

Vibrational spectroscopy of mineral-like functional materials with complex crystal structures

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The complex crystal chemical effects, like polytypism, cationic ordering, phase transitions and structures of solid solutions could be well investigated by vibrational spectroscopy methods. We studied the mineral-like borates and phosphates with the functional characteristics by the powder IR and Raman spectroscopy methods.

Huntite-like rare-earth chromium borates $R\text{Cr}_3(\text{BO}_3)_4$, where $R = \text{La} - \text{Er}$ crystallize in two space groups $R32$ and $C2/c$ and have the polytypic nature. The investigation of a system of these compounds using the full factor-group analysis allowed to assign these phases to one of two sp.gr. and to define the crystal growth conditions. In comparison of powder x-ray spectra, which are not sensible to the difference of the polytypes, the vibrational spectra of rhombohedral and monoclinic phases have the certain specific features. Main differences are observed in BO_3^{3-} stretching vibrations' region (Kurazhkovskaya, 2011). Also, we examined the IR and optical spectra of series of the solid solution $\text{NdCr}_3(\text{BO}_3)_4$ ($C2/c$) - $\text{GdCr}_3(\text{BO}_3)_4$ ($R32$), and we determined the point (compound) of morphotropic transition.

The cationic ordering in different structure positions leads to different space groups of rare-earth Zr and Hf kosnarite-like phosphates $\text{R}_{0.33}\text{Zr}_2(\text{PO}_4)_3$. In the structure of La members of this family the 0.18 a.p.f.u. La occupy unusual positions in comparison to other all rare earth phosphates, and the sp.gr. $P\bar{3}c1$ changes to $P\bar{3}$. Vibrational spectra of these compounds with different space groups are very close but have own characteristic features (Kurazhkovskaya, 2010). The study of solid solution $\text{La}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ - $\text{Yb}_{0.33}\text{Zr}_2(\text{PO}_4)_3$ also allowed to define the morphotropic transitions point. It's notable, that the maxima of ionic conductivity are close to morphotropic transition point.

The β -tridimite - like phosphates with different tetrahedral cations: Mg, Mn, Co, Zn, Ni with the large cavities for one valent cations are perspective as matrix for radioactive ^{137}Cs . But the phase transitions in these compounds decrease their stability. For these compounds three modifications were known: $P2_1/a$, $Pn2_1a$ and $Pnma$. The increasing of the temperature leads to the symmetry increasing. We made the factor group analyses for all three groups and studied the CsZnPO_4 IR spectra at the heating. So, we obtained the characteristic IR in MID region spectra of all three modifications. The spectra of Mg and Ni phases sharply differed from other ones. Moreover, there are the bands of the water vibrations and librations in spectra. We proposed the hydrolytic instability. The next investigations show that CsMgPO_4 and CsNiPO_4 adsorb the water from air at the room temperature and turn into respective hexahydrates: $\text{CsMgPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CsNiPO}_4 \cdot \text{H}_2\text{O}$. The comparison of the spectra allowed proposing the structures of CsNiPO_4 and $\text{CsNiPO}_4 \cdot 6\text{H}_2\text{O}$. These results were confirmed by Rietveld method.

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References:

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