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Optical Properties and Structure of Rare-Earth-Doped Fluoride Glasses

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博士論文

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平成8年1月

神戸大学大学院自然科学研究科 高橋 雅英

博士論文

OPTICAL PROPERTIES AND STRUCTURE OF RARE-EARTH-DOPED FLUORIDE GLASSES

(希土類含有フッ化物ガラスの光物性と構造)

平成8年1月

神戸大学大学院自然科学研究科 高橋 雅英

Preface

The present thesis is a summary of my studies carried out at Graduate School of Science and Technology, Kobe University. In this thesis, I describe a series of investigations on the optical properties and structures of rare-earthdoped fluoride glasses.

Recently, the intentional modification of light in amplitude, phase and frequency becomes fundamental technology in the optoelectronics field. Heavymetal fluoride glass system is the most promising host of optical functional materials that utilize the *f-f* transitions of rare-earth ions. Since the discovery of the ZrF₄-based glasses, a number of studies on the active applications of the rare-earth-doped heavy-metal fluoride glasses have been carried out to develop the efficient lasers and optical amplifiers. However, there are few studies which concern a correlation between the optical properties and glass structure of fluoride glasses doped with rare-earth ions.

In the present study, frequency up-conversion characteristics of Er^{3+} in the ZrF_4 -based glass, oxyfluorosilicate glass and oxyfluorosilicate vitro-ceramic systems are studied in terms of their composition. In order to understand the optical properties of rare-earth ions in ZrF_4 -based glasses, the local structures of glass-constituent cations are investigated by means of the several spectroscopies and molecular dynamics simulations. I wish the present studies will contribute for profound understanding of the rare-earth-doped heavy-metal fluoride glasses.

Rokko, Kobe January 1996

Masahide Takahashi

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General Introduction

The object of this study is to investigate the optical properties and local structure of the ZrF_4 -based glass, lead oxyfluorosilicate glass and lead oxyfluorosilicate vitro-ceramic systems doped with rare-earth ions.

Heavy-metal fluoride glasses were discovered in 1974 by Poulain *et al.* [1]. Poulain and his co-workers were interested in ZrF_4 -based crystals as laser host. The crystal structure of ZrF_4 -BaF₂ phase was found to include defects so that NaF was added with the idea of filling them. The product was not crystal but glass. It was an unexpected discovery of heavy-metal fluoride glass system. Since the discovery, systematic studies on glass-forming regions of heavy-metal fluoride glasses were carried out [2-8]. The discovery of vitreous fluoride materials was quite significant for infrared optics. These glasses are continuously transparent from 6~7 μ m in the middle-infrared to 0.25~0.30 μ m in the near ultraviolet[9-11]. Therefore, the early research of heavy-metal fluoride glasses was motivated from the interest in light transmitting materials, such as optical fibers.

Recently, the intentional modification of light becomes fundamental technology in the optoelectronics field. Heavy-metal fluoride glasses have played an important role as optical-functional materials utilizing optical transitions of rare-earth ion. This application is originated not only from high transparency of fluoride glass systems, but from the distinct characteristics of them, *i.e.*, stable incorporation of rare-earth ions and low phonon energy of lattice vibrations.

The maximum phonon energies in heavy-metal fluoride glasses are considerably lower than those in most of oxide glasses and oxide crystals[12-17]. This characteristic contributes largely to the fluorescence efficiency of optical transitions of rare-earth ions. Excited 4*f*-electrons of rare-earth ions relax through the radiative or non-radiative processes. In non-radiative process, the excited energy dissipates as heat. In other words, the excitation energy is transformed into phonons. If the host matrix has a low maximum vibrational energy, it requires a large number of phonons to relax non-radiatively. Therefore, the nonradiative decay rates would be small in heavy-metal fluoride glasses as compared with oxide glasses. The active applications of rare-earth-doped fluoride glasses that utilize the low non-radiative decay rate are fiber lasers, optical amplifiers and frequency up-converters [18-27].

The frequency up-conversion, *i.e.*, the conversion of infrared radiation to shorter wavelengths, in several rare-earth ions was first found for Yb³⁺- and Er³⁺co-doped germanate glass system[28]. Although the first observation of upconversion luminescence was in oxide system, subsequent studies of frequency up-conversion have occurred in fluoride systems because maximum phonon energy responsible for non-radiative decay is much lower in fluoride systems than in oxide systems. Many studies have been carried out to develop the efficient up-conversion lasers. The infrared pumped up-conversion laser was first reported in 1971 for Yb³⁺-Er³⁺:BaY₂F₈ crystal[29]. Since then, up-conversion lasing has been demonstrated for Pr³⁺, Ho³⁺, Er³⁺ and Tm³⁺ in crystalline hosts and fiber glass hosts[30-35]. Among these rare-earth ions, Er³⁺ ion has been widely studied. One reason is that Er^{3+} has appropriate 4*f*-levels available for IR pumping that closely match three of the most attractive laser diode wavelengths, 1.5, 0.98 and 0.8µm. Furthermore, Er³⁺ has conventionally spaced energy levels available for multi-photon absorption, and long-lived levels that contribute to up-convert IR radiation.

The mechanism of up-conversion processes has also been examined by means of excitation spectrum measurements, rate equation analyses and so on[36-38]. Several mechanisms have been proposed to account for frequency up-conversion of rare-earth ions, including excited state absorption, energy transfer up-conversion and avalanche absorption. For the case of Er^{3+} ion, a number of

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studies on the dynamics of the up-conversion process have been reported using 1.5µm source because this energy agrees with ${}^{4}I_{13/2} \leftarrow {}^{4}I_{15/2}$ transition in which the initial population state ${}^{4}I_{13/2}$ is long-lived[39,40]. The 0.98µm-excitation is also attractive for up-conversion pumping of Er³⁺ ions co-doped with Yb³⁺ ions as efficient sensitizer[41-44]. There are only a few studies of the up-conversion mechanism using 0.8µm source of which the energy agrees with ${}^{4}I_{9/2} \leftarrow {}^{4}I_{15/2}$ transition[45,46].

In the practical use of the up-conversion phosphors and lasers, glass systems are preferable compared with crystalline systems because of the ease in fabrication into thin film[47], fibrous[48-50] and bulk forms[51-53]. Last decade, therefore, extensive studies on frequency up-conversion have been carried out on rareearth-doped heavy-metal fluoride glass systems based on $ZrF_4[54,55]$, $InF_3[56]$ and $ThF_4[43,57]$. The potentiality is originated from peculiar properties of heavymetal fluoride glasses mentioned above. Host materials for these optical devices are centered in ZrF_4 -based glass system, because of its high glass forming ability. Fluorozirconate glass system doped with Er^{3+} is one of the most promising candidates as up-conversion laser materials. Although various types of investigation have been performed on the frequency up-conversion of these glasses, little has been examined concerning a correlation between up-conversion luminescence characteristics and glass compositions. Such examinations should be required in the case of designing glass compositions to control up-conversion characteristics and to enhance up-conversion efficiencies.

On the other hand, it is widely known that optical properties of rare-earth ions are affected by the structures and compositions of glass hosts. However, no structural models of fluoride glass systems have been established. The major problem in understanding the structure of fluoride glasses comes from lack of a fixed structural unit. For example, the average coordination number of F⁻ around Zr^{4+} is not an integer in fluorozirconate glass systems. This indicates that all Zr^{4+} ions do not have the same environment in the glass. Therefore, it is difficult to

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understand the fluoride glass structure in the microscopical point of view.

The local structure around rare-earth ions in heavy-metal fluoride glasses has been studied in some detail by using X-ray or neutron diffraction techniques [58-60], EXAFS analyses[61,62], fluorescence line narrowing (FLN) techniques[63] and molecular dynamics (MD) simulations[64,65]. The fluorescence properties and local environments of Eu³⁺ ions in several glass systems have been reported by using the FLN and MD techniques[66-69]. A few studies have examined a chemical bonding-states of rare-earth ions in fluoride glasses[70]. In the present study, the local structures of glass-constituent ion are investigated by using EXAFS, vibrational spectroscopies, Mössbauer spectroscopy and MD simulations.

EXAFS spectroscopy is one of the most powerful methods to examine the local structure around glass constituent ions. For fluorozirconate glasses, several studies using EXAFS spectroscopy have reported for some ions such as Zr⁴⁺, Ba²⁺ and so on[71-74].

Vibrational spectroscopies, such as Raman scattering and IR absorption, indirectly give the structural quantities. Much structural information can be obtained by comparing the vibrational energy of the glasses whose structure has unknown with that of crystals of which structure has already known[75-81].

Mössbauer spectroscopy provides useful information on characterizing the valence state and coordination environments around Mössbauer-active cations in glasses[82]. Europium is one of the appropriate elements in respect to clarifying the electron charge density at nucleus. The ¹⁵¹Eu resonance has previously been observed for Eu³⁺ in several oxide and fluoride glasses[83-86].

Recent progress of computer systems makes it possible to investigate the microscopic structures of materials such as fluoride glasses by molecular dynamics (MD) or Monte Carlo (MC) simulation. MD and MC simulations have already been applied to many topics in the material science field [87-91] and regarded as a powerful tool to understand the microscopic structures and dynamics of materials.

In the present study, optical properties and glass structure of fluoride glasses

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doped with Eu or Er ions are investigated by using several spectroscopic methods and computer simulations. Chapters 1 to 4 concern the frequency up-conversion characteristics of Er^{3+} in ZrF_4 -based glass systems under 800nm excitation. In Chapters 5 to 7, the local structures of glass constituent cations are discussed for Eu^{3+} -doped chloro-fluorozirconate glass system. Chapter 8 describes a new approach to the rare-earth-doped optical materials of polyanionic vitro-ceramics and glasses. The contents of the respective Chapters are as follows.

In Chapter 1, optical properties and up-conversion characteristics of Er^{3+} in the ZrF₄-BaF₂ glass system are discussed. The multi-phonon emission rate and cross relaxation probabilities of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states of Er^{3+} are calculated by measuring the absorption spectra and the Er concentration dependence of fluorescence lifetimes. The mechanisms of infrared-to-visible up-conversion process under 800nm excitation are also deduced from the Er concentration dependence of up-conversion intensity.

In Chapters 2 to 4, the compositional dependence of up-conversion luminescence of Er^{3+} in ZrF_4 -based glasses is clarified to design glass-composition of efficient up-conversion hosts. Factors governing up-conversion intensity in these glasses are discussed by analyzing the fluorescence spectra of Eu^{3+} in the glasses. Chapter 2 deals with the glass-modifying alkali metal dependence of Er^{3+} frequency up-conversion. The alkaline-earth fluoride dependence of Er^{3+} frequency upconversion is described in Chapter 3. In Chapter 4, the anion substitution effects on the up-conversion efficiency are examined in the ZrF_4 -BaF₂ glass system doped with Er. The glass composition chosen is a ZrF_4 -based one in which a part of F⁻ ions is replaced by other anion such as Cl⁻, Br⁻, I⁻ and O²⁻. The up-conversion efficiencies of the respective emission bands largely change, depending on the compositions. An explanation for the observed compositional dependence is discussed based on the local covalency and multi-phonon relaxation across the excited 4f state of Er^{3+} .

In Chapter 5, anion coordination environments around Zr⁴⁺ in the ZrF₄-

 $BaF_2-BaCl_2-EuF_3$ glass system are examined by the Zr K-EXAFS, Raman scattering and IR absorption spectroscopies. Changes in local structures around Zr^{4+} with substitution of Cl⁻ for F⁻ are discussed.

In Chapter 6, chemical bonding-states and fluorescence properties of Eu^{3+} in the ZrF₄-BaF₂-EuF₃ glass system in which a part of F⁻ ions is successively substituted by Cl⁻ ions are investigated by means of ¹⁵¹Eu-Mössbauer and Eu³⁺-fluorescence spectroscopies. It is shown that even a small amount of Cl⁻ substitution greatly changes the local environments around Eu³⁺.

In Chapter 7, molecular dynamics simulations are performed for the Zr-Ba-Eu-F glass system in which a part of F⁻ ions is substituted by Cl⁻ ions. Changes in local structures around each cation are investigated in terms of increasing amount of substitution of Cl⁻ for F⁻.

In Chapter 8, frequency up-conversion characteristics and local vibrational state around rare-earth ions in lead oxyfluorosilicate vitro-ceramics and glasses are investigated. Efficient up-conversion luminescence of Er^{3+} is demonstrated for the SiO₂-PbF₂ vitro-ceramics and the SiO₂-PbO-PbF₂ glasses. Local vibrational state around rare-earth ions in the vitro-ceramics and glasses is clarified by analyzing the phonon sideband of Eu^{3+} . Changes in up-conversion intensity with composition are discussed in terms of the multi-phonon relaxation.

REFERENCES

- [1] M. Poulain, M. Poulain, J. Lucas and P. Brun, Mat. Res. Bull. 10, 243 (1975).
- [2] M. G. Drexhage, B. Bendow and C. T. Moynihan, Laser Focus 10, 62 (1980).
- [3] J. J. Videau, B. Dubois and J. Portier, C.R. Acad. Sci. Paris 297, 483 (1983).
- [4] J. J. Videau, J. Portier and B. Piriou, Rev. Chem. Min. 16, 393 (1979).
- [5] T. Kanamori, K. Oikawa, S. Shibata and T. Manabe, Jpn, J. Appl. Phys. 20, L326 (1981).
- [6] J. P. Miranday, C. Jacoboni and R. de Pape, French Pat. 7907785.
- [7] M. Matecki, M. Poulain and M. Poulain, Mat. Res. Bull. 16, 749 (1981).
- [8] M. Poulain and Y. Messaddeq, Mat. Sci. Forum 32033, 131 (1988).
- [9] P. Trans, G. Sigel and B. Bendow, IEEE J. Lightwave Technol. LT-2, 566 (1984).
- [10] M. G. Drexhage, J. J. Hutta, M. J. Suscavage, R. Mossadegh and C. T. Moynihan, *Mat. Sci. Forum* 6, 509 (1985).
- [11] E. I. Cooper and C. A. Angell, J. Non-Cryst. Solids 56, 75 (1983).
- [12] C. B. Layne, W. H. Lowdermilk and M. J. Weber, Phys. Rev. B 16, 10 (1977).
- [13] G. M. Zverev, G. Y. Kolodnyi and A. M. Onishchenko, Sov. Phys. JETP 33, 497 (1971).
- [14] M. J. Weber, Phys. Rev. B 8, 54 (1973).
- [15] M. D. Shinn, W. A. Sibley, M. G. Drexhage and R. N. Brown, *Phys. Rev.* B 27, 6635 (1983).
- [16] M. J. Weber, Phys. Rev. 157, 262 (1967).
- [17] L. A. Riseberg and H. W. Moos, Phys. Rev. 174, 429 (1968).
- [18] N. Bloembergen, Phys. Rev. 2, 84 (1959).
- [19] L. F. Johnson and H. G. Guggenheim, Appl. Phys. Lett. 19, 44 (1971).
- [20] G. A. Ball and W. W. Morey, Optics Lett., 17 (6), 420 (1992).
- [21] W. H. Loh, P. R. Morkel and D. N. Payne, *IEEE Photonics Tech. Lett.*, 6, 43 (1994)
- [22] S. G. Grubb, K. W. Bennett, R. S. Cannon and W. F. Humer, *Electron. Lett.* 28, 1243 (1992).

- [23] J. Y. Allain, M. Monerie and H. Poignant, Electron. Lett. 26, 166 (1990).
- [24] J. N. Carter, R. G. Smart, A. C. Tropper and D. C. Hanna, J. Non-Cryst. Solids 140, 10 (1992).
- [25] Y. Ohishi, T. Kanamori, T. Kitagawa and S. Takahashi, Opt. Lett. 16, 1747 (1991).
- [26] R. S. Deol, D. W. Hewak, S. Jordery, A. Jha, M. Poulian, M. D. Baró and D. N. Payne, J. Non-cryst. Solids 161, 257 (1993).
- [27] Y. Ohishi, T. Kanamori, M. Shimizu, M. Yamada, Y. Terunuma, J. Temmyo,
 M. Wada and S. Sudo, *IECE Trans. Commun.* E77-B, 421 (1994).
- [28] F. Auzel, C. R. Acad. Sci. 262, 1016 (1966).
- [29] L. F. Johnson and H. J. Guggenheim, Appl. Phys. Lett. 19, 44 (1971).
- [30] T. Danger, J. Koetke, R. Brede, E. Heumann, G. Huber and B. H. T. Chai, J. Appl. Phys. 763, 1413 (1994).
- [31] J. M. Chwalek and G. R. Paz-Pujalt, Appl. Phys. Lett. 66 (4), 410 (1995).
- [32] L. Esterowitz, R. C. Eckardt and R. E. Allen, Appl. Phys. Lett. 35(3), 236 (1979)
- [33] K. Hirao, S. Todoroki and N. Soga, J. Non-Cryst.Solids 143, 40 (1992).
- [34] L. F. Johnson and H. J. Guggenheim, Appl. Phys. Lett. 19, 44 (1971).
- [35] R. K. Watts and W. C. Holton, Solid State Commun. 9, 17 (1971).
- [36] Y. Chen, D. Meichenin and F. Auzel, J. Phys.: Condense. Matter 7, 3363 (1995).
- [37] D. J. Simkin, J. A. Koningstein, P. Myslinski, S. A. Boothroyd and J. Chrostowski, J. Appl. Phys. 73 (12), 8046 (1993).
- [38] X. Zou and H. Toratani, J. Non-Cryst. Solids 181, 87 (1995).
- [39] S. A. Pollack, D. B. Chang and M. Birnbaum, Appl. Phys. Lett. 54, 869 (1989).
- [40] L. F. Johnson, H. J. Guggenheim, T. C. Rich and F. W. Ostermayer, J. Appl. Phys. 43, 1125 (1972).
- [41] D. C. Yeh, W. A. Sibley, M. Suscavage and M. G. Drexhage, J. Appl. Phys. 62, 266 (1987).
- [42] J. A. Hutchinson and T. H. Allik, Appl. Phys. Lett. 60 (12), 1424 (1992).
- [43] R. S. Quimby, M. G. Drexhage and M. J. Suscavage, *Electron. Lett.* 23(1), 32 (1987).

- [44] H. Kuroda, S. Shionoya and T. Kushida, J. Phys. Soc. Jpn 33 (1), 125 (1972).
- [45] Y. Kawamoto, R. Kanno, R. Yokota, M. Takahashi, S. Tanabe and K. Hirao, J. Solid State Chem. 103, 334 (1993).
- [46] M. Takahashi, R. Kanno, Y. Kawamoto, S. Tanabe and K. Hirao, J. Non-Cryst. Solids 168, 137 (1994).
- [47] C. Jacoboni, in Proc. 9th. Intl. Symp. Non-Oxide Glasses, (Hangzhou, China, 1994) p. 302.
- [48] D. A. Pinnow, A. L. Gentile, A. G. Standless, A. J. Timmer and L. M. Hobrock, *Appl. Phys. Lett.* 33(28), 28 (1978).
- [49] L. G. Van Uitert and S. H. Wemple, Appl. Phys. Lett. 33, 57 (1978).
- [50] C. H. L. Goodman, J. Solid-State Circuit 2, 129 (1978).
- [51] R. S. Quimby and B. Zheng, Appl. Phys. lett. 60 (9), 1955 (1992).
- [52] M. Poulain, M. Poulain and J. Lucas, Rev. Chim. Min. 16, 267 (1979).
- [53] H. Ebendorff-Heidepriem, W. Seeber and D. Ehrt, J. Non-Cryst. Solids 183, 191 (1995).
- [54] Y. Miyajima, T. Komukai, T. Sugawa and T. Yamamoto, *Opt. Fiber Technol.* 1, 35 (1994).
- [55] X. Zou, A. Shibata, H. Yanagita and H. Toratani, J. Non-Cryst. Solids 181, 100 (1995).
- [56] S. Todoroki, K. Hirao and N. Soga, J. Non-Cryst. Solids 143, 46 (1992).;
- [57] M. Moine, A. Brenier and C. Pedrine, *IEEE J. Quantum Electron.* 25 (1) 88 (1989)
- [58] J. Wasylak and L. Samek, J. Non-Cryst. Solids 129, 137 (1991).
- [59] R. Coupé, D. Loüer, J. lucas and A. Léonard, J. Am. Ceram. Soc. 66, 523 (1984).
- [60] J. Lucas, C. A. Angell and S. Tammadon, Mat. Res. Bull. 19, 945 (1984).
- [61] M. A. Marcus and A. Polman, J. Non-Cryst. Solids 136, 260 (1991).
- [62] R. M. Almeida, M. I. de Barros and M. C. Gonçalves, J. Non-Cryst. Solids 168, 144 (1994).
- [63] J. L. Adam, V. Ponçon, J. Lucas and G. Boulon, J. Non-Cryst. Solids 91, 191 (1987).

- [64] S. A. Brawer, and M. J. Weber, J. Chem. Phys. 75, 3522 (1981).
- [65] S. A. Brawer, and M. J. Weber, Phys. Rev. Lett. 45, 460 (1980).
- [66] G. Cormeir, J. A. Capobianco and A. Monteil, J. Non-Cryst. Solids 168, 115 (1994).
- [67] J. A. Capobianco, P. P. Proux, M. Bettinelli and F. Negrisolo, *Phys. Rev.* B 42(10), 5936 (1993).
- [68] G. Cormeir, J. A. Capobianco, C. A. Morrison and A. Monteil, *Phys. Rev. B* 48(22), 16290 (1993).
- [69] K. Soga, M. Uo, A. Makishima and S. Inoue, J. Am. Ceram. Soc. 78(1), 129 (1995).
- [70] S. Tanabe, K. Takahara, M. Takahashi and Y. Kawamoto, J. Opt. Soc. Am. B 22(5), 786 (1995).
- [71] Y. Kawamoto, R. Kanno, Y. Umetani, K. Tohji and H. Morikawa, Solid State Ionics 44, 181 (1991).
- [72] Y. Kawamoto, R. Kanno and Y. Umetani, Mat. Res. Bull. 26, 1077 (1991).
- [73] R. M. Almeida, M. I. Marques de Barros and M. C. Gonçalves, J. Non-Cryst. Solids 168, 144 (1994).
- [74] W. Wen-cai, C. Yu and H. Tian-dou, J. Non-Cryst. Solids 152, 172 (1993).
- [75] F. L. Galeener, A. J. Leadbetter and M. W. Stingfellow, Phys. Rev. B 27, 1052 (1983).
- [76] D. F. Horning, J. Chem. Phys., 14, 1063 (1948).
- [77] R. M. Almeida and J. D. Mackenzie, J. Chem. Phys. 74, 5954 (1981).
- [78] R. M. Almeida and J. D. Mackenzie, J. Chem. Phys. 78, 6502 (1983).
- [79] Y. Kawamoto, Phys. Chem. glasses 25, 88 (1984).
- [80] C. C. Phifer, D. Gostzola, J. Kieffer and C. A. Angell, Bull. Am. Ceram. Soc. 68, 738 (1989).
- [81] Y. Kawamoto and A. Kono, J. Non-Cryst. Solids 85, 335 (1986).
- [82] G. J. Long, in Mössbauer Spectroscopy, Applied to Inorganic Chemistry edited by G. J. Long (Plenum Press, New York, 1984), Vol. I, p. 7.
- [83] M. F. Taragin and J. C. Eisenstein, J. Non-Cryst. Solids11, 395 (1973).

