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Room Temperature Solid State Reaction Involving Structural Transformation of Covalent Oxide Network

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An interesting structural transformation from a two-dimensional (2d) covalent oxide network with a layered structure to a three-dimensional (3d) network with a tunnel structure was found at room temperature in the mixture of hydrated alkali-metal molybdenum bronze and amorphous alkali-metal molybdate. From various experimental results it was concluded that the transformation was due to a room temperature solid state reaction. © 2002 Elsevier Science (USA)

Key Words: **solid state reaction; room temperature reaction; transformation of covalent oxide network; Mo–O system.**

INTRODUCTION

Solid state reactions (SSRs) have been used to prepare many kinds of inorganic compounds. The SSRs applied to the preparations, however, are usually employed at elevated temperatures ($\gtrsim 600$ K), because of the diffusinal limitations. Recent attention of materials scientists has been focused on low temperature SSRs, because low temperatures make it possible to prepare metastable phases with interesting structures and properties (1, 2). Some room or low temperature SSRs have been known to occur in systems of coordination (2) or intermetallic compounds (3, 4) as well as soluble ionic compounds (5) (for example, $KMnO_4 + MnCl_2 \cdot 4H_2O$) with crystalline water, which affords a micro-liquid atmosphere during the reaction. In these systems considerable high mass transfer is expected because of their low melting points or low bond energies. However, no room temperature SSR, which involves some transformation of covalent networks having high bond energies and lower solubility, has been known so far, to the best of our knowledge. For the occurrence of the SSRs related to such transformations a high heating temperature is usually of essence.

Recently we found a novel room temperature SSR, which involves structural transformation of a covalent oxide network, in a molybdenum oxide system when studying structural changes of the covalent oxide network. The SSR occurred in a mixture of hydrated alkali-metal molybdenum bronze (mixed-valence compound with Mo^{V} and Mo^{VI}) having two-dimensional (2d) oxide network with a layered structure (6) and amorphous (amorphous-like) alkali-metal molybdate (monovalent Mo^{VI} compound), and led to the formation of an alkali-metal decamolybdate having a three-dimensional (3d) oxide network with a tunnel structure (7). In the present paper we will describe the details.

EXPERIMENTAL

Materials Preparation

Hydrated alkali-metal (*Na and Rb*) *molybdenum bronzes.* Hydrated sodium molybdenum bronze (*Na-br*) was prepared by chemical reduction of MoO_3 with sodium dithionate (8). Hydrated rubidium molybdenum bronze (*Rb-br*) was prepared from the hydrated sodium molybdenum bronze by ion exchange (9). Chemical compositions of Na-br and Rb-br used in the present work were $(Na{\cdot}2H_2O)_{0.25}\,H_{0.11}MoO_3$ (with $Mo^{5.64+}$ being the oxidation state of Mo) and $(Rb \cdot 0.6H_2O)_{0.22}H_{0.12}MoO_3$ (with $Mo^{5.66+}$), respectively.

Amorphous molybdate. Amorphous sodium molybdate (*Na-amr*) was precipitated from acidified Na_2MoO_4 solution. In a typical preparation the acidified solution was prepared by adding 25 ml of 6.0 M HNO_3 solution dropwise to 25 ml of 2.0 M A_2MoO_4 solution with constant stirring and then maintained at 303 K for one week for sufficient precipitation of the amorphous molybdate. The pale-yellow precipitate was collected by suction filtration, washed with distilled water, and air-dried for two days. Chemical composition of Na-amr used in the present work was $Na_{0.13}MoO_{3.07} \cdot 1.3H_2O$.

Mixing Procedure

Sufficient interfacial contact between sample particles was of essence in the reaction. M-br (M = Na, Rb) and Na-amr

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were mixed well in a proper molar ratio (usually 1:1) with an agate mortar and pestle for over a half an hour. (Although the mixing procedure was carried out under an ambient atmosphere, there was no significant incorporation of atmosphere water by the mixture during the procedure according to thermogravimetric analysis.)

