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New nonlinear optical potassium iodate $K[IO_3]$ and borates $K_3[B_6O_{10}]Br$, $KTa[B_4O_6(OH)_4](OH)_2 \cdot 1.33H_2O$—Synthesis, structures and relation to the properties

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ABSTRACT

Three optically uniaxial non-centrosymmetric potassium compounds, iodate $K[IO_3]$ and two borates $K_3[B_6O_{10}]Br$, $KTa[B_4O_6(OH)_4](OH)_2 \cdot 1.33H_2O$ have been synthesized and characterized by single-crystal X-ray diffraction. The materials were synthesized through hydrothermal techniques using initial reagents and mineralizers. All the compounds are trigonal-hexagonal: the space groups are *R3* ($K[IO_3]$), *R3m* ($K[B_6O_{10}]Br$) and *P-62m* ($KTa[B_4O_6(OH)_4](OH)_2 \cdot 1.33H_2O$). Powder second-harmonic generation (SHG) measurements on crystals, using 1064 nm Nd:YAG laser radiation, indicate the materials are all phase-matchable and have strong second-order nonlinearities. The correlation with the perovskite structure has been found and described for K,Br-borate and K-iodate. Structure-properties relation is discussed and attributed to stereo-active lone-pair on I^{5+} and asymmetrical bonds in the compounds. The role of K atoms is pronounced from crystal chemistry point of view, contributing optical nonlinearities.

1. Introduction

In the sets of ~870 noncentrosymmetric compounds, analyzed in [1] the first three ones with the maximal nonlinear optical susceptibility χ are $PbTiO_3$ (χ=42.8), $LiNbO_3$ (χ=40.68) and KIO_3 (24.7). Iodates have become an important class of NLO materials (lone-pair of I^{+5} ion may be stereo-active) and are widely investigated especially at the last time. Many complicated compositions with Li, Na, K, REE, Ti and other elements have been tested for metals with a lone-pair as Pb, Bi, Tl, V, which may be stereo active and increase IO_3-group effect [2–8]. Being promising for applications, KIO_3 crystal despite of its simplicity has up to now contradictory structural data. Five modifications I–II–III–IV–V– have been found for KIO_3 [9,10]. High temperature phase I existing at $T > 485$ K looks most promising for technical applications because of absence of ferroic domains, and better angular conditions for phase-matching. There are two structure determinations of phase I using Rietveld profile-structure refinement: based on neutron diffraction data with the resulting space group *R*3 (C_3) [11] and based on synchrotron data with the group *R*3*m* (C_{3v}) [12]. It seems, that the more reliable model is suggested in [11] for rhombohedral pseudo-cubic unit cell a_{rh}=4.4973(1) Å, α_{rh}=89.218(2)° with the conclusive proof on deviation from *R*3*m* to *R*3. Symmetry of intermediate phase II (T=345.6−485 K) is monoclinic *Cm* or *Pm* (the structure is unknown) and phase transition is characterized as ferroelectric [12]. Phase transition from phase II to the room-temperature phase III (*T*=258–345.6 K) associates most probably as ferroelastic [12]. Crystal structure III at ambient condition is triclinic *P*1 and pseudo-cubic. The unit cells transformation from I to III is given in [11]; structure determination of III is carried out using single crystal [13] and Rietveld on neutron data [14]. The earliest publication on KIO_3 [15] is apart from all publications and describes crystals synthesized by original method in water solutions at *t*=40–70 °C. High piezoelectric response was measured on these samples, but no SHG testing was performed. The structural model has been suggested in the space group *I*-43*m* in pseudo-cubic unit cell *a*=8.938(2) Å, α=89°30′ with the notation on more real *R*3*m* symmetry, but no *R*-value was given in the paper.

