



# Structure-inheriting solid-state reactions under hydrothermal conditions

Eda, Kazuo ; Uno, Yuichi ; Nagai, Noriko ; Sotani, Noriyuki ; Chen, Chen ; Whittingham, M. Stanley

---

(Citation)

Journal of Solid State Chemistry, 179(5):1453-1458

(Issue Date)

2006-05

(Resource Type)

journal article

(Version)

Accepted Manuscript

(URL)

<https://hdl.handle.net/20.500.14094/90000964>



Kazuo Eda,

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan

Tel: +81-78-803-5677, Fax: +81-78-803-5677, E-mail: [eda@kobe-u.ac.jp](mailto:eda@kobe-u.ac.jp)

### **Structure-inheriting Solid State Reactions under Hydrothermal Conditions**

Kazuo Eda,<sup>\*a</sup> Yuichi Uno,<sup>a</sup> Noriko Nagai,<sup>a</sup> Noriyuki Sotani,<sup>a</sup> Chen Chen,<sup>b</sup> and M. Stanley Whittingham<sup>b</sup>

*<sup>a</sup>Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan.*

*<sup>b</sup>Institute for Materials Research, State University of New York at Binghamton, Binghamton, NY 13902-6000, U.S.A.*

\* To whom correspondence should be addressed

## **Abstract**

We have explored several structure-inheriting solid-state reactions (SISSRs) under hydrothermal conditions for syntheses in the Co-Mo-O system. And we found an interesting hydrothermal SISSR from  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  to high-pressure (hp-) phase of  $\text{CoMoO}_4$ , which enabled us to considerably reduce the severe conditions for the synthesis of hp- $\text{CoMoO}_4$ . As similar hydrothermal SISSRs are expected to be useful tools for material syntheses, we also briefly discuss them as a means of developing novel material syntheses and designs.

**Key words:** hydrothermal synthesis, solid state reaction, soft chemistry, cobalt molybdate

## Introduction

As is now well-known, hydrothermal syntheses can lead to the formation of materials at much lower temperatures than those necessary for conventional solid-state syntheses. Some of these low-temperature syntheses may lead to intermediate states, which maintain a structural resemblance to the starting compound, as shown in Figure 1. Usually hydrothermal syntheses involve the dissolution of the starting compounds and thus the products may lose any structural resemblance to the reactants. However, when one of the reactants remains in the solid state under hydrothermal conditions it becomes possible to control the structure of the product by varying the structure of the insoluble reactant. Some such solid-state reactions (SSRs), such as ion-exchange and intercalation, under hydrothermal conditions are known [1-5]. However, further systematic research on SSRs under hydrothermal conditions is needed in order to apply them to the syntheses of new compounds with novel structures. We have been exploring, especially, the hydrothermal SSRs that lead to structural reconstruction while maintaining a structural resemblance between the starting and product compounds, and referred to them as structure-inheriting SSRs (SISSRs) under hydrothermal conditions [6-9].

Recently we have studied hydrothermal syntheses in the Co-Mo-O system and found an interesting hydrothermal SISSR, which enabled us to significantly reduce the severity of the synthesis from the prior work for the high-pressure (hp-) phase of  $\text{CoMoO}_4$ . In this paper we report this SISSR and describe briefly SISSRs expected to be useful for designing novel materials.

## Experimental

In order to investigate the effects of the solubility of the starting materials on the material formed, starting reagents consisting of various combinations of soluble and insoluble Mo and Co

sources were studied (see Table 1).  $\text{MoO}_3$  and  $\text{CoO}$  were used as the insoluble sources and were essentially insoluble in the solution before the hydrothermal treatment, whereas amorphous (am-)  $\text{MoO}_3 \cdot n\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were used as the soluble sources. Reagent grade  $\text{MoO}_3$ ,  $\text{CoO}$ , and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were purchased. The am- $\text{MoO}_3 \cdot n\text{H}_2\text{O}$  was prepared by spray-drying a molybdic acid solution, obtained by passing a  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  solution through an acid ion-exchange resin (Dow Chemical Co. Dowex 50W-X8). The hydration number  $n$  of the am- $\text{MoO}_3 \cdot n\text{H}_2\text{O}$  was determined to be about 1.1 by thermogravimetric analysis (TG-DTA). The mixture of Mo and Co sources (2.4 mmol each) was suspended or dissolved in 40ml of distilled water. For runs 5 and 6 (see Table 1), 4.8 mmol of  $\text{HCl}$  was also added to the solution to match its chlorine content to that of the solutions of runs 3 and 4. The resulting solution was put into a 60 ml Teflon-lined autoclave and heated in a forced convection oven at 453 K under autogenous pressure for the desired time. The resulting product was filtered, washed with distilled water, and dried in air at room temperature.

The pH value of the solution was measured before the hydrothermal treatment. The powder X-ray diffraction (XRD) patterns of the products were measured on a Mac Science MXP3VZ X-ray diffractometer with a graphite monochromator using  $\text{CuK}\alpha$  radiation. Thermal analysis was performed on a Mac Science TG-DTA 2010S system at a heating rate of  $10 \text{ K min}^{-1}$  in air flow. The chemical compositions of the products were determined by a HITACHI 180-80 atomic absorption spectrometer.

