Bi₂TeO₅: Synthesis, Structure, and Powder Second Harmonic Generation Properties

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Introduction

One of the continuing challenges in inorganic materials chemistry concerns the elucidation of structure−property relationships. Nowhere is this more true than with second-order nonlinear optical (NLO), i.e., second-harmonic generating (SHG), materials.[1−5] Viable SHG materials must possess the following attributes: transparency in the relevant wavelengths, ability to withstand laser irradiation, and chemical stability. Most importantly, the material in question must be crystallographically noncentrosymmetric (NCS). Mathematically it has been known for some time that only an NCS arrangement of atoms may produce a second-order NLO response.[6] We recently reviewed the known NCS oxides[3] and determined the influence of a second-order Jahn−Teller (SOJT) distortion. A SOJT distortion[7−13] is concerned with structural changes attributable to a nondegenerate ground state interacting with a low-lying excited state. The distortion occurs where the energy gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals is small *and* where there is a symmetry-allowed distortion permitting the mixing of the HOMO and LUMO states. With oxides, two families of metals can undergo SOJT distortions: octahedrally coordinated d⁰ transition metals and cations with nonbonded electron pairs. With the former, the mixing of the HOMO and LUMO is always symmetry-allowed with the energy between the orbitals correlated with the size and charge of the cation. With the latter, the stereoactive lone pair is attributable to the mixing between the s- and p-orbitals of the metal and oxygen atoms, respectively.

One way to increase the incidence of NCS is to synthesize new oxides that contain cations susceptible to SOJT distortions. Specifically, we have been investigating the syntheses of oxides that contain cations with nonbonded electron pairs.[14−16] It is

Table 1. Crystallographic Data

empirical formula: Bi₂TeO₅	fw: 625.56
$a = 11.572(1)$ Å	space group: *Abm*2 (No. 39)
$b = 16.458(2)$ Å	$T = 293.0(2)$ K
$c = 5.5245(5)$ Å	$\lambda = 0.710\ 73$ Å
$V = 1052.2(2)$ Å³	$\rho_{obsd} = 7.898$ g cm⁻³
$Z = 8$	$\mu = 72.17$ mm⁻¹
	$R(F) = 0.051^a$
	$R_w(F^2) = 0.143^b$

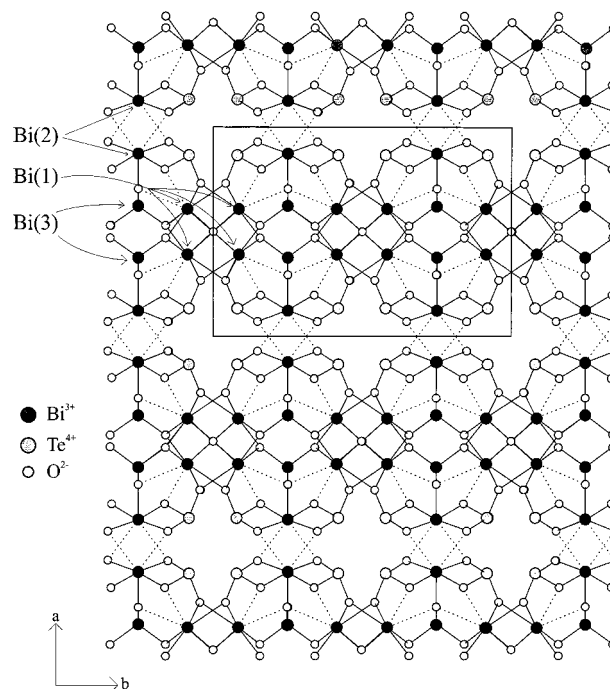$^a R = \sum ||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w(F_o^2)^2]^{1/2}$.

