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$LaAeAl_3S_7$ (Ae = Ca, Sr): Cairo pentagonal layered thioaluminates achieving a good balance between a strong second harmonic generation response and a wide bandgap†

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Breaking through the incompatibility between a strong second harmonic generation (SHG) response and a wide bandgap in an infrared nonlinear optical (IR NLO) crystal is still a huge challenge. With this in mind, we have proposed a feasible design strategy involving rational combination of highly electropositive rare-earth (Re^{3+}) and alkaline-earth metals (Ae^{2+}) as cations and a strongly covalent AlS_4 anionic group as the "NLO-active unit" into the crystal structure, which affords the successful synthesis of two new quaternary IR NLO thioaluminates: $LaAeAl_3S_7$ (Ae = Ca, Sr). Note that the unprecedented Cairo pentagonal $(AlS_4)_n$ layers in $LaAeAl_3S_7$ can be viewed as the first discovery among the structures of all reported thioaluminates and this layered structure benefits from the strong optical anisotropy that further achieves the imperative phase matchability in $LaAeAl_3S_7$. Both of them possess the widest optical bandgaps (Ca: 3.76 and Sr: 3.78 eV) in known rare-earth NLO chalcogenides. Remarkably, $LaAeAl_3S_7$ were also proven to be the first cases concurrently exhibiting wide bandgaps (>3.5 eV) and strong SHG effects (>0.5 × $AgGaS_2$) among known rare-earth NLO chalcogenides. Theoretical analysis verifies that their excellent NLO properties originate from the synergistic effect between AlS_4 and $(La/Ae)S_8$ anionic groups. This work will inspire exploration into new IR NLO candidates in rare-earth thioaluminate systems to achieve a superior property balance.

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Introduction

Nonlinear optical (NLO) crystals have shown extensive applications in tunable laser systems.[1–15] As for an excellent infrared (IR) NLO crystal, it should satisfy the following performance conditions: a wide IR transmission region, strong second harmonic generation (SHG) response, large optical bandgap, high laser damage threshold (LDT), and reliable chemical stability.[16–18] Unfortunately, there is still the undesirable incompatibility between the strong SHG response and wide bandgap in IR NLO crystals because of their inherent inverse relationship,[19,20] which is also reflected in several commercial crystals such as $AgGaQ_2$ (Q = S, Se)[21] and $ZnGeP_2$.[22] They exhibit a good SHG response but relatively narrow energy bandgaps and low LDTs, which further limit their application. Based on this, a good balance between a strong SHG response (d_{ij} > 0.5 × $AgGaS_2$) and wide bandgap (E_g > 3.5 eV) has become an urgent challenge for the discovery of new excellent IR NLO crystals and many researchers have proposed several effective design strategies and research systems.[23–29] For example, mixed alkali/alkaline-earth metal sulfides possess wide bandgaps but relatively small SHG effects; introduction of halogen ions into the structures of typical chalcogenides means the mixed-anion chalcohalides can achieve a suitable property balance but the halides will corrode and destroy the silica tubes and further enhance the difficulty of the material synthesis. Considering the above status, we have focused on other research systems and thioaluminates exhibit native advantages to obtain a wide bandgap because their strongly covalent Al–S bond has a minor influence on optical absorption. However, up to now, thioaluminates have rarely been studied in NLO and only a few NLO thioaluminates have been reported for their NLO performances such as $Al_{0.50}Dy_3(Si_{0.50}Al_{0.50})S_7$ (2.22 eV and 2 × $KTiOPO_4$ (KTP)), $Al_{0.38}Dy_3(Si_{0.85}Al_{0.15})S_7$ [30,31] (2.03 eV and 1 × KTP), $BaAl_4S_7$ [32] (3.95 eV and 0.5 × $AgGaS_2$) and $LiAlS_2$ [33] (5.13 eV and 0.2 × $AgGaS_2$). Besides, the inherent relationship between the AlS_4 anionic group and the SHG