- [84] J. M. D. Coey, A. McEvoy and M. W. Shafer, J. Non-Cryst. Solids 43, 387 (1981).
- [85] S. Tanabe, K. Hirao and N. Soga, J. Non-Cryst. Solids 113, 178 (1989).
- [86] Y. Kawamoto, in Proceedings of Japanese-French Seminar on Inorganic Fluorine Chemistry(Kyoto, 1995) p. 39.
- [87] J. Habasaki, I. Okada and Y. Hiwatari, J. Non-Cryst. Solids 183, 12 (1995).
- [88] Y. Benino, K. Hirao and N. Soga, J. Non-Cryst. Solids 183, 22 (1995).
- [89] G. Cormier, J. A. Capobianco and A. Monteil, J. Non-Cryst. Solids 152, 225 (1993).
- [90] K. Hirao and N. Soga, J. Am. Ceram. Soc. 10, 515 (1985).
- [91] H. Ogawa, Y. Shiraishi, K. Kawamura and T. Yokokawa, J. Non-Cryst. Solids 119, 151 (1990).

Chapter 1

Frequency up-conversion of Er^{3+} in ZrF_4 - BaF_2 glass system

1.1 INTRODUCTION

Fluorozirconate glass system doped with Er^{3+} is one of the leading contenders as up-conversion laser materials. Many studies have been carried out to develop the efficient up-conversion laser. The infrared pumped up-conversion laser was first reported by Johnson and Guggenheim in 1971 for Yb³⁺-Er³⁺:BaY₂F₈ crystal[1]. Since then, up-conversion lasing has been demonstrated for Er^{3+} in various crystal and glass hosts[2-5]. The mechanisms of up-conversion processes have also been examined by means of excitation spectrum measurements, rate equation analyses and so on[6-8]. Several mechanisms have been proposed to account for frequency up-conversion of rare-earth ions, including excited state absorption, energy transfer up-conversion and avalanche absorption. A number of studies about the dynamics of the up-conversion process have been reported using 1.5µm source because this energy agrees with ${}^{4}I_{13/2} \leftarrow {}^{4}I_{15/2}$ transition in which the initial population state ${}^{4}I_{13/2}$ is long-lived[9,10]. The 0.98µm-excitation is also attractive for up-conversion pumping of Er³⁺ ions co-doped with Yb³⁺ ions as efficient sensitizer[11-14]. There are only a few studies about the up-conversion

mechanism using 0.8µm source whose energy agrees with ${}^{4}I_{9/2} \leftarrow {}^{4}I_{15/2}$ transition[15,16].

In this Chapter, the up-conversion characteristics of Er^{3+} in the ZrF_4 -BaF₂ binary glass system under 0.8μ m-excitation are investigated. Non-radiative decay processes of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states are discussed by measuring the absorption and fluorescence decay spectra. Intensity parameters of optical transitions of Er^{3+} in the present glass system are calculated from absorption spectra by using Judd-Ofelt theory[17,18]. The Er concentration and excitation power dependence of upconversion emission intensity under 0.8μ m-excitation are measured to reveal the mechanism of up-conversion processes.

1.2 EXPERIMENTAL PROCEDURE

(a) Sample preparation

Glass compositions employed were $58\text{ZrF}_4 \cdot 39\text{BaF}_2 \cdot (3-x)\text{LaF}_3 \cdot x\text{ErF}_3$ (x = 0.3, 1.0, 1.5, 2.0 and 3.0). High purely reagents fluorides were used as raw materials in preparing glasses. About 5 g batches of the raw materials with an addition of a fluoridizing agent NH₄·HF were melted at 450°C for 15 minutes and subsequently at 850°C for 15 minutes in a Pt crucibles under an Ar gas atmosphere. The melts were cast into brass molds at temperatures around 100~150°C. The glasses obtained were annealed at the respective glass transition temperatures determined by a differential thermal analysis. The refractive indexes were measured with an Abbe refractometer. The densities were measured by an Archimedes's method, and the Er concentrations were calculated from the molar weights. The glass transition temperatures, T_g , refractive indexes, n_D , and Er concentration per unit volume, N, of the glasses are given in Table 1.I.

(b) Spectroscopic measurements

Emission spectra were measured with a HITACHI F-3010 fluorescence

spectrophotometer. An Xe lump and AlGaAs laser diode (SONY SLD303-XT, λ =802nm, P \leq 250mW) were used as the excitation sources of the fluorescence and up-conversion luminescence measurements, respectively. Absorption spectra were measured with a SHIMADZU UV-2200 spectrometer in the range of 220nm to 900nm. Fluorescence decay curves of Er ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states were measured on excitation with 532nm radiation of pulsed Nd:YAG laser (Spectra Physics GCR-11 & HG-2) and 650nm radiation of DCM-dye laser pumped with the pulsed Nd:YAG laser. The fluorescence signal was detected with monochromator and photomultiplier (RITSU KU-E-01) and then analyzed by a boxcar integrator (Stanford Research Systems SR-250) controlled by a personal computer. All spectral measurements are carried out at an ambient temperature.

TABLE 1.1
GLASS TRANSITION TEMPERATURES, T_{g} , Refractive Indexes, n_{D} , and
Er CONCENTRATION PER UNIT VOLUME, N, OF GLASSES
58ZrF ₄ ·39BaF ₂ ·(3-x)LaF ₃ ·xErF ₃ (x= 0.3, 1.0, 1.5, 2.0 and 3.0)

x	<i>T</i> g (°C)	n _D	N (10 ²⁰ atoms/cm ³)
0.3	301	1.5241	0.499
1.0	297	1.5228	1.659
1.5	301	1.5257	2.468
2.0	305	1.5257	3.300
3.0	309	1.5252	4.934

1.3 RESULTS

(a) Judd-Ofelt parameters

Figure 1.1 shows the UV-VIS absorption spectra of glasses 58ZrF₄·39BaF₂·(3-

x)LaF₃·3ErF₃. The absorption bands can be ascribed to transitions from the ground state (${}^{4}I_{15/2}$) to the excited states of Er³⁺ ion labeled in Fig. 1.1. The absorption spectra for the respective glasses have similar pattern. The intensities decreased for lower Er concentration. The host matrix dependence of the electric dipole (ED) transitions can be quantified by using the Judd-Ofelt(JO) theory [17,18]. The measured oscillator strength can be calculated from the integrated absorption coefficient for a particular absorption using the equation[19,20],

$$P_{\exp} = \frac{mc^2}{\pi e^2 N} \int_{band} \alpha(v) dv, \qquad (1.1)$$

where *m* and *e* are the mass and charge of electron, *N* is the number of Er ions per unit volume and $\alpha(v)$ is the absorption coefficient at frequency *v*. The ED oscillator strength for an absorption between levels *aJ* and *bJ*' in JO theory is given by

$$P_{cal}(aJ;bJ') = \frac{8\pi^2 m\bar{\nu}}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{I=2,4,6} \Omega_I |\langle aJ || U^{(I)} || bJ' \rangle|^2, \qquad (1.2)$$

where \bar{v} is the average frequency of transition, *h* is the Plank constant, *n* is the refractive index of the medium, *J* is the quantum number of angular moment of initial level in transition, Ω_t are the intensity parameters of ED transitions (JO parameters) and $|\langle a J || U^{(t)} || b J' \rangle|$ are the doubly reduced matrix elements of tensor operator $U^{(t)}$ for transition of initial state $||aJ\rangle$ to final state $||bJ'\rangle$. The three intensity parameters of ED transition are derived by fitting the measured oscillator strengths of absorption transition[Eq. 1.1] to the theoretical oscillator strength[Eq. 1.2]. The doubly reduced matrix elements of Er^{3+} in LaF₃ determined by Weber were employed[21]. All absorption bands labeled in Fig. 1.1 were used for JO calculations. The calculated JO parameters were independent of Er concentration. The three JO parameters obtained for Er^{3+} in the present glasses are 3.07 for Ω_2 , 1.25 for Ω_4 and 0.97 for Ω_6 . These JO parameters can be used to calculate sponta-

neous emission probabilities by using the equation,

$$A_{cal}(aJ;bJ') = \frac{64\pi^4 e^2}{3h(2J+1)\bar{\lambda}^3} \frac{n(n^2+2)^2}{9} \sum_{t=2, 4, 6} \Omega_t |\langle aJ || U^{(t)} || bJ' \rangle|^2,$$
(1.3)

The calculated transition probabilities and the measured fluorescence lifetimes can then be used to calculate multi-phonon relaxation rates and cross-relaxation decay rates.



Wavelength, λ / nm

Figure 1.1 UV-VIS absorption spectra of $58ZrF_4 \cdot 39BaF_2 \cdot (3-x)LaF_3 \cdot 3ErF_3$ glasses, in which the absorption bands can be ascribed to transitions from the ground state(${}^{4}I_{15/2}$) to the excited states of Er^{3+} ion labeled in figure.

(b) Fluorescence lifetime

The fluorescence decay curves of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ levels in 58ZrF₄·39BaF₂· (3-*x*)LaF₃·*x*ErF₃ (*x*= 0.3, 1.0, and 3.0) glasses are shown in Fig. 1.2. These curves were fitted by single exponential function using a least square method. The analyzed fluorescence lifetimes, τ_{exp} , are given in Table 1.II.



Figure 1.2 Fluorescence decay curves of Er in $58ZrF_4 \cdot 39BaF_2 \cdot (3-x)LaF_3 \cdot xErF_3$ glasses, (a) ${}^4S_{3/2}$ state and (b) ${}^4F_{9/2}$ state. The solid lines represent the fitted curves.

TABLE 1.II

Fluorescence Lifetimes of The ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ levels, τ_{exp} , and Root Mean Square Deviation, δ_{rms} , in $58ZrF_{4}\cdot39BaF_{2}\cdot(3-x)LaF_{3}\cdotxErF_{3}$ (x= 0.3, 1.0, 1.5, 2.0 and 3.0) Glasses

	⁴ S _{3/2}		⁴ F 9	9/2
x	$ au_{exp}(\mu s)$	$\delta_{ m rms}$ (%)	$ au_{ m exp}$ (µs)	$\delta_{ m rms}$ (%)
0.3	521	7.1	237	7.1
1.0	370	8.3	231	7.7
1.5	291	10.1		
2.0	218	7.8	208	8.3
3.0	126	4.2	182	7.7

(c) Up-conversion luminescence spectra

Figure 1.3 shows the Er concentration dependence of up-conversion luminescence spectra of glasses $58ZrF_4 \cdot 39BaF_2 \cdot (3-x)LaF_3 \cdot xErF_3$ (x = 0.3, 1.0, 1.5, 2.0and 3.0). The up-conversion emission bands were observed around 525nm, 550nm and 660nm. A faint emission band was observed around 410nm. The emission bands around 410nm, 525nm, 550nm and 660nm are assigned to the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions, respectively. In these transitions, the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ transition is thermally coupled transition of the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition[22].



Figure 1.3 Up-conversion luminescence spectra of $58ZrF_4 \cdot 39BaF_2 \cdot (3-x)LaF_3 \cdot xErF_3$ glasses.

1.4 DISCUSSION

(a) Non-radiative decay process

The total decay rate, $1/\tau_{exp}$, of an excited state can be written by,

$$1/\tau_{exp} = A + W_{MPR} + W_{ET},$$
 (1.4)

where A is the total spontaneous emission probability, W_{MPR} is the single ion non-radiative rate corresponding to the multi-phonon relaxation rate, and W_{ET} is the effective non-radiative rate due to energy transfer. At limit of zero Er concentration, W_{ET} becomes zero, since the energy transfer decreases as the average separation between ions increases. Therefore, multi-phonon relaxation rate W_{MPR} can be determined from the lifetime in the limit of zero Er concentration, τ_0 , and calculated radiative rate A_{cal} as follows,

$$W_{\rm MPR} = 1/\tau_0 - A_{\rm cal}.$$
 (1.5)

Figure 1.4 shows the Er concentration dependence of the lifetime of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states, the solid lines represent the fitted curves of lifetimes by using the formula,

$$\tau_{\exp}(N) = \tau_0 / \{1 + (N/N_q)^2\},\tag{1.6}$$

where τ_0 is the lifetime in the limit of zero concentration and N_q is the quenching concentration in which the lifetime becomes half of τ_0 . The radiative transition rates, multi-phonon relaxation rates, quenching concentrations and quantum efficiencies of emission of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states are given in Table 1.III.





TABLE 1.III

FLUORESCENCE LIFETIMES IN THE LIMIT OF ZERO Er CONCENTRATION, τ_0 , EFFECTIVE RADIATIVE TRANSITION RATES, A_{eff} , MULTI-PHONON RELAXATION RATES, W_{MPR} , QUENCHING CONCENTRATIONS, N_q , and Single Ion Quantum Efficiencies of Emission, η , of Er ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ States in 58ZrF₄·39BaF₂·(3-x)LaF₃·xErF₃ GLASSES

SLJ>	τ ₀ (μs)	A _{eff} * (s ⁻¹)	W _{MPR} (s ⁻¹)	N _q (atoms/cm ³)	η (%)
⁴ S _{3/2}	532	1372	508	2.68×10 ²⁰	73
⁴ F _{9/2}	238	1053	3149	8.84×10 ²⁰	25

* A_{eff} is the total spontaneous transition rate, $\sum A_{ij}$, in which the contribution of thermally coupled ${}^{2}H_{11/2}$ state is included by using equation [23],

 $A_{cal} = \sum_{i={}^{4}\mathrm{S}_{3n2},{}^{2}\mathrm{H}_{11/2}} g_{i}A_{i}\exp\left(-\Delta E/kT\right) / \sum_{i={}^{4}\mathrm{S}_{3n2},{}^{2}\mathrm{H}_{11/2}} g_{i}\exp\left(-\Delta E/kT\right),$

where ΔE is the energy gap between the ${}^{4}S_{3/2}$ and ${}^{2}H_{11/2}$ states, A_i is the total spontaneous emission probability from level *i* to the all lower levels and g_i is the level degeneracy.

The quenching concentration of the ${}^{4}S_{3/2}$ state is much smaller than that of the ${}^{4}F_{9/2}$ state. For ${}^{4}S_{3/2}$ state, there are several energy levels at the appropriate positions to converse excited energy. The considerable cross relaxation processes are shown in Fig. 1.5. This indicates that the non-radiative decay by cross relaxation is predominant in high Er concentration region for ${}^{4}S_{3/2}$ state, as shown in Fig. 1.6. The energy transfer decay rate of the ${}^{4}S_{3/2}$ state rapidly increases with increasing Er concentration. On the contrary, the cross relaxation does not play a dominant effect on non-radiative decay of the ${}^{4}F_{9/2}$ state because of the absence of the energy level at the appropriate positions to converse excited energy.



Figure 1.5 Considerable cross relaxation processes of the ${}^{4}S_{3/2}$ state of Er³⁺.



Figure 1.6 Er concentration dependence of ratio of energy transfer decay rate to total non-radiative decay rate.

The multi-phonon decay rate of an excited level is greatly dependent of the energy gap between the initial level and the next lower level[24]. The energy gaps of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states to the next lower level are 3050 and 2650cm⁻¹, respectively. Therefore, the multi-phonon decay rate of ${}^{4}F_{9/2}$ state is much larger than that of ${}^{4}S_{3/2}$ state.

(b) Mechanism of up-conversion process

The excitation power dependence of the up-conversion emission intensity of the ${}^{2}H_{11/2} + {}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions is shown in Fig. 1.7. The up-conversion luminescence intensity is almost proportional to the square of the excitation power for both emission bands. This indicates that up-conversion processes of both emission bands are two-photon absorption.

Figure 1.8 shows the Er concentration dependence of the up-conversion emission intensity of the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions. The Er concentration dependence of the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition is different from that of the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition. This clearly indicates that the principal mechanism of up-conversion luminescence for ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition is different from that for ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition.

First, the 800nm-to-660nm up-conversion mechanism, of which the emission is based on ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition, is discussed. The dipole-dipole energy transfer rate was shown by Dexter as follows:[25]

$$P_{d-d} = \frac{3h^4 c^4}{64\pi^5 n^4} \frac{1}{\tau_s} \left(\frac{1}{R_{sA}}\right)^6 Q_A \int_{sA} \frac{f_s(v) F_A(v)}{v^4} dv, \qquad (1.7)$$

where R_{SA} is the separation of donor and acceptor, τ_S is the radiative lifetime of the donor, $f_S(v)$ and $F_A(v)$ are the normalized lineshape function for donor emission and acceptor absorption, respectively, v is the photon energy, and Q_A is the integrated absorption cross section of acceptor. Since the energy transfer rate



Figure 1.7 Excitation power dependence of the up-conversion emission intensity of the ${}^{2}H_{11/2} + {}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition.



Figure 1.8 Er concentration dependence of the up-conversion emission intensity in glasses $58ZrF_4 \cdot 39BaF_2 \cdot (3-x)LaF_3 \cdot xErF_3$, (a) ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition and (b) ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition. Solid lines represent the fitted curves by using formulas: (a) $I(N)=aN-bN^2$ and (b) $I(N)=aN^2$ in which a and b are the constant.

between two ions depends on their distance, the efficiency of energy transfer upconversion quadratically depends on the Er concentration [Eq. 1.7]. As can be seen in Fig. 1.8, the up-conversion emission intensity of the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition increases in proportional to the square of Er concentration. This shows that the principal up-conversion process of this emission band is energy transfer upconversion. Figure 1.9 shows the up-conversion and normal fluorescence spectrum of $58ZrF_4 \cdot 39BaF_2 \cdot 3ErF_3$ glass. The normal fluorescence spectrum was measured under 395nm excitation. The intensity ratio of the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition to the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition in up-conversion spectrum is much lager than that in normal fluorescence. Under 395nm excitation, the ${}^{4}F_{9/2}$ state is populated from the ${}^{4}S_{3/2}$ state though the multi-phonon decay process across their energy gap. These facts suggest that the multi-phonon relaxation across the energy gap between the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states is not a principal process on the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ emission. In other words, most 4f-electrons are directly excited to the ${}^{4}F_{9/2}$ state under up-conversion excitation.

Figure 1.10 shows the possible energy transfer up-conversion processes of two-step excitation to the ${}^{4}F_{9/2}$ state. The energy transfer rate depends on $\tau_{\rm S}$ and $Q_{\rm A}$ [see Eq. 1.7]. The calculated radiative lifetime of donor, $\tau_{\rm S}$, and calculated absorption cross section of acceptor, $Q_{\rm A}$, for both energy transfer processes are given in Table 1.IV. The $Q_{\rm A}$ value of process II is much larger than that of process I. Therefore, the 800nm-to-660nm up-conversion emission is based on the energy transfer between ${}^{4}I_{9/2} \rightarrow {}^{4}I_{13/2}$ transition and ${}^{4}F_{9/2} \leftarrow {}^{4}I_{11/2}$ transition.

Figure 1.11 shows the up-conversion luminescence spectrum of the 50ZrF_4 · $30\text{BaF}_2\cdot15\text{LaF}_3\cdot5\text{ErF}_3$ glass under 980nm excitation[26]. The 660nm line is comparatively weak under 980nm excitation in spite of the high Er concentration (8.21×10²⁰cm⁻³) by comparison with the up-conversion spectra of the present glasses under 800nm excitation. This fact leads that Er^{3+} ions in the ${}^4I_{11/2}$ and ${}^4I_{13/2}$ states do not play a role of the donor on the energy transfer up-conversion

because Er^{3+} ion is first promoted to the ${}^{4}I_{11/2}$ state under 980nm excitation. Moreover, ${}^{4}I_{9/2}$ state may be the intermediate state of the energy transfer upconversion process under 800nm excitation. This confirms above discussions about the 800nm-to-660nm up-conversion process.



Figure 1.9 Up-conversion and normal fluorescence spectrum of 58ZrF₄·39BaF₂·3ErF₃ glass.



Figure 1.10 Possible energy transfer up-conversion processes of two-step excitation of Er^{3+} in the present glasses.


Figure 1.11 Up-conversion luminescence spectrum of the $50ZrF_4 \cdot 30BaF_2 \cdot 15LaF_3 \cdot 5ErF_3$ glass under 980nm excitation.

TABLE 1.IV

RADIATIVE LIFETIME OF DONOR, τ_{S_1} and Absorption Cross Section of Acceptor, Q_A , for the Energy Transfer OF $({}^4S_{3/2} \rightarrow {}^4I_{11/2}) \rightarrow ({}^4F_{9/2} \leftarrow {}^4I_{13/2})$ [process I] and $({}^4l_{9/2} \rightarrow {}^4I_{13/2}) \rightarrow ({}^4F_{9/2} \leftarrow {}^4I_{11/2})$ [process II]

Process	Energy transfer	$ au_{S}(ms)$	$Q_{\rm A}~(10^{-15}~{\rm cm}^2)$
Ι	$({}^{4}S_{3/2} \rightarrow {}^{4}I_{11/2}) \rightarrow ({}^{4}F_{9/2} \leftarrow {}^{4}I_{13/2})$	38.5	3.32
II	$({}^{4}I_{9/2} \rightarrow {}^{4}I_{13/2}) \rightarrow ({}^{4}F_{9/2} \leftarrow {}^{4}I_{11/2})$	34.1	30.7

The Er concentration dependence of up-conversion emission intensity of ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition is shown in Fig. 1.8. The up-conversion emission intensity is almost proportional to the Er concentration. The efficiency of excited state absorption is independent of concentration, since it involves only one ion. Therefore, the energy transfer up-conversion process is negligible for 800nm-to-550nm up-conversion. The excited state absorption is a principal process for the 550nm emission band, as shown in Fig. 1.12. This result is consistent with the previous studies[27,28].



Figure 1.12 Possible excited state absorption mechanism of two-step excitation of Er³⁺ in the present glasses.

