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Lanthanide Thioborates, an Emerging Class of Nonlinear Optical Materials, Efficiently Synthesized Using the Boron-Chalcogen Mixture Method

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The Boron-Chalcogen Mixture method was used to obtain single crystals of the previously extremely difficult to synthesize lanthanide orthothioborates to investigate their structures and their structurally connected optical behavior, such as second harmonic generation. Using a combined halide and polychalcogenide flux, the BCM method yielded single crystals of $LnBS_3$ (Ln = La, Ce, Pr, Nd), which are isostructural and crystallize in the non-centrosymmetric space group, $Pna2_1$. Second harmonic generation measurements confirmed the expectation that $LaBS_3$ would exhibit a strong SHG response, measured at 1.5 x KDP.

Thioborates are an emerging class of nonlinear optical (NLO) materials that combine the attractive NLO abilities of chalcogenides and borates, resulting in materials exhibiting a combination of highly sought-after NLO properties, specifically, the high laser damage threshold and large optical nonlinearity of borates and the wide optical and IR transmission ranges of sulfides.[1-3] The significant difficulties of their synthesis, such as difficult starting reagents and the need for high reaction temperatures and pressures, has impeded the synthesis of thioborate materials. In fact, very few have been made, despite their predicted attractive NLO behavior. Furthermore, the lack of single crystal products obtained from current thioborate synthesis reactions has made structural characterization difficult and impeded the use of this class of materials for NLO applications.

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Figure 1. An image of single crystals of (left to right) $LaBS_3$, $CeBS_3$, $PrBS_3$, and $NdBS_3$.

The family of lanthanide orthothioborates, $LnBS_3$ (Ln = Lanthanide), are of special interest due to the coupling of 'laser active' lanthanide ions with the orthothioborate unit, $[BS_3]^{3-}$, which is known to induce NLO behavior.[4,5] The first syntheses of lanthanide orthothioborates by Hunger et al. utilized high temperatures (800-1050 °C) and pressures (3 Gpa) and yielded polycrystalline powders whose structure determinations were accomplished via highly restrained Rietveld refinements.[6] The authors subsequently found that heating a pellet with nominal composition PrB_5S_9 contained in a BN crucible sealed inside a tantalum ampule under argon gas for over 30 days produced single crystals of $PrBS_3$ and they determined the first crystal structure of a lanthanide orthothioborate.[7] Unfortunately, no characterization of the physical properties of $PrBS_3$ was reported.

Synthesizing new materials that exhibit a desired property can be accomplished by numerous routes, most of them being

based on existing, successful approaches. Departing from those approaches can sometimes be extremely rewarding if one can envision a different path that is more targeted or simpler. We chose to adapt the recently reported Boron-Chalcogen Mixture (BCM) method as a new low temperature reaction route that successfully leads to single crystals of lanthanide orthothioborates, allowing us to investigate their structures and their structurally connected optical behavior, specifically, second harmonic generation.

To prepare and study lanthanide orthothioborates, $LnBS_3$, we applied a combination of the BCM and molten flux growth methods to their synthesis, as these methods are easy to use, typically yield single crystals, and are fast. We recently reported the BCM method as a facile approach for the synthesis of actinide chalcogenides from their oxides by incorporating a mixture of boron and the desired chalcogen into the reagent mixture.[8] The large difference in formation energy of B_2O_3 (i.e. $\Delta_fG°$(vitreous-B_2O_3) = −1182.5 kJ/mol) over the boron chalcogenide (e.g. $\Delta_fG°$(vitreous-B_2S_3) = −247.6 kJ/mol) favors the formation of B_2O_3 allowing elemental boron to act as an 'oxygen sponge' when heated, leaving the chalcogen to react with the other reagents.[9] This method was previously successful for the synthesis of lanthanide and transition metal sulfides from their oxides and was therefore chosen as a potentially convenient path to lanthanide thioborate materials.[10-12] By utilizing the BCM method coupled with molten flux crystal growth, plentiful single crystals of lanthanide orthothioborates (Ln = La, Ce, Pr, Nd), Figure 1, were grown at a relatively low reaction temperature of 550°C, with a reaction time of under 3 days and, importantly, using the lanthanide oxides as starting reagents. The single crystalline nature of the products allowed us to determine their structures and to investigate the NLO behavior of a phase pure sample of $LaBS_3$.