Nonlinear crystals in the borate family have been also widely investigated [1]; β-BaB_2O_4 (BBO) and LiB_3O_5 (LBO) are the two crystals already used in nonlinear optical applications. Among borates, BiB_3O_9 [16] possess highest SHG signal. Borates with the hilgardite structure $Pb_2[B_5O_9]Hal$ (*Hal*=Br, I) [17,18] also demonstrate rather strong SHG. New promising non-linear borate $K_3[B_6O_{10}]Br$ has original structure correlated to perovskite [19], its large crystals were obtained in [20]. Isostructural $K_3[B_6O_{10}]Cl$ [21] is exact replica of the original bromine compound; the analog

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with the perovskite and structure-properties relation are in agreement with the conclusions in [19]. Entry to the borates not only Pb, Bi elements with the lone pairs, but the high-polarizable atoms of niobium or tantalum makes possible to obtain crystals with enhanced non-linearity. In particular, there were produced several borates with Nb and Ta which demonstrate good piezoelectric and nonlinear optical properties: $TlNbB_2O_6$[22], $TlTaB_2O_6$ [23] and $KTaOB_2O_5$ [24]. Piezo-, ferroelectric and ferroelastic properties are found for the $K_3Ta_3B_2O_{12}$ [25,26].

In this paper, we report the syntheses, structures, second-harmonic generating properties of iodate KIO_3 and borates $K_3[B_6O_{10}]Br$, $KTa[B_4O_6(OH)_4](OH)_2 \cdot 1.33H_2O$. The correlation with the perovskite structure for K,Br-borate and K-iodate is discussed. It is suggested that electron density of active lone pairs and asymmetric bonds with the crucial role of K-atoms is most important for nonlinear optical response.

2. Experimental section

2.1. Synthesis

Single crystals of all new compounds were obtained under hydrothermal conditions. The synthesis was performed at the temperature ranging from 270 to 280 °C under a pressure of 70 atm. The experiments were carried out in standard autoclaves (volume 5–6 cm^3) lined with Teflon. The lowest and the highest temperatures of experiments were limited by kinetics of hydrothermal reactions and the instrumental capabilities, respectively. The duration of the experiments (18–20 day) corresponded to the completion of the reaction. The ration of solid and liquid phases was 1:5. As a rule in our growing experiments we are modeling processes taking place in geological environment. It is known that in the nature presence of SiO_2 component is a common thing. By reason of that, appreciable amount of SiO_2 was included into batch, special role of this additive being to enlarge viscosity of water solution. Iodate phase KIO_3 was crystallized of the components weight ratio SiO_2:B_2O_3:KIO_3=1:1:1; borate phase $K_3[B_6O_{10}]Br$ [19] was crystallized of the components weight ratio KBr:B_2O_3=1:2; borate phase $KTa[B_4O_6(OH)_4](OH)_2 \cdot 1.33H_2O$ was crystallized of the components weight ratio Ta_2O_5:B_2O_3:SiO_2=2:1:1, KF and K_2CO_3 were presented in the solution in equal proportion as mineralizers at concentration of 20 wt%. Final cooling to the room temperature was made in 24 h. Grown crystals were isolated by filtration the stock solution and washed with hot water. Colorless crystals were the only products from each reaction. KIO_3 formed large aggregates, which were lengthened up to 2 mm and break apart into small lustrous isometric cubes. K,Br-borate crystals formed opaque aggregates with the dimensions up to 1.5 mm, composed of rhombohedral, close to cube, crystals, and among the latter smaller transparent crystals were found. K,Ta-borate crystals formed turbid aggregates with the dimension up to 0.5–0.8 mm, from which was possible to separate small (~0.1 mm), half-transparent crystals without any facing. As chemical formulas of produced crystals were unknown, their compositions were tried with Jeol JSM-6480LV electronic microscope. The test revealed presence of K- and I-, K- and Br-, K- and Ta-atoms for iodate and borate compounds respectively. IR spectroscopy indicated presence of H_2O molecules and (OH)-groups in K,Ta-borate.