Measurements

X-ray diffraction (XRD) patterns of the samples were measured using a zero-background sample holder (a Si single crystal cut "off-angle") on a MAC SCIENCE MXP3V X-ray diffractometer with Cu$K\alpha_1$ radiation (0.154056 nm, 40 kV, 35 mA). The Na, Rb, and Mo contents of the samples were determined with a HITACHI 180-80 atomic absorption spectrometer with the 589.0, 780.0, and 313.3 nm lines, respectively. The oxidation state of Mo or the hydrogen content of the sample was determined by the reducing power titration. Thermogravimetric and differential thermal analyses (TG-DTA) of the samples were carried out with a MAC SCIENCE TG-DTA 2010S system.

RESULTS AND DISCUSSION

The mixture of Na-br and Na-amr. The mixture of Na-br and Na-amr (named Na–Na mixture) was maintained at room temperature for a long time. Figure 1 shows the progression of structural changes over the duration for the mixture with a 1:1 molar ratio. In the figure gradual collapse (broadening and decrease in intensity of XRD peaks) of the Na-br structure, followed by the appearance and gradual growth of an hexagonal decamolybdate structure, was observed. Similar changes were observed for the mixtures with different mixing ratios 2:1 and 1:2. Because these structural changes proceeded very slowly, successive long aging was examined. Figure 2 shows the XRD pattern of the (1:1) mixture aged for six months, together with the patterns of Na-amr and sodium decamolybdate $Na_2Mo_{10}O_{31} \cdot nH_2O$, $n =$ approx. 6 (*Na-deca*). In Fig. 2c the XRD peaks corresponding to hexagonal decamolybdate were relatively more intense and sharper than those of the mixture aged for 14 weeks (Fig. 1f) A further aging process, however, gave no changes in the XRD pattern, indicating the completion of the reaction within six months. According to the XRD patterns (Figs. 2c and 2d, which is simulated from the patterns of Figs. 2a and 2b), the pattern of the well-aged mixture is seemingly a superposition of patterns due to Na-amr and Na-deca. The decamolybdate phase in the mixture had an hexagonal lattice with $a = 1.062$ nm and $c = 0.372$ nm, which was in good accordance with that of ordinary Na-deca ($a = 1.063$ nm, $c = 0.372$ nm).

The structural changes occurred in the solid mixture (Na–Na mixture) during the simple aging process at

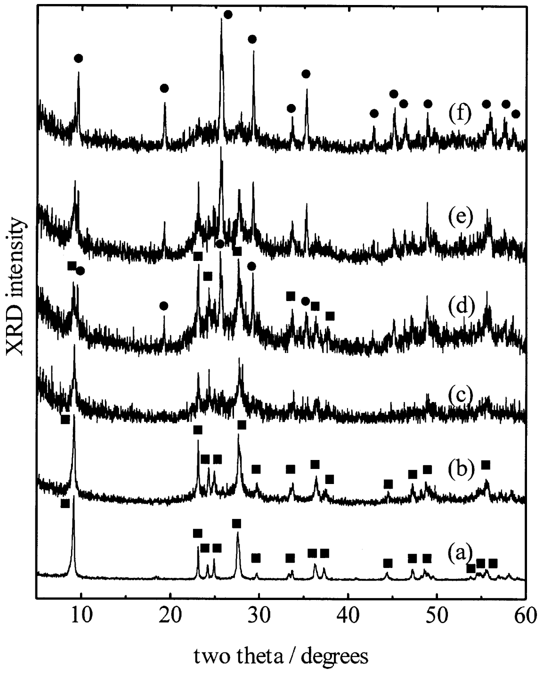

FIG. 1. The XRD patterns of Na-br (a) and of Na–Na mixtures aged for various periods: just after the mixture procedure (b), 3 weeks (c), 4 weeks (d), 6 weeks (e), and 14 weeks (f). The symbols ■ and ● indicate the phases Na-br and hexagonal decamolybdate, respectively.

