

6 Crystallography

6-1 pH Dependent Formation of Three-Dimensional Network Structures with $\{\text{Mo}_{154-x}\}$ Building Blocks

The chemical or photochemical reduction of acidified aqueous molybdate solutions leads to the formation of high-nuclearity mixed-valence polyoxometalates with sizes of typically several nanometers. In some circumstances, these nano-clusters further condense into one-, two- or three-dimensional network structures. The network structures thus formed are expected to possess large cavities between the clusters, implying the possible application of this family of compounds as gas storage materials and/or ionic conductors. Since these properties strongly depend on the network structure, the mechanism of the condensation of the polyoxometalate nano-clusters is of considerable interest. However, a comprehensive study of the formation conditions of the network structures is still lacking. Here we have prepared a series of $\{\text{Mo}_{154-x}\}$ compounds with a precisely controlled preparative procedure. Single-crystal synchrotron-radiation X-ray diffraction studies of these samples revealed the pH dependence of the condensation reactions of the polyoxometalate nano-clusters.

A study of the pH dependence of the synthetic conditions has led us to find four kinds of compounds, **1**, **2**, **3** and **4**, which were obtained from solutions carefully controlled with pHs of 3.3, 2.2, 1.7 and 1.4, respectively. Compound **1** crystallized to monoclinic space group $C2/m$ with $a = 26.9098(6)$ Å, $b = 42.9546(14)$ Å, $c = 29.4850(9)$ Å and $\beta = 94.283(1)^\circ$. Compound **2** crystallized to monoclinic $C2/m$ with $a = 42.0599(7)$ Å, $b = 40.0450(5)$ Å, $c = 22.5450(3)$ Å, and $\beta = 94.587(1)^\circ$.

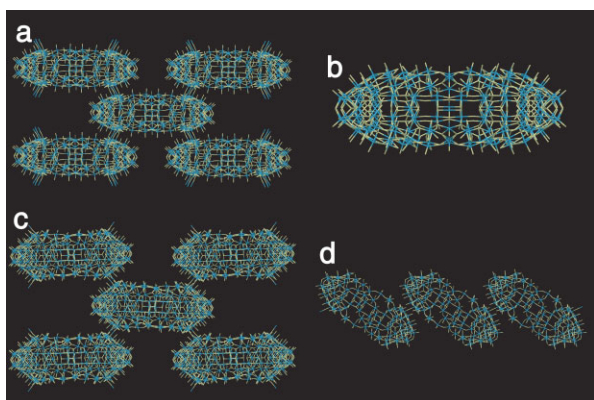


Figure 1 Structures of (a) $\{\text{Mo}_{138}\text{O}_{460}\text{O}_{16/2}\}$ in compound **1**, (b) $\{\text{Mo}_{142}\text{O}_{490}\}$ in **2**, (c) $\{\text{Mo}_{148}\text{O}_{499}\text{O}_{12/2}\}$ in **3**, and (d) $\{\text{Mo}_{150}\text{O}_{514}\text{O}_{4/2}\}$ in **4**.

Compound **3** crystallized to monoclinic $C2/c$ with $a = 59.1887(5)$ Å, $b = 47.1521(5)$ Å, $c = 31.8640(3)$ Å, and $\beta = 109.695(1)^\circ$. Compound **4** crystallized to monoclinic $C2/m$ with $a = 33.4487(5)$ Å, $b = 53.5509(10)$ Å, $c = 26.6748(10)$ Å, and $\beta = 107.175(1)^\circ$.

Synchrotron X-ray diffraction studies of these samples revealed that compounds **1**, **2**, **3** and **4** contain giant clusters formulated as $\{\text{Mo}_{138}\text{O}_{460}\text{O}_{16/2}\}$, $\{\text{Mo}_{142}\text{O}_{490}\}$, $\{\text{Mo}_{148}\text{O}_{499}\text{O}_{12/2}\}$ and $\{\text{Mo}_{150}\text{O}_{514}\text{O}_{4/2}\}$. Their structures are shown in Fig. 1. While $\{\text{Mo}_{142}\text{O}_{490}\}$ in **2** is isolated from its neighboring anions, $\{\text{Mo}_{138}\text{O}_{460}\text{O}_{16/2}\}$ in **1** is connected to four neighboring anions through 16 linker O atoms (16/2 means that each of these 16 atoms is shared by an adjacent anion), $\{\text{Mo}_{148}\text{O}_{499}\text{O}_{12/2}\}$ in **3** is connected to six neighboring anions through 12 linker O atoms, and $\{\text{Mo}_{150}\text{O}_{514}\text{O}_{4/2}\}$ in **4** is connected to two neighboring anions into a chain structure.