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†Electronic supplementary information (ESI) available: Powder XRD, performance summary, crystal data, distortion degree. CCDC 2234185 for $LaCaAl_3S_7$ and 2234186 for $LaSrAl_3S_7$, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3qi00048f

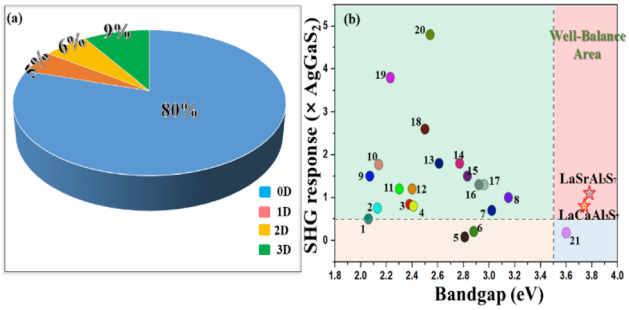

Fig. 1 (a) Dimensional distribution of AlS_4 units in the known thioaluminates (Table S1†); (b) a summary of the SHG response and bandgap among the title $LaAeAl_3S_7$ and reported rare-earth NLO chalcogenides, the well-balanced area is limited between E_g > 3.5 eV and d_{ij} > 0.5 × $AgGaS_2$. Compounds 1–21 are listed in Table S2.†

origin has not been clearly determined so far. Recent study indicates that rare-earth centered polyhedral ReS_n units make a great contribution to the origin of the NLO response, therefore, rare-earth based thioaluminates appear to have a high potentiality to break the incompatibility between the critical performances (E_g and d_{ij}) based on the synergistic effect between ReS_n and AlS_4 units. With this in mind, we have proposed one design strategy involving rational combination of rare-earth (La^{3+}) and alkaline-earth metals (Ae^{2+}) as cations into the structures of thioaluminates to achieve the birth of two new rare-earth thioaluminates: $LaAeAl_3S_7$ (Ae = Ca, Sr). Both of them exhibit the first examples of Cairo pentagon layers composed of AlS_4 tetrahedra in reported thioaluminates after a detailed survey of the Inorganic Crystal Structure Database (ICSD) (Fig. 1a) (Table S1†). Their performances were systematically measured and the results show that $LaAeAl_3S_7$ were proven to be promising IR NLO materials because of the successful breakthrough in the incompatibility between the large E_g (>3.5 eV) and strong d_{ij} (>0.5 × $AgGaS_2$). First-principles calculation analysis demonstrates that their SHG responses originate from the synergistic effect between AlS_4 and $(La/Ae)S_8$ units. Moreover, we have also summarized the critical properties (E_g and d_{ij}) in all known rare-earth chalcogenides (Fig. 1b) (Table S2†) and the survey results show that $LaAeAl_3S_7$ could be regarded as the first cases achieving the breakthrough of the "3.5 eV wall" among all reported rare-earth NLO chalcogenides.[31,34–48]

Experimental methods

Synthesis

All raw materials, including La_2S_3 powder (99.99%), Al slice (99.99%), CaS and SrS powder (99.99%), and S powder (99.99%), were purchased from Beijing Hawk Science & Technology Co., Ltd. As for air-unstable La_2S_3, SrS and CaS powder, an Ar-filled glovebox was selected to complete the whole preparation process.

Single crystals of $LaAeAl_3S_7$ were firstly synthesized with a non-stoichiometric ratio based on the raw materials of La_2S_3, CaS/SrS, Al, S = 0.37 : 1 : 3 : 3. However, under this ratio, the yield of $LaAeAl_3S_7$ was very low and many $AeAl_2S_4$ by-products were found. Thus, we gradually adjusted the proportion of raw materials after many attempts and the maximum yield (>90%) of $LaAeAl_3S_7$ was obtained under the optimal nonstoichiometric ratio of La_2S_3, CaS/SrS, Al, S = 0.56 : 1 : 3 : 3. Raw materials were loaded into vacuum-sealed silica tubes and then put into a temperature-programmed furnace with the following temperature controlling curves: heated up to 1473 K within 30 h and held for 90 h, then cooled to room temperature within 150 h. The transparent and colorless $LaAeAl_3S_7$ single crystals were obtained.

