

Nonlinear Optics

International Edition: DOI: 10.1002/anie.201602317
German Edition: DOI: 10.1002/ange.201602317**Na₂BaMQ₄ (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 Na₂BaSnS₄, Na₂BaSnSe₄, Na₂BaGeS₄, and Na₂BaGeSe₄ were successfully designed and synthesized. The compounds exhibit excellent properties with a suitable balance of band gap and NLO coefficient measured for Na₂BaSnS₄ (3.27 eV and about 17 × KDP, that is, about 17 times that of KH₂PO₄ (KDP)) and Na₂BaGeS₄ (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 d⁰ 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 KH₂PO₄ (KDP)), however only some metal chalcogenides can satisfy the above conditions and most of those have alkaline/alkaline-earth cations and easily distorted MQ₄ ligands (M = Ga, In, Ge, Sn; Q = S, Se) in their structures.^[15] Therefore, in this work, we have combined into crystal structures MQ₄ tetrahedra (M = Ge, Sn; Q = S, Se) with alkaline/alkaline-earth (Na and Ba) cations to afford four IR NLO materials Na₂BaSnS₄, Na₂BaSnSe₄, Na₂BaGeS₄, and Na₂BaGeSe₄. A suitable balance of E_g and d_{ij} values for Na₂BaSnS₄ (3.27 eV and circa 17 × KDP) and Na₂BaGeS₄ (3.7 eV and about 10 × KDP) are reported. Remarkably, these compounds undergo extraordinary structural changes from tetragonal (Na₂BaSnS₄) to trigonal systems (Na₂BaSnSe₄, Na₂BaGeS₄, Na₂BaGeSe₄).

Na₂BaSnS₄ crystallizes in the space group *I*42*d*, whereas the other three compounds crystallize in the *R*3*c* 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 Na₂BaSnS₄, the BaS₈ polyhedra are first connected with each other by sharing edges to make up wave-like ∞[BaS₆] chains, and those chains are linked together with isolated SnS₄ tetrahedra by sharing corners and edges to form layered structures (Figure 1 b). Interestingly, these layers do not exist 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 NaS₆ octahedra in one tunnel connect with each other by sharing edges, and the NaS₆ 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 Na₂BaSnSe₄, Na₂BaGeS₄, and Na₂BaGeSe₄, compound Na₂BaSnSe₄ is chosen as a representative for discussion. In the structure of Na₂BaSnSe₄, the distorted BaSe₇ polyhedra are connected

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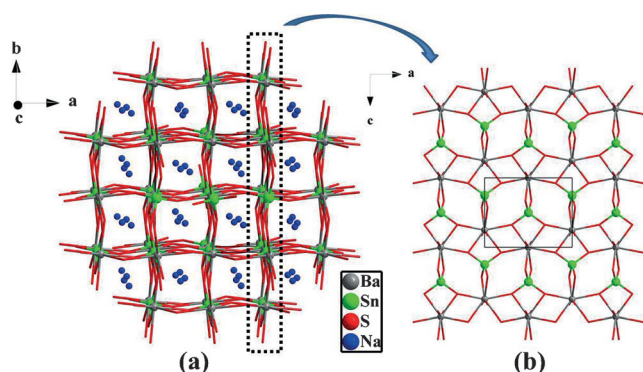


Figure 1. a) The 3D framework of Na₂BaSnS₄ with Na–S bonds omitted for clarity; b) Infinite ∞ [BaS₆] chains are connected with isolated SnS₄ units by sharing corners and edges to form a layered structure.

with the isolated SnSe₄ 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 NaSe₆ units link

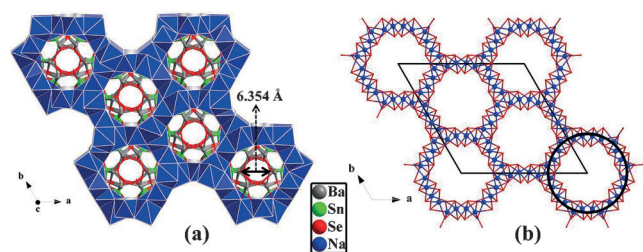


Figure 2. a) View of the tunnel structure of Na₂BaSnSe₄; b) NaSe₆ octahedra are connected together to form numerous closed rings. A 24-MR is indicated with a black line as a visual aid.

