

BARIC DISPLACEMENT OF PHASE TRANSITION IN $(\text{NH}_4)_2\text{SO}_4$ CRYSTALS

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Ammonium sulfate (AS) $(\text{NH}_4)_2\text{SO}_4$ crystals at room temperature are nonpolar and belong to the space group $Pnma$ of the orthorhombic system. Below $T_c = 223$ K, they undergo a ferroelectric phase transition without a change in the number of formula units per unit cell to the space group $Pn2a_1$. This phase transition is accompanied by a significant deformation step, while the spontaneous deformation P_c below T_c decreases in magnitude and changes sign near 83 K. The unit cell of AS crystals contains a four formula units, which possess two nonequivalent ammonium ions $\text{NH}_4^+(1)$ and $\text{NH}_4^+(2)$ in both phases. The structural studies of the para- and ferroelectric phases of AS crystals revealed ordered elements $\text{NH}_4^+(1)$, $\text{NH}_4^+(2)$ and SO_4 groups. It was concluded that SO_4 tetrahedra in the paraelectric phase do not have two equilibrium positions and move in a single-minimum potential.

The aim of this paper was to study the effect of uniaxial mechanical pressure on the temperature dependences of refractive indices n_i and the position of the phase transition (PT) point.

It was established that, in the temperature range of existence of the paraphase ($T > 223$ K), the main refractive indices increase almost linearly with a decrease in temperature: $dn_x/dT = -5.1$, $dn_y/dT = -2.9$, and $dn_z/dT = -3.8 \times 10^{-5} \text{ K}^{-1}$. At $T = 223$ K, a phase transition occurs, which is accompanied by a stepwise decrease in the refractive indices: $\delta n_z \sim 6.3$, $\delta n_x \sim 5.9$ and $\delta n_y \sim 4.1 \times 10^{-4}$. Cooling in the polar phase leads to a decrease in n_i ; in the temperature range 77–160 K, the values n_i tend to constant values and then hardly change with temperature ($dn_i/dT \sim 0$). The action of uniaxial pressures along different crystallophysical directions leads to an increase in n_i ; however, the character of temperature changes dn_i/dT and values of steps at phase transitions ($\delta n_z \sim 6.0$, $\delta n_x \sim 5.1$ and $\delta n_y \sim 5.2 \times 10^{-4}$) do not radically change. A significant change is observed in the position of the phase transition point: a uniaxial pressure σ_x shifts the phase transition point to higher temperatures ($T_c^z = 228.0$ K), while uniaxial pressures along the Z and Y axes shift it to lower temperatures ($T_c^z = 216.5$ K, $T_c^y = 218.8$ K). The baric coefficients of shift of the phase transition point have the following values: $\partial T_c / \partial y_x = +0.024$ K/bar, $\partial T_c / \partial y_y = -0.021$ K/bar, and $\partial T_c / \partial y_z = -0.046$ K/bar; the total coefficient of baric shift of the phase transition point (analog of hydrostatic pressure) $\partial T_c / \partial p = -0.043$ K/bar. These data are in good agreement with the results of differential thermal analysis of the p – T phase diagram of AS crystals under hydrostatic pressures up to $p \sim 6$ kbar, which established that hydrostatic pressure leads to a linear shift of T_c (-4.1 K/kbar).

It is known that the phase transition in the crystal under consideration is determined predominantly by the SO_4 groups, which collectively change their orientation, position, and degree of distortion at T_c , forming partial alignment of ammonium groups, which retain the possibility of reorientations below T_c . In this case, the rotations of tetrahedra around all three structure axes increase (predominantly around the X axes). A tetrahedron is frozen in one of the orientation states, which it previously occupied in the paraelectric phase.