Single crystal X-ray diffraction

Selected high-quality crystals were used for data collection on a Bruker D8 VENTURE diffractometer using Mo Kα radiation (λ = 0.71073 Å) at room temperature. A multi-scan method was used for absorption correction. The crystal structures were solved by a direct method and refined using the SHELXTL program package. After the first refinement, the formula was firstly refined to be the unbalanced "$La_2Al_3S_7$". The occupancy of La and Ca atoms in one site appeared to be 0.49 : 0.51 after the first random refinement. In order to obtain the balanced formula, we defined the actual occupancy of La and Ca atoms to be 0.5 : 0.5 and the final balanced formula is $LaCaAl_3S_7$. Similarly, this refinement process was extended to those of $LaSrAl_3S_7$ in this work. Rational anisotropic thermal parameters for all atoms were obtained by the anisotropic refinement and extinction correction. Detail refinement parameters and crystal data are shown in Table S3.†

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D2 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 10–70° with a step size of 0.02° and a fixed counting time of 1 s per step. Note that the calculated XRD patterns were derived from the respective single-crystal data. We have also carefully investigated the experimental XRD patterns of the title compounds and compared the extra peaks with those of other known related compounds.

UV–Vis–Near-IR (NIR) diffuse-reflectance spectra

Diffuse-reflectance spectra were measured by a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range of 200–1100 nm at room temperature.

Raman spectra

Hand-picked crystals were firstly put on a glass slide and then a LABRAM HR Evolution spectrometer equipped with a CCD detector by a 532 nm laser was used to record the Raman spectra.

Second-harmonic generation measurement

Through the Kurtz and Perry method, powder SHG responses were investigated by a Q-switch laser (2.09 μm, 3 Hz, 50 ns)

with different particle sizes, including 38–55, 55–88, 88–105, 105–150, 150–200, and 200–250 μm. The as-synthesized $AgGaS_2$ microcrystals were selected with the same sizes as references.

Theory calculations

In order to further investigate the relationship of structure–property, the electronic structures of the title compounds were studied by density functional theory (DFT) based on *ab initio* calculations. The exchange–correlation potential was calculated using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) with the scheme. The following orbital electrons were treated as valence electrons: La: $5s^2\ 5p^6\ 5d^1\ 6s^2$; Ca: $3p^6\ 4s^2$; Sr: $4p^6\ 5s^2$; Al: $3s^2\ 3p^1$; S: $3s^2\ 3p^4$. To achieve energy convergence, the plane-wave basis set energy cutoff was 660 eV within normal-conserving pseudo-potential (NCP). As key parameters for NLO crystals, the SHG coefficient and birefringence were also calculated. Owing to the discontinuity of exchange correlation energy, the experimental value is usually larger than that of the calculated band gap. Thus, scissors operators are used to make the conduction bands agree with the experimental values and the real-space atom-cutting method was used to analyse the contribution of anionic groups.

Results and discussion

In this work, single crystals of title $LaAeAl_3S_7$ thioaluminates were synthesized with an optimized nonstoichiometric ratio after many attempts. Submillimeter-level single-crystals were handpicked to be used for the data collection on single-crystal XRD (Table S3†). The phase-purity was verified by a powder XRD technique (Fig. S1†). The experimental PXRD patterns are basically consistent with those of the theoretical ones and a few extra tiny peaks are attributed to the $AeAl_2S_4$ by-products.