The growth in nuclearity of the clusters is in accord with an increase of the acidity of the mother liquor, which is easily rationalized because the molecular growth consumes protons. On the other hand, the condensation of the clusters into network structures, which is also a proton-consuming process, is not directly correlated with the pH of the mother liquor. The number of oxygen atoms shared by neighboring clusters are 16, 0, 12 and 4 for compounds **1**, **2**, **3** and **4**. The smaller nuclearity cluster in **1** has a total of eight clefts as shown in Fig. 2. This allows the clusters to approach closer to each other and to form highly condensed network structures. In conclusion, the network formation with the polyoxometalate nano-clusters is indirectly influenced by the pH of the mother liquor via the nuclearity and the structure of the building block nano-clusters.

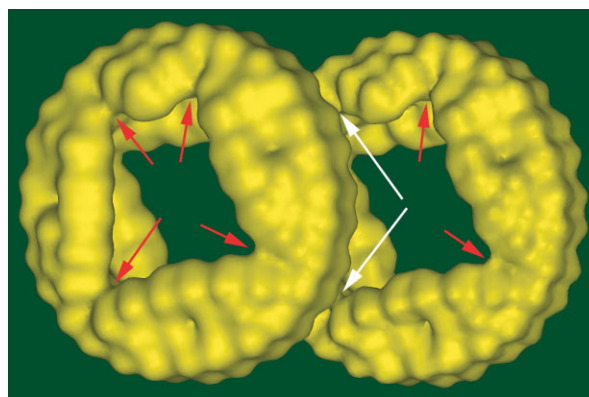


Figure 2 Molecular surface drawing of $\{\text{Mo}_{138}\text{O}_{460}\text{O}_{16/2}\}$ in compound **1** showing the intrusion of the nano-cluster into the cleft of its neighboring cluster depicted by white arrows. Red arrows indicate other clefts of the clusters, which accommodate further clusters.

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6-2 A Charge-Ordered State in Geometrically Frustrated Crystal AlV_2O_4

In spinel compounds AB_2X_4 , octahedrally coordinated B sites form a pyrochlore lattice, causing a geometrical frustration. When the B sites are occupied by mixed-valence ions, a charge frustration occurs and an interesting ground state effects such as charge ordering (CO) are often observed at low temperature.

A typical example is the spinel compound AlV_2O_4 , in which the average valence of V is 2.5+. This compound exhibits a CO transition at $T_{\text{CO}} \sim 700$ K [1,2]. The structural model reported previously [1] locates the V ions on the Kagome lattice, with those on the triangular lattices with different valences stacking alternately along the [111] direction. However, both X-ray powder-diffraction and electron-diffraction studies show the presence of a superlattice structure with a wave vector $\mathbf{q} = 1/2[111]$, a structure which was not considered in the model of [1]. In order to clarify the CO state in AlV_2O_4 , the detailed crystal structure has been investigated by making high-resolution X-ray powder-diffraction measurements.

Synchrotron X-ray powder-diffraction experiments were carried out using a multiple-detector system (MDS)

installed at BL-4B2 station [3]. A flat Ge(111) analyzer was used to improve the angular resolution. Diffraction data of AlV_2O_4 at room temperature in a 2θ range of 7 - 153° were recorded using an asymmetric 2θ scan mode at an incident angle of $\theta = 7^\circ$. The wavelength of the incident beam was $\lambda = 1.2060$ Å.

Figure 3 shows the powder patterns of AlV_2O_4 observed at room temperature. The crystal symmetry determined from the splitting of the fundamental reflections was found to be rhombohedral, in agreement with previous work [1]. Therefore each reflection was indexed using the cell parameters reported in [1], with the difference that a hexagonal axis was chosen here. Besides the fundamental reflections indexed with whole integers, superlattice reflections indexed by $h k l/2$, corresponding to reflections characterized by a wave vector $\mathbf{q} = 1/2[111]$ in a cubic axis, are also observed (Fig. 3(a)). Thus a cell twice as large as the previous one and orientated in the c direction was selected as the unit cell of the CO state. Based on this information and the results of electron-diffraction patterns, a preliminary structural model was constructed and structural refinement was performed by a Rietveld analysis based on the powder-diffraction data. The cell parameters of the new crystal structure were determined to be $a = 5.75148(3)$ Å and $c = 28.85407(14)$ Å, with a space group is $R\bar{3}m$. The