1.5 CONCLUDING REMARKS

Infrared-to-visible up-conversion characteristics of Er^{3+} were clarified for ZrF_4 -BaF₂ glass system. The non-radiative processes of $\text{Er}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ state were also discussed by measuring the absorption spectra and Er concentration dependence of fluorescence lifetimes.

Quantum efficiencies of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states are 73% and 25%, respectively, since the multi-phonon decay rate of ${}^{4}S_{3/2}$ state is much smaller than that of ${}^{4}F_{9/2}$ state. A principal non-radiative decay process of ${}^{4}S_{3/2}$ state is concentration quenching, *i.e.*, energy migration and cross relaxation in high Er concentration region. The main non-radiative decay process of the ${}^{4}F_{9/2}$ state is multi-phonon emission.

The up-conversion emission under 800nm excitation was strongly observed around 525, 550 and 660nm, and weak emission was observed around 410nm. The up-conversion emission intensity of 550nm band increases in proportional to Er concentration, and that of 660nm band increases in proportional to square of Er concentration. These results reveal that the principal up-conversion processes are excited state absorption and energy transfer for the 550nm and 660nm bands, respectively.

REFERENCES

- [1] L. F. Johnson and H. J. Guggenheim, Appl. Phys. Lett. 19, 44 (1971).
- [2] T. Danger, J. Koetke, R. Brede, E. Heumann, G. Huber and B. H. T. Chai, J. Appl. Phys. 763, 1413 (1994).
- [3] J. M. Chwalek and G. R. Paz-Pujalt, Appl. Phys. Lett. 66 (4), 410 (1995).
- [4] J. N. Carter, R. G. Smart, A. C. Tropper and D. C. Hanna, J. Non-Cryst. Solids 140, 10 (1992).
- [5] K. Hirao, S. Todoroki and N. Soga, J. Non-Cryst. Solids 143, 40 (1992).
- [6] Y. Chen, D. Meichenin and F. Auzel, J. Phys. : Condense. Matter 7, 3363 (1995).
- [7] D. J. Simkin, J. A. Koningstein, P. Myslinski, S. A. Boothroyd and J. Chrostowski, J. Appl. Phys. 73 (12), 8046 (1993).
- [8] X. Zou and H. Toratani, J. Non-Cryst. Solids 181, 87 (1995).
- [9] S. A. Pollack, D. B. Chang and M. Birnbaum, Appl. Phys. Lett. 54, 869 (1989).
- [10] L. F. Johnson, H. J. Guggenheim, T. C. Rich and F. W. Ostermayer, J. Appl. Phys. 43, 1125 (1972).
- [11] D. C. Yeh, W. A. Sibley, M. Suscavage and M. G. Drexhage, J. Appl. Phys. 62, 266 (1987).
- [12] J. A. Hutchinson and T. H. Allik, Appl. Phys. Lett. 60 (12), 1424 (1992).
- [13] R. S. Quimby, M. G. Drexhage and M. J. Suscavage, *Electron. Lett.* 23(1), 32 (1987).
- [14] H. Kuroda, S. Shionoya and T. Kushida, J. Phys. Soc. Jpn 33 (1), 125 (1972).
- [15] Y. Kawamoto, R. Kanno, R. Yokota, M. Takahashi, S. Tanabe and K. Hirao, J. Solid State Chem. 103, 334 (1993).
- [16] M. Takahashi, R. Kanno, Y. Kawamoto, S. Tanabe and K. Hirao, J. Non-Cryst. Solids 168, 137 (1994).
- [17] B. R. Judd, Phys. Rev. 127, 750 (1962).
- [18] G. S. Ofelt, J. Chem. Phys. 37, 511 (1962).
- [19] R.Reisfeld, in *Structure and Bonding*, (Springer-Verlag, Berlin, 1975) Vol. 22 p. 126.

- [20] R. S. Quimby, in *Fluoride Glass Fiber Optics*, edited by I. D. Aggarwal and G. Lu, (Academic Press, New York, 1991) p.375.
- [21] M. J. Weber, Phys. Rev. 157, 262 (1966).
- [22] M. D. Shinn, W. A. Sibley, M. G. Drexhage and R. N. Brown, *Phys. Rev.* B 27 (11), 6635 (1983).
- [23] R. Reisfeld, in *Structure and Bonding*, (Springer-Verlag, Berlin, 1975) Vol.22, p.140.
- [24] C. B. Layne, W. H. lowdermilk and M. J. Weber, Phys. Rev. B 16, 10 (1977).
- [25] D. L. Dexter, J. Chem. Phys. 21, 836 (1953).
- [26] M. Takahashi, Y. Kawamoto, K. Kadono, T. Otsuki and N. Paygambarian, unpublished data.
- [27] H. Toratani and K. Hirao, Ohyo-butsuri, 61, 43 (1992). [in Japanese]
- [28] R. Allen, L. Esterowitz and R. J. Ginther, Appl. Phys. Lett. 56, 1635 (1990).

Chapter 2

Compositional dependence of up-conversion luminescence of Er³⁺ in ZrF₄-based glass systems I. Alkaline metal dependence

2.1 INTRODUCTION

The frequency up-conversion, *i.e.*, the conversion of infrared radiation to shorter wavelengths, in several rare-earth ions was first found for $\overline{Y}b^{3+}$ - and Er^{3+} - co-doped germanate glass[1]. Although the first observation of up-conversion phenomenon was in oxide system, subsequent studies about frequency up-conversion have occurred in fluoride systems because maximum phonon energies responsible for non-radiative multi-phonon relaxation are much lower in fluoride systems than in oxide systems. For instance, the studies have been carried out on rare-earth-doped fluoride crystals, e.g., Ln:BaY₂F₈ and Ln:LiYF4 (Ln=rare-earth elements) [2,3].

In the practical use of the up-conversion phosphors and lasers, vitreous systems are preferable compared with crystalline systems because of the ease in fabrication into thin film[4], fibrous[5-7] and bulk forms[8-10]. Last decade, therefore, extensive studies on frequency up-conversion have been carried out on rare-earth-doped heavy-metal fluoride glasses based on $ZrF_4[11,12]$, $InF_3[13]$ and $ThF_4[14,15]$. Although various types of investigation have been performed

on the frequency up-conversion of these glasses, little have been examined concerning a correlation between up-conversion luminescence characteristics and glass compositions. Undoubtedly such examinations ought to be required in the case of designing glass compositions to control up-conversion characteristics and enhance up-conversion efficiencies.

The present study reports the glass-modifying alkali-fluoride dependence on up-conversion luminescence, which was examined on glasses $21.25MF \cdot 21.25LiF \cdot 52.5ZrF_4 \cdot 5ErF_3$, where *M* is Li, Na, K, Rb or Cs, and discussed based on the fluorescence and excitation experiments of Eu³⁺ ions in glasses substituted Eu for Er.

2.2 EXPERIMENTAL PROCEDURE

(a) Sample preparations

The glass compositions employed are $21.25MF \cdot 21.25LiF \cdot 52.5ZrF_4 \cdot 5LnF_3$ (M = Li, Na, K, Rb or Cs; Ln = Er or Eu). This composition means that half of the LiF in $42.5LiF \cdot 52.5ZrF_4 \cdot 5LnF_3$ was replaced by NaF, KF, RbF or CsF. It must be noted here that $42.5MF \cdot 52.5ZrF_4 \cdot 5LnF_3$ composition was considered to be more preferable for examining the alkali-fluoride dependence, but no glasses with size sufficient for up-conversion measurements could be obtained.

High purely reagents fluorides were used as raw materials in preparing glasses. About 5 g batches of the raw materials with an addition of a fluoridizing agent NH₄·HF of about 1.2 g were melted at 450°C for 15 minutes and subsequently at 750~850°C for 15 minutes in a Pt crucibles under an Ar atmosphere. The melts were cast into brass molds at temperatures around 100~150°C. The shapes of glasses obtained were thin plates about 1 mm thick. The glasses were annealed at the glass transition temperatures determined by a differential thermal analysis. The glass transition temperatures and molar volumes of the glasses are given in Table 2.I. Hereafter glasses of M = Li, Na, K, Rb and Cs are abbreviated as the Li, Na, K, Rb and Cs glass.

Glass M	<i>T</i> g (℃)	V _m (cm ³ /mol)
Li	196	0.036
Na	197	0.035
К	209	0.033
Rb	211	0.032
Cs	212	0.030

TABLE 2.I GLASS TRANSITION TEMPERATURES, T_g , and MOLAR VOLUMES, V_m , of 21.25*M*F·21.25LiF·52.5ZrF₄·5ErF₃ GLASSES (*M*= Li, Na, K, Rb or Cs)

(b) Spectroscopic measurements

The up-conversion luminescence spectra of Er³⁺ were measured in the wavelength range from 350 to 700nm with a HITACHI 850 fluorescencephotometer at room temperature, using 802nm radiation of about 0.5mm beam diameter from a GaAlAs laser diode (SONY, SLD303XT-22) with 250mW power.

In order to compare the intensity of up-conversion luminescence of the respective glasses, glass specimens were cut into the same shape $(4\times5\times1 \text{ mm}^3)$ and all the surfaces were polished into optical finish. The laser beam was irradiated perpendicular to the basal plane $(4\times1 \text{ mm}^2)$ and the up-conversion luminescence was measured from the side plane $(4\times5 \text{ mm}^2)$. The measurements for each glass was made three times to ascertain the reproducibility.

The fluorescence and excitation spectral measurements of Eu³⁺ were made with a HITACHI 850 fluorescencephotometer at room temperature, using an Xe

lump as the light source. The fluorescence spectra were measured in the wavelength range 570-660nm with 395nm excitation. The excitation spectra were measured in the wavelength range 440-475nm by monitoring the ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$ emission at 612nm.

2.3 RESULTS

(a) Er^{3+} up-conversion spectra

The up-conversion luminescence spectra of the present glasses are shown in Fig. 2.1. The spectra of the respective glasses were reproducible to about $\pm 2\%$ on three measurements. The up-conversion luminescence of Er^{3+} were observed at about 410, 525, 550 and 660nm, being assigned to the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions, respectively[16].

(b) Eu^{3+} fluorescence spectra

The Eu³⁺ fluorescence spectrum of the Li glass is shown in Fig. 2.2, where three emission bands around 578, 590 and 617nm correspond to the ${}^{5}D_{0}\rightarrow{}^{7}F_{I}$ (J=0, 1 and 2) transitions, respectively[17]. The ${}^{5}D_{1}\rightarrow{}^{7}F_{3}$ emission band is observed around 584nm and is overlapping the ${}^{5}D_{0}\rightarrow{}^{7}F_{1}$ emission band. In order to evaluate an accurate peak area of ${}^{5}D_{0}\rightarrow{}^{7}F_{1}$ emission band, the deconvolution of these two bands was performed by a curve-fitting with a Gaussian-type function using the least squares method. The example of deconvolution fitting for the Li glass is shown in Fig. 2.3. The root mean square values in the least square fitting were below 3%. Figure 2.4 shows the ${}^{5}D_{0}\rightarrow{}^{7}F_{I}$ (J=0, 1 and 2) emission spectra of Eu³⁺ in which the ${}^{5}D_{1}\rightarrow{}^{7}F_{3}$ emission was removed.



Figure 2.1 Up-conversion luminescence spectra of Er^{3+} in the 21.25*M*F·21.25LiF· 52.5ZrF₄·5ErF₃ glasses (*M*= Li, Na, K, Rb or Cs).



Figure 2.2 Eu^{3+} fluorescence spectrum of the 42.5LiF·52.5ZrF₄·5ErF₃ glass (Li glass).



Figure 2.3 Example of deconvolution fitting for the Li glass.



Figure 2.4 Fluorescence spectra of the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0, 1, and 2) transition of Eu³⁺ in the 21.25*M*F·21.25*L*iF·52.5*Z*rF₄·5EuF₃ glasses (M = Li, Na, K, Rb or Cs), in which the ${}^{5}D_{1} \rightarrow {}^{7}F_{3}$ transitions are removed by the deconvolution fittings.

(c) Eu^{3+} excitation spectra

The Eu³⁺ excitation spectra of the glasses are shown in Fig. 2.5. The phonon sidebands (PSB) associated with the pure electronic ${}^{5}D_{2} \leftarrow {}^{7}F_{0}$ transition (PET) around 21,550 cm⁻¹ are observed at higher energy sides of the PET peaks. The deconvolution of the PSB and PET peaks was carried out by the following curve-fitting method. The mixed gaussian-type and Lorentzian-type functions combined with arbitrary proportions were employed as an initial function in curve-fitting of the PET peaks because the PET peak shapes were asymmetric due to the Stark splitting of the ${}^{5}D_{2}$ state. The PSB spectra thus extracted are shown in Fig. 2.6.

2.4 DISCUSSION

As important factors governing the emission intensity of up-conversion luminescence of Er^{3+} ions in ZrF_4 -based glasses, one may anticipate the F⁻ coordination environment around Er^{3+} , which concerns the transition probability, and the phonon energy, which concerns the non-radiative decay rate due to the multi-phonon relaxation.

The covalency in the F⁻ coordination environment around Eu³⁺ can be evaluated by employing Eu³⁺ as a probe instead of Er³⁺ and by observing fluorescence for the ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ (J= 0, 1 and 2) transitions in Eu³⁺. Information about the phonon mode around Eu³⁺ can be obtained from the Eu³⁺ phonon sideband observed in the excitation spectra of Eu³⁺.

(a) Analysis of Eu^{3+} fluorescence spectra

The intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, called hypersensitive transition, is largely affected by the local environments[18]. Peacock has reported that the intensity of hypersensitive transition seems to be in proportional to covalency[19]. While the

 ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is allowed by magnetic-dipole of which the intensity is independent on the local environment. Therefore intensity ratio of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, I(0-2)/I(0-1), indicates the intensity of the hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition[20], *i.e.*, the covalency in Eu³⁺-F⁻ bonding.

The *MF* dependence of l(0-2)/l(0-1) value in the present glasses are shown in Fig. 2.7. The l(0-2)/l(0-1) values changed with the *MF* species, indicating that the covalency becomes larger in the order of the Li, Na, K and Rb glass and then becomes slightly less in the Cs glass.

(b) Analysis of phonon sideband

In the Eu³⁺ excitation spectra [see Fig. 2.5], a energy difference between PSB and PET corresponds to a phonon energy, $\hbar\omega$, and the ratio of PSB and PET in the integral peak areas corresponds to the electron-phonon coupling strength, *g*[21]. According to the Miyakawa-Dexter theory[22], the non-radiative decay rate due to the multi-phonon emission is give by,

$$W_{p}(T) = W_{0}(T)exp(-\alpha \Delta E)(n+1)^{p}$$

$$\alpha = \hbar \omega \{\ln(p/g) - 1\}$$

$$p \simeq \Delta E / \hbar \omega$$
(2.1)

where ΔE is the energy gap to the next lower level, *n* is the Plank distribution function, *p* is the phonon number concerned with multi-phonon decay and $W_0(T)$ is the decay rate at $\Delta E=0$.

The phonon energy and electron-phonon coupling strength of the glasses are given in Table 2.II. The phonon energy decreases in the order of the Li glass, the Na glass and the K glass and then increases in the order of the K glass, the Rb glass and the Cs glass, while the electron-phonon coupling strengths are almost the same for all the glasses except for the Li glass. The relative multi-phonon relaxation rates were calculated from these values by using Eq. 2.1. The calculations of the multi-phonon decay rates were made on the ${}^4l_{11/2}$ level which is

considered to be an intermediate excitation level for the multi-photon excitation processes as describes in Chapter 1. In the calculation, an energy gap to the next lower ${}^{4}I_{13/2}$ level of Er^{3+} in the crystalline LaF₃, 3643cm⁻¹[23], was employed as ΔE . The relative multi-phonon relaxation rates are shown in Fig. 2.8, where the value of the respective glasses are normalized by that of K glass. The relative multi-phonon decay rate of the Li glass is thirty times larger than those of the Na, K, Rb and Cs glasses, and those of the Na and Cs glass are several times larger than those of the K and Rb glasses.

TABLE 2.II

Phonon Energies, $\hbar\omega$, and Electron-Phonon Coupling Strengths, g, Obtained from PSB Spectra of 21.25MF·21.25LiF·52.5ZrF₄·5EuF₃ (M= Li, Na, K, Rb or Cs) Glasses

····		
М	ħω(cm⁻¹)	8
Li	427	0.015
Na	420	0.012
K	412	0.012
Rb	413	0.012
Cs	422	0.012







Figure 2.6 Phonon sideband spectra of $21.25MF \cdot 21.25LiF \cdot 52.5ZrF_4 \cdot 5ErF_3$ glasses (*M* = Li, Na, K, Rb or Cs) extracted from the excitation spectra shown in Fig. 2.5.



Figure 2.7 Glass-modifying alkaline fluoride dependence of intensity ratios of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, I(0-2)/I(0-1).



Figure 2.8 Relative multi-phonon decay rate for the energy gap across ${}^{4}I_{11/2}$ to ${}^{4}I_{13/2}$ levels of Er³⁺.

(c) MF dependence of the Er^{3+} up-conversion luminescence

The emission intensities of the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions in the glasses differ appreciably with the *MF* species [see Fig. 2.1]. Figure 2.9 shows the variation of the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ emission intensities with *MF* species, where the respective emission intensities of the Li glass are represented as unities. The alkali-fluoride dependence of these three emission bands show almost the same behaviors, *i.e.*, upconversion efficiency was the highest in the K glass and decreased in the order of the K glass, the Na glass and the Li glass.

The fluorescence and phonon sideband analysis of the present glasses disclosed that the intensity of hypersensitive transition is the maximum in the Rb glass and the multi-phonon relaxation rates is the minimum in the K glass. These two may be considered to be responsible for the *M*F dependence of the emission intensity of Er^{3+} up-conversion luminescence observed for the 21.25*M*F·21.25LiF·52.5ZrF₄·5ErF₃ glasses.



Figure 2.9 Variation of the up-conversion emission intensity of the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}, {}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions with *MF* species (*M*=Li, Na, K, Rb or Cs).

2.5 CONCLUDING REMARKS

The glass-modifying alkali-fluoride dependence of the Er^{3+} up-conversion luminescence in ZrF₄-based glasses was examined with 21.25*M*F·21.25LiF· 52.5ZrF₄·5ErF₃ glasses (*M*= Li, Na, K, Rb or Cs) to clarify the compositional effects on the design of fluoride glasses with higher up-conversion efficiencies. The Er^{3+} up-conversion fluorescence of the 21.25*M*F·21.25LiF·52.5ZrF₄·5ErF₃ glasses was observed around 410, 525, 550 and 660nm and the emission intensities changed largely with *M*F species, exhibiting the highest value in the K glass. The observed *M*F dependence may be explained based on the covalency and the multi-phonon relaxation rate in the glasses.

REFERENCES

- [1] F. Auzel, C. R. Acad. Sci. 262, 1016 (1966).
- [2] L. F. Johnson and H. J. Guggenheim, Appl. Phys. Lett. 19, 44 (1971).
- [3] R. K. Watts and W. C. Holton, Solid State Commun. 9, 17 (1971).
- [4] C. Jacoboni, in Proc. 9th. Intl. Symp. Non-Oxide Glasses (Hanrzhou, China, 1994) p. 302.
- [5] J. Y. Allain, M. Monerie and H. Poignant, Electron. Lett. 28 (2), 111 (1992).
- [6] K. Hirao, S. Todoroki and N. Soga, J. Non-Cryst. Solids 143, 40 (1992).
- [7] G. A. Ball and W. W. Morey, Opt. Lett. 17 (6), 420 (1992).
- [8] R. S. Quimby and B. Zheng, Appl. Phys. Lett. 60 (9), 1955 (1992).
- [9] Y. Chen, D. Meichenin and F. Auzel, J. Phys.: Condens. matter 7, 3363 (1995).
- [10] H. Ebendorff-Heidepriem, W. Seeber and D. Ehrt, J. Non-Cryst. Solids 183, 191 (1995).
- [11] Y. Miyajima, T. Komukai, T. Sugawa and T. Yamamoto, *Opt. Fiber Technol.* 1, 35 (1994).
- [12] X. Zou, A. Shibata, H. Yanagita and H. Toratani, J. Non-Cryst. Solids 181, 100 (1995).
- [13] S. Todoroki, K. Hirao and N. Soga, J. Non-Cryst. Solids 143, 46 (1992).
- [14] M. Moine, A. Brenier and C. Pedrine, *IEEE J. Quantum Electron.* 25 (1), 88 (1989)
- [15] R. S. Quimby, M. G. Drexhage and M. J. Suscavage, Electron. Lett. 23, 32 (1987).
- [16] M. D. Shinn, W. A. Sibley, M. G. Drexhage and R. N. Brown, *Phys. Rev.* B 27 (11), 6635 (1983).
- [17] R. Reisfeld, E. Greenberg, R. N. Brown, M. G. Drexhage and C. K. Jørgensen, Chem. Phys. Lett. 95 (2), 91 (1983).
- [18] C. K. Jørgensen and B, R, Judd, Mol. Phys. 8, 281 (1964).
- [19] R. D. Peacock, in *Structure and Bonding* (Springer-Verlag, Berlin, 1975) 22, 116.
- [20] G. Blesse, A. Bril and W. C. Nieuwpoort, J. Phys. Chem. Solids 27, 1578 (1966).

- [21] S. Tanabe, S. Todoroki, K. Hirao and N. Soga, J. Non-Cryst. Solids 122, 59 (1990).
- [22] T. Miyakawa and D. L. Dexter, Phys. Rev. B 1 (7), 2961 (1970).
- [23] W. T. Carnall, P. R. Fields and K. Rajnak, J. Chem. Phys. 49, 4450 (1968).

Chapter 3

Compositional dependence of up-conversion luminescence of Er³⁺ in ZrF₄-based glass systems II. Alkaline-earth metal dependence

3.1 INTRODUCTION

The conversion of infrared radiation to shorter wavelengths, *i.e.*, frequency up-conversion, by rare-earth-doped glasses presently receives a great interest since there is a need for higher density optical data storage and the development of near-infrared diode lasers has made the up-conversion pumping of rare-earth system possible. Among various glass systems, heavy-metal fluoride glasses are considered to be the best candidate as hosts for efficient up-conversion phosphors and lasers. This is because the maximum phonon frequencies of heavy-metal fluoride glasses are so small that the non-radiative loss due to multi-phonon relaxation can be substantially reduced[1]. Until now, frequency up-conversion phenomena have been intensively examined on heavy-metal fluoride glasses[2-5]. Although compositional dependence of up-conversion luminescence in these heavy-metal fluoride glasses is an important subject for attaining high up-conversion efficiency, there are very few papers in which such investigations have been reported[6].