Figure 1. Ball-and-stick figure of Bi₂TeO₅ is shown. The dashed lines indicate long bond contacts.

thought that the SOJT distortions observed in these materials will not only alter the symmetry from centrosymmetric to noncentrosymmetric but will also occur in a cooperative manner. The cooperative distortion will polarize the M−O bonds to give a large SHG response. We have been investigating the syntheses and characterization of new tellurites, Te⁴⁺. Recently we reported the synthesis and NLO behavior of TeSeO₄ that has a SHG efficiency 400 times that of quartz.[16] In this paper we report the synthesis and powder SHG behavior of Bi₂TeO₅. Through these powder measurements, we calculate an approximate value for $\langle d_{ijk}^{2\omega} \rangle$, the NLO bond susceptibility.

Experimental Section

Synthesis. A stoichiometric mixture of Bi₂O₃ (1.600 g, 3.43 × 10⁻³ mol) and TeO₂ (0.548 g, 3.43 × 10⁻³ mol) was thoroughly ground and pressed into pellets. The pellets were wrapped in platinum foil and introduced into a quartz tube that was evacuated and sealed. The tube was gradually heated to 690 °C (5 °C h⁻¹), held for 36 h, and cooled to room temperature. Powder X-ray diffraction (vide infra) on the resultant yellow powder indicated the material was single-phase. Crystals of Bi₂TeO₅ were prepared by placing 0.4 g of the polycrystalline Bi₂TeO₅ powder into a gold tube that was subsequently sealed.

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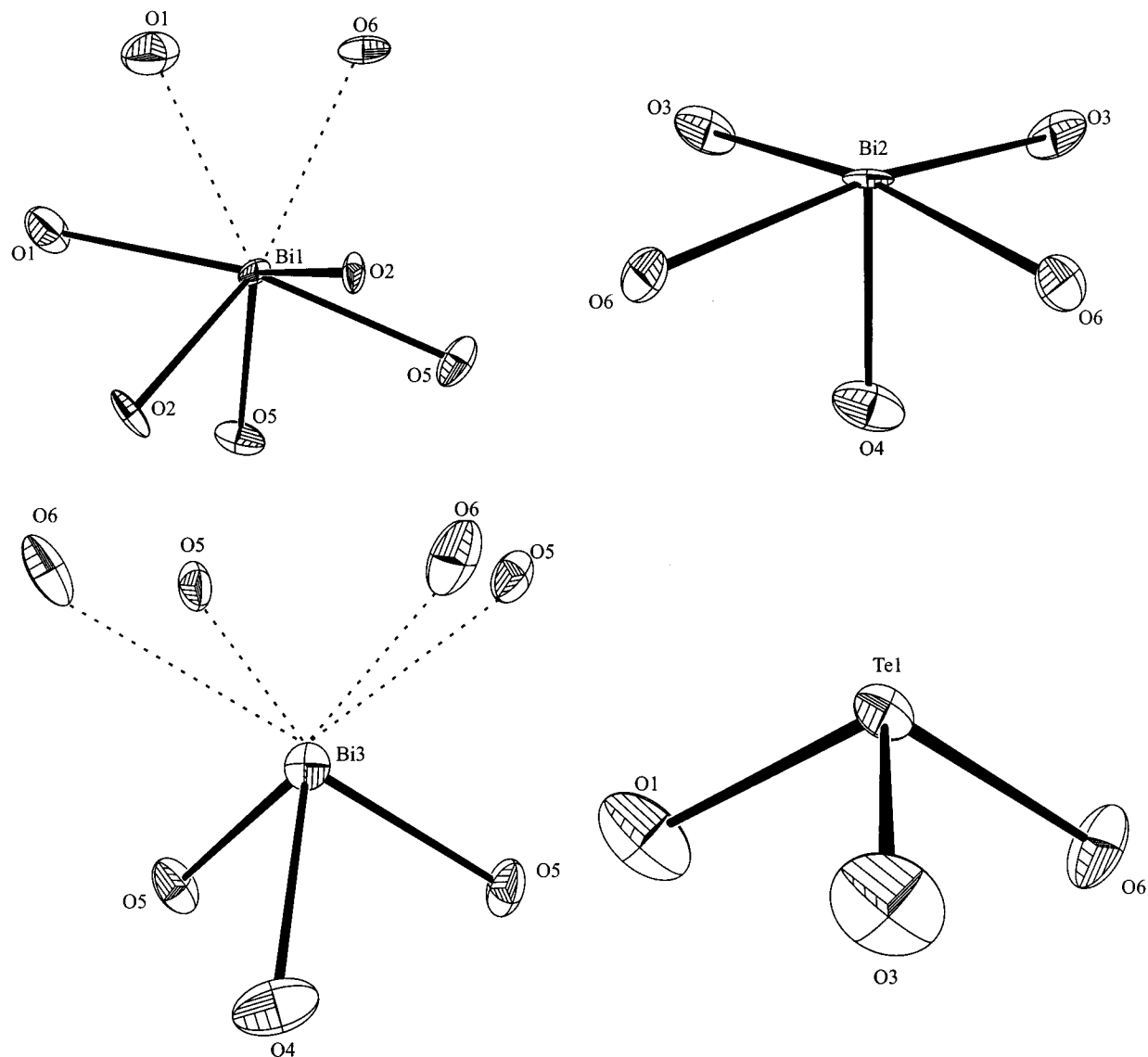(16) Porter, Y.; Bhuvanesh, N. S. P.; Halasyamani, P. S. *Inorg. Chem.*, in press.