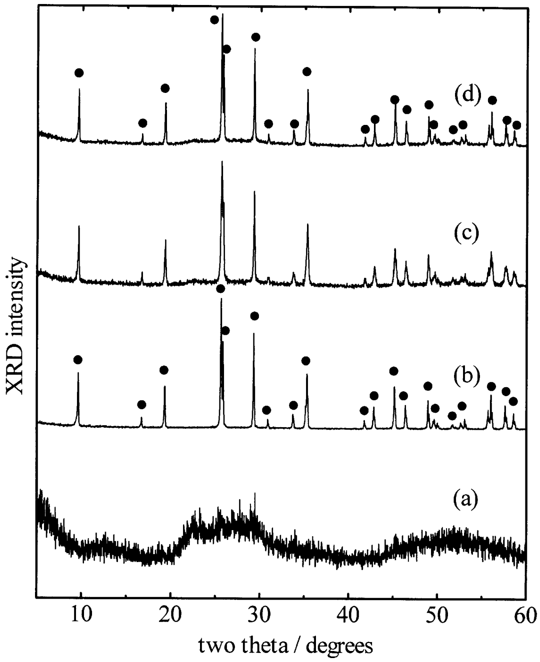

FIG. 2. The XRD patterns of Na-amr (a), Na-deca (b), and the Na–Na mixture (1:1) aged for six months (c). The pattern (d), simulated as a superposition of patterns (a) and (b) with a ratio of 5:2, is shown for comparison. The symbol ● indicates Na-deca or hexagonal decamolybdate.

room temperature. As mentioned above, Na-br (one of the starting materials) and Na-deca (the product) have different types of covalent oxide networks, which are important host structures in insertion chemistry of the Mo–O system. Thus there is the possibility that the observed structural changes are the first evidence of novel and interesting low-temperature SSRs which involve some transformation of the covalent oxide network. We, therefore, tried to examine whether the changes were due to room temperature SSR from Na-br into Na-deca.

The results of chemical analysis showed that the mixture was oxidized from $Mo^{5.84+}$ of averaged oxidation state of Mo to $Mo^{5.94+}$ during the changes, indicating some air oxidation of the mixture. A rise of temperature due to this oxidation, however, is negligible. In fact no appreciable rise of temperature was observed in the mixture for the aging duration. Furthermore, heat treatments of the mixture were performed at temperature above 400 K, but similar changes could not be obtained by the treatments. These results suggested that the observed structural changes proceeded indeed at room temperature, but not at elevated temperature due to an exothermic reaction such as the air oxidation.

In the present system it is considered that the two effects due to atmosphere (air oxidation and incorporation of water, which may result in some liquid phase reaction in the mixture) were concerned with the structural changes observed. According to visual and optical-microscopic inspections, no deliquescence of mixture (or no formation of liquid phase) was observed for the aging duration. In order to investigate (or remove) the effects, the reactions of mixtures sealed in glass ampoules were also examined. Similar structural changes with the aging process were observed for the mixture simply sealed in an ampoule, but were hindered for the mixture sealed in an evacuated ampoule. These results suggested that the structural changes were stimulated by the air oxidation, but not caused by the incorporation of water from the atmosphere directly. According to TG-DTA investigation, the water content of the 1:1 mixture was initially approx. $0.9H_2O/Mo$ (which was in accord with the value calculated from the water contents of Na-br and Na-amr) and decreased gradually to 0.8 H_2O/Mo over the aging duration. This water content is much lower than that (2.4 H_2O/M, $M = Mn$) of the system $KMnO_4 + MnCl_2 \cdot 4H_2O$ (mixed in a molar ratio of 2:3), which has been known to exhibit a room temperature SSR stimulated by a micro-liquid atmosphere (5). From these results, it was suggested that the observed structural changes were due to a reaction, which fell under the category of SSRs, although the air oxidation was concerned with the reaction.

As for the structural changes observed, the following three explanations were possible:

(1) The changes result from a reaction of Na-br with Na-amr, promoted by the air oxidation, the reaction of which leads to Na-deca as a product. (The amorphous phase observed in the well-aged mixture is attributed to some reaction byproduct or an excessive amount of Na-amr over Na-br.)