The author and co-workers are advancing a series of experiments to show

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how the up-conversion luminescence of Er^{3+} in fluoride glasses is affected by the kinds and quantities of glass-constituents. The effect of glass-modifying alkali fluorides on Er^{3+} up-conversion luminescence has been examined in the 21.25*M*F₂·21.25*L*iF·52.5*Z*rF₄·5*E*rF₃, where *M* is Li, Na, K, Rb or Cs, glasses [7]. Also the difference in Er^{3+} up-conversion luminescence with glass-forming fluorides has been examined in glasses *M*F_n-BaF₂-YF₃, where *M* is Zr, Hf, Al, Ga, In, Sc or Zn[8,9].

In the present Chapter, the compositional dependence of up-conversion luminescence of Er^{3+} on the kind of alkaline-earth ions is investigated in MF_2 -BaF₂-ZrF₄-ErF₃ (M= Mg, Ca, Sr or Ba) glass systems.

3.2 EXPERIMENTAL PROCEDURE

(a) Sample preparation

The glass compositions employed are $5MF_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5LnF_3$, where *M* is Mg, Ca, Sr or Ba, and *Ln* is Er or Eu. The detailed procedure of glass preparation has been described in Chapter 2. From now on glasses of *M*=Mg, Ca, Sr and Ba are abbreviated as the Mg, Ca, Sr and Ba glass. The glass transition temperatures and molar volumes of the glasses are given in Table 3.I.

(b) Spectroscopic measurements

The up-conversion luminescence spectra of Er^{3+} in the $5MF_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5ErF_3$ glasses were measured in the wavelength range from 350 to 780nm with a HITACHI 850 fluorescencephotometer at room temperature, using 802nm radiation from an AlGaAs laser diode (SONY, SLD303XT-22, P=250mW) as the excitation source. In order to permit a quantitative comparison of emission intensities among glasses, the measurement was performed on specimens with the same shape of $5 \times 4 \times 1 \text{mm}^3$ and its surfaces are polished into an optical finish.

The fluorescence and excitation spectra of Eu³⁺ in the glasses were measured with a HITACHI 850 fluorescencephotometer at room temperature, using an Xe lamp as the excitation source. The fluorescence measurements were carried out in the wavelength range from 550 to 650nm by 395nm excitation. The excitation spectra were measured in the wavelength range from 440 to 475nm , monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission at 615nm.

Glass M	T _g (°C)	V _m (cm ³ /mol)
Mg	329	0.028
Ca	302	0.027
Sr	313	0.028
Ва	298	0.027

Table 3.I GLASS TRANSITION TEMPERATURES, T_g , and Molar Volumes, V_m , of $5MF_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5ErF_3$ Glasses

3.2 RESULTS & DISCUSSION

(a) Up-conversion luminescence of Er^{3+}

As an example of up-conversion spectra observed for the glasses, the spectrum of the Mg glass is shown in Fig. 3.1. All the glasses gave four emission bands around 410, 525, 550 and 660nm, being assigned to the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions, respectively. Figure 3.2 shows

the dependence of intensity of the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions on the kind of substituted MF_{2} species, where emission intensity of the Ba glass is represented as unity. The alkaline-earth fluoride dependence of all the emission bands show almost the same behaviors, exhibiting the largest value in the Mg glass, almost the same value in the Ca glass and the Sr glass and the smallest in the Ba glass.

(b) Eu^{3+} fluorescence spectra

The ${}^{5}D_{0}\rightarrow{}^{7}F_{I}$ (J=1 and 2) emission spectra of Eu³⁺ in the Mg, Ca, Sr and Ba glasses are shown in Fig. 3.3 in which the ${}^{5}D_{0}\rightarrow{}^{7}F_{0}$ and ${}^{5}D_{1}\rightarrow{}^{7}F_{3}$ emissions were removed from the deconvolution fitting, as mentioned in Chapter 2. The intensity ratio of the hypersensitive ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$ transition to the ${}^{5}D_{0}\rightarrow{}^{7}F_{1}$ transition, I(0-2)/I(0-1), is shown in Fig. 3.4. The I(0-2)/I(0-1) value indicates the covalency in Eu-F bonding[10]. The intensity ratio changes with the alkaline-earth fluoride species. This change corresponds to the alkaline-earth fluoride dependence of intensity of up-conversion luminescence. The covalency is shown to be effective to the up-conversion efficiency.

(c) Analysis of the phonon sideband

Figure 3.5 shows the excitation spectra of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ in the Mg, Ca, Sr and Ba glasses. The phonon sideband (PSB) associated with the pure electric ${}^{5}D_{2} \leftarrow {}^{7}F_{0}$ transition (PET) is observed in the high energy side of PET. The separation of the PET and PSB peaks by deconvolution was carried out to evaluate the phonon energies and electron-phonon coupling strengths [see Chap. 2]. The obtained phonon energies and electron-phonon coupling strengths are given in Table 3.II. The relative multi-phonon decay rates were calculated from these values for the energy gap across the ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ state of Er³⁺[11]. Figure 3.6 shows the relative multi-phonon decay rates of each glasses, in which the value of the Mg glass is represented as unity. The relative multi-phonon decay

rate increases in the order of the Mg glass, the Cs and Sr glass and the Ba glass. This order corresponds to the order in the phonon energy, implying that, the multi-phonon decay rate is predominantly determined by the phonon energy. This change also corresponds to the alkaline-earth fluoride dependence of intensity of up-conversion luminescence. The multi-phonon relaxation rate around Eu³⁺ is shown to be effective to the up-conversion efficiency.

TABLE 3.2

Phonon Energies, $\hbar\omega$, and Electron-Phonon Coupling Strengths, *g*, Obtained from PSB spectra for $5MF_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5EuF_3$ (*M*=Mg, Ca, Sr or Ba) Glasses

M	ħω (cm ⁻¹)	8
Mg	376	0.021
Ca	384	0.024
Sr	381	0.025
Ва	392	0.023



Figure 3.1 Up-conversion spectra of Er^{3+} in the $5MgF_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5ErF_3$ glass under 802nm excitation.



Figure 3.2 Dependence of intensity of the ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions on the kind of MF_{2} species (M=Mg, Ca, Sr or Ba).



Figure 3.3 ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J= 1 or 2) emission spectra of Eu³⁺ in the Mg, Ca, Sr and Ba glasses.



Figure 3.4 Glass-modifying alkaline-earth fluoride dependence of intensity ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, I(0-2)/I(0-1).



Figure 3.5 Eu³⁺ excitation spectra of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in the $5MF_{2} \cdot 25BaF_{2} \cdot 65ZrF_{4} \cdot 5EuF_{3}$ glasses (M = Mg, Ca, Sr or Ba).



Figure 3.6 Relative multi-phonon decay rate for the energy gap across ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ states of Er³⁺ in 5*M*F₂·25BaF₂·65ZrF₄·5ErF₃ glasses (*M*= Mg, Ca, Sr or Ba), in which the value of the Mg glass is represented as unity.

3.4 CONCLUDING REMARKS

The glass-modifying alkaline-earth fluoride dependence of the up-conversion luminescence of Er^{3+} in $5MF_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5ErF_3$ (*M*=Mg, Ca, Sr or Ba) glasses was investigated to inquire a possibility of the compositional design for fluoride glasses with high up-conversion efficiencies.

Up-conversion luminescence of the glasses by 800nm excitation gave emission bands around 410, 525, 550 and 660nm. The intensities of respective bands depended on the MF_2 species, showing the largest value in the Mg glass, almost the same values in the Ca glass and the Sr glass and the smallest value in the Ba glass. Analyses of the fluorescence and excitation spectra of Eu³⁺ in glasses $5MF_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5EuF_3$ clarified that both the covalency and the multiphonon relaxation are major factors determining in the alkaline-earth fluoride dependence of up-conversion efficiency.
REFERENCES

- [1] S. Tanabe, S. Yoshii, K. Hirao and N. Soga, *Phys. Rev.* B 45, 4620 (1992).
- [2] M. D. Shinn, W. A. Sibley, M. G. Drexhage and R. N. Brown, *Phys. Rev.* B 27 (11), 6635 (1983).
- [3] R. Reisfeld, G. Katz, N. Spector, C. K. Jørgensen, C. Jacoboni and R. De Pape, J. Solid State Chem. 41, 253 (1982).
- [4] R. Reisfeld, E. Greenberg, R. N. Brown, M. G. Drexhage and C. K. Jørgensen, Chem. Phys. Lett. 95 (2), 91 (1983).
- [5] C. K. Jørgensen and B. R. Judd, Mol. Phys. 8, 281 (1964).
- [6] K. Okada, K. Miura, I. Matsuda and T. Yamashita, *Extended Abstr. of 5th Int.* Symp. on Halide Glasses. 146 (1988).
- [7] M. Takahashi, R. Kanno, Y. Kawamoto, S. Tanabe and K. Hirao, J. Non-Cryst. Solids 168, 137 (1994).
- [8] K. Takahara, R. Kanno, Y. Kawamoto, S. Tanabe and K. Hirao, Nippon Kagaku Kaisi 10, 1220 (1992). [in Japanese]
- [9] S. Tanabe, K. Takahara, M. Takahashi and Y. Kawamoto, J. Opt. Sci. Am. B 12, 786 (1995).
- [10] R. D. Peacock, in *Structure and Bonding* (Springer-Verlag, Berlin, 1975) 22, 116.
- [11] T. Miyakawa and D. L. Dexter, Phys. Rev. B 1 (7), 2961 (1970).

Chapter 4

Compositional dependence of up-conversion luminescence of Er³⁺ in ZrF₄-based glass systems III. Anion substitution effect

4.1 INTRODUCTION

The conversion of infrared radiation to shorter wavelengths, i.e., frequency up-conversion, by rare-earth-doped glasses presently receives much interest since the development of near-infrared diode laser has made the up-conversion pumping of rare-earth laser systems possible[1]. Among various glass-forming systems, heavy-metal fluoride glasses are considered to be the best candidates for producing up-conversion luminescence with high emission efficiency. This is because the maximum phonon energies of the glasses are so small that the nonradiative loss due to multi-phonon relaxation can be substantially reduced[2]. Therefore, up-conversion luminescence phenomena have been intensively examined in heavy-metal fluoride glasses[3-8]. Compositional designs for upconversion laser glasses are also an important subject in heavy-metal fluoride glass systems.

This Chapter reports the effect of anion substitution on the up-conversion properties of Er^{3+} in ZrF_4 -based glasses. The glass composition employed was $58ZrF_4$ ·39BaF₂·3ErF₃ in which part of F⁻ ions was replaces by other anions such as Cl⁻, Br⁻, I⁻ and O²⁻ ions.

4.2 EXPERIMENTAL PROCEDURE

The glass composition employed are $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaX_2 \cdot 3LnF_3$, where X is Cl, Br, I or O_{1/2}, and *Ln* is Er or Eu. The x values for the respective Xs are given in Table 4.I, together with the glass transition temperatures, T_g , and densities. High purity reagents ZrF_4 , BaF_2 , $BaCl_2$, $BaBr_2$, BaI_2 , $BaCO_3$, ErF_3 and EuF_3 were used as raw materials. About 4g batches of the raw materials were melted at 700°C for about 20min in Pt crucible under an Ar gas stream. Then the melts were poured into brass molds kept at 100°C. The glasses obtained were annealed at the respective glass transition temperatures determined by a differential thermal analysis. In the sample of O substitution (*i.e.* $BaX_2 = BaO$), small but numerous crystals precipitated in the glass matrices, giving no good quality glasses with high transparency.

x	x	Substituted F (anion%)		T_{g}	Density
		Batch	Analyzed	(C)	(greater)
F	0	0	~0.00	309	4.909
Cl	5	3	1.71	287	4.653
	10	6	3.20	285	4.603
	15	9	5.09	276	4.492
	19	12	6.23	271	4.453
	24	15	7.50	262	4.550
	29	18	8.95	249	4.394
Br	5	3	2.7	297	4.655
	10	6	5.4	287	3.463
Ι	5	3	~0.0		
	10	6	~0.0		
O _{1/2}	2.5	1.5			
	5	3			

TABLE 4.ICOMPOSITIONS AND SOME PROPERTIES OF GLASSES58ZrF₄·(39-x)BaF₂·xBaX₂·3ErF₃ (X : Cl, Br, I or O_{1/2})

Glasses obtained by Cl, Br and I substitution were subjected to X-ray fluorescence analysis to determine the amount of substituted halogen. The analyzed values of Cl, Br and I are given in Table 4.I. Since no significant amounts of I were found to remain in the I substituted glasses, no experiments were performed on these glasses.

Since the Cl and Br substituted glasses were prepared without the fluorination process, the oxygen concentration was analyzed in some of the Cl substituted glasses by using an oxygen and nitrogen analyzer (HORIBA, EMGA-2200). The analyzed oxygen concentrations in glasses of x=0, 15, and 24 were 0.469(18), 0.223(8) and 0.357(16)ppm, respectively. Therefore the oxygen of Cl substituted glasses are concluded to be negligibly small regardless of the amount of Cl substitution.

4.3 **RESULTS & DISCUSSION**

(a) Er^{3+} up-conversion luminescence

The up-conversion luminescence spectra of the $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaX_2 \cdot 3ErF_3$ glasses (X = Cl or Br) are shown in Fig. 4.1. The up-conversion luminescence of Er^{3+} were observed at about 525 and 550nm, due to the ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$, and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions, respectively, and at 660nm due to the ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. A faint emission band was observed at about 410nm, corresponding to the ${}^2H_{9/2} \rightarrow {}^4I_{15/2}$ transition. Peak wavelengths of these emission bands were almost the same in all the Cl or Br substituted glasses.

Figure 4.2 shows the up-conversion emission intensities of the green color (525 and 550nm) and red color (660nm) bands. The following three features can be seen in Figure: (1) The magnitude of the change in the emission intensities with anion substitution is much more remarkable for the CI substituted glass than for the Br substituted glasses. (2) In the CI substituted glasses, the emission intensities of both green and red bands become larger with substitution, although

substitution beyond about 6 anion% leads to a reduction of the emission intensities. (3) In the Br substituted glasses, the emission intensity of the green color slightly increases with substitution, while that of the red band remains almost unchanged.

(b) Anion coordination environment around Eu^{3+}

The fluorescence spectra of Eu³⁺ in the 58ZrF₄·(39-*x*)BaF₂·*x*BaCl₂·3EuF₃ glasses are shown in Fig. 4.3. In the luminescence spectral bands, the ${}^5D_0 \rightarrow {}^7F_2$ emission band is hypersensitive transition, depending largely on the covalency in the Eu-X (X:F or Cl) bonding. While the ${}^5D_0 \rightarrow {}^7F_1$ emission band is due to the magnetic-dipole transition, of which the strength is independent of a local structure. Therefore, the ratio of the ${}^5D_0 \rightarrow {}^7F_2$ to ${}^5D_0 \rightarrow {}^7F_1$ emission intensities, I(0-2)/I(0-1), gives information about the covalency[9].

In the emission spectra of Eu³⁺ observed for the $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses, the ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_1 \rightarrow {}^7F_3$ emission bands overlap each other, as can be seen from the assignment given in Fig. 4.3. Thus the deconvolution of each band was necessary in order to calculate the ratio of the ${}^5D_0 \rightarrow {}^7F_2$ to ${}^5D_0 \rightarrow {}^7F_1$ emission intensities. The band deconvolution was performed using a curve fitting program of the least square method [see Chap. 2]. The ${}^5D_0 \rightarrow {}^7F_1$ bands obtained for all the Cl substituted glasses by convolution fitting are shown by dotted lines of open circles in Fig. 4.3, together with the ${}^5D_0 \rightarrow {}^7F_2$ bands.

Figure 4.4 shows the I(0-2)/I(0-1) values in the $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses as a function of the analyzed amount of the Cl⁻. The compositional dependence of the I(0-2)/I(0-1) values clearly indicates that the covalency around Eu^{3+} increases with an increase of the substituted Cl amount. Since the Er^{3+} and Eu^{3+} ions can be considered to be chemically equivalent and thus to play almost the same role in the glasses, the anion coordination environments of Er^{3+} are presumed to be the same as those of Eu^{3+} .





Figure 4.1 Up-conversion luminescence spectra of the $58ZrF_4$ ·(39-x)BaF₂· xBaX₂·3ErF₃ glasses (X= Cl or Br); (a) X=Cl and (b) X=Br.



Figure 4.2 Dependence of up-conversion emission intensity of the green color region $({}^{2}H_{9/2} + {}^{4}S_{3/2} \rightarrow {}^{4}l_{15/2})$ and red color region $({}^{4}F_{9/2} \rightarrow {}^{4}l_{15/2})$ on amount of the anion substitution.



Figure 4.3 Fluorescence spectra of Eu^{3+} in the $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses.



Figure 4.4 I(0-2)/I(0-1) values in the $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses as a function of the analyzed amount of the Cl⁻.

The increasing tendency of up-conversion intensities can be ascribed to the increased probabilities of *f*-*f* transitions in the up-conversion process with successive substitution of the Cl⁻ ions for the F⁻ ions around Er^{3+} ions. In actual, however, the up-conversion luminescence intensities were reduced in the Cl substitution beyond about 6 anion%, as seen in Fig. 4.2. Accordingly there must be other factors by which up-conversion luminescence intensities are reduced with the Cl substitution.

(c) Multi-phonon decay rate

According to the Miyakawa-Dexter equation[10], the non-radiative decay rate due to the multi-phonon emission is governed by the phonon energy and electron-phonon coupling strength. The larger the phonon energy and electronphonon coupling strength results in the larger non-radiative decay rate. Consequently an increase in phonon energy and electron-phonon coupling strength reduces the lifetime and quantum efficiency of excited levels, and reduces the emission intensity of up-conversion luminescence.

The excitation spectra of ${}^{5}D_{2} \leftarrow {}^{7}F_{0}$ transition obtained for $58\text{Zr}F_{4} \cdot (39\text{-}x)\text{Ba}F_{2} \cdot x\text{Ba}\text{Cl}_{2} \cdot 3\text{Eu}\text{F}_{3}$ glasses are shown in Fig. 4.5. One can see that the phonon sideband (PSB) associated with the ${}^{5}D_{2} \leftarrow {}^{7}F_{0}$ transition overlaps closely with the pure electronic transition (PET). The deconvolution of the PSB from the PET was attempt for the Cl-substituted glasses of x=0, 10, 19 and 29. The PSB spectra of the glasses are shown in Fig. 4.6. The phonon energies and the electron-phonon coupling strengths obtained from extracted PSB spectra are given in Table 4.II. The phonon energy becomes considerably higher with the successive substitution. The multi-phonon relaxation rates for the energy gap across the ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ states of Er^{3+} was calculated by using the Miyakawa-Dexter's equation. Figure 4.8 shows the relative multi-phonon relaxation rate of excited 4f-electrons increases with the increasing amount of the anion substitution.

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Figure 4.5 Excitation spectra of ${}^{5}D_{2} \leftarrow {}^{7}F_{0}$ transition of Eu³⁺ in $58ZrF_{4} \cdot (39-x)BaF_{2} \cdot xBaCl_{2} \cdot 3EuF_{3}$ glasses.



Figure 4.6 Phonon sideband spectra of the $58ZrF_4$ ·(39-x)BaF₂·xBaCl₂·3EuF₃ glasses (x = 0, 10, 19 or 29) extracted from the excitation spectra of ${}^{5}D_{2}$ ← ${}^{7}F_{0}$ transition of Eu³⁺.



Figure 4.7 Relative multi-phonon relaxation rates for the energy gap across the ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ state of Er^{3+} , as a function of the amount of anion substitution (analyzed value).

Phonon Energies, $\hbar\omega$, and Electron-Phonon Coupling Strengths, g, Obtained from PSB Spectra of $58ZrF_4$ ·(39-x)BaF₂·xBaCl₂·3EuF₃ Glasses

Substituted F in Batch (anion%)	ስ <i>ω</i> (cm ⁻¹)	8
0	375	0.0058
6	395	0.0072
12	425	0.0072
18	435	0.0074

Such a dependence of the nonradiative decay rate on the Cl substitution amount implies that the up-conversion efficiency in the $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses decreases with the successive anion substitution. On the other hand, the Cl substitution gains the transition probability of a *f-f* transitions in up-conversion process. These two antithetical effects can explain the results shown in Fig. 4.2, in which the up-conversion intensity exhibits a maximum value at the Cl substitution of 6 anion% in the $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses.

4.4 CONCLUDING REMARKS

The effect of anion substitution on the up-conversion luminescence properties of Er³⁺ in ZrF₄-based glasses was investigated by substituting a part of the F⁻ ions in the 58ZrF₄·39BaF₂·3ErF₃ composition by Cl⁻, Br⁻, I⁻ and O²⁻ ions. The up-conversion luminescence of Er³⁺ in the glasses, which was measured by 800nm excitation of a 250mW power, gave three intense emissions around 525, 550 and 660nm, and a faint emission around 410nm. The substitution was possible only for the Cl⁻ and Br⁻ ions and the substitution ranges for the respective ions were 0~8.95 and 0~5.4 in anion%. The substitution effect on emission intensity is much more prominent in the Cl substitution than in the Br substitution. The emission intensities of the Cl substituted glasses are largely increased by the substitution, exhibiting a maximum value around 6 anion%. To investigate the local environment around Er³⁺, the emission and the phonon sideband spectra were measured for the Cl substituted glasses doped with Eu³⁺ instead of Er³⁺. The Cl substitution was found to cause the following two changes for the glasses: An increased the covalency in Eu-X (X: F or Cl) bonding, which rises the transition probabilities of up-conversion transitions and an increase in the

phonon energy, which increases the non-radiative decay rate due to multiphonon relaxation. The Cl substitution dependence of up-conversion emission intensity was deduced to be due to the competition of these two factors. The present study conclude that the substitution of Cl⁻ for a small amount of F⁻ in ZrF_4 -based glasses is highly effective for enhancing the up-conversion luminescence of Er^{3+} .

REFERENCES

- [1] E. Snitzer, J. Less-Common Metals 148, 45 (1989).
- [2] S. Tanabe, S. Yoshii, K. Hirao and N. Soga, Phys. Rev. B 45(9), 186 (1992).
- [3] R. S. Quimby and B. Zheng, Appl. Phys. Lett. 60(9), 1055 (1992).
- [4] B. Monie, A. Brenier and C. Pedrine, IEEE J. Quantum Electron. 25, 88 (1989).
- [5] D. C. Yeh, W. A. Sibley, M. Suscavage and M. G. Drexhage, J. Appl. Phys. 62, 266 (1987).
- [6] G. Özen, J-P. Denis, M. Genotelle and F. Pellé, J. Phys.: Condens. Matter 7, 4325 (1995).
- [7] J. N. Carter, R. G. Smart, A. C. Trooper and D. C. Hanna, J. Non-Cryst. Solids 140, 10 (1992).
- [8] A. S. L. Gomes and Cid. B. de Araúde, J. Lumin. 48-49, 876 (1991).
- [9] R. D. Peacock, in *Structure and Bonding* (Springer-Verlag, berlin), 22, 116 (1975).
- [10] T. Miyakawa and D. L. Dexter, *Phys. Rev.* **B** 1 (7), 2961 (1970).