Figure 2. ORTEP representations (50% probability ellipsoids) of the Bi^{3+} and Te^{4+} moieties.

Table 2. Bond Lengths (Å) and Angles (deg) for $Bi_2TeO_5^a$

atom	atom	distance	atom	atom	atom	angle
Bi(1)	O(1)	2.47(2)	O(2)	Bi(1)	O(1)	78.0(5)
Bi(1)	O(1)#2	2.729(15)	O(2)	Bi(1)	O(2)#2	71.60(12)
Bi(1)	O(2)#2	2.529(13)	O(2)	Bi(1)	O(5)#1	103.0(4)
Bi(1)	O(2)	2.166(10)	O(5)	Bi(1)	O(5)#1	76.7(3)
Bi(1)	O(5)	2.24(2)	O(5)	Bi(1)	O(1)#2	154.5(5)
Bi(1)	O(5)#1	2.29(2)				
Bi(2)	O(3)	2.38(2)	O(6)	Bi(2)	O(3)	94.2(5)
Bi(2)	O(3)#3	2.38(2)	O(6)#3	Bi(2)	O(3)	172.0(6)
Bi(2)	O(4)	2.06(2)				
Bi(2)	O(6)	2.365(14)				
Bi(2)	O(6)#3	2.365(14)				
Bi(3)	O(4)	2.14(2)	O(5)	Bi(3)	O(5)#3	87.9(8)
Bi(3)	O(5)	2.125(14)	O(5)	Bi(3)	O(4)	81.5(7)
Bi(3)	O(5)#3	2.125(14)				
Te(1)	O(1)	1.88(2)	O(3)	Te(1)	O(1)	100.3(8)
Te(1)	O(3)	1.85(2)	O(1)	Te(1)	O(6)#4	98.6(7)
Te(1)	O(6)#4	1.881(14)	O(3)	Te(1)	O(6)#4	101.6(7)

^{a} Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1$, $y + 0$, $z + \frac{1}{2}$; (#2) x, $-y + 0$, $z + \frac{1}{2}$; (#3) x, $-y + \frac{1}{2}$, z; (#4) x, y, $z - 1$.

The gold tube was heated at 920 °C for 5 h, then cooled slowly to 500 °C at 6.0 °C h^{-1} before being quenched to room temperature. The product contained yellow crystals, subsequently shown to be Bi_2TeO_5. The crystals had an approximate maximum dimension of 0.15 mm.