## Results and Discussion

**Products obtained by hydrothermal treatments of the starting materials consisting of various combinations of Mo and Co sources.** Table 1 shows the products obtained in the hydrothermal syntheses consisting of various combinations of the Mo and Co sources. The

formation of three kinds of cobalt molybdates was observed as shown in the table. They were  $\text{hp-CoMoO}_4$ ,  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$ , and  $\text{CoMo}_4\text{O}_{13} \cdot 2\text{H}_2\text{O}$  [10]. The last is apparently a new compound, while the first two are known [11-13]. The last compound has a triclinic cell with  $a=5.525(2) \text{ \AA}$ ,  $b=7.058(2) \text{ \AA}$ ,  $c=7.556(2) \text{ \AA}$ ,  $\alpha=90.011(7)^\circ$ ,  $\beta=105.252(7)^\circ$ , and  $\gamma=90.381(7)^\circ$ . Recently we succeeded in determining its crystal structure and that of an isostructural nickel molybdate; this work will be reported elsewhere.

The pH of the hydrothermal reaction medium has been shown previously to play a critical role in determining the product formed [14]. The products formed here, shown in Table 1, also depend on the pH of the initial solutions as well as on the specific starting materials. The specific reactants also play a role in determining the pH as shown in Figure 2, which shows the pH change with time for  $\text{MoO}_3$  as a function of time and temperature. The partial dissolution/hydrolysis of the molybdenum oxide creates an acidic medium, which increases at elevated temperatures where the solubility increases; as cobalt oxide is added there is a slight increase of the pH. Comparison of runs 3 and 4 with runs 5 and 6 in Table 1 proves the key role of pH. That is, the same products ( $\text{CoMo}_4\text{O}_{13} \cdot 2\text{H}_2\text{O} + \text{MoO}_3$ ) are formed from the solutions with  $\text{pH} < \text{ca. } 2$  (runs 4-6), in spite of the differences in the initial state of the solution among runs 4-6. The crystal size and crystallinity of the  $\text{CoMo}_4\text{O}_{13} \cdot 2\text{H}_2\text{O}$  were changed easily with the cooling rate after the hydrothermal treatment and the reactant concentrations of Mo and Co in the hydrothermal solution. This suggests that the  $\text{CoMo}_4\text{O}_{13} \cdot 2\text{H}_2\text{O}$  is formed via a hydrothermal dissolution-precipitation process. On the other hand the crystal size and crystallinity of  $\text{hp-CoMoO}_4$  and  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  did not change with the cooling rate and the concentrations. Therefore there is a possibility that they are formed by a solid state process, although Livage et al. reported that  $\text{hp-CoMoO}_4$  is formed via a hydrothermal solution process [13]. As mentioned by Livage et al., the formation at around 450 K of  $\text{hp-CoMoO}_4$ , which is usually prepared via a

solid-state phase transition from  $\alpha$ -CoMoO<sub>4</sub> or  $\beta$ -CoMoO<sub>4</sub> under very severe conditions (50 kbars and ca.900 K [15]), is of great interest for materials scientists. Thus it is important to reveal its formation mechanism. For comparison the details of the Livage's synthesis of hp-CoMoO<sub>4</sub> are also presented in Table 1. In Livage's synthesis, the reactants are soluble thus the hp-CoMoO<sub>4</sub> must be formed via a solution process, but an intermediate product might be initially formed. In that synthesis, hp-CoMoO<sub>4</sub> and CoMoO<sub>4</sub>·3/4H<sub>2</sub>O are formed from the same starting solution, the former is formed at 473 K and the latter at 423 K. In our run 2 both compounds are present simultaneously in the product. Therefore we investigated the formation process of hp-CoMoO<sub>4</sub> and the relation between these compounds in the formation process. The results are described in the following section.

**Formation mechanism of hp-CoMoO<sub>4</sub> and a SISSR under a hydrothermal condition.** In order to reveal the formation process, we investigated the changes of the products during the hydrothermal treatment as a function of reaction time. Figure 3 shows the progression of the structural changes of the products during the treatment of MoO<sub>3</sub> and CoO at 453 K. According to this figure, the MoO<sub>3</sub> reactant is completely dissolved within the first 5 minutes of hydrothermal treatment. Subsequently CoMoO<sub>4</sub>·3/4H<sub>2</sub>O is formed probably via a reaction between the Co and Mo species in the solution (i.e., by a hydrothermal solution process). The formation of hp-CoMoO<sub>4</sub>, accompanied with the gradual disappearance of the CoMoO<sub>4</sub>·3/4H<sub>2</sub>O, is found for the two or more day's treatment, and thus it is proposed that the initially formed CoMoO<sub>4</sub>·3/4H<sub>2</sub>O is converted gradually into hp-CoMoO<sub>4</sub>. The yields of the solid products (81.6% for the 1-day treatment and 73.8% after 3-day treatment [16]) proved the formation of hp-CoMoO<sub>4</sub> via CoMoO<sub>4</sub>·3/4H<sub>2</sub>O. The hydrothermal treatment of the same starting materials at 423 K provided CoMoO<sub>4</sub>·3/4H<sub>2</sub>O, but not hp-CoMoO<sub>4</sub>, like Livage's synthesis at 423 K. Moreover, in the case of the hydrothermal treatment of am-MoO<sub>3</sub>·*n*H<sub>2</sub>O and CoO at 453 K it took a much longer time

(about 6 days) for hp-CoMoO<sub>4</sub> to be completely formed from CoMoO<sub>4</sub>·3/4H<sub>2</sub>O, compared to the hydrothermal treatment of MoO<sub>3</sub> and CoO. Thus the formation of hp-CoMoO<sub>4</sub> seems to be related to the treatment temperature and the pH value of the solution as well as the nature of starting materials.

