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BaNbO(IO₃)₅: A New Polar Material with a Very Large SHG Response

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The search for new second-order nonlinear optical (NLO) materials is of current interest and great importance because of their applications in photonic technologies.[1] Currently, the most widely used such materials are inorganic crystals based on borates [such as β-BaB₂O₄ (BBO) and LiB₃O₅ (LBO)] and phosphates [such as KH₂PO₄ (KDP) and KTiOPO₄ (KTP)].[2,3] Metal borophosphates containing both borate and phosphate groups are also promising NLO materials.[4] Recently, we found that a combination of B−O bonds and lone-pair-containing Se(IV) cations, which are susceptible to second-order Jahn−Teller (SOJT) distortion, can also afford a new type of second-order NLO compound.[5] It has been reported that the combination of transition-metal ions having a d⁰ electronic configuration, such as W⁶⁺ or Mo⁶⁺, and lone-pair-containing Se(IV) or Te(IV) cations, both susceptible to SOJT distortions, can also form inorganic solids with excellent SHG properties as a result of the "additive" polarizations of the two types of bonds.[6] Metal iodates such as α-LiIO₃, which also contain a lone-pair cation, I⁵⁺, in an asymmetric coordination geometry, have been reported to show a wide transparency region, large second-harmonic generation (SHG) coefficients, high optical-damage thresholds, and good thermal stability.[7,8] As for metal selenites and tellurites, d⁰ transition-metal ions such as Ti⁴⁺, V⁵⁺, W⁶⁺, and Mo⁶⁺ have been introduced into metal iodate systems to aid in the formation of noncentrosymmetric (NCS) structures and enhance their SHG properties.[9,10] To the best of our knowledge, no metal iodates with added Nb⁵⁺ cations have been reported to date. The NbO₆ octahedron, which is usually moderately distorted toward a corner (the local C_4 direction),[11] may favor alignment with the asymmetric iodate groups in such a way that the two types of polarization lie along the same direction, thereby producing polar materials with a very large SHG response. Guided by this idea, we successfully obtained a new polar material, BaNbO(IO₃)₅, with a very large SHG response (∼14 times that of KDP and ∼660 times that of α-SiO₂). Herein we report its synthesis, crystal structure, and ferroelectric and NLO properties.

BaNbO(IO₃)₅ was synthesized as a single phase in 83% yield (based on Ba) by the hydrothermal reaction of Ba(IO₃)₂·H₂O (1.0 mmol), Nb₂O₅ (0.6 mmol), and I₂O₅ (9 mmol) in 5 mL of water sealed in an autoclave equipped with a Teflon liner (23 mL) at 230 °C for 4 days (see the Supporting Information). The presence of a unique phase was confirmed by powder X-ray diffraction (XRD) (Figure S1). The Ba/Nb/I molar ratio measured by microprobe energy-dispersive spectroscopy analysis was 1.1:1.3:6.0, which is close to that determined from single-crystal XRD analysis.[12] BaNbO(IO₃)₅ crystallizes in the acentric space group *Cc* (No. 9). Its anionic structure may be considered to be "zero-dimensional" (0D) and is composed of a NbO₆ octahedron linked with five IO₃⁻ groups and one terminal O²⁻ anion, with the Ba²⁺ cations acting as spacers between these anions (Figure 1 and Figure S3). Both the Nb⁵⁺ and I⁵⁺ cations are in asymmetric coordination
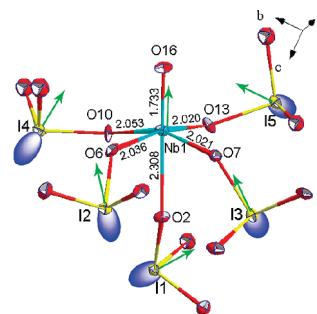

Figure 1. ORTEP drawing (with 50% probability ellipsoids) showing the "zero-dimensional" [NbO(IO₃)₅]²⁻ anion, lone pairs (blue ellipsoids), and local moments (green arrows) in BaNbO(IO₃)₅.