Chapter 5

Local structure around Zr^{4+} in ZrF_4 -Ba F_2 -Ba Cl_2 -Eu F_3 glass system

5.1 INTRODUCTION

Heavy-metal fluoride glasses, which are represented by fluorozirconate glasses, have received much attention because of potentiality of their practical application to various active optical functional materials[1-3]. The potentiality is originated from peculiar properties of the glasses, e.g. optical transparency ranging from the middle infrared to the near ultraviolet, low light-transmission losses, low phonon energies, and stable incorporation of rare-earth ions available for generating active optical functions. Host materials for these optical devices are centered in ZrF₄-based glass system, because of its high glass forming ability.

As a host matrix of these optical devices, chloro-fluorozirconate glasses have several unique characteristics. The introduction of chlorine into fluorozirconate glasses increases the refractive index, and a fiber optics with a fluoride clad / chloro-fluoride core exhibit an increased numerical aperture with extended infrared transmission[4]. There are several studies about the structures of chlorofluorozirconate glasses; Almeida *et al.* have deduced the local structure of ZrF₄-BaF₂-BaCl₂ glass by measuring Raman and IR spectra[5]. Elyamani *et al.* have reported some optical and physical properties of multi-component chlorofluorozirconate glasses[4]. Recently, Inoue *et al.* have examined the structure of fluoride glass containing chloride ions by means of computer simulation and X-ray diffraction[6]. These studies have suggested that ZrClF polyhedra are present, and that Zr-Cl bonds bring some unique characteristics to the chloro-fluorozir-conate glasses. I have also reported the local structure of ZrF_4 -BaF₂-BaCl₂-EuF₃ system glasses produced by molecular dynamics simulation[7]. Our simulation results revealed that the local structure around Zr^{4+} is hardly influenced by anion substitution of Cl for F, but the network connectivity of ZrF polyhedra is slightly influenced by the introduction of Cl⁻ ions. The Zr-Cl bonds were hardly observed in our simulation glass of which the anion ratio, [Cl]/([F]+[Cl]), is below 0.1.

EXAFS spectroscopy is one of the most powerful method to examine the local structure around glass-constituent ions. For fluorozirconate glasses, several studies using EXAFS spectroscopy have reported for some glass-constituent ions such as Zr^{4+} , Ba^{2+} and so on[8-11]. However no EXAFS analysis has been carried out for Zr^{4+} in chloro-fluoride glass system. This Chapter presents the local structure around Zr^{4+} in ZrF_4 -BaF₂-BaCl₂-EuF₃ glass systems by using Zr K-EXAFS, Raman scattering, and IR absorption spectroscopies.

5.2 EXPERIMENTAL PROCEDURE

(a) Sample preparation

Glass compositions employed are $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ (x = 0, 5, 10, 15, 19, 24, and 29). High-purity fluorides were used as the starting materials. Batches were mixed and melted in a Pt crucible at 700°C for 15 minutes under an Ar gas atmosphere and quenched into brass mold preheated about 100°C. The glasses obtained were annealed at the respective glass transition temperatures determined by a differential thermal analysis. The accurate Cl contents of the prepared glasses were determined by an X-ray fluorescence analysis. The molar volumes of the glasses were obtained by the density measurement with an Archimedean method. The refractive indexes were measured with an Abbe refractometer. From now on the x=0, 5, 10, 15, 19, 24, and 29 glasses are abbreviated as 0Cl, 3Cl, 6Cl, 9Cl, 12Cl, 15Cl, and 18Cl, respectively, in terms of the anion ratio of [Cl] to ([F]+[Cl]) in batch composition, *i.e.* 0, 3, 6, 9, 12, 15, 18%.

The analyzed Cl contents of the prepared $58ZrF_4$ ·(39-*x*)BaF₂·*x*BaCl₂·3EuF₃ glasses (*x*=0, 5, 10, 15, 19, 24, and 29) are given as the Cl/(F+Cl) values in Table 5.I, together with the refractive indexes, the glass transition temperatures and the molar volumes. The analyzed Cl contents were proportional to the Cl contents in batch composition. The glass transition temperatures decreased and the refractive indexes and molar volumes increased in proportional to the substituted Cl amounts. The respective tendencies were in agreement with previous study[4].

Cl Contents, Cl/(F+Cl), GLASS TRANSITION TEMPERATURES, T_g , Refractive Indexes, n, and Molar Volumes, V_m , of $58ZrF_4$ ·(39-x)BaF₂·xBaCl₂· $3EuF_3$ GLASSES

TABLE 5.I

Glass		Cl/(Cl+F) (anion%)		n	T. (°C)	$V_{\rm cm^3/mol}$
x	Notation	Batch	Analyzed	71	1 g (C)	
0	0Cl	0	0.00	1.5241	309	0.0273
5	3Cl	3	1.71	1.5320	287	0.0267
10	6Cl	6	3.20	1.5435	285	0.0262
15	9Cl	9	5.09	1.5507	276	0.0254
19	12Cl	12	6.23	1.5615	271	0.0249
24	15Cl	15	7.50	1.5665	262	0.0247
29	18Cl	18	8.95	1.5695	249	0.0242

(b) Zr K-EXAFS measurements

Zr K-EXAFS experiments were performed on the 0Cl ~ 18Cl glasses at the EXAFS facilities of a beam line 10B at the Photon Factory in The National Laboratory for High Energy Physics. The measurements were carried out in the transmission mode using synchrotron radiation from the storage ring running at 2.5GeV with a beam current near 250mA. All data were taken for the powder samples which were well-dispersed in the polyethylene pellet. I_0 and I were measured using ionization chambers of 17cm and 31cm long, respectively. The spectra of Zr K-edges were obtained by using Si(311) crystal monochromator.

(c) Vibration spectral measurements

Raman scattering measurements were carried out at 5cm⁻¹ resolution with a JEOL JRS-400D spectrometer, using the 488.0nm line of an Ar⁺ gas laser. The measurements were made on the 0Cl, 6Cl, 12Cl, and 18Cl glasses. IR absorption measurements were made on the 0Cl, 6Cl, 12Cl, and 18Cl glasses in the resolution of 4cm⁻¹ with a Perkin-Elmer FT-IR 1760, using the polyethylene pellet technique.

5.3 RESULTS

(a) Zr K-EXAFS analysis

The normalized X-ray absorption spectrum of glass 0Cl is shown in Figure 5.1. The Zr K-EXAFS oscillation, $k^3\chi(k)$, of 0Cl is shown in Figure 5.2. The $k^3\chi(k)$ curves were analyzed by using a "XASANAL" program[12]. Fourier transformation of $k^3\chi(k)$ was performed in the *k* range of 3.8 to 14.5Å⁻¹ to obtain the Fourier transform magnitude, $|\phi(r)|$. The obtained $|\phi(r)|$ curves are shown in Figure 5.3. Fourier backfiltering was conducted in the *r* range of 1.8 to 2.3Å and then the curve fitting of $k^3\chi(k)$ was made in the *k* region of 5.0 to 13.5Å⁻¹ by employing a one shell model where only F⁻ ions are scattering ions. The phase shift and backscattering amplitude values required in curve fitting were determined by simulation of the 0Cl glass using 2.10Å and 7.08 for Zr-F interatomic distance and F coordination number of Zr, respectively, those were obtained by a previous Xray diffraction study[13]. The features of curve fitting for the 0Cl glass is shown in Figure 5.4.

The obtained Zr^{4+} -anion interionic distance, anion coordination number of Zr^{4+} , and Debye-Waller factors in glasses 0Cl ~ 18Cl are summarized in Table 5.II

TABLE 5.II INTERIONIC DISTANCES, r_{Zr-F} , ANION COORDINATION NUMBERS OF Zr^{4+} , CN, and Debye-Waller Factors, σ , in 58ZrF₄·(39-x)BaF₂·xBaCl₂·3EuF₃ Glasses

Glass	r _{Zr-F} (Å)	СN	σ (Å ²)
0Cl	2.110 ^a	7.08 ^b	0.077
3Cl	2.108	6.59	0.077
6C1	2.108	6.87	0.080
9Cl	2.107	6.46	0.076
12Cl	2.107	6.46	0.080
15Cl	2.105	7.23	0.083
18Cl	2.104	6.46	0.078

^{a, b} Obtained by X-ray diffraction [13]



Figure 5.1 Normalized X-ray absorption spectrum of Zr K-edge in glass 0Cl.



Figure 5.2 Zr K-EXAFS oscillation, $k^{3}\chi(k)$, of glass 0Cl.



Figure 5.3 $|\phi(r)|$ curves of glasses.



Figure 5.4 Feature of curve fitting for glass 0Cl.

(b) Raman scattering spectra

The Raman scattering spectra of glasses 0Cl, 6Cl, 12Cl, and 18Cl are shown in Figure 5.5. Each glass gave a intense scattering peak which locates at around 580cm⁻¹. The accurate peak positions of the respective glasses are given in Table 5.III.

(c) IR absorption spectra

The IR absorption spectra of glasses 0Cl, 6Cl, 12Cl, and 18Cl are shown in Figure 5.6. The strong and weak absorption bands, which locate at about 500 and about 260cm⁻¹, respectively, are observed in all the spectra. The accurate band positions of the 0Cl, 6Cl, 12Cl, and 18Cl glasses are given in Table 5.III.



Figure 5.5 Raman scattering spectra of glasses 0Cl, 6Cl, 12Cl, and 18Cl.



Figure 5.6 IR absorption spectra of glasses 0Cl, 6Cl, 12Cl, and 18Cl.

Glass	Raman (cm ⁻¹)	IR (cm ⁻¹)	
0C1	575	493	
6Cl	578	496	
12Cl	574	505	
18Cl	579	514	

Table 5.III Raman Scattering and IR Absorption Bands of $58ZrF_4$ ·(39-x)BaF₂·xBaCl₂·3EuF₃ Glasses

5.4 DISCUSSION

Figure 5.7 shows the Zr K-XANES spectra of glasses. All spectra have similar profiles, and no major differences were detected between pure fluoride glass, 0Cl, and the other chloro-fluoride glasses. This fact qualitatively suggests that the anion coordination structure around Zr in fluorozirconate glasses containing chloride ions is almost the same as that in pure fluoride glass, 0Cl.

The $|\phi(r)|$ curves obtained by Fourier transformation of $k^3\chi(k)$ give radial distribution of the nearest-neighboring anions around Zr^{4+} . As can be seen from Figure 5.3, prominent peaks due to the Zr^{4+} -anion pairs locate at around 2.1Å regardless of the Cl content and, in addition, all the $|\phi(r)|$ curve profiles are almost the same. Here the following fact should be noted: Curve fitting of $k^3\chi(k)$ was attempted by employing a two-shell model that both F⁻ ions and Cl⁻ ions are

scattering ions, but the calculations were impossible for all glasses because of divergence. These facts indirectly indicate that most of the Cl⁻ ions in $58ZrF_4$ ·(39-x)BaF₂·xBaCl₂· $3EuF_3$ glasses take no part in the anion coordination to Zr^{4+} ions, and most of the Zr^{4+} ions are coordinated by F⁻ ions alone. Therefore, the Zr^{4+} - anion interionic distance and the anion coordination number of Zr^{4+} [see Table 5.II] mean the Zr^{4+} -F⁻ interionic distance, r_{Zr-F} , and the F⁻ coordination number of Zr^{4+} .

Figure 5.8 shows the r_{Zr-F} values plotted against the Cl/(F+Cl) values. As seen from the figure, r_{Zr-F} tends to slightly decrease with increasing Cl/(F+Cl) values, although such a slight decrease should be considered to be within experimental error.

The Raman bands around 580cm⁻¹ and the IR bands around 500cm⁻¹ have been assigned to the totally symmetric stretching vibration, v^{s} , and antisymmetric stretching vibration, v^{as} , of ZrF polyhedra[14,15]. As given in Table 5.III, the v^{s} frequencies remain almost unchanged in spite of the successive Cl substitution, while the v^{as} frequencies shift from 493cm⁻¹ for the 0Cl glass to 514cm⁻¹ for the 18Cl glass. From a quantum mechanical point of view, vibrations in which the dipole moment of molecules is changed are IR active and those in which the polarizability of molecule is changed are Raman active. The Raman scattering and IR absorption spectra observed for the $58ZrF_{4} \cdot (39-x)BaF_{2} \cdot xBaCl_{2} \cdot$ $3EuF_{3}$ glasses suggest that the r_{Zr-F} and CN values are almost unchanged with the Cl substitution, but the F⁻ coordination configurations around Zr^{4+} are slightly changed, causing an IR active vibration mode to shift to higher frequencies.

Finally it is concluded that, when the F⁻ ions in $58ZrF_4 \cdot 39BaF_2 \cdot 3EuF_3$ glasses were partly substituted by Cl⁻ ions, the F⁻ ions placing in the ZrF polyhedra are hardly replaced by the Cl⁻ ions, though slight amounts of replacement is not ruled out. In other words, it is presumed that the F⁻ ions participating in the Eu-F-Ba and Ba-F-Ba linkages are preferentially replaced by the Cl⁻ ions.



Figure 5.7 Zr K-XANES spectra of glasses.



Figure 5.8 Interatomic distances, r_{Zr-F} , as a function of Cl/(F+Cl) values.

5.5 CONCLUDING REMARKS

The anion coordination environments around Zr^{4+} in ZrF_4 -BaF₂-BaCl₂-EuF₃ glass system were investigated by choosing $58ZrF_4$ ·(39-*x*)BaF₂·*x*BaCl₂·3EuF₃ compositions. The Zr K-EXAFS, Raman scattering, and IR absorption spectroscopic experiments on the glasses revealed that the successive substitution of Cl for F hardly changes the anion coordination environments around Zr^{4+} .

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REFERENCES

- [1] R. S. Quimby, in *Fluoride Glass Fiber Optics* edited by I. D. Aggarwal & G. Lu (Academic Press, San Diego, 1991) p. 351.
- Y. Ohishi, T. Kanamori, M. Shimizu, M. Yamada, Y. Terunuma, J. Temmyo, M. Wada, and S. Sudo, *IECE Trans. Commun.* E77-B(4), 421 (1994).
- [3] M. Poulain, in *Fluoride Glasses* edited by A. E. Comyns (John Wiley & Sons, Chichester, 1989) p. 11.
- [4] A. Elyamani, M. Poulain, S. J. Saggese and G. H. Sigel Jr., J. Non-Cryst. Solids 119, 187 (1990).
- [5] R. M. Almeida and J. D. Mackenzie, J. Chem. Phys. 74, 5954 (1981).
- [6] H. Inoue, K. Soga and A. Makishima, Phys. Chem. Glasses 36, 1 (1995).
- [7] M. Takahashi, R. Yamamoto, R. Kanno and Y. Kawamoto, J. Phys.: Condens. Matter 7, 4583 (1995).
- [8] Y. Kawamoto, R. Kanno, Y. Umetani, K. Tohji and H. Morikawa, Solid State Ionics 44, 181 (1991).
- [9] Y. Kawamoto, R. Kanno and Y. Umetani, Mat. Res. Bull. 26, 1077 (1991).
- [10] R. M. Almeida, M. I. Marques de Barros and M. C. Gonçalves, J. Non-Cryst. Solids 168, 144 (1994).
- [11] W. Wen-cai, C. Yu and H. Tian-dou, J. Non-Cryst. Solids 152, 172 (1993).
- [12] H. Sakane, Ph.D Thesis (Osaka University, 1991).
- [13] R. Coupé, D. Louër, J. Lucas and A. Léonard, J. Am. Ceram. Soc. 66, 527 (1983).
- [14] Y. Kawamoto, Phys. Chem. Glasses 25, 88 (1984).
- [15] R. M. Almeida and J. D. Mackenzie, J. Chem. Phys. 74, 5954 (1981).

Chapter 6

Local environment around Eu³⁺ in ZrF₄-BaF₂-BaCl₂-EuF₃ glass system

6.1 INTRODUCTION

It is widely known that optical characteristics of rare-earth ions doped in glasses are affected by the structures and compositions of host glass. A number of studies have already been made on structures of rare-earth-doped fluoride glasses and local environments around rare-earth ions by means of X-ray or neutron diffraction techniques[1], EXAFS spectroscopies[2,3], fluorescence line narrowing (FLN) techniques[4] and molecular dynamics (MD) simulations[5,6]. The fluorescence properties and local environments of Eu³⁺ ions in several glass systems have been reported by using FLN and MD techniques[7-10]. However, there are only a few studies which treat a chemical bonding-states of rare-earth ions in rare-earth-doped fluoride glasses[11].

Mössbauer spectroscopy provides useful information on characterizing the valence state and coordination environments around cations in glasses[12]. Europium is one of the appropriate element in respect to clarifying the electron charge density at nucleus. The ¹⁵¹Eu resonance has previously been observed for Eu³⁺ in several oxide and fluoride glasses[13-16]. Trivalent europium is also the

most suitable element among rare earths to evaluate the changes in fluorescence characteristics because its electronic levels are quite simple[17].

In Chapter 5, I have reported about the local structure around Zr^{4+} in the Eu^{3+} -doped ZrF_4 -BaF₂-BaCl₂ glass system. EXAFS analysis clarified that the local structure around Zr^{4+} in the chloro-fluorozirconate glass system is hardly influenced by the Cl⁻ substitution.

In this Chapter, local environments around Eu^{3+} are investigated for Eu^{3+} doped ZrF₄-BaF₂-BaCl₂ glass system. The ¹⁵¹Eu Mössbauer and Eu^{3+} fluorescence spectra were measured to examine the changes on the chemical bonding-states and *f-f* transition properties of Eu^{3+} with successive Cl⁻ substitution for F⁻. Electron densities at nucleus are discussed by calculating the isomer shifts determined from the recoilless resonance absorption spectra of ¹⁵¹Eu. Ligand field strength, inhomogeneous linewidth and intensity of hypersensitive transition of Eu^{3+} are clarified by analyzing Eu^{3+} fluorescence spectra.

5.2 EXPERIMENTAL PROCEDURE

(a) Sample preparation

Glass compositions employed are $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ (x = 0, 5, 10, 15, 19, 24, and 29). High-purity fluorides were used as the starting materials. Batches were mixed and melted in a Pt crucible at 700°C for 15 minutes under an Ar gas atmosphere and quenched into brass mold preheated about 100°C, as describes in Chapter 5. The glasses obtained were annealed at the respective glass transition temperatures determined by a differential thermal analysis. The accurate Cl contents of the prepared glasses were determined by an X-ray fluorescence analysis. The molar volumes of the glasses were obtained by the density measurement with an Archimedean method. The refractive indexes were measured with an Abbe refractometer. Hereafter the x=0, 5, 10, 15, 19, 24, and 29

glasses are abbreviated as 0Cl, 3Cl, 6Cl, 9Cl, 12Cl, 15Cl, and 18Cl, respectively, in terms of the anion ratio of Cl to (F+Cl) in batch composition, *i.e.* 0, 3, 6, 9, 12, 15, 18%.

The analyzed Cl contents of the prepared $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses (*x*=0, 5, 10, 15, 19, 24, and 29) are given as the Cl/(F+Cl) values in Table 5.I in Chapter 5, together with the refractive indexes, the glass transition temperatures and the molar volumes. The analyzed Cl contents were proportional to the Cl contents in batch composition. The glass transition temperature decreased, and the refractive index and molar volume increased in proportional to the substituted Cl amounts.

(b) Spectroscopic measurements

Emission spectra were measured with a HITACHI F-3010 fluorescence spectrophotometer. The fluorescence spectra of Eu^{3+} were measured with the wavelength range from 550 to 650nm under 395nm excitation.

Room-temperature Mössbauer measurements were recorded in transmission geometry. A 0.93GBq 151 Sm₂O₃ source was used. The velocity range of the spectrometer was set between -18mm/s and 18mm/s. The velocity scale was calibrated with the magnetic hyperfine spectrum of α -Fe using a 57 Co source. The zero velocity was taken as the absorption of 151 Eu in crystalline EuF₃. Measurements were made on the 0Cl, 6Cl, 12Cl and 15Cl glasses.

5.3 **RESULTS & DISCUSSIONS**

(a) ¹⁵¹Eu-Mössbauer spectra

Isomer shift, δ , and quadropole interaction, QI, determined from ¹⁵¹Eu-Mössbauer measurements are in proportion to the *s*-electron density and electric

field gradient at ¹⁵¹Eu-nucleus, respectively[12]. That is, the δ and QI values represent the covalency and symmetry of ligand field around Eu. Figure 6.1 shows the ¹⁵¹Eu-Mössbauer spectra of 0Cl, 6Cl, 12Cl and 15Cl and crystalline EuF₃. The respective ¹⁵¹Eu-Mössbauer spectra consists of a broadened resonance line. The positions of the absorption line revealed that Eu in the present chlorofluorozirconate glasses exists only as the +3 oxidation state. No trace of Eu^{2+} was observed in measurements. The fine structure of QI was hardly detected because of large linewidth. The peak position and the linewidth at half maximum of peak, FWHM, were calculated by employing a least square fitting program of the Lorentz function. The isomer shift of ¹⁵¹Eu³⁺ was determined from the center shift of the peak with respect to crystalline EuF₃. The calculated isomer shifts and FWHMs of resonant peaks are given in Table 6.I. Although vitreous materials generally give broadened-linewidths compared with crystalline materials because of structural variation of ions from site to site, the FWHMs of ¹⁵¹Eu resonance absorption in chloro-fluorozirconate glasses are smaller than that in crystalline EuF_3 . This suggests that the quadropole interactions of ${}^{151}Eu^{3+}$ in these glasses are smaller than that in crystalline EuF₃. Crystal structure of EuF₃ is LaF₃ (tysonite) type, which has three kinds of nonequivalent anions. In the case of LaF₃, the neighbors of La comprise of 7F at 2.42-2.48Å, 2F at 2.64Å and 2F at 3.00Å[18]. The large FWHM value in crystalline EuF₃ suggests that the asymmetric lattice contributes to the electric field gradient. This implies that the anion coordination polyhedra of Eu³⁺ in chloro-fluorozirconate glasses have higher symmetry than that in crystalline EuF₃.

