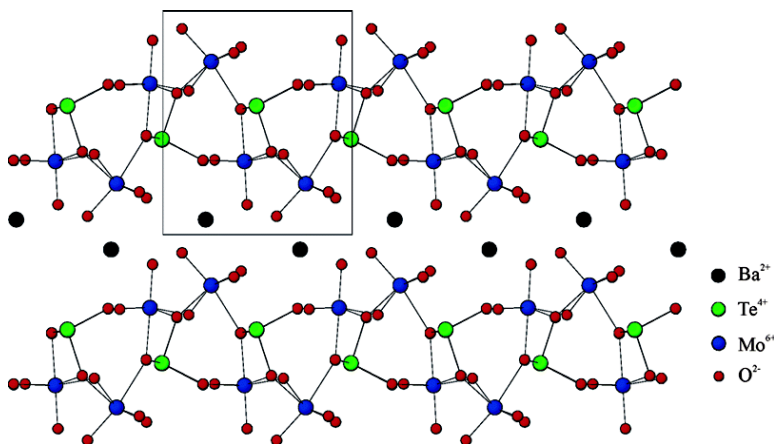


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Hyun-Seup Ra, Kang Min Ok, and P. Shiv Halasyamani

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Combining Second-Order Jahn–Teller Distorted Cations to Create Highly Efficient SHG Materials: Synthesis, Characterization, and NLO Properties of BaTeM₂O₉ (M = Mo⁶⁺ or W⁶⁺)

Hyun-Seup Ra, Kang Min Ok, and P. Shiv Halasyamani*

Department of Chemistry and the Center for Materials Chemistry, University of Houston, 136 Fleming Building, Houston, Texas 77204-5003

Received March 25, 2003; E-mail: psh@uh.edu

Second-order nonlinear optical (NLO) materials, i.e., second-harmonic generating (SHG) materials, are of current interest owing to their uses in photonic technologies.^{1–3} A requirement for all SHG materials is a noncentrosymmetric (NCS) crystal structure.⁴ Recently, a variety of strategies have been put forth to rationally design new NCS materials.^{5–10} We have focused on creating new NCS materials^{11–15} by synthesizing oxides containing cations susceptible to second-order Jahn–Teller (SOJT) distortions.^{16–22} SOJT effects involve structural changes attributable to a nondegenerate ground-state interacting with a low-lying excited state. The distortion occurs if the energy gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals is small and if there is a symmetry-allowed distortion permitting mixing of these two orbitals. The distortion can occur in two different “families” of cations, d⁰ transition metals (Ti⁴⁺, Nb⁵⁺, W⁶⁺) and cations with stereoactive lone-pairs (Se⁴⁺, Sb³⁺, Te⁴⁺), and results in asymmetric coordination environments. In this communication we report the synthesis, characterization, and SHG properties of two new materials, BaTeM₂O₉ (M = Mo⁶⁺ or W⁶⁺), in which extremely strong SHG efficiencies are observed, ~600 × SiO₂, on the order of LiNbO₃.²³ The strong SHG efficiency is attributable to the constructive addition of the Te–O and M⁶⁺–O bond polarizations. We are also able to give an estimate of β(W⁶⁺–O), by using our recently reported model.¹⁴

BaTeM₂O₉ (M = Mo⁶⁺ or W⁶⁺) were synthesized by solid-state techniques and their structures determined by standard crystallographic methods.²⁴ Polycrystalline BaTeM₂O₉ (M = Mo⁶⁺ or W⁶⁺) were synthesized by combining stoichiometric amounts of Ba₂CO₃, MoO₃ (WO₃), and TeO₂. The mixtures were heated in air to 550 °C for 36h with two intermittent re-grindings. White polycrystalline powders, subsequently shown to be BaTeMo₂O₉ (BaTeW₂O₉) were recovered. Single crystals of BaTeMo₂O₉ were grown by pouring Ba₂CO₃ (1.38 mmol) into the liquid mixture of MoO₃ (2.76 mmol) and TeO₂ (6.90 mmol) at 570 °C in a platinum crucible. The mixture was held at 570 °C for 12h and cooled slowly to 450 °C at 6 °C h⁻¹ before being quenched to room temperature. Colorless block-shaped crystals were manually extracted. Single crystals of BaTeW₂O₉ were grown by heating a mixture of Ba₂CO₃ (2.32 mmol), WO₃ (4.64 mmol), and TeO₂ (3.48 mmol) at 760 °C in a platinum crucible. The mixture was held at 760 °C for 24h and cooled slowly to 700 °C at 1 °C h⁻¹ before being quenched to room temperature. Colorless block-shaped crystals were also manually extracted. The quality of BaTeMo₂O₉ crystals was substantially better than BaTeW₂O₉.

