

Thermal expansion of calcium borates

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The high-temperature behaviour of four calcium borates ($\text{Ca}_3\text{B}_2\text{O}_6$, $\text{Ca}_2\text{B}_2\text{O}_5$, CaB_2O_4 , CaB_4O_7) has been studied by *in situ* high-temperature powder X-ray diffraction (HTXRD), differential scanning calorimetry and thermogravimetry.

The tendency of decrease in the volume expansion is observed with an increase in the B_2O_3 content in the $\text{CaO-B}_2\text{O}_3$ system as a result of the degree of polymerization increase. High anisotropy of the expansion is observed for $\text{Ca}_3\text{B}_2\text{O}_6$, $\text{Ca}_2\text{B}_2\text{O}_5$ (0D) and CaB_2O_4 (1D) based on the BO_3 triangles only: the structure highly expands perpendicular to the BO_3 planes, i. e. along the direction of the weaker bonds in the crystal structure.

$\text{Ca}_3\text{B}_2\text{O}_6$ (0D). In the trigonal structure, isolated triangles BO_3 are arranged perpendicular to the c axis. Oxygen and boron atoms oscillate perpendicularly to strong B–O bonds. Therefore, the maximum amplitude of vibration is perpendicular to the plane of the triangle.

$\text{Ca}_2\text{B}_2\text{O}_5$ (0D) undergoes two reversible polymorphic transitions at about 500 and 516 °C. The structure expands intensively along the a axis, in a direction perpendicular to the plane of borate triangles. Minimal expansion occurs along the boron-oxygen chains parallel to the c axis since the strongest bonds are realized in the chains.

CaB_2O_4 (1D). The structure contains the chains of BO_3 triangles that are located along the c axis. Planes of the triangles are approximately parallel to the (001) plane. The structure expands intensively along the a axis, in a direction perpendicular to the plane of borate triangles. Minimal expansion occurs along the boron-oxygen chains parallel to the c axis since the strongest bonds are realized in the chains.

$\alpha\text{-CaB}_4\text{O}_7$ (3D). The crystal structure is characterized by a boron-oxygen polyanion consisting of four crystallographically independent BO_3 triangles and four BO_4 tetrahedra linked via common vertices. The eight triangles and tetrahedra form a $[\text{B}_8\text{O}_{14}]^{4-}$ -unit, which is repeated throughout the structure. The maximal direction of thermal expansion in the structure coincides with an acute angle bisector of the ac parallelogram and the minimum expansion occurs along the other diagonal. The structure expands along the monoclinic axis less intensively. Such sharply anisotropic behavior could be explained using shear deformation of the monoclinic plane.

High-temperature powder X-ray diffraction experiments were performed in Saint-Petersburg State University Research Centre for XRD Studies.

The study was supported by the Russian Foundation for Basic Research (No. 18-03-00679).