Figure 6.2 shows changes in isomer shift, δ , with the substituted Cl⁻ amount, Cl/(F+Cl). The δ value increases with increasing Cl/(F+Cl). An increase of δ value can be attributed to larger participation of 6*s*-electrons to covalent bonds. The δ value of crystalline EuCl₃ is 0.3 mm/s with respect to EuF₃[19]. The difference in δ value between EuF₃ and EuCl₃ arises from a difference in bond character. The covalency in Eu-Cl bond is much larger than that in Eu-F bond. Therefore an increase in isomer shifts with increasing amount of Cl⁻ substitution means an increase in number of covalent Eu-Cl bond around Eu³⁺.

TABLE 6.I

Isomer Shifts, δ , and Linewidths At Half Maximum, FWHM, in Mössbauer Spectra of Glasses 0Cl, 6Cl, 12Cl and 15Cl, and Crystalline EuF₃

glass	δ (mm/s)	FWHM (mm/s)
0C1	-0.154	1.81
6C1	-0.082	1.47
12Cl	-0.033	1.57
15Cl	-0.016	1.48
EuF ₃	0	2.73


Figure 6.1 ¹⁵¹Eu-Mössbauer spectra of glasses 0Cl, 6Cl, 12Cl and 15Cl and crystalline EuF₃. The solid lines represent the fitted curves.



Figure 6.2 Isomer shift, δ , plotted as a function of substituted Cl⁻ amount, Cl/(F+Cl).

(b) Hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition

The intensity of most *f-f* transitions of trivalent rare-earth ions are little affected by the local environment of the ions. A few transitions, however, are very sensitive to the ion's local environments, so that these transitions are called hypersensitive transitions[20]. In the observable emission bands of Eu^{3+} , the emission line due to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is the hypersensitive transition, being sensitive to the local environment around Eu³⁺. The emission spectra of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in chloro-fluorozirconate glasses are shown in Fig. 6.3 (a), together with the magnetic dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition of which the intensity is independent on the local environment of Eu³⁺. The Cl⁻ amount, Cl/(F+Cl), dependence of the intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition normalized by that of magnetic dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, I(0-2)/I(0-1), is shown in Fig. 6.3 (b). The emission intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition increases with increasing amount of Cl⁻. Peacock reported that the intensity of hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition depends on [21]: (1) Occurrence of very small deviation from inversion symmetry causes large intensity. (2) In the same structure of ligand, the intensity changes in the order: I⁻ $>Br^>Cl^>H_2O>F^-$. (3) Hypersensitivity is proportional to the nephelauxetic ratio and to covalency. Although quite large intensity should be detected with increasing the deviation, intensity change in ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition with increasing amount of Cl⁻ are not so large in the present chloro-fluorozirconate glasses. Therefore the possibility of deviation from inversion symmetry can be disregarded, and the replacement of Cl^{-} for F^{-} at neighbors of Eu^{3+} appears without large structural changes. Figure 6.4 shows the relationship between normalized emission intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, I(0-2)/I(0-1), and the isomer shift , δ , calculated from Mössbauer spectra. Linear correlation can be seen between both values. This suggests that the intensity of hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition depends on the density of 6s-electrons at Eu nucleus. In other words, the large

intensity of hypersensitive transition is caused by an increase in covalency in $Eu^{3+}-X$ (X: F or Cl). Such a change in chemical bonding is due to the replacement of F⁻ for Cl⁻ at neighbors of Eu^{3+} . Thus, it is concluded that the replacement of Cl⁻ for F⁻ occurs at neighbors of Eu^{3+} without large structural changes, and that the hypersensitive transition appears with large intensity by the Cl⁻ substitution for F⁻.

(c) ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition of Eu^{3+}

According to the Judd-Ofelt theory [22,23], the transitions between the J=0 levels are strictly forbidden. However, the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition in the fluorescence spectra of Eu³⁺ in certain matrices can be observed with extremely low intensity[24-28]. This phenomenon can be explained based on "J-mixing" i.e. the wave functions of $I \neq 0$ state are mixing into the I=0 state by the even parity term of the crystal field[29]. In the present chloro-fluorozirconate glasses, the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition can be seen in the spectra of Eu^{3+} as shown in Fig. 6.5. Therefore the Eu³⁺ ions are placed at the crystal field having the even parity term. The intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition increases with increasing Cl⁻ amount. Tanaka *et al.* have reported that the mixture of the ${}^{7}F_{2}$ state into the ${}^{7}F_{0}$ state through the secondorder term of the crystal field potential plays a dominant effect in the intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ fluorescence of Eu³⁺ in sodium-borate and sodium-germanate glasses[25]. Figure 6.6 shows the relationship between the intensity ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, I(0-0)/I(0-1), and that of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, I(0-2)/I(0-1). There is a linear correlation between I(0-0)/I(0-1) and I(0-1)2)/*I*(0-1). Therefore, the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition is shown to be caused by the mixture of ${}^{7}F_{2}$ state into the ${}^{7}F_{0}$ state through the second order term of the crystal field potential.

The ligand field strength around Eu³⁺ and the inhomogeneous linewidth of

Eu³⁺ fluorescence can be estimated from the spectral profiles of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition because both ${}^{5}D_{0}$ and ${}^{7}F_{0}$ states of transition are non-degenerated J=0 levels. The peak position and FWHM of emission line of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition represent the ligand field strength and inhomogeneous linewidth, respectively. Changes in the peak positions of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition with the Cl/(F+Cl) are shown in Fig. 6.7. The ligand field strength around Eu^{3+} decreases with increasing Cl/(F+Cl). This change indicates that the Cl⁻ exists around Eu³⁺. Figure 6.8 shows the FWHMs of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition as a function of the Cl/(F+Cl). It is particularly interesting that the FWHM of emission peak of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition becomes narrower with increasing Cl/(F+Cl). Such trend can be also seen in Mössbauer spectra of ¹⁵¹Eu³⁺ in the present chloro-fluorozirconate glasses. The FWHM of resonance absorption peak [see Fig. 6.1 and Table 6.1] have no shoulder, and the FWHM of glass 18Cl is smaller than that of glass 0Cl. A decrease in inhomogeneous linewidth of fluorescence suggests that the present chloro-fluorozirconate glass system has a potentiality to the rare-earth-doped laser materials because the stimulated emission cross section is inversely proportional to the effective linewidth of the fluorescence line shape[8].



Figure 6.3 (a) Emission spectra of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in glasses 0Cl, 3Cl, 6Cl, 9Cl, 12Cl, 15Cl and 18Cl. (The intensities are normalized by the intensities of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition.),



Figure 6.3 (b) Cl⁻ amount,Cl/(F+Cl), dependence of the intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition normalized by that of magnetic dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, I(0-2)/I(0-1). The contribution of ${}^{5}D_{1} \rightarrow {}^{7}F_{3}$ transition is removed by decomvolution fitting on the calculation as mentioned in Chapter 2.



Figure 6.4 The relationship between the normalized intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, I(0-2)/I(0-1), and the isomer shift, δ . The dotted line is guide for the eye.



Wavelength / nm

Figure 6.5 Emission spectra of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition of Eu³⁺ in glasses 0Cl, 3Cl, 6Cl, 9Cl, 12Cl, 15Cl and 18Cl. (The intensities are normalized by the intensities of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition.)



Figure 6.6 The relationship between the normalized intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, I(0-0)/I(0-1), and that of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, I(0-2)/I(0-1). The solid line is guide for the eye.



Figure 6.7 The variation of the peak position of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition, E(0-0), with the substituted Cl⁻ amount, Cl/(F+Cl). The errors are calculated from the resolution of the spectrophotometer.



Figure 6.8 Relationship between the full width at half maximum of ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition, FWHM(0-0), and the substituted Cl⁻ amount, Cl/(F+Cl).

5.4 CONCLUDING REMARKS

The local environments around Eu^{3+} in ZrF_4 -Ba F_2 -Ba Cl_2 glass system have been examined by means of ¹⁵¹Eu-Mössbauer and Eu^{3+} -fluorescence spectroscopies. The glass composition employed was $58ZrF_4 \cdot (39-x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ (x=0, 5, 10, 15, 19, 24, and 29).

It was found from ¹⁵¹Eu-Mössbauer measurement that the isomer shifts of ¹⁵¹Eu³⁺ decrease with increasing Cl⁻ concentration. Eu³⁺ fluorescence measurements revealed that the ligand field strength around Eu³⁺ and the inhomogeneous linewidth of Eu³⁺ fluorescence decrease, and the intensity of hypersensitive ⁵ $D_0 \rightarrow$ ⁷ F_2 transition increases with increasing the Cl⁻ amount. These experimental results conclude that Cl⁻ substituted for F⁻ are present at neighbors of Eu³⁺, causing no large structural changes.

REFERENCES

- [1] J. Wasylak and L. Samek, J. Non-Cryst. Solids 129, 137 (1991).
- [2] M. A. Marcus and A. Polman, J. Non-Cryst. Solids 136, 260 (1991).
- [3] R. M. Almeida, M. I. de Barros and M. C. Gonçalves, J. Non-Cryst. Solids 168, 144 (1994).
- [4] J. L. Adam, V. Ponçon, J. Lucas and G. Boulon, J. Non-Cryst. Solids 91, 191 (1987).
- [5] S. A. Brawer, and M. J. Weber, J. Chem. Phys. 75, 3522 (1981).
- [6] S. A. Brawer, and M. J. Weber, Phys. Rev. Lett. 45, 460 (1980).
- [7] G. Cormeir, J. A. Capobianco and A. Monteil, J. Non-Cryst. Solids 168, 115 (1994).
- [8] J. A. Capobianco, P. P. Proux, M. Bettinelli and F. Negrisolo, *Phys. Rev.* B 42(10), 5936 (1993).
- [9] G. Cormeir, J. A. Capobianco, C. A. Morrison and A. Monteil, *Phys. Rev.* B 48(22), 16290 (1993).
- [10] K. Soga, M. Uo, A. Makishima and S. Inoue, J. Am. Ceram. Soc. 78(1), 129 (1995).
- [11] S. Tanabe, K. Takahara, M. Takahashi and Y. Kawamoto, J. Opt. Soc. Am. B 22(5), 786 (1995).
- [12] G. J. Long, in Mössbauer Spectroscopy, Applied to Inorganic Chemistry edited by G. J. Long (Plenum Press, New York, 1984), Vol. I, p. 7.
- [13] M. F. Taragin and J. C. Eisenstein, J. Non-Cryst. Solids 11, 395 (1973).
- [14] J. M. D. Coey, A. McEvoy and M. W. Shafer, J. Non-Cryst. Solids 43, 387 (1981).
- [15] S. Tanabe, K. Hirao and N. Soga, J. Non-Cryst. Solids 113, 178 (1989).
- [16] Y. Kawamoto, in Proceedings of Japanese-French Seminar on Inorganic Fluorine Chemistry (Kyoto, 1995) p. 39.
- [17] S. Todoroki, K. Hirao and N. Soga, J. Appl. Phys. 72 (12), 5853 (1992).
- [18] A. F. Wells, in Structural Inorganic Chemistry, Fifth Edition (Clarendon Press, Oxford, 1984) p. 420.

- [19] G. Gerth, P. Kienle and K. Lunchner, Phys. Lett. 27A(17), 557 (1968).
- [20] C. K. Jørgensen and B. R. Judd, Mol. Phys. 8, 281 (1964).
- [21] R. D. Peacock, in *Structure and Bonding* (Springer-Verlag, Berlin, 1975) 22, p.116.
- [22] B. R. Judd, Phys. Rev. 127, 750 (1962).
- [23] G. S. Ofelt, J. Chem. Phys. 37, 551 (1962).
- [24] M. A. Saltzberg and G. C. Farrington, J. Solid State Chem. 83, 272 (1989).
- [25] M. Tanaka and T. Kushida, Phys. Rev. B 52(6), 4171 (1995).
- [26] Y. Nageno, H. Takebe, K. Morinaga and T. Izumitani, J. Non-Cryst. Solids 169, 288 (1994).
- [27] K. Soga, H. Inoue and A. Makishima, J. Lumin. 55, 17 (1993).
- [28] W. C. Nieuwport and G. Blasse, Solid State Commun. 4, 227 (1966).
- [29] M. Tanaka, G. Nishihara and T. Kushida, Phys. Rev. B 49 (24), 16917 (1994).

Chapter 7

Molecular dynamics simulation of ZrF₄-BaF₂-BaCl₂-EuF₃ glass system

7.1 INTRODUCTION

The rare-earth-doped fluoride glasses (RDFG) have unique characteristics; high transmittance from middle-infrared to near-ultraviolet region[1], incorporation of rare-earth elements at high content (up to 30mol%) and low phonon energies[2]. RDFG has wide applications as optical devices such as laser oscillators and optical fiber amplifiers[3-5]. It is widely known that the optical properties of fluorescent ions doped in glasses are greatly affected by structures of the glasshost. Although many experimental studies have already been made on the structures of RDFG[6-10], there are only a few studies which treat the fluorescence properties of rare-earth ions in RDFG in terms of the glass structures except for the following studies; Adam *et al.*[11] investigated the geometries of Eu^{3+} in fluorozirconate glass using site-selective spectroscopy, Todoroki *et al.* [12] reported the relationship between up-conversion luminescence of Er^{3+} and phonon energy around rare-earth ions, and Soga *et al.* [13] studied the fluorescence properties of Eu^{3+} and local phonon modes around Eu^{3+} ions in ZrF₄-based glasses containing Cl⁻. These groups tried to relate the optical properties of RDFG

and its structures.

Recent progress in computer systems makes it possible to investigate the microscopic structures of materials such as fluoride glasses by molecular dynamics (MD) or Monte Carlo (MC) simulation. MD and MC simulations have already been applied to many topics in the materials science field [14-19] and are regarded to be a powerful tool for understanding the microscopic structures and dynamics of materials.

In Chapter 4, I have confirmed from experiments that emission efficiency of rare-earth ions in ZrF_4 glasses which contain a small amount of Cl^- ions as impurities are higher than those in pure ZrF_4 glasses [20]. Elyamani *et al.* reported that the absorption edge shifts to a longer wavelength with increasing amount of substitution of Cl^- for F^- [21]. These findings are particularly of interest because they all suggest that the glass structures are greatly affected by a small amount of Cl^- substitution.

In this chapter, I have performed MD simulations for ZrF_4 -BaF₂-EuF₃ systems to investigate the changes in glass structures with increasing amount of Cl⁻ substitution for F⁻. In particular, the local structures around each cation (Zr^{4+} , Eu^{3+} and Ba^{2+}) are extensively analyzed by calculating the anion coordination numbers around the cation. The power spectra of velocity autocorrelation functions are calculated as well. The substitution of Cl⁻ is carried out up to 10% in total number anions ([Cl]/([Cl]+[F])×100.). This substitution range is within the experimentally obtained glass-forming range by means of a melting method [see Chap. 5 & Chap. 6].

7.2 SIMULATION METHODOLOGY

In the present MD simulations, all ions interact through Busing approximation of the Born-Mayer-Huggins type of potential without any dispersion terms.

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The potential energy (U_{ij}) between ions *i* and *j* is given by

$$U_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + f_0 \left(b_i + b_j \right) \exp \frac{a_i + a_j - r_{ij}}{b_i + b_j},$$
(7.1)

where Z_i is the point charge located on the ion *i*, r_{ij} is the distance between ions *i* and j, $e=1.6022\times10^{-19}$ C and $f_0=6.9472\times10^{-18}$ J. a_i and b_i are the size and softness parameters, which were empirically determined to reproduce the structures of various crystals containing the ion species at room temperature. The potential parameters used in the present calculations are listed in Table 7.I. I have carried out MD simulations for three glass compositions, 55ZrF₄·(35-x)BaF₂·xBaCl₂· 10EuF₃ with x=0, 8, and 16. These compositions correspond to 0, 5, and 10 % Cl⁻ in total anions. From now on, I refer these three glasses of x=0, 8, and 16 as 0Cl, 5Cl, and 10Cl, respectively. The unit cell contains 420 ions. The periodic boundary conditions are used as usual. The long-range corrections for potentials and forces due to the Coulomb term are treated by Ewald's method[22]. Temperatures and pressures are controlled by a simple scaling method. The initial ionic configurations were generated randomly; the initial velocities used were such that Boltzmann distribution was followed at simulation temperatures. The equations of motion were integrated with a time step of 2.5fs. The simulation schedule of each stage, i.e. equilibration, cooling, annealing and data analysis is summarized in Table 7.II.

The power spectra of the velocity autocorrelation functions for each ion are calculated using the MD data during 1,600 steps after the annealing process. Bond angle distribution functions are also calculated by averaging over 3,000steps of MD data. In order to reduce statistical errors, simulations were carried out three times for each glass composition using different initial configurations.

ion	Z	a (Å)	b (Å)
F-	-1	1.500	0.090
Cl-	-1	1.970	0.095
Zr ⁴⁺	+4	1.380	0.072
Ba ²⁺	+2	1.800	0.077
Eu ³⁺	+3	1.510	0.075

 $TABLE \ 7.I \\ POTENTIAL \ PARAMETERS \ USED \ FOR \ ZrF_4-BaF_2-BaCl_2-EuF_3 \ GLASS \ System$

TABLE 7.II SCHEDULE OF THE PRESENT MD SIMULATIONS

Stage	Start step	End step	Temperature (K)	Cooling rate (K/step)
Equilibration	1	10,000	2,000	0
Cooling	10,001	17,000	2,000 to 300	-1
Annealing	17,001	27,000	300	0
Data analyses	27,001	31,600	300	0

7.3 RESULTS & DISCUSSION

(a) Structure of Zr-Ba-Eu-F glass

Figure 7.1 shows a schematic diagram of 55Zr-35Ba-10Eu-320F glass (0Cl) at 300K. Zr-F and Eu-F bonds are shown by the solid lines. One can see that the network structures of ZrF_4 glasses are built up by linking $ZrF_n(n=7 \text{ or } 8)$ polyhedra by edge or corner sharing. EuF_n polyhedra also play a part in building up the network. Ba²⁺ ions, however, locate in the intersticial positions of ZrF_n and EuF_n polyhedra which construct the three dimensional network.



Figure 7.1 Schematic diagram of 55Zr-35Ba-10Eu-320F (0Cl) glass at 300K.

(b) Local structures around Zr^{4+}

The pair correlation functions $g_{Zr-X}(r)$ and the running coordination numbers $N_{Zr-X}(r)$ for $Zr^{4+}-X^-$ pair (X:F or Cl) are shown in Figure 7.2. One can observe only very small peaks on the $g_{Zr-Cl}(r)$ curves in the r range from 2.5 to 3.0Å for 5Cl and 10Cl. Thus I can say that very few Cl⁻ ions exist around Zr^{4+} . The $g_{Zr-F}(r)$ curves show that the average interionic distances between Zr^{4+} and F⁻ are 2.10Å and almost constant, being independent of the anion substitutions. As is observed on $N_{Zr-X}(r)$ curves in Fig. 7.2, the total anion coordination numbers around Zr^{4+} are about 7.7 in all glass compositions 0Cl, 5Cl and 10Cl. The curve profiles of $N_{Zr-X}(r)$ are quite similar to each other. Thus the average interionic distances between Zr^4 and F⁻, and the total anion coordination numbers around Zr^{4+} are independent of the anion substitution.

The power spectra of the velocity autocorrelation functions for Zr^{4+} and F⁻ are shown in Figure 7.3. The spectra for Zr^{4+} and F⁻ show a same tendencies. Both spectra have a peak around 800cm⁻¹. Thus it can be assigned to the stretching vibration Zr-F bonds. One can see that the peak frequency of this mode is independent of the anion substitutions. This is consistent with my previous experimental study in which I have reported that the frequency of the stretching vibration of Zr-F bonds is independent of Cl⁻ substitution in ZrF_4 glasses[23]. Both the MD and the experimental results show that Zr^{4+} ions are surrounded only by F⁻ ions and that very few Cl⁻ ions coordinate to Zr^{4+} within the substitution range 0-10anion% of Cl⁻.

Table 7.III shows the distributions of the number of F^- ions which are present in ZrF_n polyhedra. For 0Cl system, only the polyhedra of n=7 or 8 exist. However those with n=6 or 9 are also observed in the 5Cl and 10Cl systems. The network connectivity of ZrF_n polyhedra is also studied by counting numbers of F^- ions in the corner-shared configuration and those in the edge-shared configuration. Those are shown in Table 7.III. It is found that the corner-shared F^- decreases and

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the edge-shared F^- increases with increasing amount of Cl⁻ substitution. The increase of edge-shared F^- contributes to keep the F^- coordination number around 7.7 using a smaller amount of F^- ions.

Table 7.III Anion Coordination Number around ${\rm Zr}^{4+}$ and Interconnectivity of ZrF_n Polyhedra

Sample	Anio arou	Anion coordination number around Zr ⁴⁺ (%)				Interconnectivity of ZrF _n polyhedra (%)	
	5	6	7	8	9	Corner-shared F ⁻	Edge-shared F ⁻
0C1	0	0	28.7	71.3	0	91	9
5Cl	0	1.8	26.0	70.4	1.82	88	12
10Cl	0.1	5.0	62.8	31.9	0.2	79	21



Figure 7.2 Pair correlation functions $g_{Zr-X}(r)$ and running coordination numbers $N_{Zr-X}(r)$ for $Zr^{4+}-X^-$ (X=F or Cl) pair: (a) $g_{Zr-X}(r)$; (b) $N_{Zr-X}(r)$.



Figure 7.3 Power spectra of the velocity autocorrelation functions for Zr^{4+} and F^{-} .

The distributions of F-Zr-F bond angles are shown in Figure 7.4. The width of the peak around θ =75° increases with increasing Cl⁻ substitution. F-Zr-F bond angle is distributed in wider range as Cl⁻ substitution increases.

From the present MD results, it is found that the average Zr^{4+} -F⁻ interionic distance and the average F⁻ coordination number around Zr^{4+} are not greatly affected by the anion substitution. However, the variation of the number of F⁻ in ZrF_n polyhedra and the network structures of ZrF_n polyhedra are found to be affected by the anion substitution.



Figure 7.4 Distributions of F-Zr-F bond angles.