(2) They are due to a self-conversion of Na-br into Na-deca, stimulated by the air oxidation. In this case Na-amr is unchanged during the aging process.

(3) They are ascribed to an accidental combination of crystallization of Na-amr into Na-deca and the structural collapse of Na-br into an amorphous phase.

To prove explanations (2) and (3), two types of examinations were performed. First, variation in the Na-amr content of the mixture was examined using an XRD intensity comparison technique with Si powder as an internal standard. Then it was ascertained that the relative intensity of the broad hump in the range 20–30° of the XRD pattern, due to the amorphous phase, decreased to six-tenths of the initial one during the changes, indicating the consumption of the amorphous molybdate. These results conflicted with explanation (2). Next, the behaviors of Na-amr and Na-br under the same aging process were examined separately. As for Na-amr there was no significant structural change during the one-year aging. On the other hand Na-br showed an increase in the oxidation state from $Mo^{5.68+}$ to $Mo^{5.83+}$ at room temperature, but the original Na-br structure remained unchanged. In order to produce the more oxidized state for Na-br, the aging process was also performed at 340 K. According to the chemical analysis, the oxidation state of Mo increased from $Mo^{5.68+}$ to $Mo^{5.96+}$ during the (one-year) aging. Figure 3 shows the progression of the structural changes of Na-br under the aging process at 340 K. In this figure it can be seen that the original Na-br structure ($a = 0.384$ nm, $b = 1.926$ nm, and $c = 0.374$ nm) gradually turned into another structure, giving new XRD peaks. The newly appeared peaks were, however, indexed with an orthorhombic lattice with $a = 0.396$ nm, $b = 1.867$ nm, and $c = 0.372$ nm, which exhibits a strong filiation with the original Na-br structure, indicating that the 2d covalent network of the Na-br structure was preserved even when Na-br was nearly oxidized to the highest oxidation state ($Mo^{6.0+}$). These results did not support explanations (2) and (3).

Rb–Na mixture. In order to prove explanation (1), the evidence of mass transfer between the two phases during the changes was examined using another mixture (named *Rb–Na mixture*), where the two starting phases (Rb-br and Na-amr) contained different kinds of alkali-metal cations Rb^+ and Na^+, respectively. Figure 4 shows the

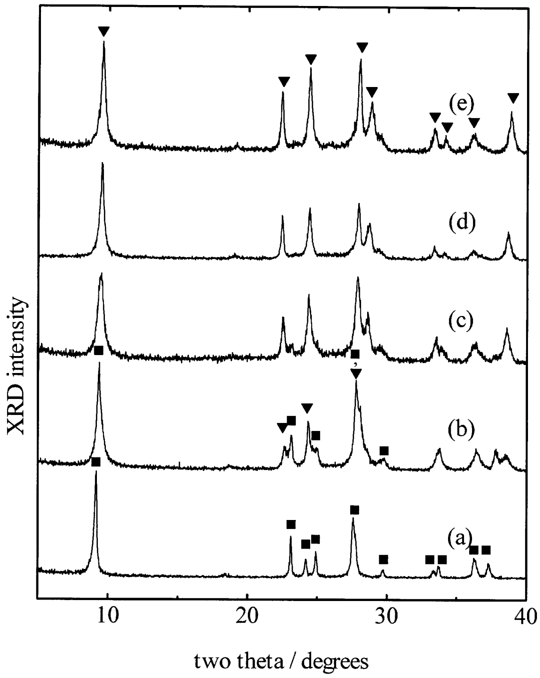

FIG. 3. The XRD patterns of Na-br aged for various periods at 340 K: as prepared (a), 2 months (b), 4 months (c), 5 months (d), and 1 year (e). The symbols ■ and ▼ indicate Na-br and newly appeared peaks, respectively.