According to the literature [11-13,17], three polymorphs of CoMoO<sub>4</sub> are known. The formation of hp-CoMoO<sub>4</sub> from CoMoO<sub>4</sub>·3/4H<sub>2</sub>O seems not to agree with the Ostwald step rule [18], because hp-CoMoO<sub>4</sub> is the densest of the three (4.78, 4.57, 5.58 g/cm<sup>3</sup> for  $\alpha$ -,  $\beta$ -, and hp-CoMoO<sub>4</sub>'s, respectively) and is much denser than CoMoO<sub>4</sub>·3/4H<sub>2</sub>O (3.76 g/cm<sup>3</sup>). Thus we propose that the formation is related to a constrained process, that is, to a solid-state process rather than to a solution process. The fact, mentioned above, that the crystal size and crystallinity of CoMoO<sub>4</sub>·3/4H<sub>2</sub>O and hp-CoMoO<sub>4</sub> do not depend on the cooling rate and the concentrations of Mo and Co probably suggests a solid state formation of hp-CoMoO<sub>4</sub> from CoMoO<sub>4</sub>·3/4H<sub>2</sub>O. Because the CoMoO<sub>4</sub>·3/4H<sub>2</sub>O precipitates here tend to form a hard mass during the hydrothermal treatment, we checked to see if the morphology of the CoMoO<sub>4</sub>·3/4H<sub>2</sub>O sample is retained after the transformation into hp-CoMoO<sub>4</sub>. The CoMoO<sub>4</sub>·3/4H<sub>2</sub>O product was removed from the hydrothermal solution after a 1-day treatment. Then a part of the product was changed into hp-CoMoO<sub>4</sub> by treating it in the same hydrothermal solution for a further two days. Figure 4 shows that the morphology of the CoMoO<sub>4</sub>·3/4H<sub>2</sub>O is retained after transforming into the hp-CoMoO<sub>4</sub>, supporting the hypothesis that the transformation is a solid-state process.

This solid-state transformation occurs at temperature much lower than the usual solid-state transformation of hp-CoMoO<sub>4</sub> from  $\alpha$ -CoMoO<sub>4</sub> or  $\beta$ -CoMoO<sub>4</sub> (50 kbars and ca.900 K). Thus, it is expected that there is stronger affinity between the structures of CoMoO<sub>4</sub>·3/4H<sub>2</sub>O and hp-CoMoO<sub>4</sub> than between those of hp-CoMoO<sub>4</sub> and  $\alpha$ -CoMoO<sub>4</sub>/ $\beta$ -CoMoO<sub>4</sub>. Although the crystal structure of CoMoO<sub>4</sub>·3/4H<sub>2</sub>O was not known until quite recently, we successfully



determined its crystal structure and compared it to those of the three  $\text{CoMoO}_4$  polymorphs [19]. This comparison revealed that  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  consists of structural building units (shown in Figure 5) similar to those found in  $\text{hp-CoMoO}_4$ , and confirmed the strong structural affinity between  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  and  $\text{hp-CoMoO}_4$ . That is, these two phases consist of similar lengthened types of  $[\text{CoO}_6]_4$  units, differing from  $\alpha$ - and  $\beta$ - $\text{CoMoO}_4$ 's that are composed of the condensed types. And the lengthened types of  $[\text{MoO}_n]_4$  units in  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  and  $\text{hp-CoMoO}_4$  have similar arrangements of the  $\text{MoO}_n$  polyhedra, so that the pseudo  $[\text{MoO}_4]_4$  unit of  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  may turn easily into the  $[\text{MoO}_6]_4$  unit of  $\text{hp-CoMoO}_4$  by small translational and/or rotational displacements of corresponding  $\text{MoO}_n$  polyhedra. Thus we regard the formation reaction of  $\text{hp-CoMoO}_4$  from  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  as a SISSR.

This SISSR under hydrothermal conditions enables us to markedly reduce the prior severe synthetic conditions of  $\text{hp-CoMoO}_4$ . Thus similar SISSRs under hydrothermal conditions are expected to be useful tools for material syntheses and designs. Therefore we discuss briefly below SISSRs under hydrothermal conditions, which are useful for material design.

**SISSRs under hydrothermal conditions for material design.** In order to synthesize materials with desired structures and/or compositions, we have often to add or remove some structural units or some constituting elements from the starting materials. There may be three types of SISSRs under hydrothermal conditions: (i) addition, (ii) elimination, and (iii) substitution ones.