X-ray Diffraction. Although the structure of Bi_2TeO_5 has been reported,[17] we felt it important to redetermine the structure to better understand the SHG properties. Our data confirm that Bi_2TeO_5 crystallizes in the noncentrosymmetric orthorhombic space group *Abm*2 (No. 39) with $a = 11.572(1)$ Å, $b = 16.458(2)$ Å, $c = 5.5245(5)$ Å, and $V = 1052.2(2)$ Å^3. The cell refined from powder data, $a = 11.599$-(8) Å, $b = 16.456(5)$ Å, and $c = 5.519(2)$ Å, compares well to the single-crystal data. Table 1 summarizes the crystallographic data for the material. Complete crystallographic data have been deposited as a CIF (see Supporting Information).

Thermogravimetric Measurements. Thermogravimetric analysis was carried out, on polycrystalline Bi_2TeO_5, in air at a heating rate of 5 °C/min to 900 °C with a Seiko 320 TG/DTA. No weight loss or phase change was observed up to 900 °C. The absence of a phase change suggests that Bi_2TeO_5 is pyroelectric rather than ferroelectric.

Infrared Measurements. Infrared spectra were recorded on a Matteson FTIR 5000 spectrometer in the 400–4000 cm^{-1} range with the sample pressed between two KBr pellets. Infrared data: ν_{Bi-O}, 572 cm^{-1}; ν_{Te-O}, 664 and 754 cm^{-1}.

Second-Order Nonlinear Optical Measurements. Powder SHG measurements were performed on a modified Kurtz-NLO[18] system using

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1064 nm light. A Continuum Minilite II laser, operating at 1 Hz, was used for all measurements. The average energy per pulse was 3 mJ. Since the SHG efficiency of powders has been shown to depend strongly on particle size,[18,19] polycrystalline Bi_2TeO_5 was ground and sieved (Newark Wire Cloth Company) into distinct particle size ranges, <20, 20−45, 45−63, 63−75, 75−90, 90−125, and 125−138 μm. To make relevant comparisons with known SHG materials, crystalline SiO_2 was also ground and sieved into the same particle-size ranges. All of the powders were placed in separate capillary tubes. The SHG, i.e., 532 nm green light, radiation was collected in reflection and detected by a photomultiplier tube (Oriel Instruments). To detect only the SHG light, a 532 nm narrow-band-pass interference filter was attached to the tube. A digital oscilloscope (Tektronix TDS 3032) was used to view the SHG signal.

Results and Discussion

Because the structure of Bi_2TeO_5 has been published,[17] only a brief description will be given here. Bi_2TeO_5 has a three-dimensional structure consisting of Bi^{3+} and Te^{4+} cations. The Bi^{3+} are observed in both five- and three-coordinate environments, whereas the Te^{4+} is three-coordinate. A ball-and-stick representation of the structure is given in Figure 1 with dashed lines indicating long atom contacts. Both the Bi^{3+} and the Te^{4+} are in asymmetric coordination environments owing to their nonbonded electron pair (see Table 2 and Figure 2). As with $TeSeO_4$,[16] it is important to determine the "net" direction of the lone pair polarizations in order to understand the origin and magnitude of the SHG response. In Bi_2TeO_5, the lone pair on Te^{4+} points in one of four directions, [1 1 0], [−1 1 0], [1 −1 0], and [−1 −1 0] (see Figure 1). When taken as a whole, the lone pair polarizations associated with Te^{4+} cancel. The same phenomenon occurs for Bi(1), where the lone pair polarization points in the same directions as Te^{4+} (see Figure 1). For Bi(2), the lone pair points approximately in the [1 0 0] and [−1 0 0] directions but with the lone pair tilted roughly 15° toward the *c* axis. The net effect of this tilt is to produce a small moment in the [0 0 1] direction. The final Bi^{3+} cation, Bi(3), has its lone pair always pointing parallel to the [0 0 −1] direction, producing a very large moment in that direction. Thus, from a structural approximation, the SHG efficiency may be attributed to mainly Bi(3) because the lone pair polarizations attributable to the other metal cations effectively cancel.

