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KMnVO₄ and Na₃MnV₂O_{7.5}: New oxygen-deficient perovskite type structures.Hamdi Ben Yahia^a, Etienne Gaudin^a, Jacques Darriet^a^a*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 ABO₃ can be non-stoichiometric because of the presence of A-site or oxygen-site vacancies. During studies on K₂O-MnO-V₂O₅ and Na₂O-MnO-V₂O₅ ternary systems, we have identified the new KMnVO₄ and Na₃MnV₂O_{7.5} 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 (K₂Mn)[MnV₂O₈ and (Na₃)[MnV₂O_{7.5}. The atoms between brackets and square brackets occupy the A and B sites, respectively. The structures of KMnVO₄ and Na₃MnV₂O_{7.5} 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 Mn²⁺ and V⁵⁺ are six and four coordinated, respectively. The originality in the KMnVO₄ structure is that the Mn²⁺ cations occupy both the A and B sites.

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Superionic phase-transitions in the minerals of the pearceite-polybasite groupLuca Bindi^a, Michel Evain^b, Annie Pradel^c,
Stephanie Albert^c, Michel Ribes^c, Silvio Menchetti^a^a*Dipartimento di Scienze della Terra, Università di Firenze, Italy. ^bLaboratoire de Chimie des Solides, Université de Nantes, France. ^cLaboratoire 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)₁₆M₂S₁₁ 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)₆(As,Sb)₂S₇]²⁻, and a second module layer (labeled B), with general composition [Ag₉Cu₄S₄]²⁺. 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.

[1] Bindi L., Evain M., Menchetti S., *Acta Cryst.*, 2006, B62, 212.[2] Evain M., Bindi L., Menchetti S., *Acta Cryst.*, 2006, B62, in press.[3] Bindi L., Evain M., Menchetti S., *Can. Miner.*, 2006, accepted.