(c) Local structures around Eu^{3+}

The pair correlation functions $g_{Eu-X}(r)$ and the running coordination numbers $N_{Eu-X}(r)$ for $Eu^{3+}-X^-$ (X:F or Cl) pair are shown in Figure 7.5. As can be seen from $g_{Eu-X}(r)$ curves, the average interionic distances of the Eu³⁺-F⁻ and Eu³⁺-Cl⁻ pairs are 2.41Å and 2.96Å, respectively. These are mostly independent of the anion substitution. $N_{Eu-X}(r)$ curves for 0Cl has a clear shoulder at 2.5Å as is seen on that of Zr-F pair. $N_{Eu-X}(r)$ curves for 5Cl and 10Cl show two discernible shoulders at 2.5Å and 3.0Å. The former shoulder corresponds to Eu-F pair; the latter corresponds to Eu-Cl pair. The total anion coordination numbers around Eu³⁺ are approximately 9.5 at a distance 3.5Å for all glass compositions treated in this work. Figure 7.6 shows the distributions of coordination number of F and Cl⁻ around Eu³⁺. I used the threshold distance of 3.0Å for Eu-F bonds and that of 4.0Å for Eu-Cl bonds. The average F^- coordination numbers around Eu³⁺ are 8.1, 7.4 and 5.7 for 0Cl, 5Cl and 10Cl, respectively. For 0Cl system, the number of F⁻ ions in the EuF_n polyhedra is 7, 8, 9 or 10, and the principal number is 8. This result almost consistent with experimental data of Lucas et al. obtained from X-ray and MD investigations on a ZB glass[24]. For 5Cl system, the principal F⁻ coordination number is also 8. However the rate of eight-F⁻-coordinated Eu³⁺ is smaller than that for 0Cl system and the many six-F⁻-coordinated Eu³⁺ freshly exists. For 10Cl system, F⁻ coordination numbers around Eu³⁺ distributes widely from 2 to 9 and the principal number of F⁻ around Eu³⁺ is 5. The Cl⁻ coordination numbers around Eu^{3+} for 5Cl is 0, 1 or 2; that for 10Cl is 0, 1, 2, 3, 4, or 5. The average Cl⁻ coordination numbers are 0.6 for 5Cl and 1.78 for 10Cl. The Cl⁻ coordination number increases with decreasing F⁻ coordination number around Eu³⁺. All these results indicate that the substituted Cl⁻ coordinates to Eu³⁺, and the coordination number of Cl⁻ around Eu³⁺ seems to increase proportionally with increasing amount of Cl⁻ substitution.



Figure 7.5 Pair correlation functions $g_{Eu-X}(r)$ and running coordination numbers $N_{Eu-X}(r)$ for $Eu^{3+}-X^-$ (X:F or Cl) pair: (a) $g_{Eu-X}(r)$; (b) $N_{Eu-X}(r)$.



Figure 7.6 Distribution of the coordination number of F^- and Cl^- around Eu^{3+} : (a) for 0Cl; (b) for 5Cl; (c) for 10Cl.

The distribution functions of F-Eu-F bond angles in EuX₇ (X:F and/or Cl) polyhedra are shown in Figure 7.7. The average F-Eu-F angles for the 5Cl and 10Cl systems become smaller than that for the 0Cl system in which no Cl⁻ ions exists in EuX₇ polyhedra. This is attributable to the fact that the ionic radius of Cl⁻ is larger than that of F⁻.

Figure 7.8 shows the power spectra of the velocity autocorrelation functions for Eu^{3+} , F^- and Cl^- obtained from Fourier transformation of the velocity autocorrelation functions. A small shoulder appears for 5Cl and 10Cl systems on the

higher-energy side of the peak around 250 cm^{-1} . I have experimentally observed that the phonon energy coupled to Eu^{3+} in ZrF_4 glass systems shifts to a higher energy region by the substitution of Cl^- for F⁻[see Chapter 4]. The shoulder on the higher-energy side of the power spectra obtained by simulations agree with the experiments. This high energy peak in the spectra for Eu^{3+} seems to correlate to that for Cl^- . I suppose that the existence of Cl^- produces the high-energy phonon modes around Eu^{3+} .



Figure 7.7 Distribution of F-Eu-F bond angles in EuX₇ (X:F and/or Cl) polyhedra.



Figure 7.8 Power spectra of the velocity autocorrelation functions for Eu³⁺, F⁻ and Cl⁻.

The local structure changes around Eu^{3+} with the anion substitution are summarized as follows; (i) Cl⁻ substituted for F⁻ exists around Eu^{3+} , and Cl⁻ coordination numbers around Eu^{3+} increase in proportion to Cl⁻ concentration. (ii) The total anion coordination number around Eu^{3+} is independent of the Cl⁻ concentration. In other words, F⁻ coordination number decrease with increasing Cl⁻ coordination number. (iii) The F-Eu-F bond angle distribution shifts to a smaller-angle region. (iv) The existence of Cl⁻ produces the high-energy (high frequency) phonon modes around Eu^{3+} .

(d)Local structure around Ba²⁺

The pair correlation functions $g_{Ba-X}(r)$ and the running coordination numbers $N_{Ba-X}(r)$ for $Ba^{2+}-X^-$ (X:F or Cl) pair are shown in Figure 7.9. The distribution of $Ba^{2+}-X^-$ interionic distance is much wider than that of $Zr^{4+}-X^-$ or $Eu^{3+}-X^-$. The Cl⁻ coordination number around Ba^{2+} is the largest of all. Since Ba^{2+} is a network-modifying cation in the glass systems, the anions are weakly bonded to Ba^{2+} and construct BaF_nCl_m polyhedra.

The Cl⁻ coordination numbers around the cations increase in order Zr^{4+} , Eu^{3+} and Ba^{2+} . This can be explained by comparing the interionic potential energies between those cations and anions. The potential curves for the cation-anion pairs are depicted in Figure 7.10. The minima in the potential curves for cation-Cl⁻ pairs are shallower than that for cation-F⁻ pairs in all cases. Thus the total potential energy increases with the anion substitution of Cl⁻ for F⁻. The energy differences at the minimum of the potential curves between cation-F⁻ pair and cation-Cl⁻ pair are 0.88×10^{-18} J, 0.52×10^{-18} J, and 0.28×10^{-18} J for Zr^{4+} , Eu^{3+} and Ba^{2+} , respectively. Thus the substituted Cl⁻ ions preferentially coordinate to Ba^{2+} or Eu^{3+} to keep the total potential energy lower.



Figure 7.9 Pair correlation functions $g_{Ba-X}(r)$ and running coordination numbers $N_{Ba-X}(r)$ for $Ba^{2+}-X^-$ (X:F or Cl) pair: (a) $g_{Ba-X}(r)$; (b) $N_{Ba-X}(r)$.



Figure 7.10 Potential curves for the cation-anion pairs.

7.4 CONCLUDING REMARKS

I have carried out MD simulations for ZrF_4 -BaF₂-EuF₃ glass systems to investigate changes in the local structures around glass containing cations with increasing amount of the substitution of Cl⁻ for F⁻. Three glass compositions have been studied, those are 0Cl, 5Cl and 10Cl.

It is found from the present MD simulations that the F⁻ coordination number around Zr^{4+} is approximately 7.7 and independent of Cl⁻ concentration. The F⁻ coordination numbers around Ba²⁺ and Eu³⁺ are found to decrease with Cl⁻ concentration increase. Instead of this, Cl⁻ coordination numbers around Ba²⁺ and Eu³⁺ increase. The total anion coordination numbers around Eu³⁺ remain unchanged. These MD results clearly shows that Cl⁻ substituted for F⁻ mostly exists around Ba²⁺ or Eu³⁺ cation. Only very few Cl⁻ exist around Zr⁴⁺ in the Cl⁻ substituted ZrF₄ glasses treated in the present work. The power spectra obtained by the present simulations also support this.

I have investigated also the network structures of ZrF_n polyhedra and F-Zr-F bond angle distributions. MD results show that the distribution of numbers of F⁻ ions in ZrF_n becomes wider as the amount of Cl⁻ ions increase. The F-Zr-F bond angle distribution also becomes wider with Cl⁻ substitution.

REFERENCES

- [1] B. Bendow, in *Fluoride Glass Fiber Optics*, edited by I. D. Aggarwal & G. Lu (Academic Press, San Diego, 1989) p. 85.
- [2] R. S. Quimby, in *Fluoride Glass Fiber Optics*, edited by I. D. Aggarwal and G. Lu, (Academic Press, New York, 1991) p.375.
- [3] K. Hirao, S. Todoroki and N. Soga, J. Non-Cryst. Solids 143, 40 (1992).
- [4] R. S. Deol, D. W. Hewak, S. Jordery, M. Poulain, M. D. Baró and D. N. Payne, J. Non-Cryst. Solids 161, 257 (1993).
- [5] T. Danger, J. Koetke, E. Heumann, G. Huger and B. H. T. Chai, J. Appl. Phys. 76, 1413 (1994).
- [6] J. M. D. Coey, A. McEvoy and M. W. Shafer, J. Non-Cryst. Solids 43, 387 (1981).
- [7] R. M. Almeida, M. I. de Baros Marques and M. C. Gonçalves, J. Non-Cryst. Solids 168, 144 (1993).
- [8] P. Sant-Cruz, F. Auzel, A. Sadoc, J. Dexpert-Ghys, P. Henoc, D. Morin, S. Hubert and J. Grannec, J. Non-Cryst. Solids 161, 70 (1993).
- [9] W. Wang, Y. Chen and T. Hu, J. Non-Cryst. Solids 152, 172 (1993).
- [10] S. Tanabe, K. Takahara, M. Takahashi and Y. Kawamoto, J. Opt. Soc. Am. B 12(5), 786 (19956).
- [11] J. L. Adam, V. Ponçon, J. Lucas and G. Boulon, J. Non-Cryst. Solids 91, 191 (1987).
- [12] S. Todoroki, K. Hirao and N. Soga, J. Non-Cryst. Solids 143, 46 (1992).
- [13] K. Soga, H. Inoue and A. Makishima, J. Lumin. 55, 17 (1993).
- [14] J. Habasaki, I. Okada and Y. Hiwatari, J. Non-Cryst. Solids 183, 12 (1995).
- [15] Y. Benino, K. Hirao and N. Soga, J. Non-Cryst. Solids 183, 22 (1995).
- [16] G. Cormier, J. A. Capobianco and A. Monteil, J. Non-Cryst. Solids 152, 225 (1993).
- [17] K. Hirao and N. Soga, J. Am. Ceram. Soc. 10, 515 (1985).
- [18] H. Ogawa, Y. Shiraishi, K. Kawamura and T. Yokokawa, J. Non-Cryst. Solids 119, 151 (1990).

- [19] K. Hirao and N. Soga, J. Am. Ceram. Soc. 10, 515 (1985).
- [20] Y. Kawamoto, R. Kanno, R. Yokota and M. Takahashi, J. Solid State Chem. 103, 334 (1993).
- [21] A. Elyamani, M. Poulain, S. J. Saggese and G. H. Sigel Jr., J. Non-Cryst. Solids 119, 187 (1990).
- [22] P. P. Ewald, Ann. Phys., NY 64, 64, 253 (1921).
- [23] M. Takahashi, R. Kanno, Y. Kawamoto and K. Kadono, J. Phys. :Condens. Matter 7, 7797 (1995).
- [24] J. Lucas, D. Louër and C. A. Angell, Mater. Sci. Forum 6, 499 (1985).

Chapter 8

Frequency up-conversion and local vibrational states of rare-earth-doped lead oxyfluorosilicate vitro-ceramics and glasses

8.1 INTRODUCTION

Heavy-metal fluoride glasses are one of the promising materials to apply the active optical devices that utilize *f-f* transitions of rare-earth ions, *i. e.* optical amplifiers[1], lasers[2] and so on. This can be explained in terms of the multiphonon relaxation. The multi-phonon relaxation rate exponentially increases with increasing the phonon energy of host matrix[3]. The maximum phonon energy of fluoride glass system is much smaller than that of oxide glass system. The multi-phonon emission probability of excited rare-earth ions in fluoride glasses is much smaller than that in oxide glass systems. Therefore, the fluorescence of rare-earth ions in fluoride glasses are generally more efficient than that in oxide glasses. However, problems such as low chemical and mechanical stabilities become serious for the fibers and waveguides fabrication for fluoride systems[4]. On the contrarily, oxide glass systems. Especially, SiO₂-based glass system is chemically stable and easy to fabricate into various waveguide structure.

The vitro-ceramic system, comprising the oxide glassy and fluoride crystalline phase, has potentiality to apply the efficient and the chemically and mechani-
cally stable host materials doped with rare-earth ions. Auzel and his co-workers have reported the vitro-ceramic hosts for rare-earth luminescence[5]. The general formula of their materials is M_nO_m -PbF₂ (M: B, Si, P, Ge or Te) doped with rare-earth oxides, such as Er_2O_3 or Tm_2O_3 . They found that the green up-conversion efficiency of Er^{3+} -doped materials are as high as those obtained from the Er^{3+} :YF₃ host. Recently, Wu *et al.* have clarified the blue up-conversion luminescence properties of Er^{3+} in GeO₂-PbF₂ vitro-ceramics doped with Yb³⁺[6]. They have reported that the blue up-conversion emissions centered at 406 and 480nm are due to three- and two-photon absorption processes, respectively, and that the energy transfer between Yb³⁺ and Er^{3+} depends on temperature. Wang and Ohwaki have reported that the transparent vitro-ceramics co-doped with Er^{3+} and Yb^{3+} exhibit the efficient up-conversion[7].

In this study, the compositional dependence of the intensity of Er^{3+} upconversion luminescence was clarified for Er^{3+} -doped SiO₂-PbF₂ vitro-ceramics system, and the local vibrational states around rare-earth ions were examined for the SiO₂-PbF₂ vitro-ceramics system doped with Eu₂O₃. The local vibrational states were analyzed by using phonon sideband associated with the Eu ${}^{5}D_{2}\leftarrow {}^{7}F_{0}$ transition. On the other hand, the infrared-to-green up-conversion of Er^{3+} was demonstrated for the SiO₂-PbO-PbF₂ glass system. To my knowledge, this is the first observation among the SiO₂-based glass system. The local vibrational states were also clarified by phonon sideband spectra. From these results, it was deduced that the cluster-like structure containing Pb-Eu-F plays a dominant effect on the up-conversion luminescence on the SiO₂-PbO-PbF₂ glasses doped with Er₂O₃.

8.2. EXPERIMENTAL PROCEDURE

(a) Sample preparation

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The vitro-ceramic compositions employed are given in Table 8.I. High-purity

reagents SiO₂, PbF₂, La₂O₃, Eu₂O₃ and Er₂O₃ were used as the starting materials. Batches were well-mixed and melted in a Pt crucible with a cover at 1000°C for 1 hour. The melts were then poured into brass molds preheated about 200°C. The obtained samples were white plates. The vitro-ceramics obtained were annealed at 350°C for 4 hours.

Vitreous samples were synthesized by using a conventional melting method. The mixtures of starting materials were melted in a Pt crucible with a cover at 1000°C for 15 minutes, and then poured into brass molds preheated about 130°C. The obtained glasses were annealed for 2 hours at the respective glass transition temperatures determined by a differential thermal analysis. The colorless and pale pink transparent glass samples were obtained for Eu₂O₃- and Er₂O₃-doped glasses, respectively. The respective samples were cut into a size of 5×5×1mm and their surfaces were polished into an optical finish. The glass forming region of SiO₂-PbO-PbF₂ glass system doped with 1mol% of Er₂O₃ are systematically clarified. The glass compositions employed in the present spectroscopic study are given in Table 8.II.

(b) Spectroscopic measurements

The up-conversion luminescence and fluorescence spectra were measured with a HITACHI F-3010 fluorescence spectrophotometer. A Xe lump and AlGaAs diode laser (λ =802nm, P=250mW) were used as the visible and infrared excitation sources, respectively. The up-conversion spectra of Er³⁺-doped vitro-ceramics were recorded with the refractive geometry, as shown in Fig. 8.1. To remove the incidence of the scattered excitation light into the spectrometer, IR-cut-filter was used.

Notation	SiO ₂	PbF ₂	La ₂ O ₃	Eu(Er) ₂ O ₃
20S-V	20	75	2.5	2.5
27S-V	27	68	2.5	2.5
35S-V	35	60	2.5	2.5
40S-V	40	55	2.5	2.5
50S-V	50	45	2.5	2.5
60S-V	60	35	2.5	2.5
10E-V	27	68	4.0	1.0
15E-V	27	68	3.5	1.5
20E-V	27	68	3.0	2.0
25E-V	27	68	2.5	2.5
30E-V	27	68	2.0	3.0
35E-V	27	68	1.5	3.5
40E-V	27	68	1.0	4.0

 TABLE 8.I

 COMPOSITIONS OF LEAD OXYFLUOROSILICATE VITRO-CERAMICS

 TABLE 8.II

 COMPOSITIONS OF LEAD OXYFLUOROSILICATE GLASSES

Notation	SiO ₂	PbO	PbF ₂
20S-G	20	48	32
25S-G	25	45	30
30S-G	30	42	28
35S-G	35	39	26
40S-G	40	36	24
0P-G	30	70	0
5P-G	30	65	5
10P-G	30	60	10
15P-G	30	55	15
20P-G	30	50	20
25P-G	30	45	25
28P-G	30	42	28

Er₂O₃ (1mol%) or Eu₂O₃ (0.5mol%) were added to these compositions.



Figure 8.1 Experimental geometry of up-conversion luminescence measurements for Er³⁺-doped vitro-ceramics.

8.3 RESULTS

8.3.1 SiO₂-PbF₂ vitro-ceramic system

(a) Up-conversion luminescence properties of vitro-ceramics

Figure 8.2 shows the changes on the up-conversion luminescence spectra with increasing amount of SiO_2 . Four up-conversion emission bands located around 410, 525, 550 and 660nm can be seen in each spectrum. Although the

present vitro-ceramics contain a large amount of SiO₂, the up-conversion luminescence can be detected with high efficiency. Figure 8.3 shows the SiO₂content dependence of up-conversion emission intensity. The intensity of upconversion luminescence rapidly increases with decreasing amount of SiO₂. Figure 8.4 shows the Er^{3+} -concentration dependence of up-conversion emission intensity of 550nm band. The concentration quenching occurs above 2mol% of Er_2O_3 in batch composition.

(b) Phonon sideband

Figure 8.5 shows the excitation spectra of Eu^{3+} . Phonon sidebands associated with the pure electric ${}^{5}D_{2}\leftarrow {}^{7}F_{0}$ transition can be observed on the higher-energy region of the transition. The splitting of pure electric transition (PET) by Stark effect is not observed in each spectrum. In the respective spectra, two phonon sideband (PSB) peaks can be seen at around 250cm⁻¹ and 950cm⁻¹. The intensity of PSB peaks changes with increasing content of SiO₂, that is, the intensity of lower energy peak around 250cm⁻¹ decreases and that of the higher energy peak around 950cm⁻¹ increases.



Figure 8.2 Infrared-to-visible up-conversion luminescence spectra of the present vitro-ceramics.



Figure 8.3 SiO₂-content dependence of up-conversion emission intensity.



Figure 8.4 Er³⁺-concentration dependence of 550nm up-conversion emission intensity.



Figure 8.5 Excitation spectra of ${}^{5}D_{2} \leftarrow {}^{7}F_{0}$ transition of Eu³⁺ in the present vitroceramics.

8.3.2 SiO₂-PbO-PbF₂ glass system

(a) Glass-forming region

Figure 8.6 shows the glass-forming area of the Er_2O_3 -containing (1mol%) lead oxyfluorosilicate glasses obtained in this study.

(b) Up-conversion spectra

Figure 8.7 shows the SiO₂-content dependence of up-conversion spectra of the glasses. Up-conversion emission bands can be clearly observed around 525 and 550nm. Figure 8.8 shows the SiO₂-content dependence of up-conversion emission intensity of 550nm band (${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition). The up-conversion intensity decreases with increasing amount of SiO₂.

Figure 8.9 shows the PbF_2 -content dependence of up-conversion spectra. Figure 8.10 shows the PbF_2 -content dependence of up-conversion emission intensity. The up-conversion intensity appears to increase with increasing content of PbF_2 .

(c) Phonon sideband spectra

Figure 8.11 shows the excitation spectra of Eu^{3+} in the present lead oxyfluorosilicate glasses; (a) SiO₂-content dependence and (b) PbF₂-content dependence. The Stark splitting of PET is clearly observed for glasses 15P-G, 10P-G, 5P-G and 0P-G. Such a splitting is also observed on the excitation spectra of Eu^{3+} -doped sodium silicate glasses[8]. Phonon sidebands associated with the pure electric ${}^{5}D_{2}$ $\leftarrow {}^{7}F_{0}$ transition can be observed at around 250cm⁻¹ and 950cm⁻¹ on the higherenergy region of the transition. These energy ranges are similar to the phonon energies obtained from the PSB of the present vitro-ceramics.



Figure 8.6 Glass-forming area of the Er₂O₃-containing (1mol%) lead oxyfluorosilicate glasses.



Figure 8.7 SiO₂-content dependence of up-conversion spectra of Er³⁺ in the lead oxyfluorosilicate glasses.



Figure 8.8 SiO₂-content dependence of up-conversion emission intensity of 550 nm band (${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transition) of Er³⁺ in the lead oxyfluorosilicate glasses.



wavelength / mm

Figure 8.9 PbF_2 -content dependence of up-conversion spectra of Er^{3+} in the lead oxyfluorosilicate glasses.



Figure 8.10 PbF₂-content dependence of up-conversion emission intensity of Er^{3+} in the lead oxyfluorosilicate glasses.



Figure 8.11 Excitation spectra of Eu^{3+} in the lead oxyfluorosilicate glasses: (a) SiO₂-content dependence; (b) PbF₂-content dependence.

8.4 DISCUSSION

8.4.1 SiO₂-PbF₂ vitro-ceramic system

(a) Local vibrational state around Eu^{3+}

The dominant PSB peaks are found at the energy shift of 250 and 950cm⁻¹ [see Fig. 8.5]. Hereafter the former peak is abbreviated as PSB²⁵⁰ and the latter peak, being PSB⁹⁵⁰. The PSB²⁵⁰ is very close to the PET peak. In order to obtain the phonon energy and the electron-phonon coupling strength, the curve decomposition on the PET and PSB²⁵⁰ peaks was carried out by using a least squares fitting program of mixed Lorenztian-and-Gaussian function [see Chap. 2]. Figure 8.12 shows the PSB²⁵⁰ and PSB⁹⁵⁰ spectra of the present vitro-ceramics. The PSB⁹⁵⁰ can be found in the spectra of 40S-V and 50S-V. The phonon energies are calculated from the energy difference between the center of PSB and that of PET. The phonon energies of both peaks are almost independent of the content of SiO₂. The intensity of PSB²⁵⁰ decreases whereas that of PSB⁹⁵⁰ increases with increasing SiO₂ content (decreasing PbF₂ content). This fact suggests that the PSB²⁵⁰ and PSB⁹⁵⁰ are concerned with the vibration due to the Pb-X and Si-X (X=O or F) bond, respectively. The vibrational spectroscopy has been reported for lead oxyhalosilicate glasses [9]. Table 8.III gives the results of Raman study of lead oxyhalosilicate glasses.