XRD patterns of the Rb–Na mixture with a molar ratio of 1:1, together with the patterns of Rb-br and Na-amr. Changes with the aging procedure similar to those of the Na–Na mixture were observed. (The oxidation state of Mo changed from $Mo^{5.83+}$ to $Mo^{5.95+}$ during the changes.) The crystalline phase in the well-aged mixture (Fig. 4d) had a hexagonal lattice with $a = 1.059$ nm and $c = 0.373$ nm. This a value was intermediate between those of Na-deca ($a = 1.063$ nm) and Rb-deca ($a = 1.055$ nm), suggesting the coexistence of Na^+ and Rb^+ in the tunnel sites of the hexagonal decamolybdate structure. This result supported the transfer of Na^+ or Rb^+ between Na-amr and Rb-br (that is, explanation (1)).

To obtain further information about the changes in the respective phases of the mixtures (especially in the amorphous phase, which was less informative in X-ray diffractometory), heat treatments of the mixtures at the different aging stages were performed both in air and in N_2. Figures 5 and 6 show the XRD patterns of the samples heat-treated in air and in N_2, respectively. According to these figures, Na-amr turned mainly into MoO_3 with the heat treatments at 793 K, regardless of atmosphere (air and N_2). Rb-br provided, as the heat-treatment products, $Rb_2Mo_5O_{16}$ and hexagonal decamolybdate in air (Fig. 5b), while $Rb_{0.3}MoO_3$ and MoO_3 under N_2 (Fig. 6b). Heat-treatment products from the mixture just after the mixing procedure were explained roughly with those from Rb-br and Na-amr (Figs. 5c and 6c). However, the mixture aged for six months gave quite different products (Figs. 5d and 6d), indicating that considerably large structural and/or compositional changes occurred in both crystalline and amorphous phases of the mixture over the aging duration. According to the figures hexagonal decamolybdate was the major phase in the heat-treatment products from the well-aged mixture. We supposed that it was derived from the crystalline phase in the mixture (hexagonal decamlybdate phase, Fig. 4d) or that the phase retained its structure even after the heat treatments. To prove this hypothesis, we examined the heat treatments of the decamolybdate, which mainly contained Rb^+ in its tunnel sites, and ascertained that its structure was retained even after heat treatments at 773 K both under N_2 and in air. Thus it was suggested that phases other than the hexagonal one in the products (Fig. 5d and 6d) were derived mainly from the amorphous phase in the well-aged mixture. As mentioned above, the original amorphous phase (Na-amr) gave mainly MoO_3 after the heat treatments (regardless of atmosphere). Only a very minor amount of MoO_3 was, however, observed in the products from the well-aged mixture. Especially for the heat treatment under N_2 a mixed-valence ($Mo^V + Mo^{VI}$) compound $Na_{0.9}Mo_6O_{17}$ was formed instead of MoO_3 (Fig. 5d). This compound is, of course, attributed to one of the

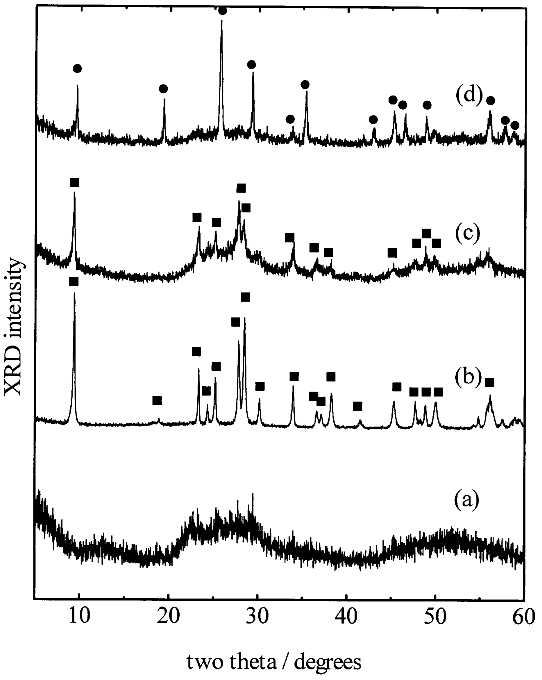

FIG. 4. The XRD patterns of Na-amr (a), Rb-br (b), and of Rb–Na mixtures just after the mixing procedure (c) and after six-months aging at room temperature (d). The symbols ■ and ● indicate Rb-br and hexagon decamolybdate structure.