environments attributed to SOJT effects. The Nb⁵⁺ cation undergoes intraoctahedral distortion toward the terminal oxide ligand, that is, a corner (C_4[001]) distortion (see Figure 1), resulting in one "short" [1.733(7) Å], one "long" [2.308(8) Å], and four "normal" [2.020(8)−2.053(8) Å] Nb⁵⁺−O bonds. The magnitude of the out-of-center distortion (Δd) was estimated to be 0.63.[11] All five I⁵⁺ cations are in distorted trigonal-pyramidal environments, being coordinated by three oxygen atoms. The I−O distances range from 1.780(9) to 1.899(7) Å, comparable to those reported in other metal iodates.[7,8] It should be mentioned that the above 0D anionic units are further interconnected by weak I1−O4 bonds with lengths of 2.452(9) Å into a chain along the *a* axis (Figure S3b). The Ba²⁺ ion is surrounded by 10 oxygen atoms, one from a terminal O²⁻ anion and nine from IO₃ groups in a unidentate fashion, with Ba−O distances in the range 2.623(7)−3.162(9) Å. The results of bond valence calculations (Ba, 2.28; Nb, 4.84; I, 4.86−5.01) indicate that the Ba, Nb, and I atoms are in oxidation states of +2, +5, and +5 respectively.[13]

The IR spectrum of BaNbO(IO₃)₅ shows the characteristic absorption bands of ν_Nb−O (924 cm⁻¹) and ν_I−O (478−833 cm⁻¹) (Figure S4).[9,14] Its UV absorption spectrum reveals little absorption from 0.35 to 2.5 μm (Figure S5). The optical diffuse reflectance spectrum indicates an optical band gap of 3.64 eV (Figure S6), and hence, BaNbO(IO₃)₅ is a wide-band-gap semiconductor. The thermogravimetric analysis (TGA) curve (Figure S7) shows that BaNbO(IO₃)₅ is stable up to 420 °C but then continually loses weight up to 700 °C. The sharp weight loss corresponds to the decomposition of the compound through thermal disproportionation, which releases 2.5 molecules of I₂ and 6.25 molecules of O₂.[9,10] The total weight loss of 73.8% at 700 °C was close to the calculated value of 74.5%. The differential scanning calorimetry (DSC) diagram of BaNbO(IO₃)₅ exhibits two endothermic peaks at 456 and 593 °C, indicating that the compound melts incongruently.

The acentric structure of BaNbO(IO₃)₅ prompted us to measure its SHG properties. SHG measurements on sieved powder samples (80−100 mesh) using 1064 nm radiation[15] revealed that BaNbO(IO₃)₅

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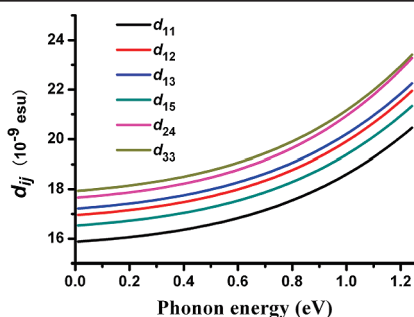‡ Graduate School of the Chinese Academy of Sciences.

Figure 2. Calculated frequency-dependent SHG coefficients of BaNbO-$(IO_3)_5$.

exhibits a very large SHG response, ∼14 times that of KDP and ∼660 times that of α-SiO_2. Furthermore, the compound was found to be phase-matchable (Figure S8). The extremely large SHG efficiency can be attributed to the synergistic effect of the polarizations of the asymmetric NbO_6 octahedra and the IO_3^- anions (Figure 1).

Piezoelectric measurements in a random direction on a single crystal with a size of 0.6 × 1.0 × 2.0 mm^3 gave a p_{33} value of ∼8.1 pC/N, which is much smaller than that of $Li_2Ti(IO_3)_6$.[10a] Ferroelectric measurements revealed a small maximum spontaneous polarization of 0.414 $\mu C/cm^2$ (Figure S9). Hence, the coefficients are very small, and the ferroelectric properties are negligible.[9,10] It is unlikely that the dipole moments associated with the asymmetric IO_3 polyhedra are reversible.[9,10] Thus, the polarization reversibility is limited to the small contribution from the Nb^{5+} cation.