As for the addition SISSRs under hydrothermal conditions we have not found any real examples yet. Structural reconstructions under hydrothermal conditions, which are induced by addition reactions such as insertion or intercalation, are related examples. As for the last two types of SISSRs under hydrothermal conditions we have found examples in hydrothermal syntheses of M-Mo-O system ( $\text{M}=\text{Co}, \text{K}$ ), as shown in Figure 6. The present SISSR from  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  to  $\text{hp-CoMoO}_4$  is regarded as an elimination SISSR under the hydrothermal

condition. In this reaction dehydration takes place with structural reconstruction. Other than dehydration, leaching [20,21] of the starting materials under hydrothermal conditions may lead to interesting elimination SISSRs. The formation of  $K_{0.3}MoO_3$  from  $H_xMoO_3$  (Fig. 6(b)), which we found earlier [9], is attributed to a substitution SISSR under a hydrothermal condition. Structural retention under solid-state ion-exchange reactions under hydrothermal conditions is now quite common, with one famous example being the hydrothermal synthesis of hydroapatite by Roy et al. [1].

All the SISSRs mentioned above are related to the reactions used in ordinary soft chemistry. Various solid-state reactions concerning ordinary soft chemistry will provide many interesting SISSRs under hydrothermal conditions. Therefore, the presence of a large number of them is expected, although not so many SISSRs under hydrothermal conditions have been reported so far. Because many hydrates with a range of structures such as  $CoMoO_4 \cdot 3/4H_2O$  can be prepared via solution reactions even under ambient conditions, exploring their hydrothermal treatment might lead to some interesting SISSRs and some new compounds with novel structures. We believe that some presently considered hydrothermal solution reactions might in fact be occurring in the solid state with partial structural retention. Searching various SISSRs under hydrothermal conditions and analyzing them systematically will provide novel soft chemical tools useful for material designs, and could lead to a more rational approach to the synthesis of new materials.

## **Acknowledgement**

The work at Binghamton was supported by the National Science Foundation under grant DMR0313963, and we thank Dr. Masao Hashimoto for helpful discussions of the results of the present study.

## References

- [1] D. M. Roy, S. K. Linnehan, *Nature*, **247** (1974) 220.
- [2] W. Eysel, D. M. Roy, *Z. Kristallogr Bd* **141** (1975) 11.
- [3] K. Yanagisawa, J.C. Rendon-Angeles, N. Ishizawa, S. Oishi, *Am. Miner.*, **84** (1999) 1861.
- [4] Q. Feng, K. Kajiyoshi and K. Yanagisawa, *Chem. Lett.*, **32** (2003) 48.
- [5] R. Suárez-Orduña, J. C. Rendón-Angeles, J. López-Cuevas, K. Yanagisawa, *J. Phys.: Condens. Matter* **16** (2004) S1331.
- [6] K. Eda, K. Chin, M.S. Whittingham, *Chem. Lett.*, **28** (1999) 811.
- [7] K. Chin, K. Eda, N. Sotani, M.S. Whittingham, *J. Solid State Chem.*, **164** (2002) 81.
- [8] K. Eda, K. Chin, N. Sotani, M.S. Whittingham, *J. Solid State Chem.*, **177**, (2004) 916.
- [9] K. Eda, K. Chin, N. Sotani, M. S. Whittingham, *J. Solid State Chem.*, **178**, (2005) 158.
- [10]  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  (Calcd: Co 41.3 wt%, Mo 25.4 wt%,  $\text{H}_2\text{O}$  5.81 wt%; Found: Co 39.5 wt%, Mo 24.7 wt%,  $\text{H}_2\text{O}$  5.36 wt%),  $\text{hp-CoMoO}_4$  (Calcd: Co 26.9 wt%, Mo 43.9 wt%; Found: Co 25.9 wt%, Mo 43.9 wt%),  $\text{CoMo}_4\text{O}_{13} \cdot 2\text{H}_2\text{O}$  (Calcd: Co 8.58 wt%, Mo 55.9 wt%,  $\text{H}_2\text{O}$  5.25 wt%; Found: Co 8.66 wt%, Mo 56.1 wt%,  $\text{H}_2\text{O}$  5.35 wt%)
- [11] G. W. Smith, J. A. Ibers, *Acta Cryst.*, **19** (1965) 269.
- [12] J. A. Rodriguez, S. Chaturvedi, J. Hanson, A. Albornoz, J. L. Brito, *J. Phys. Chem.*, **B102** (1998) 1347.
- [13] C. Livage, A. Hynaux, J. Marot, M. Nogues, G. Férey, *J. Mater. Chem.*, **12** (2002) 1423.
- [14] T. Chirayil, E. A. Boylan, M. Mamak, P. Y. Zavalij, M. S. Whittingham, *Chem. Commun.*, (1997) 33.
- [15] M. Wiesmann, H. Ehrenberg, G. Wltschek, P. Zinn, H. Weitzel, H. Fuss, *J. Magn. Magn. Mater.*, **150** (1995) L1.
- [16] For the 1-day treatment 0.4551 g of the  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  precipitate was obtained from the reactant mixture {0.3455 g (2.4 mmol) of  $\text{MoO}_3$  and 0.1798 g (2.4 mmol) of  $\text{CoO}$ }, while 0.3879 g of the  $\text{hp-CoMoO}_4$  precipitate for the 3-day treatment.
- [17] A.W. Sleight, B. L. Chamberland, *Inorg. Chem.*, **7** (1968) 1672.
- [18] (a) W. Ostwald, *Z. Phys. Chem.* 22, (1897) 289. (b) D. Turnbull, *Metall. Trans.*, **A124** (1981) 695.
- [19] K. Eda, Y. Uno, N. Nagai, N. Sotani, M. S. Whittingham, *J. Solid State Chem.*, **178** (2005) 2791.
- [20] N. S. P. Bhuvanesh, S. Uma, G. N. Subbanna, J. Gopalakrishnan, *J. Mater. Chem.*, **5** (1995) 927.
- [21] K. Eda, A. Sukejima, N. Sotani, *J. Solid State Chem.*, **159** (2001) 51.