Both materials crystallize as clear, colorless faceted blocks. The compounds have two-dimensional layered structures consisting of MO₆ (M = Mo⁶⁺ or W⁶⁺) octahedra linked to asymmetric TeO₃ polyhedra. The anionic layers are separated by Ba²⁺ cations (see Figure 1). The bond distances for Mo⁶⁺–O (W⁶⁺–O) range from

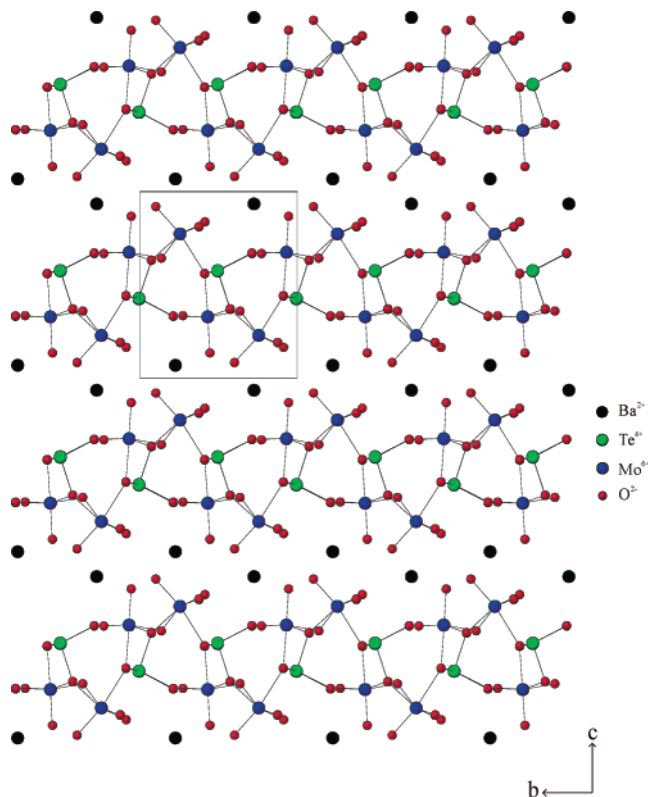


Figure 1. Ball-and-stick diagram of BaTeMo₂O₉. Note the asymmetric coordination environments in both Te⁴⁺ (green spheres) and Mo⁶⁺ (blue spheres) cations.

1.728(9)–2.233(7) Å (1.73(2) – 2.22(2) Å), whereas the Te–O bonds range from 1.867(8)–2.024(19) Å. Both the M⁶⁺ and Te⁴⁺ cations are in asymmetric coordination environments attributable to SOJT distortions. These distortions polarize the MO₆ and TeO₃ polyhedra. Interestingly for the two materials the intra-octahedral distortions are not the same. In BaTeMo₂O₉, the two unique Mo⁶⁺ cations distort along the local C₃ [111] direction, toward a face, of their respective octahedra. This out-of-center distortion produces three ‘short’ (1.728(9)–1.847(9) Å) and three ‘long’ (2.036(8)–2.233(7) Å) Mo⁶⁺–O bonds (see Figure 2). In BaTeW₂O₉, the two unique W⁶⁺ cations distort either along the local C₂ [110] direction, toward an edge, or the local C₃ [111] direction, resulting in two ‘short’ (1.73(2) Å and 1.77(2) Å), two ‘normal’ (1.90(2) Å and 1.99(2) Å), and two ‘long’ (2.22(2) Å × 2) W⁶⁺–O bonds, and for the C₃–W⁶⁺ distortion three ‘short’ (1.73(2)–1.85(2) Å) and three ‘long’ (2.09(2)–2.14(2) Å) W⁶⁺–O bonds. For Te⁴⁺, an asymmetric coordination environment is observed owing to the stereoactive lone-pair. Bond valence calculations for the M⁶⁺ (M = Mo⁶⁺ or

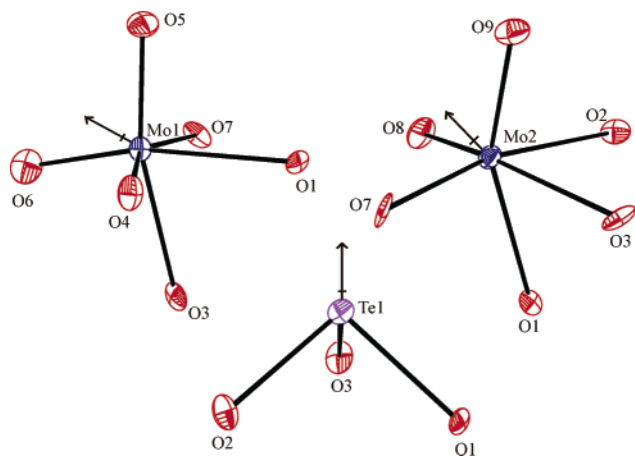


Figure 2. ORTEP (50% probability ellipsoids) in BaTeMo₂O₉ showing the asymmetric coordination environments of the Mo⁶⁺ and Te⁴⁺ cations. The approximate direction of the dipole moment in each polyhedra is also shown.

