New Low-Temperature Synthetic Method of Complex Inorganic Solids: Amorphous Route Based on Amorphous Nature of Soluble Giant Clusters

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The amorphous nature of molybdenum giant clusters (molybdenum blue species) was used to prepare compositionally well-arranged precursors (homogeneous amorphous phase), which are suitable for lower temperature syntheses of alkali-metal molybdenum oxide bronzes. Then, it was confirmed that soluble giant clusters such as molybdenum blue species afforded very attractive merits for materials syntheses.

Complex inorganic solids are generally synthesized by repeated grinding and firing at elevated temperatures of the reactant mixtures. The higher firing temperature is of essence of overcoming the diffusional limitations. Such a higher temperature procedure causes sometimes several disadvantages: products with large particle size as well as an inaccessibility of metastable phases which have interesting structures and properties. This recognition has stimulated solid state chemists to develop new synthetic techniques, by which the reaction proceeds at low temperature, such as sol–gel processing.[1–4]

Sol–gel approaches have been investigated extensively to succeed in obtaining a number of metal oxides such as Al_2O_3, Nb_2O_5, MoO_3, WO_3, as well as mixed-metal oxides at lower temperatures.[5] Although the higher valent oxides could be readily obtained by these sol–gel methods, little was known about obtaining lower valent oxides. Manthirm's group and we have independently proposed some low-temperature synthetic routes for lower valent oxides, in which non-stoichiometric single-phase compounds being homogeneous in wide compositional ranges (amorphous precipitates obtained by reducing aqueous oxometalate species with $NaBH_4$ or KBH_4 for Manthiram group[6,7] and intercalation compounds for us[8,9]) are used as starting materials for the syntheses. In these routes, however, compositional control of the single-phase compounds is not so easy, because their compositions depend on various parameters such as temperature, solution pH, concentration, etc. Thus products usually contain some by-products.

"Amorphous molybdenum blue" has been known since C.W. Scheele in 1793.[10] Recently Müller's group revealed that it consisted of extremely large ring-shaped, mixed-valent cluster with large open space, indicating that its amorphous character results from the difficulties of positioning extremely large anions into a highly ordered lattice.[11] This amorphous character can be expected to provide an effective preparation route of compositionally well-controlled, homogeneous materials suitable for low-temperature syntheses. The present author attempted to use this method to prepare starting materials of alkali metal molybdenum oxide bronzes having very attractive properties, such as pulse sign memory effects and ac response to a dc bias[12] It was confirmed that the method was very convenient for low-temperature syntheses of complex solids. This idea opens new perspectives for materials syntheses. In the present paper, therefore, the above results are presented briefly.

Aqueous molybdic acid was prepared by ion-exchanging aqueous sodium molybdate with an ion-exchange resin (Dow Chemical Co. Dowex 50W-X8). The solution was reduced with H_2/Pd treatment to prepare pure lower valent molybdic acid (without foreign ions) consisting of the molybdenum giant cluster species.[13] The presence of these species in the solution was confirmed by UV–vis (ca. 750 nm band) and Raman spectroscopy (ca. 800, 530, 460, 330, and 220 cm^{-1} bands).[11] The reduction power of the lower valent molybdic solution was measured by cerimetric titration and was adjusted to match that of target material by mixing with the original higher valent molybdic acid solution or by additional reduction with the H_2/Pd treatment. Aqueous alkali carbonates were added as alkaline sources in correct molar ratio to the aqueous molybdic acid with well-arranged reduction power in order to lead to the target composition like as H_xMoO_y (molybdic acid) + x/2 $A_2CO_3 \rightarrow A_xMoO_y + x/2\ CO_2\uparrow + x/2\ H_2O$.

Amorphous solids with well-arranged compositions were obtained simply by vacuum drying the resulting solutions. X-ray diffraction (XRD) investigations revealed that amorphous solids could be obtained in wide ranges of compositions, independent of the kinds of alkaline sources. The amorphous solids were fired at elevated temperatures to obtain target materials. Figure 1 shows thermogravimetory–differential thermal analysis (TG–DTA) curves recorded with the amorphous solid prepared with the sodium content of 0.17 Na/Mo (mole ratio) and Mo of average oxidation state 5.50+ (at a heating rate of 10 $K{\cdot}min^{-1}$ in a nitrogen atmosphere). We see a broad, strong endothermic peak centered around 390 K and a very sharp exothermic peak at 608 K (DTA). The endothermic peak is followed with a large weight loss (TG) and corresponds to dehy-