Table 1. Co-Mo-O products obtained by the hydrothermal treatment of various starting materials at 453 K for 3 days

run	Mo <sup>a</sup> source	Co <sup>a</sup> source	additives	initial state <sup>b</sup>	pH <sup>c</sup>	products
1	<u>MoO<sub>3</sub></u>	<u>CoO</u>	-	solid	4.1	hp-CoMoO <sub>4</sub>
2	am-MoO <sub>3</sub> · <i>n</i> H <sub>2</sub> O	<u>CoO</u>	-	solid+solution	2.1	CoMoO <sub>4</sub> ·3/4H <sub>2</sub> O, hp-CoMoO <sub>4</sub> , CoMo <sub>4</sub> O <sub>13</sub> ·2H <sub>2</sub> O
3	<u>MoO<sub>3</sub></u>	CoCl <sub>2</sub> ·6H <sub>2</sub> O	-	solid+solution	3.9	MoO <sub>3</sub>
4	am-MoO <sub>3</sub> · <i>n</i> H <sub>2</sub> O	CoCl <sub>2</sub> ·6H <sub>2</sub> O	-	solution	1.9	CoMo <sub>4</sub> O <sub>13</sub> ·2H <sub>2</sub> O, MoO <sub>3</sub>
5	<u>MoO<sub>3</sub></u>	<u>CoO</u>	HCl	solid	1.6	CoMo <sub>4</sub> O <sub>13</sub> ·2H <sub>2</sub> O, MoO <sub>3</sub>
6	am-MoO <sub>3</sub> · <i>n</i> H <sub>2</sub> O	<u>CoO</u>	HCl	solid+solution	1.6	CoMo <sub>4</sub> O <sub>13</sub> ·2H <sub>2</sub> O, MoO <sub>3</sub>
ref. 13 <sup>d</sup>	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	CoCl <sub>2</sub> ·6H <sub>2</sub> O	succinic acid, KOH	solution	3	hp-CoMoO <sub>4</sub>

<sup>a</sup> Underlined are the compounds that remain essentially in the solid state in the solutions before the hydrothermal treatment.

<sup>b</sup> The state of the solution before the hydrothermal treatment.

<sup>c</sup> pH value of the solution before the hydrothermal treatment.

<sup>d</sup> The product obtained by the hydrothermal treatment at 473 K for 3 days.

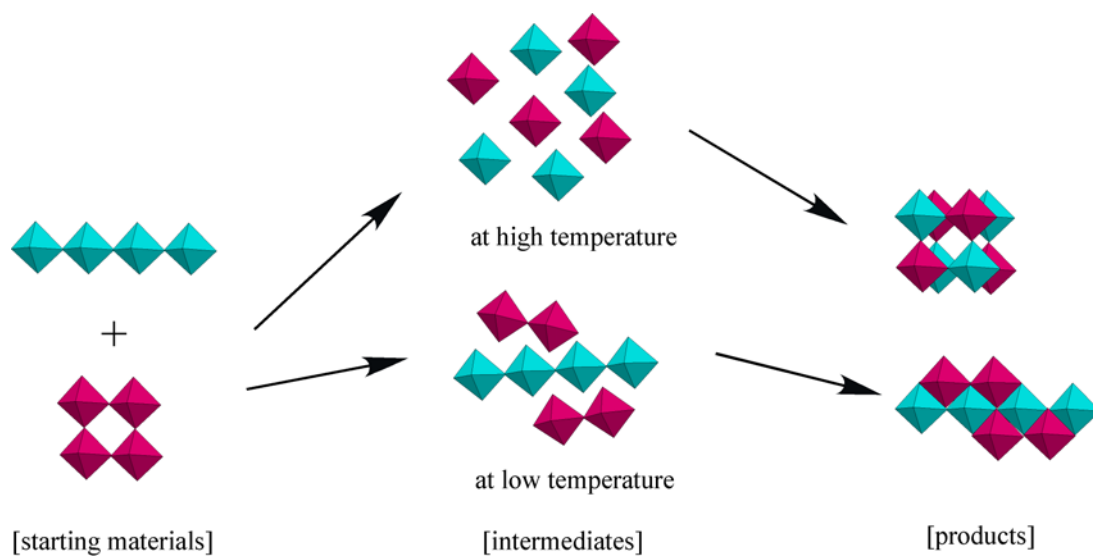


Fig. 1 Conceptual schemes of material formation.