$LaAeAl_3S_7$ (Ae = Ca, Sr) crystallize in the $P\bar{4}2_1m$ space group of the tetragonal system. In view of their similar structures, $LaCaAl_3S_7$ was selected as the representative to depict their structural features. La and Ca atoms are located at the one site with the occupied ratio (0.5 : 0.5). One AlS_4 unit is linked to four AlS_4 units to form a $[Al_5S_{16}]^{17-}$ windmill cluster and these clusters further link together to compose the 2D Cairo pentagonal layers located at the *ab* plane. $(La/Ca)S_8$ polyhedra were located within the interlayers to bridge adjacent layers together to compose the overall 3D network. In this work, various link modes of AlS_4 units in structures of thioaluminates were also summarized and most of them (about 80%) possess the 0D link modes after the survey in the ICSD (Fig. 1a) (Table S1†). In addition, only three of the thioaluminates ($Rb_4Al_2S_5$,[49] $Bi_2Al_4S_8$ [50] and *Cccm*-$SrAl_2S_4$ [51]) exhibit 1D $(AlS_4)_n$ chains but the link modes of the AlS_4 units in the 1D chains are different, for example, AlS_4 units connect with each other by edge-sharing to form similar 1D chains in $Bi_2Al_4S_8$ (Fig. S2a and b†) and *Cccm*-$SrAl_2S_4$ (Fig. S2e and f†), which is different to the way AlS_4 units link together by edge and corner-sharing to form a 1D chain structure in $Rb_4Al_2S_5$ (Fig. S2c and d†). Note that the ratio of the 3D network is only 9% and seven of them possess 3D networks formed by AlS_4 units. For instance, AlS_4 units link together by corner-sharing to form a 3D network and Ba atoms are located within the 3D tunnels to form the whole structure of $BaAl_4S_7$ (Fig. S3c†). In particular, Al atoms have two different coordination modes: AlS_4 and AlS_6 units in the structure of $Ln_6Al_{3.3}S_{14}$ [52] and AlS_6 units link together by sharing faces to form a 1D chain structure and AlS_4 units are existed in isolation (Fig. S3a and b†). Note that 2D $(AlS_4)_n$ layers were also rarely discovered and only a few ternary thioaluminates exhibit 2D layered structures, such as $FeAl_2S_4$,[53] $TlAlS_2$ [54] and $AeAl_2S_4$ [55] (Ae = Ca, Sr). Although they have layered structures, the link modes of their AlS_4 units are different to those in the title $LaAeAl_3S_7$ (Fig. 2b and e). Therefore, the Cairo pentagonal layers in the title $LaAeAl_3S_7$ can be viewed as the first discovery in the known thioaluminates. For instance, 6-membered rings (MRs) exist in the structure of $CaAl_2S_4$ and its interlayer spacing (1.654 Å) is smaller