To synthesize the lanthanide orthothioborates, the lanthanide oxide (Ln_2O_3 for Ln = La, Pr, Nd or CeO_2), boron, and sulfur were loaded into a carbon crucible (0.5 in OD x 0.25 in ID x 2 in L) in a 1:20:30 molar ratio. In a nitrogen filled glovebag, 0.05 grams of K_2S and then 0.25 grams of a NaI-CsI eutectic flux were layered on top of this mixture inside the carbon crucible which was subsequently placed into a carbon-coated fused silica tube. The fused silica tube was evacuated, sealed, and placed in a furnace set to step to 400 °C and then ramp to 550 °C in 2 hours where it dwelled for 48 hours. The furnace then slow-cooled to 350 °C in 20 hours and was then shut off to return to room temperature. To isolate the single crystals, the flux was dissolved in methanol, aided by sonication, and the crystals isolated via vacuum filtration.

The four compositions thus obtained, $LnBS_3$ (Ln = La, Ce, Pr, Nd), all crystallize in the non-centrosymmetric space group $Pna2_1$ and are isostructural. The crystal structures, Table 1, are consistent with the one previously published for $PrBS_3$.[7] The flux approach used in our synthesis, which relies on alkali halide eutectics, is known to work well for the crystallization of a multitude of chalcogenide phases.[13-18] However, to accomplish the synthesis of lanthanide orthothioborate phases, $LnBS_3$, it was found to be essential to supplement the low temperature halide melt with a polychalcogenide flux, another low

temperature melt, that is known to be stable at lower reaction temperatures. The combination of the alkali halide eutectic flux with the potassium polychalcogenide flux afforded high quality single crystals of the target compounds suitable for X-ray diffraction studies. These crystals represent the first single crystal growth of $CeBS_3$ and $NdBS_3$ that allows for the refinement of their crystal structures, and the single crystal structure of $LaBS_3$ is reported herein for the first time.

Table 1. Crystallographic data for lanthanide orthothioborates, LnBS3.

Formula	$LaBS_3$	$CeBS_3$	$PrBS_3$	$NdBS_3$
Formula weight	245.90	247.11	247.90	251.23
Space group, Z	$Pna2_1$, 4			
a, Å	7.6766(2)	7.6059(2)	7.5432(2)	7.4818(2)
b, Å	6.0445(1)	6.0181(1)	6.0072(1)	6.0037(1)
c, Å	8.9940(2)	8.9311(2)	8.8897(2)	8.8530(2)
V, Å³	417.33(1)	408.80(1)	402.82(1)	397.66(1)
R_1 (I >2σ(I))	0.0076	0.0079	0.0094	0.0080
wR_2 (all data)	0.0177	0.0174	0.0204	0.0178

The structure of the lanthanide orthothioborates, $LnBS_3$ (Ln = lanthanide), is shown in Figure 2 and is comprised of two building units: 9-coordinate, LnS_9, lanthanide sulfide distorted tricapped trigonal prisms and trigonal planar, $[BS_3]^{3-}$, orthothioborate units. The $LnBS_3$ 3-dimensional crystal structure is composed of corrugated sheets consisting of distorted kagome nets formed by the sulfur atoms. The sheets are stacked parallel to the b-c plane along the a-axis. In each kagome-net layer, every other sulfur triangle is occupied by a boron cation forming the BS_3 unit and the distorted hexagonal holes in the kagome lattice are filled with lanthanide cations. An alternation of the orientation of the orthothioborate unit between layers results in an ABAB stacking. Each LnS_9 polyhedron is surrounded by 6 orthothioborate units, 3 edge-sharing and 3 corner-sharing, and 12 neighboring LnS_9 polyhedra; 8 corner sharing, 2 face-sharing, and 2 edge sharing. The B—S distances range from 1.7981(26) to 1.8243(21) Å and the Ln—S distances range from 2.8579(5) to 3.3182(4) Å. The boron located in the middle of the BS_3 unit is very slightly out of the plane created by the triangle of sulfur atoms the magnitude of which slightly varies for the different lanthanide element; 0.0747, 0.0739, 0.0782, 0.0786 Å from the plane for Ln = La, Ce, Pr, and Nd, respectively.

