

Polarized IR-microscope spectra of guanidinium hydrogenselenate single crystal

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Abstract

The polarized IR-microscope spectra of $C(NH_2)_3 \cdot HSeO_4$ small single crystal samples were measured at room temperature. The spectra are discussed with the framework of oriented gas model approximation and group theory. The stretching νOH vibration of the hydrogen bond with the $O \cdots O$ distance of 2.616 Å gives characteristic broad AB-type absorption in the IR spectra. The changes of intensity of the AB bands in function of polarizer angle are described. Detailed assignment for bands derived from stretching and bending modes of selenate anions and guanidinium cations were performed. The observed intensities of these bands in polarized infrared spectra were correlated with theoretical calculation of directional cosines of selected transition dipole moments for investigated crystal. The vibrational studies seem to be helpful in understanding of physical and chemical properties of described compound and also in design of new complexes with exactly defined behaviors.

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1. Introduction

The most important role in structure of new compounds is reserved for weak intermolecular interactions such as hydrogen bonds [1,2]. A vibrational spectroscopy is a very good tool for study of the behavior of hydrogen bonds in a crystal. The influences of the hydrogen bond network on the optical properties of the crystals were already discussed [3]. Crucial role in this study can be reserved for vibrational polarized light spectra on monocrystal's samples. These results could be compared directly with theoretical calculation of optical properties [4].

The new family of compounds with guanidinium cation were discovered and investigated as potential materials for non-linear optics (NLO). Molecules with symmetry close to three-fold rotational (octupolar molecules) can exhibit non-zero β , despite being non-polar [5]. A number of molecules as well as molecular ions of D_{3h} (or C_3 or D_3) symmetry have been shown to display promising properties.

The choice of guanidinium ion $C(NH_2)_3^+$ for detailed investigations is not accidental. The guanidinium ion can form a broad family of hydrogen-bonded crystals, but this cation is relatively simple chemical species [6] whose structure is related to those of amides and proteins in which there is considerable current interest. Some of these organic molecules have the delocalized electron systems and are of particular interest in NLO investigation because of their potentially large non-linear optical response [7].

The crystal structure and powder vibrational spectra of $C(NH_2)_3 \cdot HSeO_4$ at various temperatures were investigated previously [8]. The studies did not explain all chemical and physical behaviors of described compounds. The appearance of a phase transition seems to be not clear. If this phenomenon has to do with the many hydrogen bonds in the crystal, polarized IR spectra may provide a satisfactorily answer. This crystal belongs to centrosymmetric space group ($P2_1/n$), but detailed vibrational studies of chemical interactions between organic (guanidinium ion) and inorganic (hydrogenselenate ion) parts can be helpful in work on next guanidinium cation family compounds. The results obtained during analysis of polarized vibrational spectra for investigated crystal could be

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used to discuss a design strategy for the molecular engineering for new crystals with similar crystallographic structure.

The second problem which should be explained after detailed vibrational study, concern the “rigidity” of guanidinium cation (the shape of this cation is not deformed by chemical interaction, practically). This configuration is very stable and the symmetry is virtually D_{3h} . The ion is almost flat. This property is independent from neighborhood of different chemical anions and interactions. In this configuration planarity of the CN_3 groups skeleton correspond to sp^2 hybridization of the carbon atom. The understanding of this behavior is very important in design of new compounds without inverse center, which will be interesting in technological applications.

2. Experimental

The crystals of $C(NH_2)_3 \cdot HSeO_4$ were obtained by a slow evaporation at constant temperature ($20^\circ C$) of the water solution containing guanidine cations (guanidinium carbonate) and selenate anions (selenic acid) in stoichiometric ratio 1:1. The transparent single crystals were very small (size $3\text{ mm} \times 2\text{ mm} \times 1\text{ mm}$ approx.) therefore were not suitable for standard IR and Raman polarized measurement. The polarized IR-microscope studies for investigated crystal with this small size were possible only. The attempt to growth of deuterated analogue was not successful.

The crystals were oriented using X-ray and polarizing microscope methods. Two samples were prepared. One sample was parallel to $b(Z)$ axis. The second one, the $ac(XY)$, was perpendicular to the $b(Z)$ axis. The polarized reflection spectra from (0 1 0) plane using Specular Reflectance Mode of IR-microscope were acquired at every 10° with respect to the X axis. The relationship between X, Y principal optical axis and crystallographic a and c axis are shown in Fig. 2. The IR-microscope polarized single crystal spectra of $ac(XY)$ plane were recorded for one sample with different setting and fixed polarizer. For each specular spectrum new reference set was measurement. The reflectance spectra from a polished sample perpendicular to (0 1 0) face, with polarization of the radiation parallel to $b(Z)$ crystallographic axis was recorded too.