To gain further insights into the band structure and optical properties of BaNbO$(IO_3)_5$, theoretical calculations based on density functional theory (DFT) were performed using the total-energy code CASTEP.[16]

The results of band structure calculations (Figure S10) indicate that BaNbO$(IO_3)_5$ is a direct-gap semiconductor with a band gap of 2.55 eV, which is significantly smaller than the experimental value as a result of the limitations of DFT methods. The bands just above the Fermi level are predominately derived from Nb 4d, I 5p, and some O 2p states, whereas the band just below the Fermi level is composed of O 2p, I 5p, and Nb 4d states that mix with small amounts of I 5s states (Figure S11).

The linear optical response properties of BaNbO$(IO_3)_5$ were examined through calculation of the complex dielectric function $\varepsilon(\omega)$ = $\varepsilon_1(\omega)$ + i$\varepsilon_2(\omega)$. The imaginary part [$\varepsilon_2(\omega)$] of the frequency-dependent dielectric function of BaNbO$(IO_3)_5$ shows anisotropy along different dielectric axis directions (Figure S12a). The curves of the average imaginary and real parts of the dielectric function were obtained as ε_{ave} = (ε_x + ε_y + ε_z)/3 (Figure S12b). The average imaginary part reveals the strongest adsorption peak at ∼5.71 eV, which can be mainly assigned to electronic interband transitions from the O 2p state to I 5p and Nb 4d states. The average static dielectric constant is $\varepsilon(0)$ = 4.50. The dispersion of the refractive index, which was calculated using the formula $n^2(\omega) = \varepsilon(\omega)$, indicates an order of $n^z > n^y > n^x$ (Figure S13). The values of n^x, n^y, and n^z at 1064 nm were calculated to be 2.128, 2.157, and 2.163, respectively.

The space group of BaNbO$(IO_3)_5$ belongs to class m and has 10 nonvanishing tensors of second-order susceptibility. Under the restriction of Kleinman's symmetry, only six independent SHG tensor components (d_{11}, d_{12}, d_{13}, d_{15}, d_{24}, and d_{33}) remain. The frequency-dependent SHG tensor components of BaNbO$(IO_3)_5$ ars plotted in Figure 2. The values of d_{11}, d_{12}, d_{13}, d_{15}, d_{24}, and d_{33} at a wavelength of 1064 nm (1.165 eV) for BaNbO$(IO_3)_5$ are 1.98 × 10^{-8}, 2.12 × 10^{-8}, 2.15 × 10^{-8}, 2.06 × 10^{-8}, 2.24 × 10^{-8}, and 2.26 × 10^{-8} esu,

respectively. These values are close to our experimental value, which is 14 times that of KDP ($d_{36} = 1.1 \times 10^{-9}$ esu).

In summary, by the combination of the Nb^{5+} cation, which has a d^0 electronic configuration, and the lone-pair-containing iodate anion, a new SHG material, BaNbO$(IO_3)_5$ has been prepared. It represents the first compound in the Ae/A−Nb^{5+}−I^{5+}−O system (Ae = alkaline-earth; A = alkali). It exhibits a very large SHG signal (∼14 times that of KDP) and is phase-matchable. It has also high thermal stability and a wide transparent region. On the basis of these arguments, it is concluded that this compound is potentially a new candidate for second-order NLO materials. Currently we are exploring other compounds in the Ae/A−Nb^{5+}−I^{5+}−O system and trying to grow larger-sized BaNbO$(IO_3)_5$ crystals in order to further study its optical properties.

Supporting Information Available: Details of crystallographic studies (CIF), physical property measurements, and theoretical calculations for BaNbO$(IO_3)_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for BaNbO$(IO_3)_5$: M_r = 1120.74; monoclinic; *Cc*; *a* = 13.9886(11) Å, *b* = 7.4843(4) Å, *c* = 14.8896(10) Å, β = 112.969(3)°; *V* = 1435.27(17) $Å^3$; *Z* = 4; D_{calc} = 5.187 g cm^{-3}. The final least-squares refinements converged at R1 (wR2) = 0.0317 (0.0837) and S = 1.076 for 2685 reflections with $I > 2\sigma(I)$. More details about the crystallographic studies are given in the Supporting Information.
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