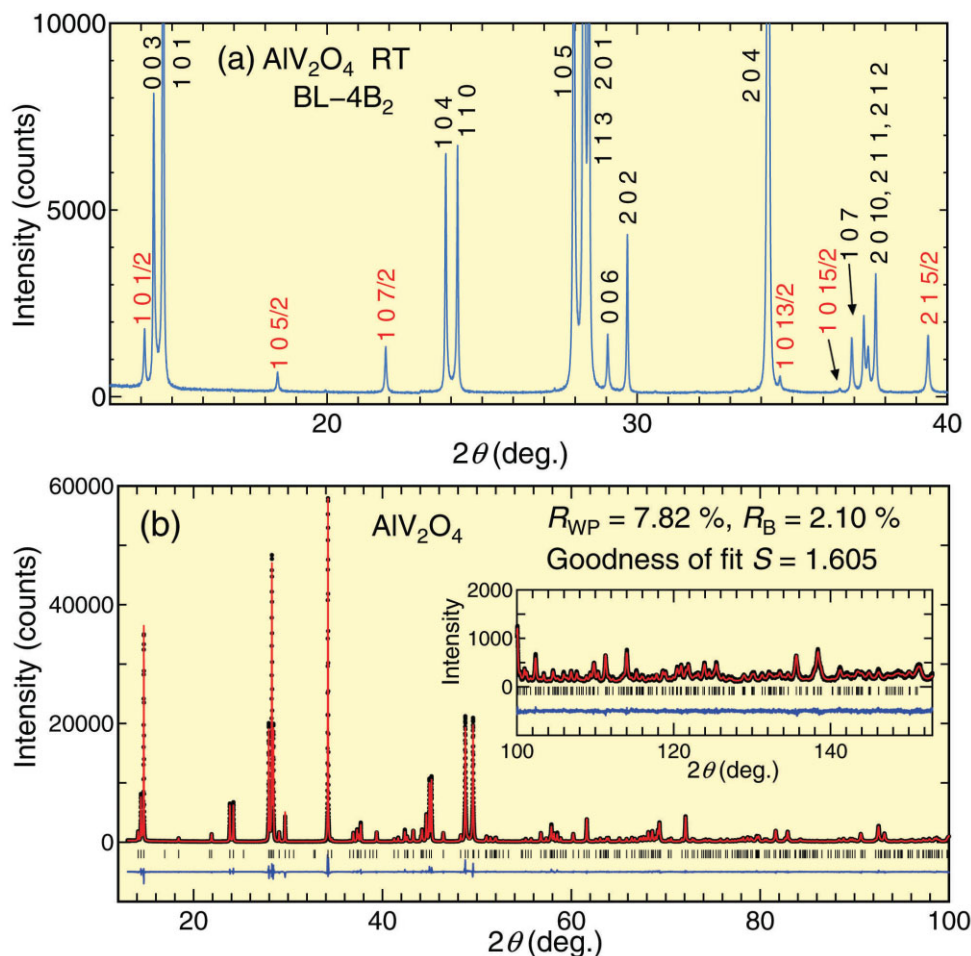


Figure 3 Whole X-ray powder-diffraction pattern of AlV_2O_4 . (a) The indices are based on the rhombohedral symmetry with a lattice constant of $a \sim 5.75$ Å and $c \sim 14.43$ Å (hexagonal axis choice) [1], where superlattice reflections indexed by $h k l/2$ are also observed. (b) The result of the Rietveld analysis.

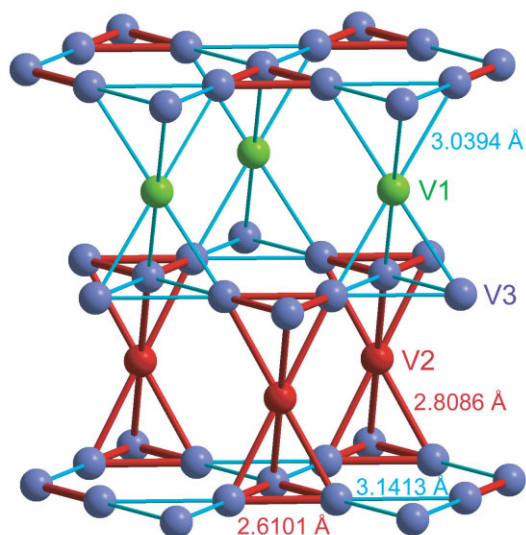


Figure 4
The crystal structure in the CO phase of AlV_2O_4 , where only the V atoms are shown. The thick red bonds show the “heptamer” V clusters.

overall quality of the fitting was fairly good (Fig. 3(b)) [4]. The newly determined crystal structure of the CO state is shown in Fig. 4. This structural model indicates three crystallographically independent sites occupying the V atom sites: two V atoms (V1 and V2) on the triangular lattice and one V atom (V3) on the Kagome lattice. There are four different V-V bond lengths. Two of them

are short (V3-V3: 2.6101 Å, V2-V3: 2.8086 Å) and the others are long (V3-V3: 3.1413 Å, V1-V3: 3.0394 Å). The shorter V3-V3 bonds form “trimers” on the Kagome lattice and all the V2 atoms are sandwiched by two V3 trimers. As a result, seven V atoms form a V cluster, a “heptamer”. Studies of the magnetic properties of the crystal have shown that this V heptamer forms a spin-singlet state [4]. Further, the origin of the stabilization of the V heptamer is a strong bonding of the d - d direct overlap of the V t_{2g} orbitals.

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