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Crystal growth, crystal structure, vibrational spectroscopy, linear and nonlinear optical properties of guanidinium phosphates

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ABSTRACT

Of the three guanidinium phosphates GuH_2PO_4 (space group $P2_1/c$), $Gu_2HPO_4 \cdot H_2O$ (space group $P\bar{4}2_1c$) and $Gu_3PO_4 \cdot \frac{3}{2} H_2O$ (space group Cc) crystal structures and a vibrational spectroscopy study are presented. Large single crystals of GuH_2PO_4 and $Gu_2HPO_4 \cdot H_2O$ are grown. Refractive indices and their dispersion in the wavelength range 365 nm – 1083 nm are determined and used for the analysis of phase matching conditions for collinear SHG in the case of the non-centrosymmetric crystals of $Gu_2HPO_4 \cdot H_2O$. The crystals are not phase-matchable within their transmission range. Both independent components of the SHG tensor of $Gu_2HPO_4 \cdot H_2O$, determined by the Maker fringe method, are given, with $d_{14} = 0.23$ pm/V and $d_{36} = 0.22$ pm/V. In addition, the thermal stability and the anisotropy of thermal expansion of GuH_2PO_4 and $Gu_2HPO_4 \cdot H_2O$ is reported.

1. Introduction

In the family of compounds of the trigonal guanidinium cation $[C(NH_2)_3]^+$ (abbreviated "Gu" in the following) a series of members are known with crystal structures of polar symmetry, which either show ferroelectric behaviour, such as $GuClO_4$ [1], $GuBF_4$ [1,2], $Gu_4Cl_2SO_4$ [3,4] or $Gu_4Br_2SO_4$ [5], or are non-ferroelectric polar crystals with remarkable physical effects, such as pyroelectricity or piezoelectric effect. A prominent example for the latter case is the hexagonal (point group 6*mm*) guanidinium iodide, GuI, which possesses a pyroelectric coefficient as high as 60 μC m^{-2} K^{-1} at room temperature [6–8] (which amounts approximately one quarter of the pyroelectric coefficient of the ferroelectric $BaTiO_3$ [9]).

According to their nonlinear optical (NLO) properties given in literature, several guanidinium compounds also may be classified as attractive NLO crystals. The suitability of the guanidinium cation as a polarizable acentric structural constituent of nonlinear optical crystals has been analysed theoretically by Zyss [10] and exemplified by the development of the NLO material guanidinium monohydrogen L-tartrate [11]. Remarkable coefficients of the second harmonic generation (SHG) tensor [d_{ijk}^{SHG}] were also found for the tetragonal guanidinium zinc sulfate (point group $\bar{4}2m$) [12], and, although the refractive indices of the crystals do not allow (collinear) SHG phase matching, $Gu_2Zn(SO_4)_2$ turned out to be an attractive material for cascaded $\chi^{(2)}$-$\chi^{(3)}$ nonlinear processes [13]. Here, stimulated Raman scattering (SRS) is involved as $\chi^{(3)}$-based NLO process. Attractive properties of SHG, SRS and cascaded $\chi^{(2)}$-$\chi^{(3)}$ nonlinear processes are also reported for another guanidinium compound, the orthorhombic (point group 222) bis(guanidinium) zirconium bis(nitrilotriacetate) hydrate ($Gu_2Zr(NTA)_2 \cdot H_2O$) [14,15]. This non-ferroelectric crystal also shows exceptional large piezoelectric constants ($d_{123} = 62(2)$, $d_{231} = 1.5(2)$, $d_{312} = 16.6(3)$ pC N^{-1}) [15].