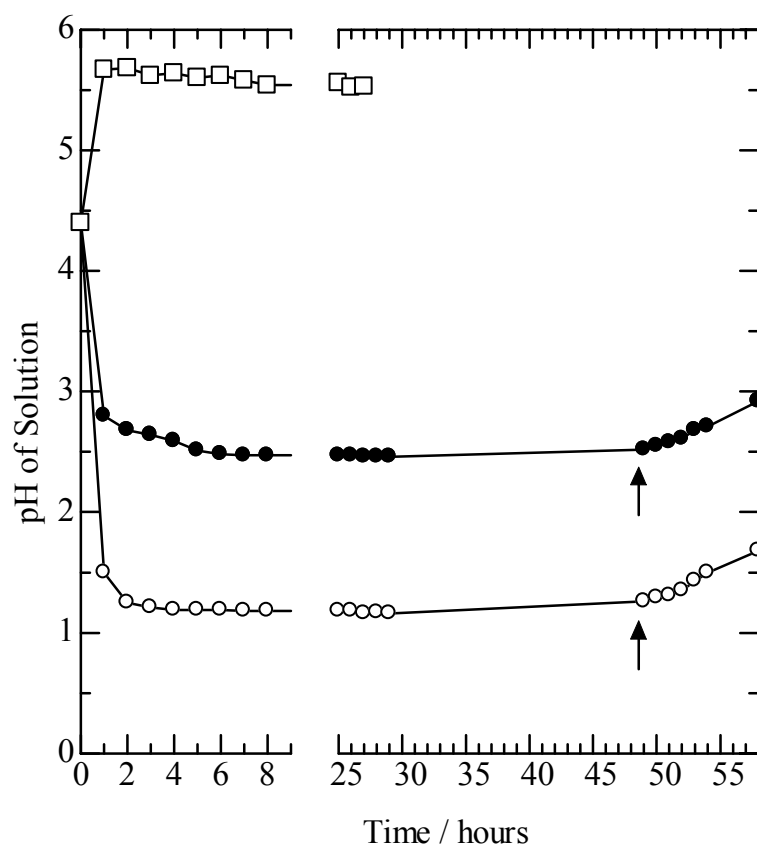


Fig. 2 The pH of solutions prior to hydrothermal synthesis for MoO<sub>3</sub> (0.01 mol in 100 ml water) at room temperature (●) and at 353 K (○), and the effect of adding CoO (0.01 mol). Arrows indicate the addition of CoO. After 1 week the pH values were 2.92 and 1.68 respectively. For comparison the data for ammonium molybdate is also presented (□).

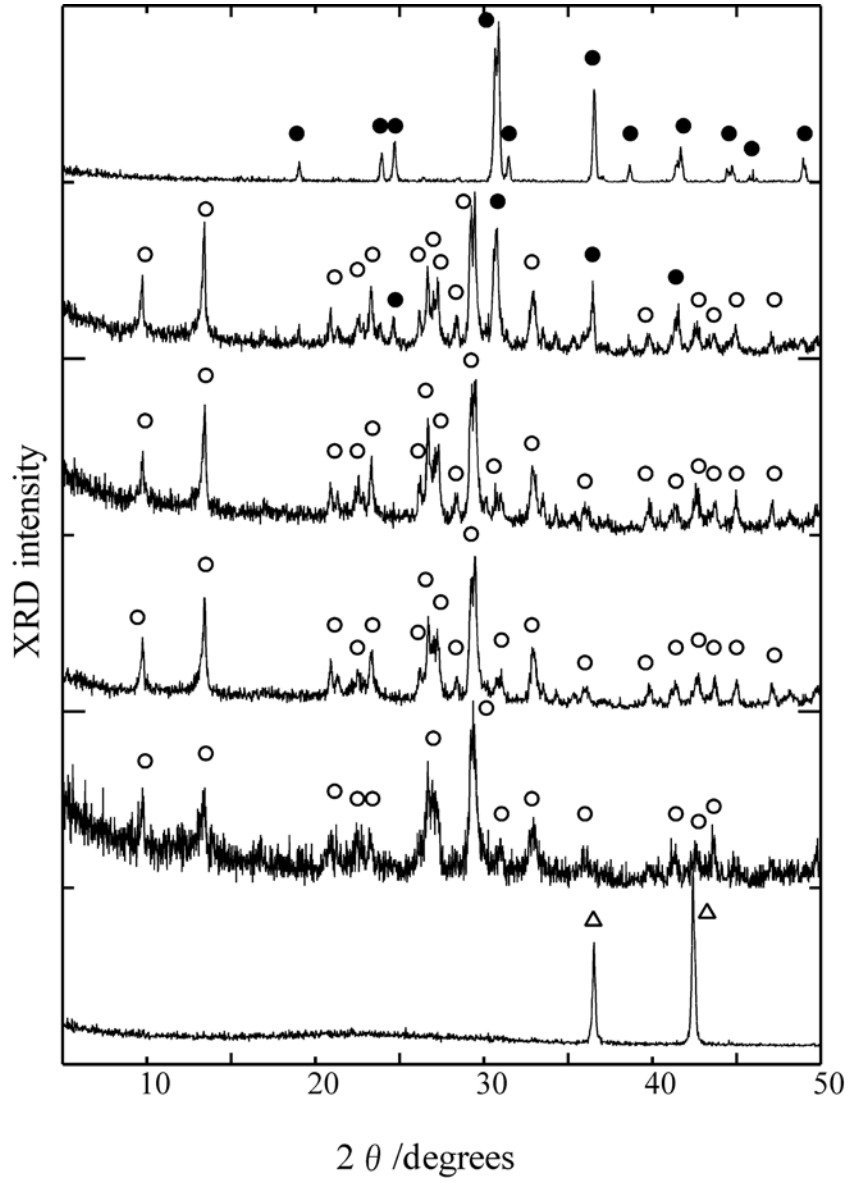


Fig. 3 The XRD patterns of the samples obtained by the hydrothermal treatments of  $\text{MoO}_3 + \text{CoO}$  at 453 K for 5 minutes (a), 3 hours (b), 12 hours (c), 1 day (d), 2 days (e), and 3 days (f). Symbols  $\Delta$ ,  $\circ$ , and  $\bullet$  indicate  $\text{CoO}$ ,  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$ , and  $\text{hp-CoMoO}_4$ , respectively.