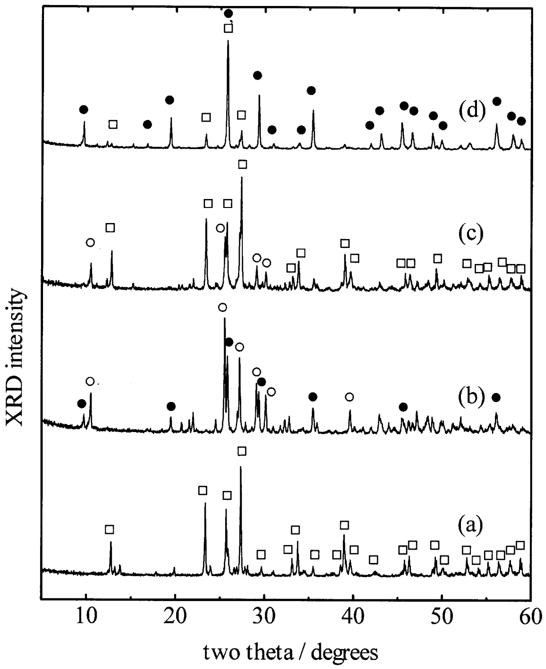

FIG. 5. The XRD patterns of the heat-treatment products (at 773 K in air) from Na–amr (a), Rb-br (b), and Rb–Na mixtures just after the mixing procedure (c) and after six-months aging at room temperature (d). The symbols □, ●, and ○ indicate MoO_3, Rb-deca, and $Rb_2Mo_5O_{16}$, respectively.

products derived from the amorphous phase, which was originally a Mo^{VI} compound, in the mixture. Thus it was suggested that some transfer of electron, oxygen, or Mo^{V} occured between Rb-br (mixed-valent Mo^{V} + Mo^{VI} compound) and Na-amr (monovalent Mo^{VI} compound) during the aging process, supporting explanation (1).

SSR of M (M = Na, Rb)-br with Na-amr into M-deca. The results mentioned above elucidated that the structural changes of the mixtures during the aging process were due to a room temperature SSR of M-br with Na-amr into M-deca, followed by air oxidation.

According to the literatures (6, 7), M-br and M-deca have well-extended covalent oxide networks, as shown in Fig. 7. These networks consist of double chains of edge-sharing MoO_6 octahedra linked by common corners, but have different manners of linkage. The double chains are linked only with the bonds perpendicular to the chain's plane in M-br, while they are linked with the bonds both parallel and perpendicular to the plane in M-deca (Fig. 7). Therefore, it is suggested that switchover of covalent bonds concerning the linkage occurs in the SSR discussed.

Na-amr has not been well studied so far. It was rather soluble in water, suggesting that it did not have any stout covalent network, unlike M-br and M-deca. According to X-ray absorption near edge structure (XANES) investigation, it consists of MoO_6 octahedra. A detailed structure of it, however, has not been made clear yet, although we have been making various efforts. We only suppose that the rather high solubility of Na-amr and the micro-liquid atmosphere afforded by crystalline water in the mixture allow the mass transfer related to the present room temperature SSR. A detailed mechanism concerning the transformation of the covalent network has not been revealed yet. As a future problem we will try to make the mechanism clear.

CONCLUSION

In Na-Na and Rb-Na mixtures an interesting structural transformation from a hydrated bronze structure with a 2d covalent oxide network to an hexagonal decamolybdate structure with a 3d covalent oxide network was found at room temperature for the first time. On the basis of various examinations we concluded that the transformation was due to a room temperature SSR of M-br with M'-amr, which involved structural transformation of the covalent oxide network. Speaking strictly some oxidation also occurs during the transformation and the total reaction is expressed as $M\text{-br(s)} + M'\text{-amr (s)} + O_2\text{(g)} \rightarrow M\text{-deca (s)}$.