The title compounds all crystallize in the non-centrosymmetric space group $Pna2_1$ and contain the $[BS_3]^{3-}$ unit, which literature suggests can lead to especially good SHG materials. To test for SHG, as well as test the predictions, SHG measurements were performed on ground crystals of $LaBS_3$. The lanthanum member was chosen for SHG testing as it does not exhibit any f-f transitions that cause coloration. The SHG measurements revealed that $LaBS_3$ is indeed SHG active with an SHG intensity

COMMUNICATION

1.5 times that of the standard reference sample of potassium dihydrogen phosphate (KDP), Figure 3, though non-phase-matchable, Figure 4, when irradiated with 1064 nm light. $LaBS_3$ has a calculated band gap of 2.9 eV, Figure S12. Fluorescence measurements are described in the SI.

crystals of kinetic phases, including a variety of chalcogenides.[15–17] The critical component is the low melting flux, usually an alkali halide salt, that acts as the solvent at
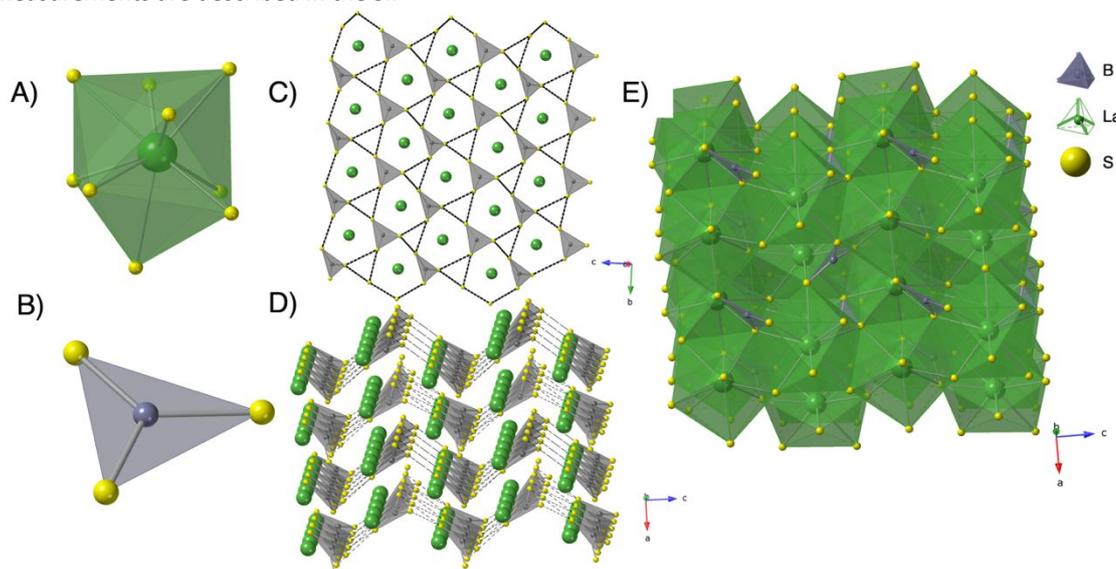
Figure 2. A schematic of the $LnBS_3$ structure showing the (A) LnS_9 and (B) BS_3 building blocks as well as an (C) illustration of the corrugated kagome nets, (D) how they stack within the structure, and (E) an image of the overall crystal structure.

High temperature solid state chemistry generally leads to the formation of the thermodynamic phases that have high temperature stability. Hydrothermal and flux routes operate at lower temperatures and, while able to crystallize thermodynamic phases, can also lead to kinetic/metastable
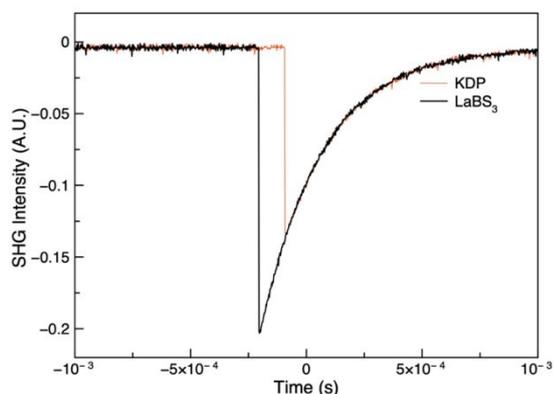
Figure 3. Powder SHG data of a sample of $LaBS_3$ compared to a standard sample of KDP with a particle size between 90-125 μm.