All polarized IR-microscope spectra were measured at room temperature. The sample was fixed on the microscope stage in air atmosphere. The auto moving function of microscope stage was switched off.

The specular reflectance spectra were run on Perkin-Elmer AutoIMAGE IR-microscope, attached to a Spectrum 2000 FT-IR spectrometer with L_{N_2} cooled MCT detector (spectral region $4000\text{--}600\text{ cm}^{-1}$, resolution 4 cm^{-1} , number of scans 500, aperture $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$). The auto-focus function was applied to find and store information regarding the position across the monocrystal was. The standard build-in controllable polarizer was used.

The absorbance spectra were calculated from specular reflectance spectra by Kramers–Kronig transforma-

tion module from Perkin-Elmer Spectrum version 2.00 software.

The powder infrared spectra were measured using a Bruker IFS-88 spectrometer with resolution of 2 cm^{-1} . The samples in Nujol suspensions were used.

A mini color CCD camera attached to the IR-microscope recorded photographs of the surface of the measured crystals.

3. The crystal structure and vibrational selection rules

The $C(NH_2)_3 \cdot HSeO_4$ crystallises in $P2_1/n$ space group of the monoclinic system. There are four formula units per primitive unit cell [8]. The crystal is build up of hydrogenselenate anions that are connected by hydrogen bonds forming infinite chains (Fig. 1a). These chains are parallel to the b crystallographic axis and form planes parallel to the (0 1 1) crystallographic plane. The hydrogen bonds linking the hydrogenselenate anions into chains are medium strong with $O(2)\text{--}H(1)\cdots O(1)\#1$ distance equals $2.616(6)\text{ \AA}$. The O2 oxygen atom plays a role of proton donor, whereas the O1 oxygen atom is an acceptor of proton in hydrogen bond. The Se–O2 bond is the longest in hydrogenselenate anion. The Se–O1 bond is the shortest one.

The second type of crystal sublattice is built up of guanidinium cations $C(NH_2)_3^+$ (Fig. 1b). The cation has symmetry similar to D_{3h} , but this relationship is disturbed by second hydrogen bond network, because all oxygen atoms from hydrogenselenate anions participate in other hydrogen bonds joining the $HSeO_4^-$ ions with nitrogen atoms from guanidinium cations. The bonds are very weak with distances: $N(1)\text{--}H(12)\cdots O(3) = 2.902\text{ \AA}$, $N(1)\text{--}H(11)\cdots O(4) = 2.989\text{ \AA}$, $N(2)\text{--}H(21)\cdots O(4) = 2.923\text{ \AA}$, $N(2)\text{--}H(22)\cdots O(2) = 3.082\text{ \AA}$, $N(3)\text{--}H(31)\cdots O(3) = 2.910\text{ \AA}$ and $N(3)\text{--}H(32)\cdots O(1) = 2.983\text{ \AA}$. The weak hydrogen bonds change C–N distances in guanidine ion and investigated cation does not have D_{3h} symmetry exactly. The C–N distances are different and equal to: 1.287 (C–N(1)), 1.307 (C–N(2)) and 1.335 (C–N(3)) \AA . The differences were found in the N–H distances in guanidinium ion. The bonds $N(1)\text{--}H(11)$ and $N(1)\text{--}H(12)$ are equal to 0.829 and 0.558 \AA , respectively. The distances $N(2)\text{--}H(21)$ and $N(2)\text{--}H(22)$ are similar and equal: 0.694 and 0.684 \AA , whereas the bonds $N(3)\text{--}H(31)$ and $N(3)\text{--}H(32)$ are equal to 0.750 and 0.778 \AA , respectively. The guanidinium ion is almost flat, but the very small (ca. 3°) deviation of hydrogen atoms from C–N plane is observed. The projection on ac plane of guanidinium selenate structure is presented in Fig. 2 (above: the hydrogenselenate hydrogen bond network; below: the second motif of crystallographic structure—guanidinium cations).

The X-ray diffraction study of the crystal structure reveals that the hydrogenselenate anions (deformed tetrahedrons) and the guanidinium cations occupy the C_1 positions in the primitive unit cell.

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