

MS16-P1 Studies of structural changes in $K_9H_7(SO_4)_8 \cdot H_2O$ single crystals with temperature. Tatiana Chernaya, Irina Makarova, Igor Verin, Vadim Grebenev, Valentina Dolbinina, *Shubnikov Institute of Crystallography RAS, Russia*
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Crystals $K_9H_7(SO_4)_8 \cdot H_2O$ belongs to a fairly large family of $M_mH_n(XO_4)_{(m+n)/2}$ ($M = K, Rb, Cs, NH_4; X = S, Se$), for which characteristic features are the presence of high-temperature ferroelastic phase transitions. These crystal family is important from the point of view of basic knowledge about structural mechanisms of superionic conductivity and for creating promising materials for hydrogen fuel cells. It was carried out the researches of dielectric and optical properties of the crystals $K_9H_7(SO_4)_8 \cdot H_2O$ [1]. The measurements at temperatures 295 - 460 K revealed the anomaly with an increase of the conductivity more than by three orders of magnitude at ≈ 413 K. As a result of X-ray diffraction structural studies of single-crystal samples $K_9H_7(SO_4)_8 \cdot H_2O$ [2] on an Xcalibur S diffractometer equipped with a 2D CCD-detector at temperatures 295 - 473 K the crystal structure of low-temperature phase was defined and refined: monoclinic symmetry, sp. gr. $P2_1/c$, $Z=4$, $a=7.073(1)$, $b=19.813(1)$, $c=23.496(1)$ Å, $\beta=95.33(1)^\circ$ ($R_{int}=1.7\%$, $R_w/R=1.73/1.73\%$, 295 K); the crystal structure parameters of high-temperature phase: orthorhombic symmetry, sp. gr. $Pcan$, $Z=8$, $a=7.178(1)$, $b=19.866(1)$, $c=23.343(1)$ Å, ($R_{int}=5.58\%$, $R_w/R=3.49/2.63\%$, 413 K). It should be noted that the interval of the orthorhombic phase is fairly wide - 413 - 473 K. The obtained structural data confirmed the previously proposed mechanism of conductivity in crystals of this family: the appearance of a high protonic conductivity is connected with the formation of a qualitatively new system of hydrogen bonds.

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MS16-P2 Synthesis and high-temperature characterization of mullite-type $(Al_{1-x}Ga_x)_4B_2O_9$. K. Hoffmann^{1,2}, M. Mangir Murshed¹, Reinhard X. Fischer², Th. M. Gesing¹ ¹*Solid state chemical crystallography, Inorganic Chemistry, University of Bremen, Germany;* ²*Crystallography, FB5 Geosciences, University of Bremen, Germany*
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$Al_4B_2O_9$ (A_2B) aluminum borates and gallium borate $Ga_4B_2O_9$ (G_2B) belong to the family of mullite-type materials. Two different mullite-type modifications are reported for A_2B . We synthesized well crystallized A_2B as the monoclinic $C2/mp$ polymorph, formed in an enlarged unit cell with all lattice parameters doubled [1] with respect to the orthorhombic structure ($Pbam$) [2], which we assume to represent a meta-stable A_2B state. The corresponding gallium compound G_2B is described in $C2/m$ as well [3], however, its structure significantly differ from that of A_2B . For easier comparison we have transformed G_2B into space group $I112/m$ which results in a monoclinic angle $\gamma = 90.43^\circ$ instead of $\beta = 135.24^\circ$. Here we report on the synthesis of $(Al_{1-x}Ga_x)_4B_2O_9$ compounds carried out at different temperatures. The crystalline samples were synthesized following the nitrate decomposition method [4] for the aluminum-rich compounds, which was modified, according to Cong et al. [3], for the gallium-rich phases. Gallium could be incorporated into the A_2B structure up to $x \approx 0.7$, synthesized at 1173 K. The aluminum incorporation into the G_2B structure produced at 873 K is approximately the same.

While G_2B is reported to be stable up to 923 K [3] before the binary oxides are formed, A_2B decomposes to $Al_{18}B_4O_{33}(A_9B_2) + B_2O_3$ above 1323 K. Both end-members are characterized between 298 K and 1423 K by means of temperature-dependent X-ray powder diffraction data Rietveld refinements. The cell volume of G_2B expands linearly with a thermal volume expansion coefficient $\alpha_V = 2.04(1) \cdot 10^{-5} K^{-1}$. This expansion has been mainly contributed by the expansion in the crystallographic a - and b -direction; the c -lattice parameter (parallel to the mullite-type octahedral chains) and γ remain nearly constant. The decomposition of G_2B was observed at 1073 K. The linear thermal volume expansion of A_2B can be divided into two linear steps with a point of intersection at about 473 K. Expansion coefficients of $\alpha_V = 1.38(1) \cdot 10^{-5} K^{-1}$ between 273 K and 473 K and then $\alpha_V = 2.25(1) \cdot 10^{-5} K^{-1}$ up to 1373 K are determined. Alike G_2B , the monoclinic angle (β) remains almost constant. The expansion of the lattice parameters a and b (parallel to the octahedral chains) is linear over the whole temperature range. The thermal expansion behavior of the c -direction is similar to the volume effect, leading to two different expansion coefficients within the investigated temperatures. Such a non-linear expansion was earlier also observed for sinter mullites [5].

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