Powder SHG measurements on sieved polycrystalline Bi_2-TeO_5 revealed a SHG efficiency 300 times that of quartz. In addition, the material is not phase-matchable (see Figure 3). That is, as the particle size becomes substantially larger than the coherence length of the material, the SHG intensity decreases rapidly. Our experiments also revealed Bi_2TeO_5 is damaged under prolonged laser irradiation. We observed after several laser shots (∼10) that the capillary tube became black. This phenomenon did not occur when the tube was empty. On the basis of the intensity ratio between a nonphase-matchable material and quartz (which is also not phase-matchable), one can
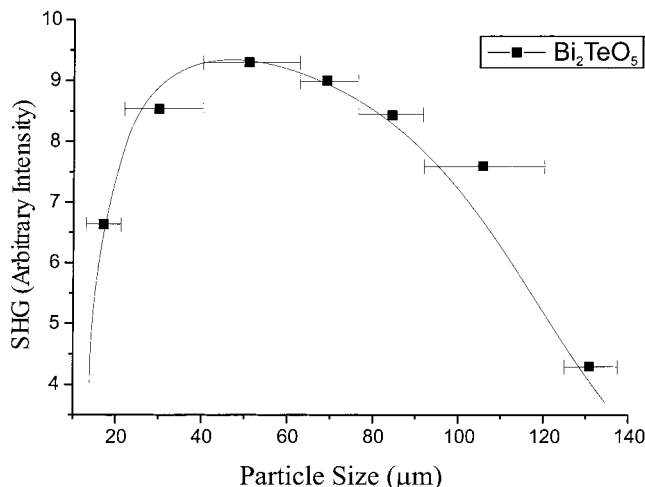
Figure 3. Phase-matching, i.e., particle size vs SHG intensity, data for Bi_2TeO_5. The curve drawn is to guide the eye and is not a fit to the data.

calculate the average NLO bond susceptibility, $\langle d_{ijk}^{2\omega} \rangle$.[18] For nonphase-matchable materials, the intensity ratio can be written[18]

$$\frac{I^{2\omega}(Bi_2TeO_5)}{I^{2\omega}(SiO_2)} = \frac{\left[(\langle d_{ijk}^{2\omega}\rangle^2)\frac{l_c^2}{2r}\right](Bi_2TeO_5)}{\left[(\langle d_{ijk}^{2\omega}\rangle^2)\frac{l_c^2}{2r}\right](SiO_2)} \quad (1)$$

The coherence length l_c is 20 μm for SiO_2 and is assumed to be 10 μm for Bi_2TeO_5, whereas the average particle size r is taken to be 50 μm for both materials.[18] The value of $\langle d_{ijk}^{2\omega} \rangle^2(SiO_2)$ can be calculated on single-crystal work and is $\langle d_{ijk}^{2\omega} \rangle^2(SiO_2) = 7.62 \times 10^{-2}$ pm²/V².[20] Setting eq 1 equal to 300 and solving for $\langle d_{ijk}^{2\omega} \rangle(Bi_2TeO_5)$ result in a value of 9.56 pm/V. Bi_2TeO_5 is found in crystal class $mm2$, which has three independent d_{ijk} moduli, $d_{113} = d_{311}$, $d_{223} = d_{322}$, and d_{333},[6] assuming Kleinman symmetry is valid.[21] Thus, it is not possible to calculate the specific d_{ijk} moduli solely on the basis of the $\langle d_{ijk}^{2\omega} \rangle(Bi_2TeO_5)$ value.

In summary, we have demonstrated that although Bi_2TeO_5 is SHG-active, with an efficiency 300 times that of quartz, the material is not phase-matchable.

Supporting Information Available: X-ray crystallographic file, in CIF format, and experimental and calculated powder X-ray diffraction patterns for Bi_2TeO_5. This material is available free of charge via the Internet at http://pubs.acs.org.

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