together to form a so-called 24-membered-ring (24-MR) motif by sharing edges, and other units (BaSe₇ and SnSe₄) 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 SnSe₄ tetrahedra (assumed to be a fake layer), and the innermost layer is a tunnel formed with interconnected BaSe₇ 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 Na₂BaSnS₄ (3.27 eV) and Na₂BaGeS₄ (3.70 eV) are much larger than those of commercial IR NLO crystals, such as AgGaQ₂ (Q=S, Se) and ZnGeP₂,^[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 MQ₄ units extended over all of the compounds (Figure 3). Moreover, a pulse laser was used to assess the LDTs of the compounds with AgGaS₂ (AGS) as a reference and the results of Na₂BaSnS₄ (27.8 MW cm^{−2}) and Na₂BaGeS₄ (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). Na₂BaSnS₄ and Na₂BaGeS₄ 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 Na₂BaSnS₄ and Na₂BaGeS₄ are circa 0.5 and 0.3 times that of AGS with type-I phase-matching, respectively. Given that the SHG coefficient of AGS ($d_{\text{powder}} \approx 11 \text{ pm V}^{-1}$) is about 33 times of that of KDP ($d_{\text{powder}} \approx 0.33 \text{ pm V}^{-1}$),^[15] Na₂BaSnS₄ and Na₂BaGeS₄ exhibit good SHG responses about 17 and 10 times that of KDP. For Na₂BaSnS₄ theoretical d_{ij} values and birefringence (Δn) measure $d_{ij} = 4.63 \text{ pm V}^{-1}$ and $\Delta n = 0.07$, and for Na₂BaGeS₄

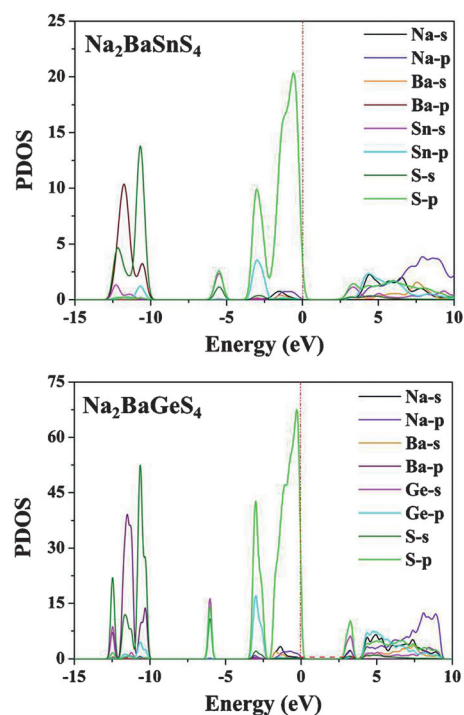


Figure 3. Projected density of states (PDOS) of Na₂BaSnS₄ and Na₂BaGeS₄.

$d_{ij} = 3.76 \text{ pm V}^{-1}$ and $\Delta n = 0.037$, which agree well with the experimental results (Table 1). In combination, it is clear that $\text{Na}_2\text{BaSnS}_4$ and $\text{Na}_2\text{BaGeS}_4$ 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 ($M = \text{Ge, Sn}$; $Q = \text{S, Se}$), 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 trans-

Table 1: Optical properties of the IR NLO materials.

Materials	$\text{Na}_2\text{BaSnS}_4$	$\text{Na}_2\text{BaGeS}_4$	LiGaS_2 ^[24,25]	LiInS_2 ^[24,25]
E_g [eV]	3.27	3.7	4.15	3.57
d_{ij} ($\times \text{KDP}$)	17	10	15	19
Δn	0.070	0.037	0.04	0.04

formation from tetragonal to trigonal systems. Measurement of the optical properties shows that $\text{Na}_2\text{BaSnS}_4$ and $\text{Na}_2\text{BaGeS}_4$ 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 $\text{Na}_2\text{BaSnS}_4$ and $\text{Na}_2\text{BaGeS}_4$, which indicates that these materials can effectively avoid the performance defects (low LDTs and TPA) of commercial IR NLO materials.

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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