

**m19.p01****KMnVO<sub>4</sub> and Na<sub>3</sub>MnV<sub>2</sub>O<sub>7.5</sub>: New oxygen-deficient perovskite type structures.**Hamdi Ben Yahia<sup>a</sup>, Etienne Gaudin<sup>a</sup>, Jacques Darriet<sup>a</sup><sup>a</sup>*Institut de Chimie de la Matière Condensée de Bordeaux, Université Bordeaux I, 87 Avenue du Docteur Schweitzer, 33608 Pessac Cedex, France. E-mail: benyahia@icmcb-bordeaux.cnrs.fr***Keywords: crystal structure determination, perovskite structures, relationships**

Cubic (or pseudo-cubic) perovskite ABO<sub>3</sub> can be non-stoichiometric because of the presence of A-site or oxygen-site vacancies. During studies on K<sub>2</sub>O-MnO-V<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>O-MnO-V<sub>2</sub>O<sub>5</sub> ternary systems, we have identified the new KMnVO<sub>4</sub> and Na<sub>3</sub>MnV<sub>2</sub>O<sub>7.5</sub> compounds. Crystallographic studies have confirmed the composition of the phases and established that the structures correspond to new types of ordered anionic defect cubic perovskites with cationic ordering on the A and B sites. The compound formulas can be expressed as (K<sub>2</sub>Mn)[MnV<sub>2</sub>O<sub>8</sub> and (Na<sub>3</sub>)[MnV<sub>2</sub>O<sub>7.5</sub>. The atoms between brackets and square brackets occupy the A and B sites, respectively. The structures of KMnVO<sub>4</sub> and Na<sub>3</sub>MnV<sub>2</sub>O<sub>7.5</sub> have been refined from single crystal X-ray diffraction in the P21/n and C2/c space groups, with the unit cell parameters  $a = 12.081(2) \text{ \AA}$ ,  $b = 5.645(7) \text{ \AA}$ ,  $c = 23.804(12) \text{ \AA}$  and  $\beta = 103.45(2)^\circ$  and  $a = 5.6190 \text{ \AA}$ ,  $b = 17.1010 \text{ \AA}$ ,  $c = 7.4090 \text{ \AA}$ , and  $\beta = 89.93^\circ$ , respectively. In both structures, the B site cations Mn<sup>2+</sup> and V<sup>5+</sup> are six and four coordinated, respectively. The originality in the KMnVO<sub>4</sub> structure is that the Mn<sup>2+</sup> cations occupy both the A and B sites.

**m19.p02****Superionic phase-transitions in the minerals of the pearceite-polybasite group**Luca Bindi<sup>a</sup>, Michel Evain<sup>b</sup>, Annie Pradel<sup>c</sup>,  
Stephanie Albert<sup>c</sup>, Michel Ribes<sup>c</sup>, Silvio Menchetti<sup>a</sup><sup>a</sup>*Dipartimento di Scienze della Terra, Università di Firenze, Italy.* <sup>b</sup>*Laboratoire de Chimie des Solides, Université de Nantes, France.* <sup>c</sup>*Laboratoire de Physicochimie de la Matière Condensée, Montpellier, France. E-mail: lbindi@geo.unifi.it***Keywords: ionic conductivity, phase transitions, polytypism**

The minerals of the pearceite-polybasite group, general formula (Ag,Cu)<sub>16</sub>M<sub>2</sub>S<sub>11</sub> with  $M = \text{Sb, As}$ , have been recently structurally characterized [1,2,3]. On the whole, all the structures can be described as a regular succession of two module layers stacked along the  $c$  axis: a first module layer (labeled  $A$ ), with general composition [(Ag,Cu)<sub>6</sub>(As,Sb)<sub>2</sub>S<sub>7</sub>]<sup>2-</sup>, and a second module layer (labeled  $B$ ), with general composition [Ag<sub>9</sub>Cu<sub>4</sub>S<sub>4</sub>]<sup>2+</sup>. In the  $B$  layer of the pearceite structure silver cations are found in various sites corresponding to the most pronounced probability density function locations of diffusion-like paths. We have shown for the first time that the observed structural disorder in the  $B$  layer is strongly related to the fast ion conduction character exhibited by these minerals. Conductivity and calorimetric measurements as well as *in situ* single-crystal X-ray diffraction experiments show that all the members of the pearceite-polybasite group present the same high temperature structure and are observed at room temperature either in the high temperature fast ion conductivity form (pearceite) or in one of the low temperature fully ordered (222), partially ordered (221) or still disordered (111) forms, with transition temperatures slightly above or below room temperature.

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