Nonlinear Optics

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Na_2BaMQ_4 (M = Ge, Sn; Q = S, Se): Infrared Nonlinear Optical Materials with Excellent Performances and that Undergo Structural Transformations

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Abstract: *Infrared nonlinear optical (IR NLO) materials with excellent performances are particularly important in laser technology. However, to design and synthesize an efficient IR NLO material with a balance between the optical band gap and the NLO coefficient is still a huge challenge. With this in mind, four new IR NLO materials Na_2BaSnS_4, $Na_2BaSnSe_4$, Na_2BaGeS_4, and $Na_2BaGeSe_4$ were successfully designed and synthesized. The compounds exhibit excellent properties with a suitable balance of band gap and NLO coefficient measured for Na_2BaSnS_4 (3.27 eV and about 17 × KDP, that is, about 17 times that of KH_2PO_4 (KDP)) and Na_2BaGeS_4 (3.7 eV and about 10 × KDP), demonstrating that the systems satisfy the key requirements as promising IR NLO candidates. Remarkably, the new compounds also undergo a novel structural transformation from tetragonal to trigonal systems, the first time that this has been reported for quaternary metal chalcogenides.*

Infrared nonlinear optical (IR NLO) materials are of great importance in developing new light sources (2–20 μm) by frequency conversion technology.[1] The application of commercial IR NLO materials[2–4] in IR-based technologies is seriously limited because of their low laser-damage thresholds (LDTs) or harmful two-photon absorption (TPA). Over the past two decades, researchers have conducted extensive investigations into new IR NLO materials and several efficient design strategies have been proposed. The first strategy involved the incorporation of asymmetric building blocks into crystal structures, such as second-order Jahn–Teller distorted d^0 metal centers or cations with lone electron pairs,[5–9] which are conducive to obtain strong second-harmonic generation (SHG) responses (d_{ij}), but will result in relatively narrow band gaps (E_g). Essentially, a high LDT value in a material strongly depends on the material having a large E_g.[10] Thus, IR NLO materials with small E_g values have limited use in high-power lasers. The second design strategy incorporates electropositive elements (alkaline or alkaline-earth metals) or highly electronegative halide anions into the crystal structures in order to enlarge the E_g values of the products leading to the generation of high LDTs.[11–13] Note that a large E_g value was found to conflict with a large SHG response in one NLO material.[14]

Thus, the development of materials exhibiting a suitable balance between the properties of NLO materials is still urgently required. According to previous research, a good IR NLO material should demonstrate a critical balance between E_g values (> 3.0 eV) and d_{ij} values (> 10 × KDP, that is, more than 10 times the value of KH_2PO_4 (KDP)), however only some metal chalcogenides can satisfy the above conditions and most of those have alkaline/alkaline-earth cations and easily distorted MQ_4 ligands (M = Ga, In, Ge, Sn; Q = S, Se) in their structures.[15] Therefore, in this work, we have combined into crystal structures MQ_4 tetrahedra (M = Ge, Sn; Q = S, Se) with alkaline/alkaline-earth (Na and Ba) cations to afford four IR NLO materials Na_2BaSnS_4, $Na_2BaSnSe_4$, Na_2BaGeS_4, and $Na_2BaGeSe_4$. A suitable balance of E_g and d_{ij} values for Na_2BaSnS_4 (3.27 eV and circa 17 × KDP) and Na_2BaGeS_4 (3.7 eV and about 10 × KDP) are reported. Remarkably, these compounds undergo extraordinary structural changes from tetragonal (Na_2BaSnS_4) to trigonal systems ($Na_2BaSnSe_4$, Na_2BaGeS_4, $Na_2BaGeSe_4$).

Na_2BaSnS_4 crystallizes in the space group $I\bar{4}2d$, whereas the other three compounds crystallize in the $R3c$ space group. For all compounds, the calculated bond valences and global instability index (GII) prove that all of their crystal structures are reasonable (see Tables S1 and S2 in the Supporting Information).

In the structure of Na_2BaSnS_4, the BaS_8 polyhedra are first connected with each other by sharing edges to make up wave-like $_\infty[BaS_6]$ chains, and those chains are linked together with isolated SnS_4 tetrahedra by sharing corners and edges to form layered structures (Figure 1 b). Interestingly, these layers do not existed in isolation, but are further connected with the common S atoms to form a 3D tunnel structure with Na cations located inside the tunnels (Figure 1 a). Note that the NaS_6 octahedra in one tunnel connect with each other by sharing edges, and the NaS_6 octahedra in the different tunnels still interlink by sharing corners to make up framework structure. Remarkably, the location of all of the Na atoms in the tunnels means that moisture absorption by the compound is effectively prevented, unlike for other alkali-metal-containing compounds.[16] This feature also ensures its chemical stability, which is consistent with the experimental observation that it is stable in air for a long time.