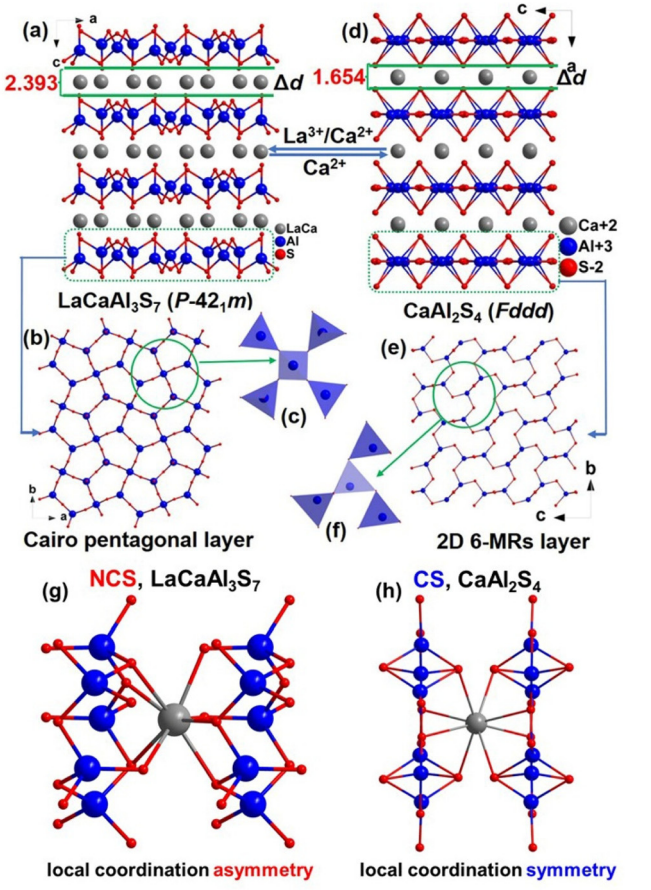

Fig. 2 (a) The crystal structure of $LaCaAl_3S_7$ along the *b*-axis; (b) the 2D layer is composed of AlS_4 units in $LaCaAl_3S_7$; (c) the windmill configuration $[Al_5S_{16}]^{17-}$ cluster; (d) the crystal structure of $CaAl_2S_4$ along the *b*-axis; (e) the 2D layer is composed of AlS_4 units in $CaAl_2S_4$; (f) the connection mode of AlS_4 unit in $CaAl_2S_4$; (g) the local coordination asymmetry between $(La/Ca)S_8$ and AlS_4 units in $LaCaAl_3S_7$; and (h) the local coordination symmetry between CaS_8 and AlS_4 in $CaAl_2S_4$.

than that of $LaCaAl_3S_7$ (2.393 Å) (Fig. 2a and d). Besides, AlS_4 is connected with three AlS_4 units in $CaAl_2S_4$ which is different to the $[Al_5S_{16}]^{17-}$ windmill cluster in the $LaCaAl_3S_7$ (Fig. 2c and f). Moreover, one $(La/Ca)S_8$ is linked to ten AlS_4 units but the inherent link modes are different and not symmetrical, showing local asymmetry in the $LaCaAl_3S_7$, which is also different to that (local coordination symmetry) in the $CaAl_2S_4$ (Fig. 2g and h). We have also calculated the distortion degrees (Δd) of $(La/Ae)S_8$ in the $LaAeAl_3S_7$ and AeS_8 dodecahedra in $AeAl_2S_4$ (Table S4†) and the results show that $(La/Ae)S_8$ have a larger Δd (Sr: 2.763‰; Ca: 2.686‰) in $LaAeAl_3S_7$ than those of SrS_8 (0.030–0.092‰) and CaS_8 (0.0007–0.140‰) in $AeAl_2S_4$. Such a large Δd is beneficial to achieve the local coordination asymmetry and promotes a potential structural change from centrosymmetric (CS) $AeAl_2S_4$ to NCS $LaAeAl_3S_7$.

Diffuse-reflectance spectra of $LaAeAl_3S_7$ were measured and their optical bandgaps are 3.76 for $LaCaAl_3S_7$ and 3.78 eV for $LaSrAl_3S_7$, respectively (Fig. 3a and b), which are much larger than that of commercial $AgGaS_2$ (2.64 eV) and comparable to other famous NLO crystals such as $BaAl_4S_7$ [32] (3.95 eV), $LiZnPS_4$ [56] (3.44 eV), $K_3Ga_3PS_8Cl$ [57] (3.60 eV), $BaGa_2SiS_6$ [58] (3.75 eV) and Li_2ZnSiS_4 [59] (3.90 eV). Note that $LaAeAl_3S_7$ exhibit the widest optical bandgaps and they can be also viewed as the first cases to achieve the breakthrough of "3.5 eV wall" in all the reported rare-earth NLO chalcogenides. Analysis into the calculated electronic structures and density of states (DOS) shows that the title $LaAeAl_3S_7$ are indirect-bandgap compounds and their theoretical bandgaps are 2.505 for $LaCaAl_3S_7$ and 2.527 eV for $LaSrAl_3S_7$, respectively (Fig. 3c and d). As can be seen from their DOS diagrams, the top of the valence band (VB) and the bottom of the conduction band (CB) region are mainly occupied by the S-p and La-d with a minor contribution of Al-p orbitals and Ae-s,p orbitals producing a negligible effect on the optical bandgaps. Therefore, optical absorptions in $LaAeAl_3S_7$ are determined by the inherent electronic transition in La–S units (Fig. 3e and f). Note that the wide bandgap has a huge influence on improving the inherent laser damage threshold (LDT), thus, their LDTs were measured under the 1.06 μm laser with the commercial $AgGaS_2$ as reference. Both of them have a high laser damage resistance of about 9.0 times that of $AgGaS_2$, which are comparable to those of IR NLO sulfides such as $KYGeS_4$ [39] (10 × $AgGaS_2$), $LiGaGe_2S_6$ [60] (6 × $AgGaS_2$), Li_2ZnSiS_4 [59] (10 × $AgGaS_2$) and $Li_{0.6}Ag_{0.4}GaS_2$ [61] (8.6 × $AgGaS_2$). The measured Raman spectra exhibit no obvious absorption peaks in the wavenumber range from 500 to 4000 cm^{-1}, indicating wide IR transmission ranges (2.5–20 μm) (Fig. 4a and b). Several Raman peaks located at 300–500 cm^{-1} are attributed to the Al–S bond interaction, such as (334, 374, 423, 500 cm^{-1}) for $LaCaAl_3S_7$ and (334, 422, 498 cm^{-1}) for $LaSrAl_3S_7$, which are similar to those of other known thioaluminates, such as $K(AlS_2)(GeS_2)$[62] (375 cm^{-1}) and Ba_2AlSbS_5.[63] Other peaks located at 200–300 cm^{-1} belong to the La–S bond vibration, which are similar to those of the previously reported La_2S_3.