2.2. Crystallographic determination

The experimental intensities for K-iodate and K,Ta-borate were collected using Xcalibur S diffractometer equipped with CCD area detector using graphite-monochromated Mo Ka radiation. For K,Ta-borate except normal sharp reflections from a single crystal, Debye crystallogramm or powder pattern was detected in a form of weak circles centered on primary beam and that was the evidence of component of disorder in the best small half-transparent crystal. Full spheres of data were collected in omega scan for both compounds with the exposure time of 1.5 s per frame for K-iodate and 50 s per frame for K,Ta-borate and with control frames measurements during the process of data collection to check stability of all measurements. The absorption, calculated after structure determination, was negligible because of small μr_{av}=0.43 for KIO_3 and μr_{av}=0.69 for K,Ta-borate. The data were integrated using CrysAlis program, with the intensities corrected for Lorentz and polarization factors; the calculations were carried out using SHELXS-97 and SHELXL-97 [27,28]. The structures drawing was made using ATOMS [29]. Description of diffraction experiment for $K_3[B_6O_{10}]Br$, details of structure solving using Patterson method in polar space group *R*3*m*, *a*=10.124(3), *c*=8.867(2) Å and structure refinement are given in [19].

The unit cell of K-iodate was close to cubic; three angles were equal, but have deviation from 90°. Cubic symmetry was tested in the space group *I*-43*m* as in [15]. Patterson map peaks allowed to fill special position 6*b*, 2*a*, 8*c* by K, K, I or by I, I, K. Both variants revealed O-atoms with the acceptable coordination for heavy atoms, but the results were not reasonable and show up: the actual symmetry is not cubic, but trigonal rhombohedral with the rhombohedral setting of experimental data corresponded to a_{rh}=8.9481(8) Å, α_{rh}=89.95(1)°. Space group *R*3*m* apparently was not suitable: mirror plane doubled O-positions in I–O ambrella-like groups. Space group *R*32 was tested first in direct methods, SHELXS-97. Two I-atoms: in 2*c* position (symmetry 3) and in 6*f*, and four K-atoms: in 1*a*, 1*b*-positions (symmetry 32) and 3*e*, 3*d* positions (symmetry 2) were located and were similar to previous cubic model. Then 8 independent O-atoms with the correct I–O distances were found. Despite good R_{hkl}=0.0585, chemical formula and the model have double amount of oxygen atoms because of presence 2-fold axis. Thus the symmetry was lowered up to *R*3. In this final space group two independent I-atoms were located in positions 1*a*, (*xxx*), *x*~1/4 and ~3/4 (what caused pseudo-cubic I-lattice) and other two—in common position close to previous special. K-atoms also confirm pseudo-cubic I-lattice being in 1*a*, (*xxx*), *x*~0 and ~1/2. Chemical formula KIO_3 requested 8 independent O-atoms with *Z*=8, however, high pseudosymmetry doubled it up to 16 on residual density maps. The selection of the half real O-positions was made on the base of interatomic distances I–O, O–O and polar umbrella-like groups topology. List squares procedure was carried out with the correction of anomalous scattering and refinement of weighting scheme in the anisotropic approximation of thermal displacement for all the atoms. Flack parameter −0.02(5) showed that the absolute configuration was correctly determined for *R*3 mono-axial single crystal under investigation.

The unit cell of K,Ta-borate corresponded to hexagonal (trigonal) system. The structure was solved from the first principles using Patterson method. The extinctions of reflections were not observed, thus possible space group should be acentric (SHG signal) and without any screw axis or glide planes. The model was proposed first in most low-symmetrical *P*3 space group. The refinement of three heavy atom positions with the assumption of zero coordinates for the first atom, Ta1, revealed mirror plane m_z and the symmetry was set up to *P*-6. In this case, the positions of heavy atoms, namely Ta1, Ta2, K, were added by O1 atom, which coordinated a certain atom in tetrahedron with the only 3 vertices. Introduction of horizontal two-fold axis gave full tetrahedron of O1 and new O2 atoms, which was centered by B, what followed from the typical B–O interatomic distances. Thus, the correct final space group was *P*-62*m*. Two oxygen positions for