

$\text{RbMo}_2\text{P}_2\text{O}_{10}(1-x) \text{H}_2\text{O}$ and $\text{CsMo}_2\text{P}_2\text{O}_{10}$. The main difference between these compounds is the filling of the tunnel by the alkaline ions and water.

$\text{K}_3\text{Mo}_4\text{P}_4\text{O}_{22} \text{H}_2\text{O}$ exhibits also a leucophosphate structure but the tetraoctahedral units are built up from one Mo(III)O_6 octahedron sharing one edge with one Mo(IV)O_6 octahedron and each of them sharing also one corner with one Mo(V)O_6 octahedron. So this compound has not really a mixed valency Mo(IV)/Mo(V) but $\text{Mo(III)/Mo(IV)/Mo(V)}$. The Mo(III) and the Mo(IV) are spread randomly over the two edge-sharing octahedra. We obtained a new mixed valent monophosphate containing also tetraoctahedral units: $\text{Cs}_6\text{Mo}_7\text{P}_7\text{O}_{37} \text{H}_2\text{O}$. In these units the edge sharing octahedra contain Mo(IV) and the other ones Mo(V) . Beside the tetraoctahedral units the framework exhibits trioctahedral units containing only Mo(V) in which two octahedra share one edge and share also one of their common oxygen atoms with the third octahedron of the unit.

Recently we have isolated compounds with a Mo(V)/Mo(VI) valency. Three of them ($\text{NaMo}_3\text{P}_3\text{O}_{16}$, $\text{AgMo}_3\text{P}_3\text{O}_{16}$ and $\text{KMo}_3\text{P}_2\text{O}_{14}$) have their different valency well located, the two others $\text{Cs}_3\text{Mo}_4\text{P}_4\text{O}_{22}$ and $\text{Rb}_3\text{Mo}_4\text{P}_4\text{O}_{22}$ have the Mo(V) and the Mo(VI) spread randomly over the same sitting. In $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and in $\text{AgMo}_3\text{P}_3\text{O}_{16}$ the two Mo(V)O_6 octahedra have each their own sitting while the Mo(VI) is surrounded by a triangular bipyramid of oxygen allowing the formulation $\text{AMo}_2^{\text{V}}\text{octaMo}^{\text{VI}}\text{bipyP}_3\text{O}_{16}$. In $\text{KMo}_3\text{P}_2\text{O}_{14}$ layer structure one observes one octahedral site for Mo(V) and the two Mo(VI) are respectively located in an octahedron and a bipyramid allowing the formulation $\text{KMo}^{\text{V}}\text{octaMo}^{\text{VI}}\text{octaMo}^{\text{VI}}\text{bipyP}_2\text{O}_{14}$. In spite of their same formula and their same basic units $\text{Mo}_2\text{P}_2\text{O}_{15}$ forming similar $[\text{Mo}_2\text{P}_2\text{O}_{13}]_{\infty}$ layers, $\text{Cs}_3\text{Mo}_4\text{P}_4\text{O}_{22}$ and $\text{Rb}_3\text{Mo}_4\text{P}_4\text{O}_{22}$ exhibit dissimilar frameworks principally due to different way of stacking the layers.

It is worth pointing out that in the compounds we synthesized, the mixed valency of molybdenum involving Mo(V) arises only when the frameworks exhibit polyoctahedral units built up from edge sharing or/and corner sharing octahedra. One observes also that the molybdenyl oxygen of the octahedron is never shared with another polyhedron.

PS-08.04.48 STUDY ON THE LAW OF MINUTE CHANGE IN CRYSTAL STRUCTURE. By Zhang Hanqing, Institute of Mineral Deposits of Chinese Academy of Geological Sciences, He Zhuwen and Xu Li, China University of Science and Technology

The crystal structure varies minutely with the change of its composition and the environments which it is situated in. Those changes could be indicated in different ways. Researchers previously proposed a lot of expressing methods when they compared these structures, such as unit cell parameters, volume of lattice cell, bond lengths and bond angles, deformation of ligands, the changes of thermal parameters of each ion, and so on. Based on the study of the minute variation of some type structures in recent years, the authors find that: (1) The change of coordinates of characteristic ions or of the relative value of each parameter can be used to indicate the law of minute change in crystal structure; (2) On condition that the space group is unchanging, no matter how the tiny the change of crystal structure is, the ligand form can become different but the symmetry of ligand can be unchanged. In this paper, we discuss the law of the minute change in crystal structure, taking the examples spinel, wurtzite, nickeline, rutile, calcite, and pyrite type structure etc.

Spinel (AB_2O_4) The space group of spinel is $\text{Fd}\bar{3}m$. In its crystal structure, the O^{2-} ion cumulate and arrange closely with each other, and produce tetrahedral and octahedral voids. A ions occupy the

tetrahedral voids with coordinates $(1/4, 1/4, 1/4)$. B ions are located in the $(3/8, 5/8, 3/8)$ octahedral. The coordinates of O^{2-} ion are (u, u, u) . Because of the special sites of A and B ions, their symmetry and coordinates are not changing when composition, temperature and pressure vary. However, O^{2-} ions may move along the 3 axes (i.e. u will possess different values). Thus, AO_4 tetrahedral and BO_6 octahedral will react differently. The four O^{2-} ions will move (in or out) along the four A-O directions of an AO_4 tetrahedron at the same time, and still form a regular tetrahedron, only the ligand size will change. The six O^{2-} ions of a BO_6 octahedron will move along the $[111]$ direction of the unit cell simultaneously. Thus the regular octahedron will distort and become a flat tened or elongated trigonal anti-prism. The relation between each parameter and the u value is as indicated in the block diagram (fig. 1). From this we can see that there are two mutate points ($u=0.375$ and $u=0.3875$) which influence the crystal structure as the u value is changing. So, the structure can be divided into five regions, the main characters of each and is as in figure 1.

Conclusion: (1) The coordination polyhedron of ions suited in structure can be used to discuss the law of minute change in crystal structure; (2) The move of ions in crystal structure should follow the symmetry rules of the space group; (3) The form and size of ligand in structure can change, but its symmetry is constant. That is to say, the minute change in crystal structure is the adjusted result of form and size of each ligand. The law of minute change in crystal structure can be reflected from the locus of ion movement.