Thermal behavior of pseudovaterite $NdBO_3$

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There are known pseudovaterite, aragonite and H-modifications of $NdBO_3$ [1-3]. Here we present thermal behavior of pseudovaterite $NdBO_3$ including its thermal expansion.

Polycrystalline sample of pseudovaterite $NdBO_3$ was prepared through hydrothermal method. Starting materials were high purity Nd_2O_3 and H_3BO_3. Reagents were mixed in stoichiometric proportions and finely grounded, and then the charge was put to autoclave with 40 ml of NaOH solution (0.2 M) at the temperature 493 K for 2 weeks. At the result a metastable hexagonal phase of $NdBO_3$ pseudovaterite type first discovered in [1] has formed according to X-ray powder diffraction data. Thermal behavior of the sample has been studied in air from 293 to 1163 K by means of high-temperature X-ray powder diffraction data collected using a Stoe Stadi P X-ray diffractometer (CuKα radiation) with a high-temperature camera (Buehler GMbh).

The HTXRD patterns of pseudovaterite remain without any changes up to 973 K. On further heating peaks of the aragonite modification appear. The thermal expansion is determined in linear approximation in temperature range of 293-943 K before phase transition beginning. Thermal expansion of pseudovaterite $NdBO_3$ is close to isotropic one: $\alpha_a = 11.5$, $\alpha_c = 10$, $\alpha_V = 33$, $\langle\alpha\rangle = \alpha_v/3 = 11\times10^{-6}$ C^{-1}. Pseudovaterite $NdBO_3$ shows average linear thermal expansion close to that of other M^{3+} borates for example it is about 12.7×10^{-6} C^{-1} for Bi^{3+}-borates [4].

The crystal structure of this phase has not been yet determined up to now. There are two structural models for the hexagonal phase of MBO_3 where M = Y and *RE* (Sm-Lu) [1, 5]. Both models are built up from alternative layers of and BO- and *RE*O-polyhedra along *c* axis: one present crystal structure with isolated BO_3 triangles planes of those disposed parallel to *c*-axis [4], another - with isolated tetrahedra [3]. *RE*O-polyhedra sharing corners form framework in both models. By high-temperature borate crystal chemistry principles [4, 6] if crystal structure is based on isolated BO_3 triangles the most thermal expansion should be expected in directions to perpendicular to a plane of triangles and minimal to parallel the plane of BO_3; in the case of crystal structure with isolated BO_4 tetrahedra thermal expansion is expected close to isotropic. Hence thermal expansion pseudovaterite $NdBO_3$ is good agreement with both crystal structures: pseudovaterite minimally expands along *c* axis and slight more intensive along a axis and such behavior of expansion could be caused by disposition of the BO_3 triangles parallel to *c* axis while the expansion is close to as it should be expected in case of existence of BO_4 tetrahedra.

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