SPECTROSCOPIC INVESTIGATION OF THE CRYSTAL STRUCTURE OF THE BINARY SYSTEM LiIO$_3$–HIO$_3$


The lattice dynamics of the pseudo-binary system LiIO$_3$–HIO$_3$ has been investigated by means of the IR and Raman spectroscopies and the NQR technique. The spectral changes, observed in the 2600–400 cm$^{-1}$ region, indicate the formation of variable “intermolecular” hydrogen bonds O–H···O in the system between the quasi molecular halogenate groups IO$_3^-$, HIO$_3$ and H(IO$_3$)$_2^-$. By the analysis of low-frequency Raman spectra of the mixed crystals Li$_{1-x}$H$_x$IO$_3$ with varying the concentration $x$ in the range from 0 to 1, the critical $x$ values of HIO$_3$ content were evaluated at which the hydrogen bonds of different strength are formed and the different crystal structure of the binary system is observed. Thus for the concentration range 0 – 0.22 the IR absorption spectra show wide and weak O–H stretching bands. That concentration range corresponds to $\alpha$-modification LiIO$_3$ crystal doped by protons (C$\alpha^P$ space group). Within the intermediate concentration range $0.06 < x < 0.22$ two separate crystals $\alpha$-LiIO$_3$ and 2LiIO$_3$·HIO$_3$ (with unknown crystal structure) exist as it follows from the NQR data. For concentrations $x > 0.35$ the vibrational spectra of the system correspond to Li-doped orthorhombic $\alpha$-HIO$_3$ crystal. From the NQR and Raman data the amorphous (“glass”) phase was detected in the concentration range 0.22 – 0.35. Our results help to solve some contradictions concerning the binary system structure obtained by different experimental methods.