phases that would not survive very high temperatures, decomposing into binaries and ternaries. What is without a doubt true, however, is that while thermodynamic phases might be thermally more stable, they are finite in number, especially when contrasted with kinetic/metastable phases that comprise a vast frontier. While plentiful, kinetic phases are synthetically challenging to obtain, especially relative to thermodynamic phases.[19] The molten flux growth method has proven to be a successful approach for the creation of single
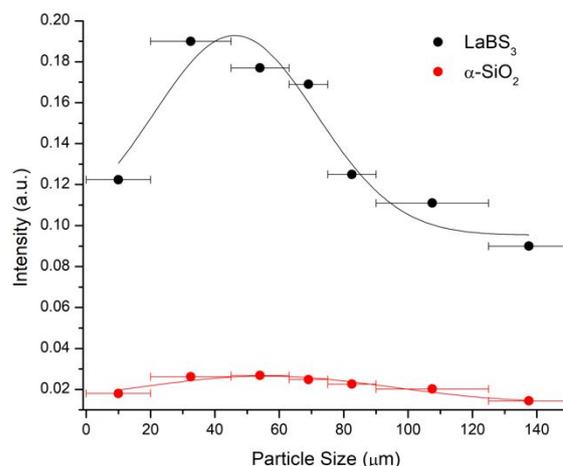
Figure 4. Powder SHG phase-matching experiment on $LaBS_3$ compared to a standard α-SiO_2 with particle size ranges of <20, 20-45, 45-63, 63-75, 75-90, 90-125, and 125-150 μm. The lines are not fits to data, but to guide the eye.

elevated temperatures in which the reagents dissolve. The addition of the 'liquid component' aids in the diffusion of reagents, greatly reducing reaction times, and the extensive choice of alkali halide melting points offers a large range of reaction temperatures that can be utilized. For the synthesis of chalcogenides compounds in particular, low melting polychalcogenide fluxes have been employed that have been the key to the discovery and crystal growth of numerous chalcogenide phases.[23-28] At the low temperatures afforded by polychalcogenide fluxes, the incorporation of chalcometallate molecular building blocks (i.e. $[SiS_4]^{4-}$, $[VS_4]^{3-}$, etc.) into the resulting compounds becomes increasingly possible which greatly influences their structures and resulting properties.[19]

For the growth of the lanthanide orthothioborates reported herein, a NaI-CsI eutectic flux was employed to access a reaction temperature of 550 °C, speed up the reaction time, and to aid in single crystal growth. The addition of the K_2S polychalcogenide flux was to potentially help increase the possibility of molecular building block incorporation into the final reaction product. Finally, the BCM method was applied to these reactions allowing for the use of the lanthanide oxides as starting reagents greatly assisting in the ease of reaction setup. The combination of these three components resulted in a new unprecedented low temperature synthetic route used herein to obtain single crystals of lanthanide orthothioborates, $LnBS_3$, in only 3 days, which contain the orthothioborate, $[BS_3]^{3-}$, molecular unit that is known to induce NLO behaviors, a phenomenon validated by the strong SHG activity of $LaBS_3$. The successful low temperature approach to these compounds, which were previously thought to only form during high temperature and pressure synthetic routes, opens an entirely new energy landscape, potentially leading to the discovery of many new kinetic thioborate materials with promising optical properties. As a further demonstration to validate this low temperature approach, we used the same procedure used to prepare $LnBS_3$ to obtain single crystals of BaB_2S_4, one of the best SHG materials known to date.[29] This reaction resulted in a phase pure sample of BaB_2S_4 with crystals up to a millimeter in size; synthesis details, crystal images, and the powder X-ray diffraction pattern can be found in the SI. We are in the process of extending this synthetic approach to other thioborate compositions to investigate their physical properties. This synthetic method coupled with the ease of access to chalcogenide materials afforded by the BCM method and the single crystal growth abilities of the molten flux growth technique will undoubtably boost research in the field of NLO active thioborates.

Author Contributions

Breton – conceptualization, investigation, sample synthesis, structure determination, writing. Morrison – fluorescence measurements, writing, reviewing. Lacroix and Halasyamani – SHG measurements, reviewing. zur Loye – conceptualization, methodology, writing, reviewing.

Conflicts of Interest

The authors declare no conflicts of interest

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