BARIC DISPLACEMENT OF PHASE TRANSITION IN (NH₄)₂SO₄ CRYSTALS

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Ammonium sulfate (AS) ((NH₄)₂SO₄) 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 Pn2₁a₁. 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 NH₄⁺(1) and NH₄⁺(2) in both phases. The structural studies of the para- and ferroelectric phases of AS crystals revealed ordered elements NH₄⁺(1), NH₄⁺(2) and SO₄ groups. It was concluded that SO₄ 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: \( \frac{dn_x}{dT} = -5.1, \frac{dn_y}{dT} = -2.9, \) and \( \frac{dn_z}{dT} = -3.8 \times 10^{-5} \) 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 \( \sigma_x \) shifts the phase transition point to higher temperatures \( (T_c^\ast = 228.0 \) K), while uniaxial pressures along the Z and Y axes shift it to lower temperatures \( (T_c^\ast = 216.5 \) K, \( T_c^\ast = 218.8 \) K). The baric coefficients of shift of the phase transition point have the following values: \( \partial T_c / \partial \sigma_x = 0.024 \) K/bar, \( \partial T_c / \partial \sigma_y = -0.021 \) K/bar, and \( \partial T_c / \partial \sigma_z = -0.046 \) 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 SO₄ 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.