

MS15-P7 Growth, polymorphism and structure of Nd₂MoO₆ Single Crystals

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The Ln₂Mo(W)O₆ compounds (1:1), so-called oxymolybdates, can be synthesized with all the rare-earth elements and attract the attention due to their chemical resistance, high refractive index, luminescence intensity. Earlier it was found that these molybdates have a tetragonal structure of La₂MoO₆-type or a monoclinic structure of Nd₂WO₆-type depending on the ionic radius of the rare earth element. In the case of large cations (La, Pr, Nd) the oxymolybdates synthesized at above 1000 °C have a tetragonal structure. Earlier the Nd₂MoO₆ monoclinic phase was obtained for the first time under the firing at 900°C, which has the irreversible phase transition at 1010°C into the tetragonal phase.

The purpose of the present work was growth, study of polymorphism and structure of Nd₂MoO₆ single crystals.

All the oxymolybdates single crystals were obtained by crystallization from a molten solution at a maximum temperature of 1250°C. The oxymolybdates with large cations (La, Pr, Nd) had a plate-like shape, the others crystallized as isometric prisms. The monoclinic Nd₂MoO₆ single crystals were obtained by slow melt at 800 °C temperature.

X-ray diffraction study of two Nd₂MoO₆ single crystals obtained at two different temperatures, were carried out using a diffractometer XCalibur S. Analysis of diffraction patterns from single crystal Nd₂MoO₆ obtained at temperatures above 1000°C revealed the presence of additional lines not indicated within a unit cell with parameters established earlier: $a=4.089$, $c=15.99\text{\AA}$. This contradiction was eliminated by fold increase of cell volume by choosing of the cell with the basis vectors $a=a_0 + b_0$, $b=-a_0 + b_0$, $c=2c_0$ as a result of the tetragonal cell (sp. gr. I4₁/acd) was obtained with $a=5.664(1)$, $c=31.621(1)\text{\AA}$. The refinement of the structure of Nd₂MoO₆ single crystals obtained at a temperature of about 800 °C revealed the monoclinic cell (sp. gr. I2/c) with $a=15.903(1)$, $b=11.391(1)$, $c=5.527(1)\text{\AA}$, $\beta=91.169(1)^\circ$. The refined structural models of both tetragonal and monoclinic Nd₂MoO₆ single crystals confirmed that oksimolibdatah polymorphic transformations occur in an extremely low speed and appears continuously over a wide temperature range. The results clarify the structural models of tetragonal and monoclinic samples confirmed that oxymolybdates polymorphic transformations occur in an extremely low speed and appears continuously over a wide temperature range.

The study was supported by the RFBR (pr.no.14-02-00531) and pr. NSh-6617-2016-5.

Keywords: molybdates, single crystals, X-ray diffraction study

MS15-P8 Crystal chemistry of the wyllieite group of phosphate minerals

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The wyllieite group of minerals contains Na-Mn-Fe-Mg-Al-bearing phosphates which occur in rare-elements granitic pegmatites; their crystal structure is topologically identical to the alluaudite structure. However, the ordering of cations in wyllieite-type phosphates induces a splitting of the M(2) and X(1) sites of alluaudite into the M(2a) M(2b) and X(1a) X(1b) sites, with a concurrent change of space group from $C2/c$ to $P2_1/n$. Three samples of minerals belonging to the wyllieite group were structurally investigated: wyllieite from the Buranga pegmatite, Rwanda (A), wyllieite from the Malpensata pegmatite, Italy (B), and qingheite from the Santa Ana pegmatite, Argentina (C). Their crystal structures have been refined, based on single-crystal X-ray diffraction data, to $R_f = 2.72\%$ (A), 3.53% (B), and 2.46% (C); unit-cell parameters are: $a = 11.954(2)$, $b = 12.439(2)$, $c = 6.406(1)\text{\AA}$, $\beta = 114.54(1)^\circ$ (A); $a = 11.983(1)$, $b = 12.423(1)$, $c = 6.381(1)\text{\AA}$, $\beta = 114.54(1)^\circ$ (B); $a = 11.878(3)$, $b = 12.448(2)$, $c = 6.438(2)\text{\AA}$, $\beta = 114.49(1)^\circ$ (C). The structure consists of kinked chains of edge-sharing octahedra stacked parallel to {101}. These chains are formed by a succession of M(2a)-M(2b) octahedral pairs, linked by slightly larger M(1) octahedra. Equivalent chains are connected in the b direction by the P(1), P(2a) and P(2b) phosphate tetrahedra to form sheets oriented perpendicular to [010]. These interconnected sheets produce channels parallel to c , channels that contain the large X sites. The X(1a) site is a distorted octahedron, whereas the X(1b) site can be described as a very distorted cube. The morphology of the X(2) site corresponds to a very distorted gable disphenoid with a [7 + 1] coordination, similar to the A(2)' site of the alluaudite structure. The structural features of these phosphates are compared to those of other wyllieite-type phosphates: ferrosemaryite, rosemeryite, and qingheite-(FeII). These new structural data indicate that Al is predominant on the M(2a) site in the investigated samples, with Fe(II), Fe(III) or Mg on the M(2b) site. Variations of unit-cell parameters, of bond distances, and of distortion coefficients among members of the wyllieite group are discussed in detail.

Keywords: phosphate minerals, wyllieite group, crystal chemistry