Through the typical Kurtz–Perry method, we have investigated the powder SHG responses of $LaAeAl_3S_7$ with different

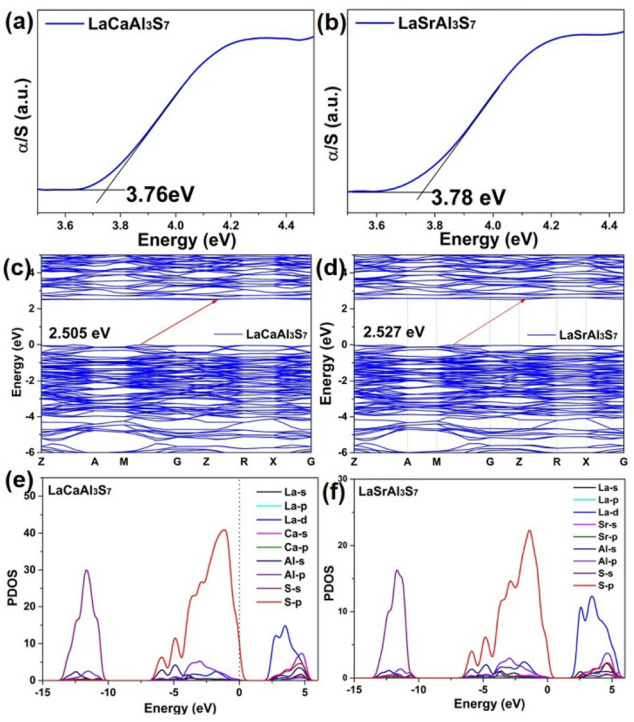

Fig. 3 Experimental optical bandgaps of $LaCaAl_3S_7$ (a) and $LaSrAl_3S_7$ (b); (c–f) band structures and PDOS of the title compounds.

