RAMAN SPECTRA AND PRETRANSITION STATE OF THE CRISTALLINE POTASSIUM PERCHLORATE IN THE REGION OF STRUCTURAL PHASE TRANSITION OF THE FIRST KIND

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The present work is a spectroscopic study of the processes of molecular relaxation in crystalline potassium perchlorate (KClO₄). In previous work we studied the Raman spectra and molecular relaxation in sodium perchlorate [1].

At room temperature KClO₄ is a rhombic crystal (low-temperature phase II). At 574 K a phase transition occurs. The high-temperature phase I has a cubic structure; at T=855 K the crystal melts [2].

Vibrational spectra of perchlorates studies in many works [3]. The molecular anion ClO₄⁻ is characterized by the following vibrations: ν₁(A) is the stretching totally symmetrical vibration (935 cm⁻¹); ν₂(E) (462 cm⁻¹) is the twice degenerate vibration; ν₃(F) is the thrice degenerate vibration (1102 cm⁻¹); ν₄(F) is the thrice degenerate vibration (628 cm⁻¹).

Investigations were carried out by the Raman spectroscopic method using a DFS-24 spectrometer [4]. Raman spectra were excited by an argon laser (λ=488 nm). On passing through a filter (488 nm) the radiation was scattered by the sample and directed to the inlet slot (100–150 μm) of the spectrometer. As a dispersion element, a diffraction grating was used. The scattered radiation was recorded by a photoelectric receiver connected via an amplifier to a recorder. The discharge current force of a gas tube of the laser was 24–30 A. The sample was crushed in a mortar and placed into a quartz cuvette in a furnace. The temperature of the sample was maintained with an accuracy of ±1 K by a VRT-2 high-current regulator and measured by a calibrated chromel-alumel thermocouple. Raman spectra were recorded in the field of the totally symmetrical oscillation ν₁(A). The parameters of reorientation with respect to polarized Raman lines were evaluated based on the temperature dependences of their widths.

The processes of vibrational dephasing and orientational relaxation make the basic contribution to the width of the spectral band. This requirement is entirely satisfied with the ν₁(A) lines of the tetrahedral ion of potassium perchlorate.

We have investigated the temperature dependence of the position of the maximum and the width of the spectral contour corresponding to the vibration ν₁(A) of the anion ClO₄⁻ in crystalline potassium perchlorate in the temperature range 298 – 583 K. It was noted that at temperatures up to 500 K the temperature dependence of the width is exponential; then its slope becomes smoother, which can be associated with saturation of the rotation mobility of the anion. A further increase in the temperature causes the instability of the low-temperature crystalline phase and the transition to a new high-temperature crystalline phase. In the temperature range 500 – 570 K there is a pretransition state. In the region of the phase transition one observes bending of the temperature dependences of the frequency and the width.

For the low-temperature phase, we made calculations in accordance with the procedure described in [1] and evaluated the following parameters: J is the effective moment of inertia; τₑc is the collision-to-collision time; ε is the angular step of diffusion.

An analysis of the experimental data and reorientation times allows the assessment that in KClO₄ the reorientation proceeds following the Frenckel type, i.e., it represents the activation process.

To describe the dynamics of molecular anions in the investigated substance, we have employed, as a tool, the time correlation functions (TCF) G(t), which make it possible to quantitatively characterize the process of relaxation of the vibrational states of particles, caused by interaction and motion, in a time domain.

An analysis of the TCFs and relaxation times shows that as long as the temperature increases, the contribution of homogeneous broadening δₑ to the spectral band width increases. This can be associated with the fact that upon heating the processes of vibrational dephasing enhanced (the collision of ions increases). At the same time, the contribution of the inhomogeneous broadening δᵢ changes slightly. Crystal heating leads, on the one hand, to destruction of inhomogeneities, and on the other hand, to acceleration of the diffusion transitions of anions to new local surroundings. The competition of these two processes causes weak changes in δᵢ. It is seen that if at low temperatures G(t) is almost of the Gaussian form, with an increase in the temperature G(t) approaches the exponential form of the contour. In this case, the contribution of Gₛ(t) decreases, while that of Gᵢ(t) increases, which can be explained by the predominance of the mechanisms associated with the interaction of particles and by the decrease of the contribution due to the system inhomogeneity.

The processes of molecular relaxation in crystalline potassium perchlorate are investigated by the method of Raman spectroscopy in the field of totally symmetrical oscillation ν₁(A) of the anion ClO₄⁻. The parameters of reorientation in relation to the polarized Raman lines are evaluated from the temperature dependences of line widths. It is established that in KClO₄ the reorientation represents the activation process. Time correlation functions are obtained and the times of vibrational and orientational relaxation are determined, which show that with an increase in temperature the contribution of homogeneous broadening increases while that of the inhomogeneous one remains practically unchanged.

References