Synthesis and thermal behavior of borate $CaBi_2B_4O_{10}$:Eu

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For the first time this borate was obtained and studied by the DSC method in the CaO-Bi_2O_3-B_2O_3 system [Egorysheva et al., 2008]. A homogeneous samples of $CaBi_2B_4O_{10}$:*x*Eu (x = 0-30 at.%) were obtained by solid-phase synthesis at 630 °C / 20-26 hours. The initial reagents were $CaCO_3$ (e.c.), H_3BO_3 (e.c.), Bi_2O_3 (e.c.), taken in a stoichiometric ratio.

The compound is isostructural to the borate of $SrBi_2B_4O_{10}$ [Krzhizhanovskaya et al., 2009]. $CaBi_2B_4O_{10}$ crystallizes in the triclinic system, *P*–1 space group (a = 6.6704 (1), b = 6.8317 (1), c = 9.5775 (1) Å, α = 94.33, β = 108.48, γ = 101.34 °, V = 401.37 Å3, Z = 2). $CaBi_2B_4O_{10}$ is a borate whose polyanion is represented by isolated tetraborate group $[B_4O_9]$. Two triangles BO_3 and tetrahedron BO_4 form a triborate ring to which another single triangle BO_3 is attached.

$CaBi_2B_4O_{10}$ was studied *in situ* on a Rigaku "Ultima IV" powder diffractometer (CoKα radiation, 2θ = 10–70°, temperature range 25–700 °C, pitch 25 °C) and the DSC method. Above 650 ° C, the texture of the diffraction pattern increases, which apparently indicates the effects of premelting. Melting occurs at a temperature of 729 °C according to DSC. Thermal expansion is sharply anisotropic. The coefficients and parameters of the thermal expansion tensor at 25 °C: $\alpha_{11} = 3\times10^{-6}$, $\alpha_{22} = 15\times10^{-6}$, $\alpha_{33} = 7\times10^{-6}$, $a_\alpha = -3\times10^{-6}$, $a_\beta = 5\times10^{-6}$, $a_\gamma = 3\times10^{-6}$,$\alpha_V = 25\times0^{-6}$ °C^{-1}, at 600 °C: $\alpha_{11} = 0.5\times10^{-6}$, $\alpha_{22} = 22\times10^{-6}$, $\alpha_{33} = 13.5\times10^{-6}$, $a_\alpha = -3\times10^{-6}$, $a_\beta = 10\times10^{-6}$, $a_\gamma = 2\times10^{-6}$, $\alpha_V = 36\times10^{-6}$°C^{-1}.

The parameters *a*, *b*, *c* increase by 0.45, 0.8 Å, 0.6 Å, and the angles α, β, γ change by -0.25°, 0.6°, 0.2° in the temperature range 25–700 °C. A sharp change in the angle β indicates the presence of shear deformation in the plane of *ac*. The sharp increase in the parameter *b* with increasing temperature may be due to the position of the tetraborate groups ($[B_4O_9]$), which are perpendicular to the axis *b*.

X-ray studies were performed at the St. Petersburg State University Resource Center "X-ray diffraction methods of research". Luminescent properties of samples $CaBi_2B_4O_{10}$:*x*Eu (x = 0-30 at.%) are studied. The study was supported by RFBR (Project No. 18-03-00679).

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