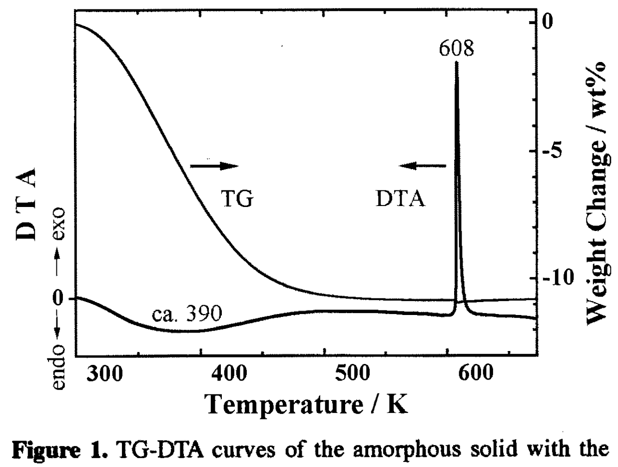

Figure 1. TG-DTA curves of the amorphous solid with the Na content of 0.17 Na/Mo and the average oxidation state of $Mo^{5.50+}$.

dration of crystallization water of the sample. The dried samples for all compositions prepared contained such crystallization water (5–13 wt% of the sample). The sharp endothermic peak is attributed to crystallization. This was confirmed by the XRD investigation. That is, the sample retained the amorphous nature (absence of discernible Bragg reflections) before the exothermic peak, while after the peak it turned into the target material ($Na_{0.90}Mo_6O_{17}$), excepting a very minor amount of unidentified by-product (probably monoclinic-Mo_4O_{11}), showing sharp Bragg reflections (Figure 2b).

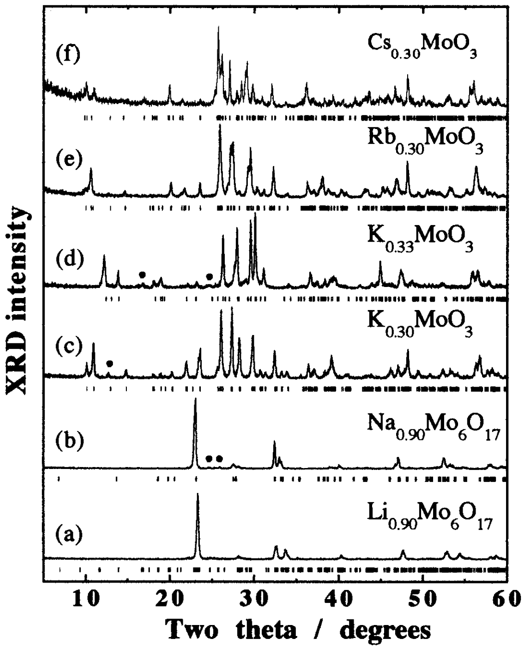

Figure 2. XRD patterns of final products (fired at 673 K) with 0.17 Li/Mo, Mo$^{5.50+}$ (a); 0.17 Na/Mo, Mo$^{5.50+}$ (b); 0.28 K/Mo, Mo$^{5.72+}$ (c); 0.33 K/Mo, Mo$^{5.67+}$ (d); 0.30 Rb/Mo, Mo$^{5.70+}$ (e); and 0.30 Cs/Mo, Mo$^{5.70+}$ (f). Calculated peak positions of corresponding bronzes (shown by chemical formulas) are drawn below the respective patterns. Symbol ● indicates by-products.

According to detailed investigations, the bronze was formed drastically at the exothermic peak and there was no need of long-term firing at elevated temperature for the formation. Many kinds of alkali metal molybdenum oxide bronzes were also easily obtained as almost single-phases through the present route at lower temperature around 600 K, some 200–300 K below those used in the ordinary methods (Figure 2, Cu Kα radiation). (These bronzes were identified by comparing with XRD patterns simulated with literature crystal data.[14])

Soluble amorphous solids of the lower valent molybdic acid are also easily obtained by vacuum drying and are storable. In the present method compositional adjustment is very easily achieved only by mixing solutions in proper molar ratio: mixing higher- and lower- valent molybdic acid and appropriate quantity of alkali carbonate to adjust the reduction power and the composition. Furthermore, the rheological properties of the resulting solution will allow the formation of fibers or films by such techniques as spinning, dip-coating or impregnation. Finally it should be mentioned that the present work provides not only attractive synthetic routes of molybdenum oxide bronzes but also a novel strategy of materials syntheses, which uses specific features of giant clusters.

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