Of the other three compounds prepared $Na_2BaSnSe_4$, Na_2BaGeS_4, and $Na_2BaGeSe_4$, compound $Na_2BaSnSe_4$ is chosen as a representative for discussion. In the structure of $Na_2BaSnSe_4$, the distorted $BaSe_7$ polyhedra are connected

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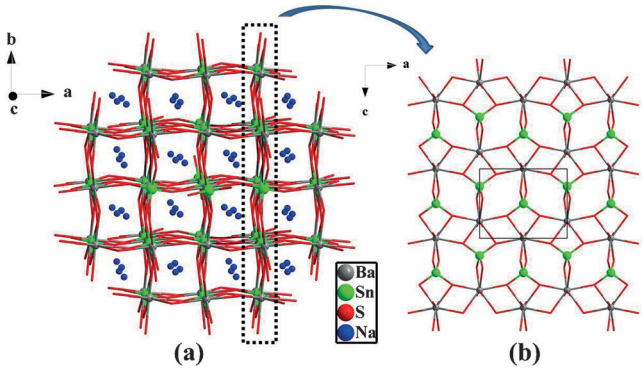

Figure 1. a) The 3D framework of Na_2BaSnS_4 with Na–S bonds omitted for clarity; b) Infinite $_\infty[BaS_6]$ chains are connected with isolated SnS_4 units by sharing corners and edges to form a layered structure.

with the isolated $SnSe_4$ units by sharing corners or edges to make up the tunnel structure, with the diameter of the tunnel measuring about 6.354 Å (Figure 2a). The $NaSe_6$ units link

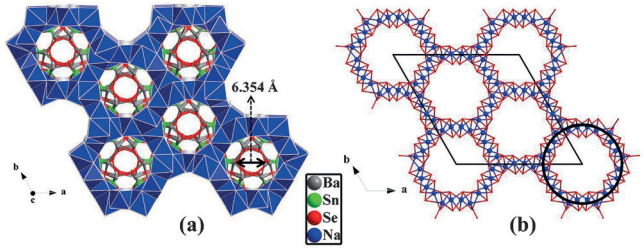

Figure 2. a) View of the tunnel structure of $Na_2BaSnSe_4$; b) $NaSe_6$ octahedra are connected together to form numerous closed rings. A 24-MR is indicated with a black line as a visual aid.

together to form a so-called 24-membered-ring (24-MR) motif by sharing edges, and other units ($BaSe_7$ and $SnSe_4$) locate within the 24-MR (Figure 2b). Alternatively, the structure can be described in terms of a build-up of three layers (Figure 2a), in which the outermost layer is the 24-MR, the middle layer is composed of six isolated $SnSe_4$ tetrahedra (assumed to be a fake layer), and the innermost layer is a tunnel formed with interconnected $BaSe_7$ units. It should be noted that previously reported transformations of space groups in metal chalcogenides with different M^{IV} (M^{IV}=Si, Ge, Sn) or Q (Q = S, Se) atoms have mainly been of two types,[17–21] the first between the biaxial crystals, and the second from the biaxial crystals to the uniaxial crystals (see Table S3 and Figures S2–S4). However, this is the first time that space group transformation from tetragonal to trigonal and structural changes from the 2D layered structure to the 24-MR and tunnel structures has been reported for quaternary metal chalcogenides.

The optical spectra (employing Raman and IR spectroscopies and measuring the E_g values) of the four new compounds were measured (Table S4, Figure S5). The results show that every compound exhibits a wide transparent region of about 20 μm that covers the two critical atmospheric windows (3–5 and 8–14 μm), important wavelengths for applications in areas such as telecommunications, laser guidance, and explosives detection. Moreover, experimental E_g values of Na_2BaSnS_4 (3.27 eV) and Na_2BaGeS_4 (3.70 eV) are much larger than those of commercial IR NLO crystals, such as $AgGaQ_2$ (Q = S, Se) and $ZnGeP_2$,[22,23] implying that they can be expected to avoid TPA of common laser radiation and exhibit high LDTs for future practical application. As for the structure–performance relationship, theoretical band gaps were calculated (Table S4, Figures S6, S7) and the analysis of projected density of states (PDOSs) indicates that the optical absorptions can be mainly attributed to the contribution of the MQ_4 units extended over all of the compounds (Figure 3). Moreover, a pulse laser was used to assess the LDTs of the compounds with $AgGaS_2$ (AGS) as a reference and the results of Na_2BaSnS_4 (27.8 MW cm^{-2}) and Na_2BaGeS_4 (43.5 MW cm^{-2}) are about 5 and 8 times greater than that of AGS (5.4 MW cm^{-2}), respectively, suggesting that these materials may be promising for application in high-energy laser systems.

