

Matrix-infrared spectroscopy as a tool to monitor admixtures in mineralsD. Marinova^{1*}, M. Wildner², D. Stoilova¹ and M. Georgiev³

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Matrix-infrared spectroscopy provides important information about the type of the admixtures included in minerals, either as isomorphous (isodimorphous) substitutions or as distinct phase inclusions. The vibrational spectra of distinct phase inclusions are similar to those of the respective neat compounds. However, the vibrational spectra of isomorphously included guest ions are essentially determined by both the site-symmetry, which is assumed to be the same as that of the respective host ions (substitutional type of mixed crystals), and the potential at the lattice sites where the guest ions are located, as shown by the extend of energetic distortion of the matrix-isolated ions.

In the present study, several phases belonging to the large number of natural and synthetic compounds with kröhnkite-type chains have been synthesized as model phases. The crystal structures of $\text{Na}_2\text{Me}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Me} = \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) and $\text{K}_2\text{Me}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Me} = \text{Zn}, \text{Cd}$) were determined from X-ray single-crystal diffraction data and those of $\text{K}_2\text{Me}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{Me} = \text{Co}, \text{Ni}$) by X-ray powder diffraction. The structures are build up from $\text{MeO}_4(\text{H}_2\text{O})_2$ octahedra and XO_4 tetrahedra forming infinite kröhnkite-type octahedral-tetrahedral chains, which are linked by alkali cations to layers and further to a three-dimensional framework via hydrogen bonds. The sodium cobalt, nickel and zinc compounds as well as the potassium cobalt, nickel and cadmium compounds crystallize in the triclinic space group $P\bar{1}$ (type A), the sodium cadmium selenate in the monoclinic space group $P2_1/c$ (type D), and the potassium zinc chromate in the monoclinic space group $C2/c$, thus representing a new structural type (type H).

The vibrational behavior of SO_4^{2-} guest ions included in these chromate and selenate matrices has been studied by infrared spectroscopy. It has been established that the extent of energetic distortion of the SO_4^{2-} guest ions as deduced from the values of $\Delta\nu_{\text{as}}$ (site-group splitting) and $\Delta\nu_{\text{max}}$ (the difference between the highest and the lowest wavenumbered components of the stretching and bending modes), depends on both the electronic configurations of the Me^{2+} ions and the degree of covalency of the respective $\text{Me}^{2+}\text{--O}$ bonds. The matrix-isolated SO_4^{2-} guest ions are stronger distorted in the selenates than in the chromates due to the smaller unit-cell volumes of the selenate host compounds as compared to those of the chromate ones and the different ionic radius of the K^+ and Na^+ ions. The smaller Na^+ ions cause a stronger electrostatic field (shorter Na--O bonds), thus leading to remarkably larger values of $\Delta\nu_{\text{as}}$ and $\Delta\nu_{\text{max}}$ of the guest ions in the sodium compounds.