W⁶⁺) and Te⁴⁺ cations result in values ranging from 5.82–6.25 and 3.91–4.04, respectively.^{25,26}

Infrared data on polycrystalline BaTeMo₂O₉ and BaTeW₂O₉ revealed M⁶⁺–O and Te–O stretches between 840 and 900 cm⁻¹ and 600–800 cm⁻¹. The vibrations at 600 and 474 cm⁻¹ can be assigned to M–O–Te bends. The assignments are consistent with those previously reported.²⁷ Thermogravimetric analyses on the materials indicated the compounds are stable up to 650 °C. Above 650 °C, decomposition occurs to BaMo₄ (M = Mo⁶⁺ or W⁶⁺) and unidentified amorphous products.

Both of the reported materials crystallize in the NCS space group P2₁ (No. 4). NLO measurements on polycrystalline BaTeMo₂O₉ and BaTeW₂O₉ revealed extremely strong SHG responses of 600 and 500 × SiO₂ respectively—on the order of LiNbO₃.²³ *The very large SHG responses are directly attributed not only to the polarization from the M⁶⁺–O and Te–O bonds (see Figure 2), but more importantly to the constructive addition of these polarizations.* Additional powder SHG measurements indicated both materials are type-1 phase-matchable.²³ From the SHG efficiency and phase-matching behavior, we are able to estimate ⟨d_{eff}⟩_{exp}, the bulk NLO susceptibility, for each material. For BaTeMo₂O₉ (BaTeW₂O₉), ⟨d_{eff}⟩_{exp} is 28 (22) pm/V. Since ⟨d_{eff}⟩_{exp} ∝ β(M–O), the bond hyperpolarizability, it should be possible to estimate β for a given Mⁿ⁺–O bond once the crystal structure, the type-1 phase-matching behavior, and ⟨d_{eff}⟩_{exp} are known. We have developed such a model and recently published a table of β's for a variety of Mⁿ⁺–O bonds.¹⁴ The model also works in “reverse”, that is β for the various Mⁿ⁺–O bonds can be input into the relevant equations, and ⟨d_{eff}⟩_{calc} may be obtained. For BaTeMo₂O₉, using β(Te⁴⁺–O) = 130 × 10⁻⁴⁰ m⁴/V and β(Mo⁶⁺–O) = 305 × 10⁻⁴⁰ m⁴/V results in ⟨d_{eff}⟩_{calc} = 20 pm/V, which is in reasonable agreement with ⟨d_{eff}⟩_{exp} = 28 pm/V.

For BaTeW₂O₉ a different situation occurs. A β(W⁶⁺–O) of 570 ± 130 × 10⁻⁴⁰ m⁴/V has been reported.²⁸ This value seems erroneously large, given that third-row transition metals are less polarizable than second-row transition metals and that the magnitude of the out-of-center distortion for W⁶⁺ is smaller than Mo⁶⁺. Since in BaTeW₂O₉, the W⁶⁺–O and Te⁴⁺–O bond polarizations constructively add, we may use ⟨d_{eff}⟩_{exp} and β(Te⁴⁺–O) to estimate β(W⁶⁺–O). In doing so, we arrive at a value of β(W⁶⁺–O) of 230 × 10⁻⁴⁰ m⁴/V. This value is consistent with the smaller polarizability and magnitude of the intra-octahedral distortion of W⁶⁺ compared with Mo⁶⁺.

In summary, we have demonstrated that highly efficient SHG materials can be designed by synthesizing oxides containing cations susceptible to SOJT distortions. In BaTeM₂O₉ the polarizations attributable to the M⁶⁺–O and Te⁴⁺–O bonds constructively add, resulting in the large SHG responses. On the basis of the powder SHG measurements, we have also determined a more reasonable value for β(W⁶⁺–O), 230 × 10⁻⁴⁰ m⁴/V.

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Supporting Information Available: Two X-ray crystallographic files in CIF format and a calculated and observed X-ray diffraction pattern for BaTeMo₂O₉. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- For BaTeMo₂O₉ (BaTeW₂O₉) colorless faceted crystals, 0.03 mm × 0.05 mm × 0.08 mm (0.20 mm × 0.30 mm × 0.40 mm), were used. Single-crystal data were collected on a Siemens SMART diffractometer equipped with a 1K CCD area detector using graphite monochromated Mo Kα radiation at 293 K. The data were integrated using the Siemens SAINT [SAINT, Version 4.05; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995] program, with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. ψ -Scan absorption corrections were applied. The structures were solved by direct methods using SHELXS-97 [Sheldrick, G. M. SHELXS-97: A program for automatic solution of crystal structures; University of Goettingen; Goettingen, Germany, 1997.] and refined using SHELXL-97 [Sheldrick, G. M. SHELXL-97: A program for crystal structure refinement; University of Goettingen; Goettingen, Germany, 1997.]. Crystal data for BaTeMo₂O₉ (BaTeW₂O₉): monoclinic, P2₁, *a* = 5.5407(5) (5.490(2)) Å, *b* = 7.4661(7) (7.446(3)) Å, *c* = 8.8448(9) (8.887(3)) Å, β = 90.841(2)° (90.370(6)°), *V* = 365.80(6) (363.3(2)) Å³, *Z* = 2 (2), *R*(*F*) = 0.0313 (0.0601), *G*O_F = 1.078 (1.082).
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