The non-centrosymmetric tetragonal (point group $\bar{4}2m$) bis(guanidinium) hydrogen phosphate monohydrate, $Gu_2HPO_4 \cdot H_2O$, and the isomorphic arsenate, $Gu_2HAsO_4 \cdot H_2O$, were treated as subjects for the ab initio calculation of hyperpolarizabilities β_{ijk} of

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their structural constituents [16]. The author of this work also states the observation of nonlinear optical response of the crystals and concludes, based on the results, that the two compounds should be promising NLO materials [16]. Liu et al. [17] reported on crystal growth and some physical properties of $Gu_2HPO_4 \cdot H_2O$, including refractive indices and their dispersion in the visible wavelength range. The authors classify the bis(guanidinium) hydrogen phosphate monohydrate as an optically positive "phase matchable nonlinear optical material in the visible and UV region" [17]. Results of single crystal growth and of an investigation of optical properties of $Gu_2HPO_4 \cdot H_2O$ were also reported in Ref. [18], recently.

Motivated by the promising properties of compounds containing the guanidinium cation and continuing our work on guanidinium salt crystals we investigated the phases obtained from aqueous solutions of reaction products between guanidinium carbonate Gu_2CO_3 and phosphoric acid H_3PO_4, namely the above mentioned hydrogen phosphate $Gu_2HPO_4 \cdot H_2O$, the dihydrogen phosphate GuH_2PO_4 and the neutral phosphate $Gu_3PO_4 \cdot \frac{3}{2} H_2O$. Surprisingly, for the latter two compounds no structural information could be found in literature, and, surprisingly, we found, in contrast to the data given in Ref. [17], optically negative character of the crystals of $Gu_2HPO_4 \cdot H_2O$. In the present work we report on crystal structure determination and a vibrational spectroscopy study of all three guanidinium orthophosphates. Large single crystals of $Gu_2HPO_4 \cdot H_2O$ and GuH_2PO_4 were grown, which were used for the investigation of their thermal expansion and the determination of precision refractive indices in the visible and near infrared wavelength region. For crystals of the non-centrosymmetric $Gu_2HPO_4 \cdot H_2O$ and $Gu_3PO_4 \cdot \frac{3}{2} H_2O$ second harmonic generation (SHG) was investigated, including the determination of the SHG tensor [d_{ijk}^{SHG}] for $Gu_2HPO_4 \cdot H_2O$.

2. Experimental

2.1. Crystal structures

The crystal structures of the three guanidinium orthophosphates $Gu_2HPO_4 \cdot H_2O$, GuH_2PO_4 and $Gu_3PO_4 \cdot \frac{3}{2} H_2O$ were determined by single crystal X-ray diffraction using single crystals with typical size of 0.2 × 0.2 × 0.2 mm^3, which were obtained from reaction of guanidinium carbonate and phosphoric acid in aqueous solution. All structure data were collected at 296 K with a STOE IPDS2 diffractometer. Experimental details of data collection, structure solution and structure refinement are given in the Electronic Supplementary Material in Tables 1S and 2S (Supplementary Materials), CIF files of the three crystal structures are available upon request at Fachinformationszentrum (FIZ) Karlsruhe under CSD-No. 427995 ($Gu_2HPO_4 \cdot H_2O$), CSD-No. 427996 (GuH_2PO_4) and CSD-No. 427994 ($Gu_3PO_4 \cdot \frac{3}{2} H_2O$).

2.2. Vibrational spectroscopy

The infrared spectra were recorded using nujol and fluorolube mull (KBr windows) techniques on a Thermo Nicolet 6700 FTIR spectrometer with 2 cm^{-1} resolution and Happ-Genzel apodization in the 400 - 4000 cm^{-1} region. The Raman spectra were recorded on a Thermo Nicolet 6700 FTIR spectrometer equipped with the Nicolet Nexus FT Raman module (2 cm^{-1} resolution, Happ–Genzel apodization, 1064 nm Nd:YVO_4 laser excitation, 600 mW power at the sample) in the 100 - 4000 cm^{-1} region.

2.3. Crystal growth

Growth of large single crystals was performed for the two compounds GuH_2PO_4 and $Gu_2HPO_4 \cdot H_2O$ (see Fig. 4). The compounds were synthesized from guanidinium carbonate (Gu_2CO_3) and phosphoric acid (H_3PO_4) in a molar ratio 1 : 2 (for GuH_2PO_4) and 1 : 1 (for $Gu_2HPO_4 \cdot H_2O$) in aqueous solution. A subsequent purification by recrystallization of the guanidinium phosphates yielded the starting materials for crystal growth.