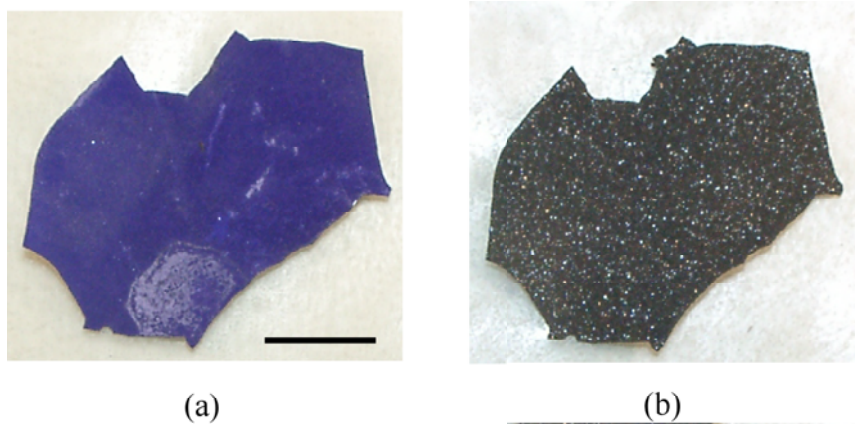


Fig. 4 Optical photographs of the samples: (a) before and (b) after the transformation from  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  to  $\text{hp-CoMoO}_4$  during the hydrothermal treatment at 453 K. The scale bar indicates 5 mm.



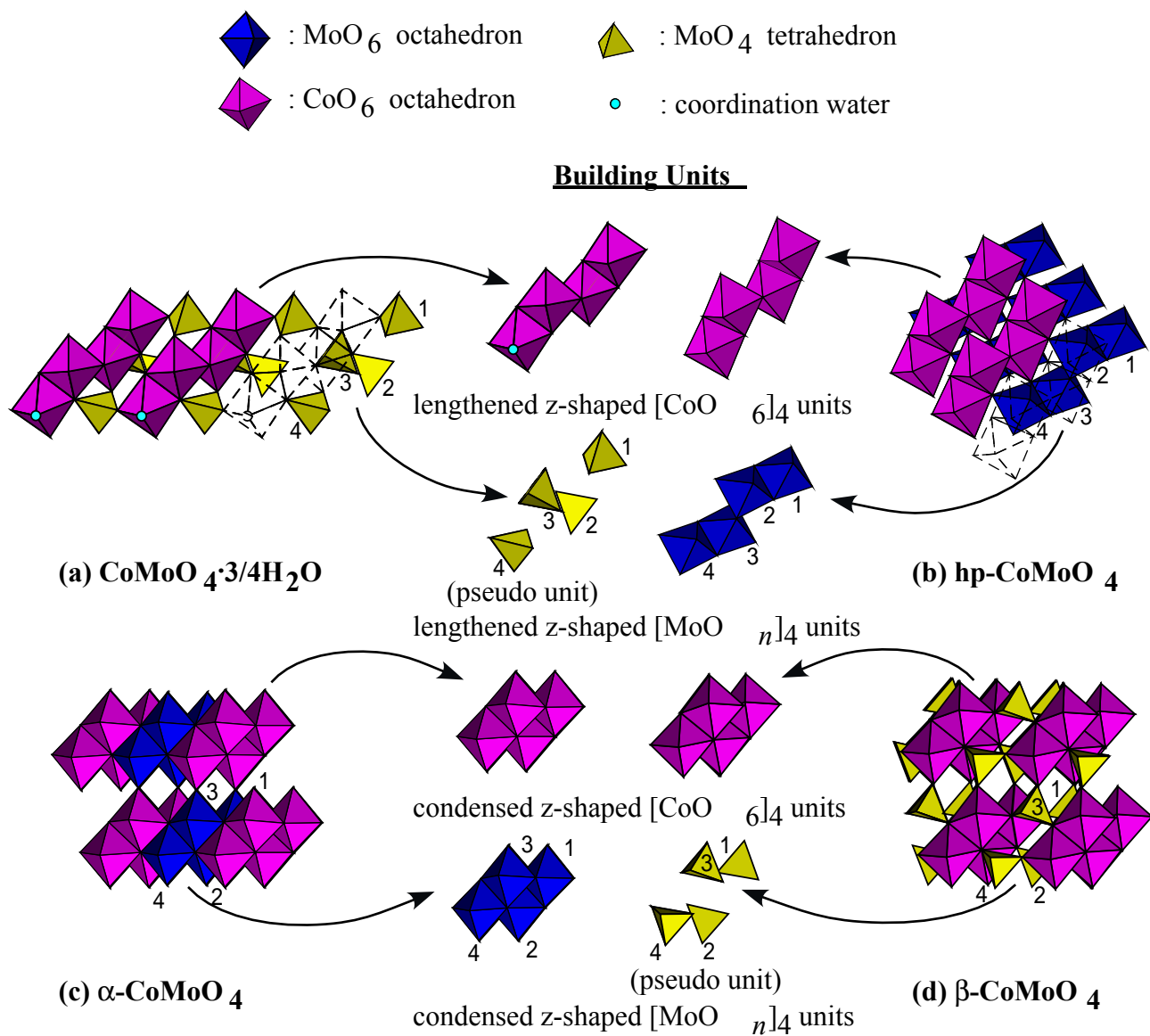
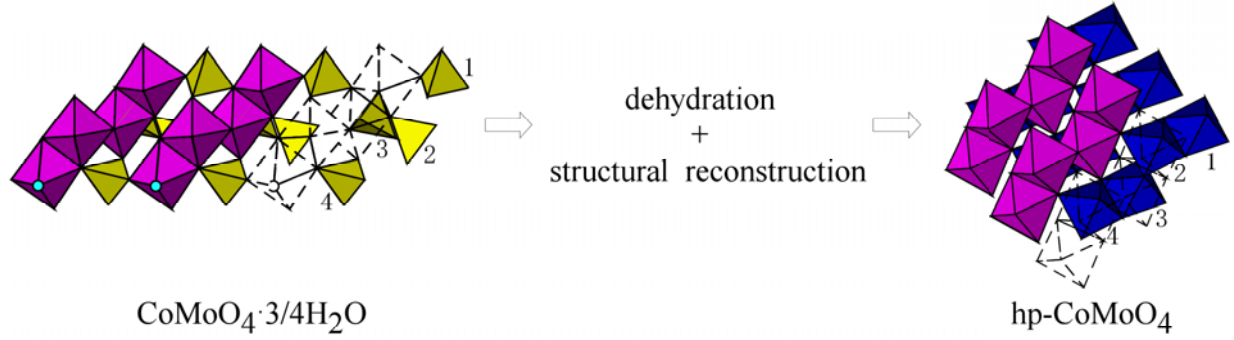


