

Phase Transition and H₂O Motions in [Ba(H₂O)₄](ClO₄)₂ Studied by Differential Scanning Calorimetry, Infrared Spectroscopy and Inelastic/Quasielastic Incoherent Neutron Scattering

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Compounds of the type: [M(H₂O)_x](ClO₄)₂ ($x = 4-6$) are particularly interesting molecular materials because of the occurrence of different reorientational motions of the complex cations, H₂O ligands and ClO₄⁻ anions. Polymorphism of several similar (M = Ni, Mg, Mn, Co, Fe, Cr) compounds have been investigated up to now [1-5].

One phase transition at: $T_c^h = 210.6$ K (onset on heating) and $T_c^c = 204.6$ K (onset on cooling) was determined for [Ba(H₂O)₄](ClO₄)₂ in the temperature range of 90–300 K by means of differential scanning calorimetry (DSC). The thermal hysteresis of the phase transition temperature T_c equal to ca. 6 K and the heat flow anomaly sharpness suggest that the detected phase transition is a first-order one. The relatively high entropy change ($\Delta S \approx 16.8$ J·mol⁻¹·K⁻¹) connected with observed phase transition indicates high degree of dynamical disorder. We have performed infrared (FT-MIR) and neutron scattering (IINS/QENS) measurements in order to establish relationship between the observed phase transition and reorientational motions of the H₂O ligands. Fourier transform middle infrared spectra were measured in the temperature range of 16–295 K. On cooling the sample no characteristic changes in the FT-MIR spectra are observed till 220 K, where the splitting of the band connected with $\rho(\text{H}_2\text{O})$ mode at ca. 720 cm⁻¹, can be distinctly seen. In addition to this at ca. 200 K a new weak shoulder band at ca. 1652 cm⁻¹ starts to appear. It suggests that in the vicinity of the phase transitions at T_c the crystal symmetry is reduced. On the other hand we can not see any narrowing of the bands during cooling. In the high temperature phase the bands are not broadened. It means that particular groups (H₂O and/or ClO₄⁻) do not perform fast ($\tau_R \approx 10^{-12}$ s) stochastic reorientational motion (even in high temperature phase) at least from point of view of infrared spectroscopy and correlation time characteristic for this method. Moreover, from our infrared measurements one can conclude that in the investigated compound there exist hydrogen bonds. The neutron scattering (IINS, QENS) studies performed with NERA time of flight spectrometer (Dubna in Russia) in the temperature range of 20–270 K did not give the evidence of fast (correlation time $\tau \approx 10^{-11}-10^{-12}$ s) stochastic reorientational motions of H₂O (180° flips) ligands in high and low temperature phases. The QENS maximum does not show any broadening (characteristic for the so called ODDIC crystals) above the phase transition temperature. This conclusion, consistent with infrared measurements, is also supported by the proton-weighted phonon density functions $G(\nu)$ calculated in one phonon harmonic approximation from the time-of-flight IINS spectra. The $G(\nu)$ spectra obtained at temperatures 20, 175, 200, 225, 270 K show some separate peaks characteristic for ordered phase. Concluding the H₂O groups do not perform fast stochastic reorientation (within picoseconds time scale) in the temperature range of 20–270 K. There are possible much slower reorientations ($\tau_R \approx 10^{-4}-10^{-5}$ s) of the whole complex cation [Ba(H₂O)₄]²⁺.

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