The crystals of both compounds were grown from aqueous solutions using two different methods: By controlled slow cooling within the temperature range from ~315 K down to ~308 K, and by controlled evaporation of the solvent at constant temperature of ~313 K. For both methods a typical growth period of 10 − 12 weeks was applied. Small single crystals of $Gu_3PO_4 \cdot \frac{3}{2} H_2O$ for crystal structure determination were obtained by reaction of Gu_2CO_3 with H_3PO_4 in a molar ratio of 3 : 2 in aqueous solution. Note, however, that during this reaction also GuH_2PO_4 crystallized as a second (and dominant) phase.

2.4. Thermal stability

By means of thermogravimetric analysis, using a commercial thermobalance Perkin Elmer TGA7, the thermal stability of the grown crystals GuH_2PO_4 and $Gu_2HPO_4 \cdot H_2O$ was investigated. Optically clear, inclusion-free single crystal fragments of both compounds were crushed to coarse powders and immediately inserted each into the thermobalance. The measurements were performed in nitrogen atmosphere within the temperature range 315 K − 600 K with an applied heating rate of 1 K/min.

2.5. Thermal expansion

The temperature dependence and anisotropy of thermal expansion of both crystals, GuH_2PO_4 and $Gu_2HPO_4 \cdot H_2O$ was investigated using a commercial inductive dilatometer (Perkin Elmer TMA7). All measurements were performed on single crystal samples with three heating/cooling cycles for each sample orientation and a heating rate of ±1 K/min. During the measurements dry nitrogen atmosphere had been applied to prevent H_2O condensation on the samples. Temperature dependent measurements of sample length L started from base temperature $T_0 = 145$ K and ranged to 293 K. The $\Delta L/L_0$ versus $\Delta T = T - T_0$ data ($\Delta L = L - L_0$, L_0 = sample length at base temperature T_0) were fitted with a polynomial of type $\Delta L/L_0 = A \cdot \Delta T + B \cdot (\Delta T)^2 + C \cdot (\Delta T)^3 + \ldots$. For all measurements a polynomial of second rank turned out to be sufficient. From the first derivative of this polynomial

$$\frac{\mathrm{d}}{\mathrm{d}\Delta T}\left(\frac{\Delta L}{L_0}\right) = A + 2B \cdot \Delta T = \alpha'_{11}(\Delta T)$$

the temperature dependent thermal expansion coefficients α'_{11} for each sample orientation with sample face normal $\boldsymbol{e}'_1$ (with $\boldsymbol{e}'_1 = u_{1i}\boldsymbol{e}_i$, u_{1i} being the direction cosines of $\boldsymbol{e}'_1$ with respect to the axes $\boldsymbol{e}_i$ (i = 1, 2, 3) of the Cartesian crystal physical system $\{\boldsymbol{e}_i\}$) were calculated. The Cartesian reference system $\{\boldsymbol{e}_i\}$, to which in the following all tensorial properties and all transformations refer, is related to the crystallographic system $\{\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}\}$ by $\boldsymbol{e}_3 = {}^1/_c\boldsymbol{c}$, $\boldsymbol{e}_2 = {}^1/_b\boldsymbol{b}$ and $\boldsymbol{e}_1 = \boldsymbol{e}_2 \times \boldsymbol{e}_3$, see also Fig. 12.

2.6. Linear optical properties

Non-polarized transmission spectra of GuH_2PO_4 and $Gu_2HPO_4 \cdot H_2O$ were recorded at room temperature with a spectrophotometer Perkin Elmer Lambda 950, using a plate-shaped crystal sample of orientation (001) and thickness 1.06 mm for GuH_2PO_4, and of orientation (110) and thickness 0.90 mm in the case of $Gu_2HPO_4 \cdot H_2O$.