

Ferroelastic phase transition in the family of crystals of double salts of fluorides according to vibrational spectroscopy data

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In this work we synthesized and investigated single crystals of heptafluorides $(\text{NH}_4)_2\text{SnF}_6 \cdot \text{NH}_4\text{F}$, $(\text{NH}_4)_2\text{TiF}_6 \cdot \text{NH}_4\text{F}$ and $(\text{NH}_4)_2\text{GeF}_6 \cdot \text{NH}_4\text{F}$ with different structures at room temperature. Considerable difference of the central ions radii of the in this series of fluoride double salts $(\text{NH}_4)_3\text{Me}^{4+}\text{F}_7$ (Me^{4+} : Sn, Ti, Ge) results in a different sequences of structural phase transitions, and a general task of these investigations is possible ferroic phases among these sequences. In the process of structural studies, an unusual sequence of phase transitions in $(\text{NH}_4)_3\text{TiF}_7$ was founded: $Pa\bar{3} \leftrightarrow Pm\bar{3}m$ and $P4/mbm \leftrightarrow Pbam \leftrightarrow P12_1/c1 \leftrightarrow Pa\bar{3}$ in fluoride $(\text{NH}_4)_3\text{GeF}_7$. For a deeper understanding of the nature of the observed structural transformations, studies of the dynamics of the crystal lattice are necessary; vibrational spectroscopy is traditionally used to study ferroelectric materials and establish the composition – property relations. The studies of the Raman and IR spectra performed in this work made it possible to determine the features of the structural distortions caused by changes in the chemical pressure during the replacement of the central atom.

An important feature of the vibrational spectra of all investigated crystals is the appearance of a number of new lines due to decrease of the local symmetry of ammonium tetrahedra. The phase transition in $(\text{NH}_4)_3\text{TiF}_7$ at 360 K was found to be associated with fluorine octahedra disordering while the second transition at 285 K – with the ordering processes of TiF_6 octahedra; below the temperature of the second transition a new line appears at 97 cm^{-1} as a result of a bond length shortening between the free fluorine atom F and the NH_4 group. The phase transition mechanism in $(\text{NH}_4)_3\text{SnF}_7$ at 360 K is associated with the ordering of structural units, the octahedral polyhedra of SnF_6 are ordered in the $Pa\bar{3}$ phase, and the lines that appear at 488 and 297 cm^{-1} relate to F7 vibrations. In the germinate crystal, the $P4/mbm$ ($T_1 = 278 \text{ K}$) – $Pbam$ ($T_2 = 268 \text{ K}$) – $P12_1/c1$ transitions are of the second order, the proximity of temperatures T_1 and T_2 causes the spectral parameters to change only slightly. The transition between monoclinic and cubic $Pa\bar{3}$ phases at 229 K is a first-order transformation associated with the ordering of ammonium groups with decreasing temperature. Thus the replacement of the central atom leads not only to changes in the type of transitions, but to different degrees of structural disorder also. All studied compounds are ferroelastics.

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References

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