Raman shift	Assignment			
842	Q ⁰			
925	Q^1			
970	Q ²			
1055	Q ³			

TABLE 8.III Assignments of Various Bands in the Raman Spectra for 17.2PbF2.54.3PbO.28.5SiO2 Glass [9]



Figure 8.12 PSB²⁵⁰ and PSB⁹⁵⁰ spectra of Eu³⁺ in the lead oxyfluorosilicate vitro-ceramics.

In Table 8.III, Si atom in each Q^n state shows a specific chemical shift in ²⁹Si NMR spectra where *n* represents the number of non-bridging oxygens bonded to an Si atom. Osaka *et al.* have reported that no Si-F bonds are formed in oxy-halosilicate glasses [9]. Considering from the vibrational energy, the PSB⁹⁵⁰ is assigned to Si-O symmetric stretching vibrations of the Q^1 or Q^2 tetrahedra (Q^1 and Q^2 units include 1 and 2 non-bridging oxygen, respectively). On the other hand, the vibrational energy of Pb-X (X=O or F) seems to be low due to the large effective mass of Pb²⁺ ion as compared with Si-O vibration. Therefore, the PSB²⁵⁰ can be assigned to Pb-O or Pb-F vibration.

The electron-phonon coupling strength can be calculated from the intensity ratio of PSB to PET[10]. Figure 8.13 shows the SiO₂-content dependence of the electron-phonon coupling strength of PSB²⁵⁰ and PSB⁹⁵⁰. The electron-phonon coupling strengths of PSB²⁵⁰ and PSB⁹⁵⁰ are abbreviated as g^{250} and g^{950} , respectively. The g^{950} value increases, and the g^{250} value decreases with increasing SiO₂ content. The g^{950} values are almost zero up to 25mol% of the SiO₂ content. This suggests that silicate glass phase and lead fluoride crystalline phase microscopically separate and that Eu³⁺ preferentially places at lead fluoride phase. The similar phenomenon has been reported for Er:PbF₂-GeO₂ vitro-ceramic systems by Auzel [5]. The PbF₂-GeO₂ vitro-ceramics are microscopically separated into germanate glass phase and lead halide crystalline phase, and the most Er³⁺ are placed in lead halide crystalline phase. The increase of g^{950} value with increasing SiO₂ content indicates the increase in a number of the Q¹ or Q² unit around Eu³⁺.



Figure 8.13 SiO₂-content dependence of the electron-phonon coupling strength of PSB²⁵⁰ and PSB⁹⁵⁰ of Eu³⁺ in the lead oxyfluorosilicate vitro-ceramics.

(b) Multi-phonon relaxation rate

The multi-phonon relaxation rates, W(T), are expressed by Miyakawa-Dexter's equation[3],

$$W(T) = W_0(T) \exp(-\alpha \Delta E)(n+1)^p,$$

$$\alpha = \hbar \omega^{-1} \{ \ln(p/g) - 1 \},$$

$$p \approx \Delta E / \hbar \omega,$$
(8.1)

where ΔE is the energy gap to the next lower level, $W_0(T)$ is the decay rate at $\Delta E=0$, *n* is the Plank constant, $\hbar \omega$ is phonon energy, *g* is electron-phonon coupling strength, *p* is the phonon number concerned with multi-phonon decay. Table 8.IV gives the maximum phonon energies of the typical oxide and fluoride glass systems obtained from Raman study. The maximum phonon energies of oxide glasses are much larger than that of fluoride glasses. Therefore the multi-phonon decay rate of excited 4*f*-electrons in fluoride glass systems is much smaller than that in oxide glass systems.

TABLE 8.IV THE MAXIMUM PHONON ENERGIES OF TYPICAL OXIDE AND FLUORIDE GLASS SYSTEMS DETERMINED FROM RAMAN STUDY

Oxide glass system[11]		Fluoride glass system[12-14]	
System	Energy (cm ⁻¹)	System	Energy (cm ⁻¹)
B ₂ O ₃	1350	ZrF ₄	580
P_2O_5	1100	AlF ₃	630
SiO ₂	1000	InF ₃	500
GeO ₂	900	HfF ₄	580
TeO ₂	800	ZnF ₂	400

As shown in Eq. 8.1, multi-phonon relaxation rates can be calculated from the phonon energy and electron-phonon coupling strength determined from PSB spectra. Figure 8.14 shows the SiO₂-content dependence of the relative multiphonon relaxation rate across the Er ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ energy gap (about 3500cm⁻¹). The multi-phonon relaxation rate of the present vitro-ceramics depends on the g^{950} value. Figure 8.15 shows the relationship between the Er³⁺ up-conversion intensity and the g^{950} value. The up-conversion intensity is greatly dependent of the g^{950} value. In other words, Si-O stretching vibration of the Q¹ or Q² unit coupled with the 4*f*-electrons of rare-earth ions plays a dominant effect on the multi-phonon relaxation rate. From the above considerations, the up-conversion emission intensity of the present rare-earth-doped vitro-ceramics depends on the multi-phonon emission rate across the 4*f*-state.

8.4.2 SiO₂-PbO-PbF₂ glass system

(a) SiO₂ content dependence

As can be seen in Fig. 8.11 (a), dominant PSB peaks are found at around 250 and 950cm⁻¹. The respective changes on the intensity of PSB in lead oxyfluoro-silicate glasses are the same as those in lead oxyfluorosilicate vitro-ceramics. The SiO₂-content dependence of PSB spectra obtained from excitation spectra of Eu³⁺ is shown in Fig 8.16. The peak profile of each PSB remains almost unchanged, but the intensity of PSB changes with increasing amount of SiO₂. The intensity of PSB²⁵⁰ decreases and that of PSB⁹⁵⁰ increases with increasing amount of SiO₂. Figure 8.17 shows the SiO₂-content dependence of electron-phonon coupling strength of PSB²⁵⁰ and PSB⁹⁵⁰. The electron-phonon coupling strength of PSB²⁵⁰, g²⁵⁰, decreases and that of PSB⁹⁵⁰, increases with increasing SiO₂ content.



Figure 8.14 SiO₂-content dependence of the relative multi-phonon relaxation rate across the Er ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ energy gap.



Figure 8.15 Relationship between the Er^{3+} up-conversion intensity and the g^{950} value of PSB⁹⁵⁰.



Figure 8.16 SiO₂-content dependence of PSB spectra of Eu³⁺ in the lead oxyfluoro-silicate glasses.



Figure 8.17 SiO₂-content dependence of electron-phonon coupling strength of PSB²⁵⁰ and PSB⁹⁵⁰.

Figure 8.18 shows the SiO₂ content dependence of the relative multiphonon relaxation rate across the Er ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ energy gap (about 3500cm⁻¹). In a similar manner to the present vitro-ceramics, the g^{950} value plays a dominant effect on the multi-phonon relaxation of excited 4*f*-electrons.



Figure 8.18 SiO₂ content dependence of the relative multi-phonon relaxation rate across the Er ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ energy gap.

(b) F^{-} concentration dependence

Figure 8.19 shows the PSB spectra extracted from the excitation spectra of Eu^{3+} with PbF₂ content. The intensity of PSB⁹⁵⁰ remains almost unchanged, but the peak profile of PSB⁹⁵⁰ changes with the PbF₂ content. For the 0P-G glass, PSB around 1100cm⁻¹ is observed, and this high-energy phonon contributes largely to the multi-phonon decay of excited 4*f* ions. The intensity of PSB²⁵⁰ rapidly increases with increasing amount of F⁻, in spite of the same SiO₂ content. This suggests that the local environment around rare-earth ions greatly changes with the amount of F⁻. These results show that the Pb-F bond preferentially presents around rare-earth ions in the lead oxyfluorosilicate glass system, and that the cluster-like structure of fluoride-rich phase containing Pb, Eu and F exists. This cluster-like structure contributes to the efficient up-conversion in the present glass system.



Figure 8.19 PSB spectra of Eu³⁺ in the lead oxyfluorosilicate glasses.

8.5 CONCLUDING REMARKS

The compositional dependence of infrared-to-visible up-conversion luminescence of Er^{3+} were investigated for the SiO₂-PbF₂ vitro-ceramic and SiO₂-PbO-PbF₂ glass systems. The local vibrational states around rare-earth ions in these systems are also examined by measuring the phonon sideband spectra of Eu^{3+} .

The efficient up-conversion luminescence was demonstrated for SiO_2 -PbF₂ vitro-ceramics doped with Er_2O_3 . Two kinds of phonon modes were coupled with the 4*f*-electrons of Eu^{3+} in the present vitro-ceramics. The energies of these phonons were about 250 and 950cm⁻¹ corresponding to the Pb-F and Si-O vibrations, respectively. The phonon sideband at around 250cm⁻¹ is predominant for composition of low SiO_2 content up to 30mol%. The multi-phonon decay rate greatly depends on the electron-phonon coupling strength of the phonon sideband at 950cm⁻¹.

The up-conversion luminescence was demonstrated for SiO_2 -PbO-PbF₂ glass system. The local structure around rare-earth ions greatly depends on the amount of F⁻. The fluoride-rich cluster-like structure containing Pb, Eu and F ions is found in the lead oxyfluorosilicate glasses.

REFERENCES

- [1] Y. Ohishi, T. Kanamori, M. Shimizu, M. Yamada, Y. Terunuma, J. Temmyo,
 M. Wada, and S. Sudo, *IECE Trans. Commun.* E77-B(4), 421 (1994).
- [2] M. C. Briertly and C. A. Millar, Electron. Lett. 24, 438 (1988).
- [3] T. Miyakawa and D. L. Dexter, *Phys. Rev.* B 1(7), 2961 (1970).
- [4] A. B. Seddon, in *Fluoride Glasses*, edited by A. E. Comyns (J. Wiley & Sons, Chichester, 1989) p. 157.
- [5] F. Auzel, D. Pecile and D. Morin, J. Electrochem. 122(1), 101 (1975).
- [6] W. Wu, J. P. Denis, G. Özen, Ph. Goldner and F. Pellé, Solid State Commun.
 85(4), 351 (1993).
- [7] Y. Wang and J. Ohwaki, Appl. Phys. Lett. 63 (24), 3268 (1993).
- [9] A. Osaka, Y. H. Wang, M. Kobayashi and Y. Miura, J. Non-cryst. Solids 105, 63 (1988).
- [10] S. Tanabe, S. Todoroki, K. Hirao and N. Soga, J. Non-Cryst. Solids 122, 59 (1990).
- [11] C. B. Layne, W. H. Lowdermilk and M. J. Weber, Phys. Rev. B 16(1), 10 (1977).
- [12] M. Takahashi, R. Kanno, Y. Kawamoto and K Kadono, J. Phys.:Condens. Matter 7, 7797 (1995).
- [13] Y. Kawamoto and A. Kono, J. Non-Cryst. Solids 85, 335 (1986).
- [14] K. Takahara, M. Takahashi, Y. Kawamoto and K. Kadono, unpublished data (1993).

Summary

In the present study, the optical properties and glass structure of the ZrF₄based glasses doped with Eu or Er ions are investigated by means of several spectroscopic methods and computer simulations. Besides, frequency upconversion properties and local vibrational states of rare-earth ions are examined for mixed-anion vitro-ceramics and glasses. The results of respective Chapters are summarized as follows.

In Chapter 1, the non-radiative relaxation processes of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states and frequency up-conversion properties of Er³⁺ are clarified for binary ZrF₄-BaF₂ glass system. It is shown that the quantum efficiencies of the ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ states are 73% and 25%, respectively. Non-radiative decay rate of the ${}^{4}S_{3/2}$ state rapidly increases with increasing Er concentration, because cross relaxation becomes a principal non-radiative decay process in high Er concentration region. The dominant non-radiative decay process of the ${}^{4}F_{9/2}$ state is the multi-phonon relaxation. Under 800nm excitation, the up-conversion luminescence is strongly observed at around 525, 550 and 660nm, and weak emission is observed at around 410nm. The mechanism of infrared-to-visible up-conversion is discussed based on the Er concentration and excitation power dependence of the emission intensity. The up-conversion emission intensities of the 550nm and 660nm bands quadralically depend on the excitation energy. This indicates that the twophoton absorption is the main mechanism for these up-conversion luminescence. The up-conversion emission intensity of 550nm band increases in proportional to Er concentration, but that of 660nm band increases in proportional to square of Er concentration. These results reveal that the principal up-conversion

processes for 550nm and 660nm bands are excited state absorption and energy transfer, respectively.

In Chapter 2, compositional variation of the Er^{3+} up-conversion luminescence in the ZrF₄-based fluoride glasses is examined with the glass-modifying alkali-fluoride in 21.25*M*F·21.25LiF·52.5ZrF₄·5ErF₃ (*M* = Li, Na, K, Rb or Cs) glasses. Up-conversion luminescence of the glasses with 800nm excitation gives emission bands around 410, 525, 550 and 660nm. Emission intensities of these bands change remarkably, depending on alkali-fluoride species. An explanation for the observed alkali-fluoride dependence is based on the covalency in Er^{3+} -F⁻ bonding and multi-phonon decay across the excited 4*f*-levels. Those are evaluated from fluorescence and excitation spectra of Eu^{3+} in glasses substituted Eu for Er.

In Chapter 3, the glass-modifying alkaline-earth-fluoride dependence of upconversion emission intensity is investigated using $5MF_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5ErF_3$ (*M* = Mg, Ca, Sr or Ba) glasses. Up-conversion luminescence of the glasses by 800nm excitation gives emission bands around 410, 525, 550 and 660nm. The intensity of respective bands depends on the alkaline-earth-fluoride species, being the largest value in the Mg glass, almost the same values in the Ca glass and the Sr glass and the smallest value in the Ba glass. Analyses of the fluorescence and excitation spectra of Eu³⁺-substituted glasses clarify that the alkaline-earth-fluoride dependence of up-conversion luminescence intensity is determined by both covalency in Er^{3+} -F⁻ bonding and phonon energy coupled with 4*f*-electrons of Er^{3+} .

In Chapter 4, the anion substitution effect on the up-conversion luminescence intensity has been examined in ZrF_4 -BaF₂-ErF₃ glass system in which a part of F⁻ ions is replaced by other anions such as Cl⁻, Br⁻, I⁻ and O²⁻ ions. Prominent enhancement of up-conversion emission intensity is observed on the substitution of Cl for F. The Cl substitution brings about two effects, of which one is an increase in the covalency in Er^{3+} -F⁻ bonding and the other is an increase in both phonon energy and electron-phonon coupling strength. The former raises the transition probability in the up-conversion process, leading to an enhancement of the emission intensity, while the latter increases the multi-phonon relaxation in the up-conversion process, leading to a reduction of the emission intensity. Due to these antithetical effects on the up-conversion process, the up-conversion emission intensity of the Cl substituted glasses exhibits a maximum value around the $58ZrF_4.20BaF_2.19BaCl_2.3ErF_3$ composition. The substitution of small amount of Cl for F is concluded to be quite effective for enhancing the upconversion efficiency of ZrF_4 -based glasses.

In Chapter 5, the anion coordination environments around Zr^{4+} in ZrF_4 -BaF₂-BaCl₂-EuF₃ glass system are examined by the Zr K-EXAFS, Raman scattering and IR absorption spectroscopies. These spectroscopic analyses reveal that the anion coordination environments around Zr^{4+} are hardly changed by the successive substitution of Cl for F.

In Chapter 6, the chemical bonding-states and fluorescence properties of Eu^{3+} ions in ZrF_4 -BaF₂-EuF₃ glass system in which a part of F⁻ ions is successively substituted by Cl⁻ ions have been investigated by means of the ¹⁵¹Eu-Mössbauer and Eu³⁺-fluorescence spectroscopies. Mössbauer spectra indicate that Eu in the present chloro-fluorozirconate glasses exists only as the +3 oxidation state. Isomer shift of ¹⁵¹Eu³⁺ increases with increasing amount of Cl⁻. An increase of isomer shifts can be ascribed to larger participation of 6*s*-electrons to covalent bonds. This change on chemical bonding-state of Eu³⁺ corresponds to the intensity of hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition in Eu³⁺ fluorescence. This shows that the intensity of hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition depends on the covalency in Eu³⁺-anion bonding. The intensity of ${}^5D_0 \rightarrow {}^7F_0$ transition increases with increasing Cl⁻ amount. Ligand field strength around Eu³⁺ and inhomogeneous linewidth of Eu³⁺ fluorescence calculated from fluorescence spectra of ${}^5D_0 \rightarrow {}^7F_0$ transition decreases with increasing amount of Cl⁻. These results reveal that Cl⁻ substituted for F⁻ exists at the neighbors of Eu³⁺ in chloro-fluorozirconate glasses.

In Chapter 7, molecular dynamics simulations are performed for ZrF_4 -BaF₂-EuF₃ glass system in which 0, 5, and 10% of F⁻ ions are substituted by Cl⁻ ions. Changes in local structures around each cation are investigated in terms of increasing amount of substitutions of Cl⁻ for F⁻. The average coordination number of F⁻ around Zr⁴⁺ is found to be approximately 7.7 and is independent of the amount of Cl⁻ substitution. The power spectra of the velocity autocorrelation functions are also calculated. The Zr-F stretching mode observed around 800cm⁻¹ shows no shift with Cl⁻ substitution. These results show that the local structure around Zr⁴⁺ is not greatly affected by the small amount of Cl⁻ substitution. The F⁻ coordination number around Eu³⁺ at a radius of 3.0Å and that around Ba²⁺ at a radius of 3.5Å are found to decrease from 8.0 to 5.6 and from 9.2 to 5.1, respectively, as the Cl⁻ fraction increases. This means that Cl⁻ ions substituted for F⁻ exist almost around the Eu³⁺ or Ba²⁺ cation. These results are confirmed with the experimental results described in Chapters 5 and 6.

In Chapter 8, the infrared-to-visible up-conversion properties of Er^{3+} have been examined for SiO₂-PbF₂ vitro-ceramic system and SiO₂-PbO-PbF₂ glass system. For the vitro-ceramic system, efficient up-conversion luminescence under 800nm excitation can be observed at around 525, 550 and 660nm, and the intensity of up-conversion emission bands is greatly dependent on the amount of SiO₂. The up-conversion intensity increases with decreasing SiO₂ fraction. The local vibrational states and the multi-phonon relaxation rates are investigated for Eu^{3+} -doped vitro-ceramics. Two kinds of vibrational mode, of which the energies are about 950 and 250cm⁻¹, are coupled with 4*f*-electrons, and their intensities are dependent of the SiO₂ fraction. The 950cm⁻¹-phonon plays a dominant effect on the multi-phonon relaxation of excited 4*f*-electrons of rare-earth ions. For the SiO₂-PbO-PbF₂ system glasses, the 800nm-to-550nm up-conversion luminescence is observed for the first time among SiO₂-based glass systems. The analysis of phonon sideband spectra reveals that the cluster-like structure containing Pb, Eu and F ions exists in the glass matrix.

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List of Publications

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- Chapter 2. M. Takahashi, R. Kanno, Y. Kawamoto, S. Tanabe and K. Hirao, "Compositional dependence of Er³⁺ upconversion luminescence in MF-LiF-ZrF₄ glasses (M:alkali metals)", J. Non-cryst. Solids 168, 137 (1994).
- Chapter 3. M. Takahashi, R. Kanno, Y. Kawamoto, S. Tanabe and K. Hirao, "Compositional dependence of upconversion luminescence of trivalent Erbium ions in fluorozirconate glasses, II. alkaline earth fluoride dependence", *Mat. Res. Bull.* 28, 557 (1993).
- Chapter 4. Y. Kawamoto, R. Kanno, R. Yokota, M. Takahashi, S. Tanabe and K. Hirao, "Compositional dependence of upconversion luminescence of trivalent Erbium ions in fluorozirconate glasses, III. anion substitution effect", J. Solid State Chem. 103, 334 (1993).
- Chapter 5. M. Takahashi, R. Kanno, Y. Kawamoto and K. Kadono, "Local structure around Zr⁴⁺ in ZrF₄-BaF₂-BaCl₂-EuF₃ glasses", *J. Phys.:Condens. Matter* 7, 7797 (1995).
- Chapter 6. M. Takahashi, R. Kanno and Y. Kawamoto, "Mössbauer and fluorescence spectroscopic study on local environment around trivalent europium ions in chloro-fluorozirconate glasses", J. Appl. Phys., submitted.
- Chapter 7. M. Takahashi, R. Yamamoto, R. Kanno and Y. Kawamoto, "Molecular dynamics simulation of Eu³⁺-doped chlorofluorozirconate glasses", J. Phys.: Condens. Matter 7, 4583 (1995).
- Chapter 8. M. Takahashi, M. Kano, R. Kanno and Y. Kawamoto, "Frequency upconversion and local vibrational states of rare-earth-doped lead oxyfluorosilicate vitro-ceramics", J. Appl. Phys., in preparing.

Other publications not contained in this thesis

- M. Shojiya, M. Takahashi, R. Kanno, Y. Kawamoto and K. Kadono, "Upconversion luminescence of Er³⁺ in chloride glasses based on ZnCl₂ or CdCl₂", *Appl. Phys. Lett.* 65, 1874 (1994).
- K. Kadono, H. Higuchi, M. Takahashi, Y. Kawamoto and H. Tanaka, "Upconversion luminescence of Ga₂S₃-based sulfide glasses containing Er³⁺ ions", J. Non-cryst. Solids 184, 309 (1995).
- S. Tanabe, K. Takahara, M. Takahashi and Y. Kawamoto, "Spectroscopic studies of radiative transitions and upconversion characteristics of Er³⁺ ions in simple pseudoternary fluoride glasses MF_n-BaF₂-YF₃ (M:Zr, Hf, Al, Ga, Sc, In or Zn)", J. Opt.Soc. Am. B 12(5), 786 (1995).
- M. Shojiya, M. Takahashi, R. Kanno, Y. Kawamoto and K. Kadono, "Upconversion luminescence of Er³⁺ in CdX₂ system glasses (X=Cl. Br, I)", *Appl. Phys. Lett.* 67, 2453 (1995).
- M. Takahashi, H. Shigemura, M. Shojiya, H. Higuchi and Y. Kawamoto, "Local structure and optical properties of ZrF₄-based glass doped with Ni²⁺", *Photon factory Activity Report* 1994, #12 in press.