

Infrared spectroscopic studies of $\text{Cs}_2\text{Ni}(\text{XO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$) and of NH_4^+ ions

included in $\text{M}_2\text{Ni}(\text{XO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Cs}, \text{Rb}; \text{X} = \text{S}, \text{Se}$)

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The solubility in the three-component $\text{Cs}_2\text{SO}_4 - \text{NiSO}_4 - \text{H}_2\text{O}$ system was studied at 25 °C by the method of isothermal decrease of supersaturation. It has been established that a double salt, $\text{Cs}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, crystallizes from the ternary solutions within a wide concentration range.

Infrared spectra of neat Tutton compounds $\text{Cs}_2\text{Ni}(\text{XO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$) as well as those of ammonium doped rubidium and cesium sulfate and selenate matrices are presented and discussed in the regions of the normal modes of the tetrahedral ions and water librations. The ammonium ions included in the sulfate matrices exhibit three bands corresponding to ν_4 (C_1 site symmetry of the host cations). However, the inclusion of ammonium ions in the rubidium and cesium selenate matrices leads to the appearance of four bands in the region of ν_4 . At that stage of our knowledge we assume that some kind of disorder of the ammonium ions included in the selenate lattices occurs due to the strong proton acceptor capability of the SeO_4^{2-} ions (stronger than that of the SO_4^{2-} ions). This fact facilitates the

formation of polyfurcate hydrogen bonds by the ammonium ions in the selenate matrices, thus leading probably to increasing in the coordination number of these ions, i.e. to a disorder of the ammonium guest ions.

The strength of the hydrogen bonds formed in the cesium Tutton compounds as well as that of the hydrogen bonds formed in the rubidium and cesium salts containing isomorphously included ammonium ions as deduced from the frequencies of the water librations is also discussed. The spectroscopic experiments show that the bands corresponding to water librations in the spectra of the mixed crystals $M_{1.85}(NH_4)_{0.15}Ni(XO_4)_2 \cdot 6H_2O$ ($M = Rb, Cs; X = S, Se$) broaden and shift to lower frequencies as compared to those in the spectra of the neat rubidium and cesium compounds, thus indicating that weaker hydrogen bonds are formed in the mixed crystals. These spectroscopic findings are owing to the decrease in the proton acceptor strength of the SO_4^{2-} and SeO_4^{2-} ions as a result of the formation of hydrogen bonds between the host anions and the guest ammonium cations (*anti-cooperative* or proton acceptor competitive effect).