Fig. 5 Crystal structures and  $\text{Mo}_n$  building units of  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  and the three  $\text{CoMoO}_4$  polymorphs.

(a) Elimination SISSR under hydrothermal condition



(b) Substitution SISSR under hydrothermal condition

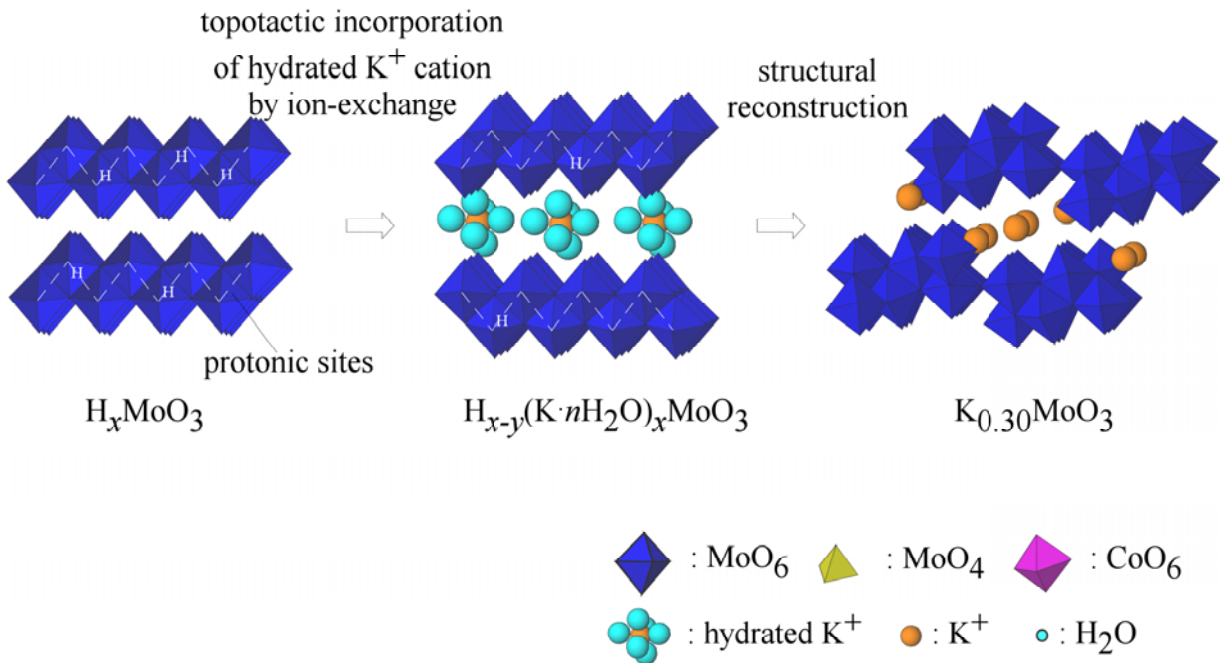


Fig. 6 Two types of SISSRs under hydrothermal conditions, found in the hydrothermal syntheses of M-Mo-O system (M=Co,K).