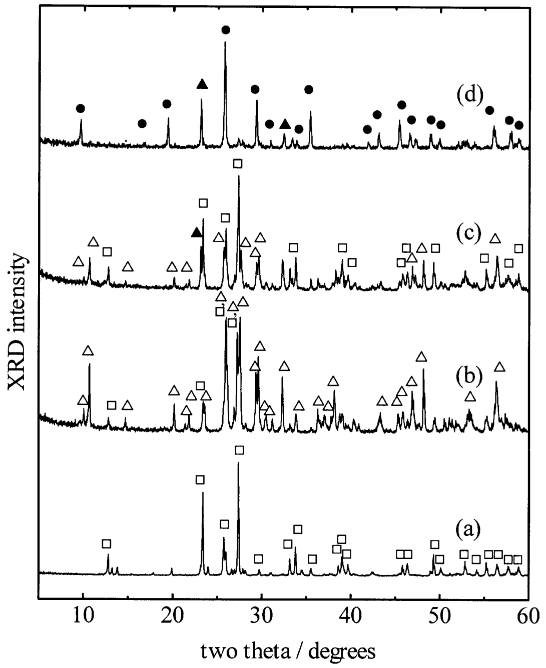

FIG. 6. The XRD patterns of the heat-treatment products (at 773 in N_2) from Na-amr (a), Rb-br (b), and Rb–Na mixtures just after the mixing procedure (c) and after six-months aging at room temperature (d). The symbols □, △, ▲, and ● indicate MoO_3, $Rb_{0.3}MoO_3$, $Na_{0.9}Mo_6O_{17}$, and hexagonal decamolybdate, respectively.

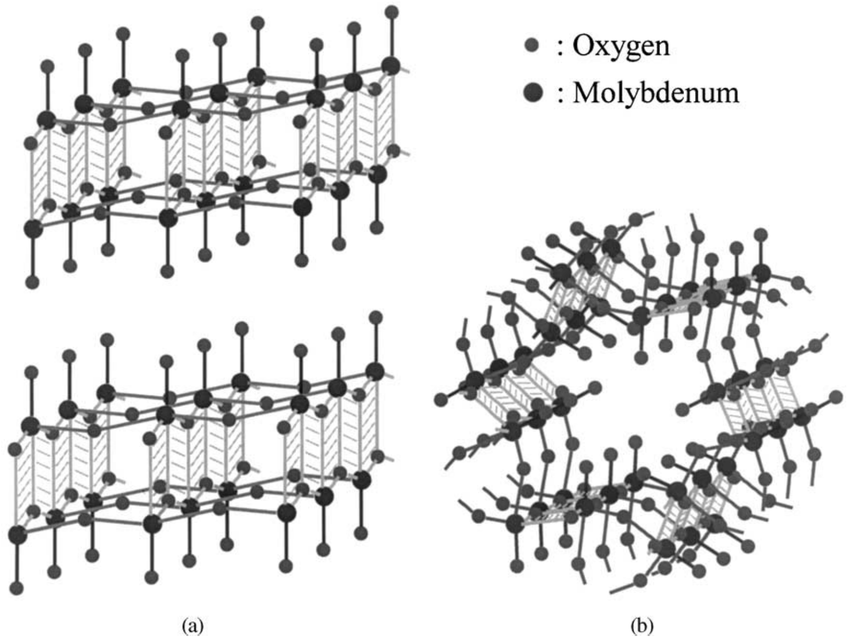

FIG. 7. Schematic models of hydrated alkali-metal molybdenum bronze *M*-br (a) and alkali-metal decamolybdate *M*-deca (b). Alkali-metal ions are excluded and the planes of the double chains, consisting of edge-sharing MoO_6 octahedra, are shaded. (Only five-sixths of the Mo sites are randomly occupied in *M*-deca.)

For the occurrence of transformation of covalent oxide networks, a high temperature is usually of the essence because of their high bond energies. In these (high-temperature) cases the transformation is completed momentarily and therefore investigation of the mechanisms of the transformation is difficult. However, in the present system the transformation proceeds very slowly and its mechanism is easy to investigate. We hope that the present system is fully investigated and opens a new prospect on material designs concerning covalent oxide networks.

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