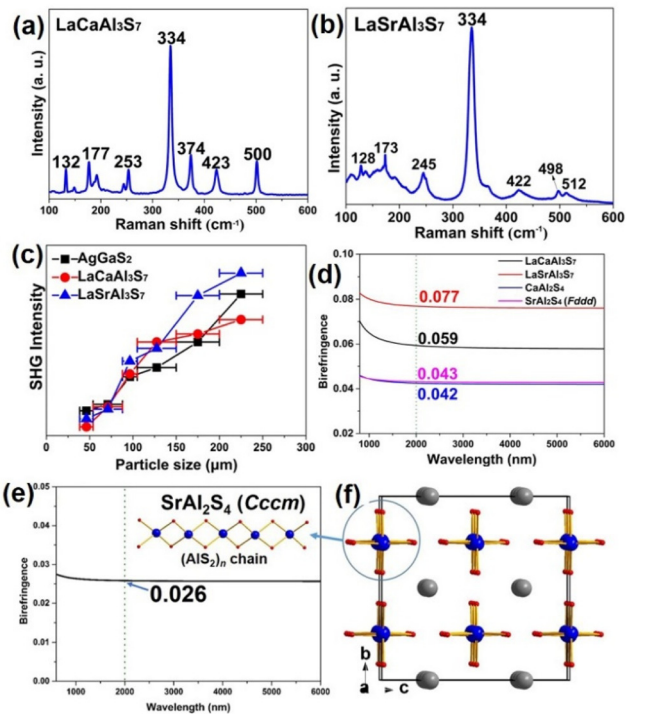

Fig. 4 Raman spectra of $LaCaAl_3S_7$ (a) and $LaSrAl_3S_7$ (b); (c) powder SHG response *versus* particle size for $LaAeAl_3S_7$ with $AgGaS_2$ as reference; (d) calculated birefringences for $LaAeAl_3S_7$ and $AeAl_2S_4$; (e) calculated birefringence for *Cccm*-$SrAl_2S_4$; and (f) the 1D $(AlS_2)_n$ chain in *Cccm*-$SrAl_2S_4$.

particle sizes under 2.09 μm pulse laser and the as-synthesized $AgGaS_2$ crystal as reference was selected. The measured results show that SHG intensity displays a similar growing trend with the increasing particle size. At the maximum particle size (200–250 μm), the title $LaAeAl_3S_7$ possess large SHG responses about 0.8 times that of $AgGaS_2$ for $LaCaAl_3S_7$ and 1.1 × $AgGaS_2$ for $LaSrAl_3S_7$, respectively (Fig. 4c), which are comparable to those of wide-bandgap NLO chalcogenides such as $LiZnPS_4$ [56] (0.8 × $AgGaS_2$), $KYGeS_4$ [39] (1.0 × $AgGaS_2$), $Li_{0.6}Ag_{0.4}GaS_2$ [61] (1.1 × $AgGaS_2$), $Na_2ZnGe_2S_6$ [64] (0.9 × $AgGaS_2$) and $[Ba_4Cl_2][ZnGa_4S_{10}]$[65] (1.1 × $AgGaS_2$). In view of the fact that the NLO coefficient (d_{36}) of $AgGaS_2$ is 13.0 pm V^{-1},[66] we have also calculated the theoretical NLO coefficients (d_{ij}) and their maximal d_{ij} are 6.83 for $LaCaAl_3S_7$ and 7.02 pm V^{-1} for $LaSrAl_3S_7$, respectively, which are basically consistent with the experimental results. The origin of the NLO effect was analyzed by the SHG-density calculation and the results show that their NLO origin was derived from the synergistic effect between AlS_4 and $(La/Ae)S_8$ anionic groups (Fig. 5). Note that the SHG responses (0.8–1.1 × $AgGaS_2$) of $LaAeAl_3S_7$ are larger than that (0.5 × $AgGaS_2$) of $BaAl_4S_7$, which also further verifies that incorporation of lanthanide (Ln) atoms into crystal structures provides a great strategy to enhance the SHG response. Moreover, we have also calculated the birefringence *versus* wavelength curves for title the $LaAeAl_3S_7$ and they exhibit a large optical anisotropy (Δn = 0.059 for Ca and 0.077 for Sr@2 μm), such a large Δn also further verifies the rationality of experimental phase-matching (PM) behavior. Herein, we have also calculated the Δn of $CaAl_2S_4$ (*Fddd*) and $SrAl_2S_4$ (*Fddd* and *Cccm*) and the results show that *Fddd*-$AeAl_2S_4$ exhibit a relatively larger Δn (0.042 and 0.043) than that of *Cccm*-$SrAl_2S_4$ (0.026) (Fig. 4d). In general, the whole birefringence has a close relationship with the microscopic anisotropic polarizability of functional groups. In the title $LaAeAl_3S_7$, coplanar AlS_4 units connect with each other to compose the Cairo pentagonal layers and such layered structures are beneficial to the optical anisotropy. We have also calculated the contribution of anionic groups (AlS_4 and $(La/Ae)S_8$) on the birefringences of title $LaAeAl_3S_7$ by the real-space atom-cutting method and the calculated results show that the AlS_4 unit provides the main contribution (~76%) on the birefringence with a minor contribution (~24%) of the $(La/Ca)S_8$ unit in $LaCaAl_3S_7$, which is similar to those in $LaSrAl_3S_7$ (AlS_4: 80%; $(La/Sr)S_8$: 20%). Besides, anisotropic distortions (Δd) of $(La/Ae)S_8$ units in title $LaAeAl_3S_7$ are much larger than those of $AeAl_2S_4$, which also contributes to the improvement of birefringence. Thus, the microscopic addition of AlS_4 and $(La/Ae)S_8$ groups makes the $LaAeAl_3S_7$ exhibit a relatively larger optical anisotropy than those of *Fddd*-$AeAl_2S_4$ (2D layer), *Cccm*-$SrAl_2S_4$ ($(AlS_2)_n$ chain) (Fig. 4e and f) and $BaAl_4S_7$ (Δn = 0.0328, 3D network) since the contribution of alkaline-earth cations on birefringence is negligible. Therefore, combination of Cairo pentagonal layers and lanthanides into crystal structures is conducive to improving optical anisotropy, which provides a useful structure-directing design for the discovery of new potential PM NLO crystals. To sum up, considering the overall performances of title $LaAeAl_3S_7$, they exhibit wide bandgaps (E_g: 3.76–3.78 eV), large SHG responses (d_{ij}: 0.8–1.1 × $AgGaS_2$), high LDTs (9.0 × $AgGaS_2$) and good chemical stability, indicating that title $LaAeAl_3S_7$ could be viewed as the first cases satisfying the excellent property balance (E_g > 3.5 eV and d_{ij} > 0.5 × $AgGaS_2$) in rare-earth NLO chalcogenides.