The NLO properties of the four compounds were recorded by using a 2.09 μm laser (Table S4, Figures S8, S9). $Na_2BaSnSe_4$ and $Na_2BaGeSe_4$ are found to be nonphase-matchable and their SHG maximum intensities are about 1.3 and 0.9 times that of AGS at the particle size of 55–88 μm, respectively. In addition, the SHG effects of Na_2BaSnS_4 and Na_2BaGeS_4 are circa 0.5 and 0.3 times that of AGS with type-I phase-matching, respectively. Given that the SHG coefficient of AGS ($d_{powder} \approx 11$ pm V^{-1}) is about 33 times of that of KDP ($d_{powder} \approx 0.33$ pm V^{-1}),[15] Na_2BaSnS_4 and Na_2BaGeS_4 exhibit good SHG responses about 17 and 10 times that of KDP. For Na_2BaSnS_4 theoretical d_{ij} values and birefringence (Δn) measure $d_{ij} = 4.63$ pm V^{-1} and $\Delta n = 0.07$, and for Na_2BaGeS_4

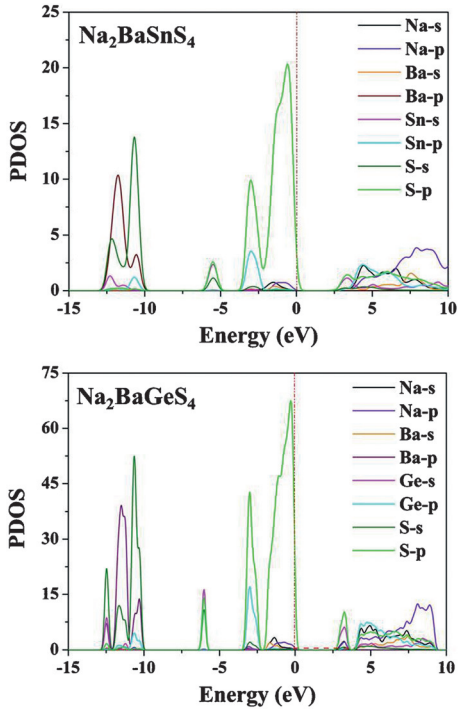

Figure 3. Projected density of states (PDOS) of Na_2BaSnS_4 and Na_2BaGeS_4.

$d_{ij} = 3.76\ pm\ V^{-1}$ and $\Delta n = 0.037$, which agree well with the experimental results (Table 1). In combination, it is clear that Na_2BaSnS_4 and Na_2BaGeS_4 exhibit properties suitable for IR NLO applications (with d_{ij} values, large E_g values, and suitable Δn) and which are comparable to those of outstanding IR NLO materials, such as $LiGaS_2$ and $LiInS_2$,[24,25] that have been verified to output IR energy.

In summary, a new family of IR NLO compounds, Na_2BaMQ_4 (M = Ge, Sn; Q = S, Se), were successfully synthesized. The compounds crystallize in two different space groups ($I\bar{4}2d$ versus $R3c$), demonstrating for the first time in quaternary metal chalcogenides a structural transformation from tetragonal to trigonal systems. Measurement of the optical properties shows that Na_2BaSnS_4 and Na_2BaGeS_4 satisfy the essential conditions to be considered as excellent IR NLO crystals, such as high LDTs, large SHG responses, wide transmission region, and suitable birefringence values. Furthermore, a good balance between large NLO coefficients and high LDTs is found in Na_2BaSnS_4 and Na_2BaGeS_4, which indicates that these materials can effectively avoid the performance defects (low LDTs and TPA) of commercial IR NLO materials.

Table 1: Optical properties of the IR NLO materials.

Materials	Na_2BaSnS_4	Na_2BaGeS_4	$LiGaS_2$[24,25]	$LiInS_2$[24,25]
E_g [eV]	3.27	3.7	4.15	3.57
d_{ij} (× KDP)	17	10	15	19
Δn	0.070	0.037	0.04	0.04

Experimental Section

Single crystals of four compounds were prepared in vacuum-sealed silica tubes by the solid-state method. See the Supporting Information for more details.

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Keywords: alkali metals · alkaline earth metals · nonlinear optics · solid-state structures · structure–property relationships

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