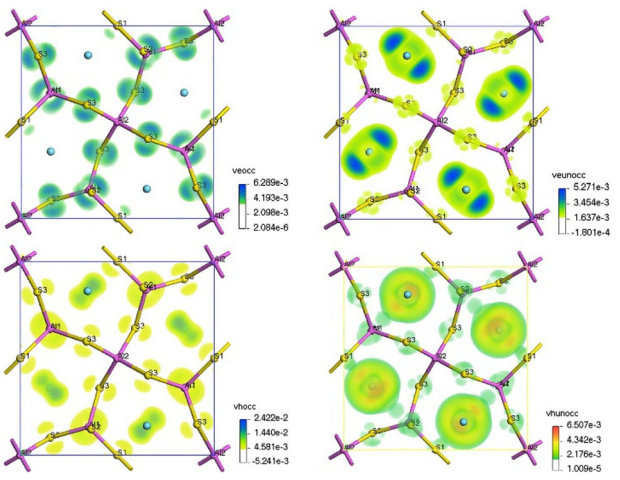

Fig. 5 Calculated SHG-density diagrams in the occupied and unoccupied states of $LaAeAl_3S_7$.

Conclusions

In summary, two new $LaAeAl_3S_7$ thioaluminates were firstly synthesized and their measured performances verify them to be potential IR NLO candidates. Synergistic contributions between $(La/Ae)S_8$ and AlS_4 units afford strong NLO responses in $LaAeAl_3S_7$. The novel Cairo pentagonal layered structures in $LaAeAl_3S_7$ have the benefit of improving the optical anisotropy, which provides a structure-directing strategy for the discovery of PM crystals. This study indicates that Ln-based thioaluminates could be expected to be feasible research systems for the breakthrough in the incompatibility between a strong SHG response and a wide bandgap to achieve the imperative property balance.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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