

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Physical Chemistry Chemical Physics

ARTICLE

Li₃AlSiO₅: The First Aluminosilicate as a Potential Deep-ultraviolet Nonlinear Optical Crystal with the Quaternary Diamond-like Structure

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xinglong Chen,^{a,b} Fangfang Zhang,^{*a} Lili Liu,^{a,b} Bing-Hua Lei,^{a,b} Xiaoyu Dong,^a Zhihua Yang,^{*a} Hongyi Li,^{a,c} and Shilie Pan^{*a}

Deep-ultraviolet (deep-UV) nonlinear optical (NLO) crystals play a crucial role in the modern laser frequency conversion technology. Traditionally, the exploration of deep-UV NLO crystals is mainly focused on borates, while, the finding of phosphates recently opens up a novel and promising non-boron pathway for designing new deep-UV NLO crystals. Extending this pathway to aluminosilicates leads to the discovery of Li₃AlSiO₅, the first NLO crystal in this system. It crystallizes in the polar space group *Pna*2₁ (no. 33) with the quaternary diamond-like structure composed by the LiO₄, AlO₄ and SiO₄ tetrahedral groups. The compound exhibits a deep-UV cut-off edge below 190 nm and is phase matchable with moderate powder second harmonic generation (SHG) intensity (0.8 × KH₂PO₄). The calculated band gap by PBE0 is 7.29 eV, indicating that the cut-off edge of Li₃AlSiO₅ crystal can be down to 170 nm. In addition, the compound is nonhygroscopic and thermally stable up to ~ 1472 K. These results suggest that Li₃AlSiO₅ is a potential deep-UV NLO crystal. First-principles studies were performed to elucidate the structure-property relationship of Li₃AlSiO₅.

Introduction

Almost immediately after the invention of the laser at the beginning of the 1960s, the SHG signal in crystalline quartz was first observed by Franklin.¹ Since then crystals with NLO properties have attracted extensive commercial and academic interest.^{2,3} Various high-performance NLO crystals have been obtained after continuous intensive studies over the past 50 years. The most advanced, commercially available benchmark NLO crystals include β-BaB₂O₄,⁴ LiB₃O₅,⁵ KH₂PO₄ (KDP),⁶ KTiOPO₄,⁷ AgGaQ₂ (Q = S, Se)⁸ and ZnGeP₂,⁹ which have been widely used as optoelectronic devices in the optical spectrum from ultraviolet (UV) to infrared (IR) region. In contrast, NLO crystals that can be practically used in deep-UV region (below 200 nm) are relatively rare but in urgent demand.

Generally speaking, deep-UV NLO crystals must meet a series of extremely rigorous prerequisites that include not only the

noncentrosymmetric crystallographic structure and phase-matching capability, but also a wide transparency window down to the deep-UV spectral region.¹⁰ To satisfy the abovementioned requirements, the dominant research field has been focused on the beryllium borate system. Numerous beryllium borates were reported as deep-UV NLO crystals including KBe₂BO₃F₂ (KBBF),¹¹ Sr₂Be₂B₂O₇,¹² NaBeB₃O₆,¹³ Na₂CsBe₆B₅O₁₅,¹⁴ Na₂Be₄B₄O₁₁ and LiNa₅Be₁₂B₁₂O₃₃,¹⁵ etc. While until now, KBBF is the sole practically applicable NLO crystal working below 200 nm by direct SHG. However, KBBF has a great difficulty to grow in large size because it exhibits a strong layering growth tendency and decomposes easily at a relatively low temperature.¹⁶ Furthermore, the containing beryllium is highly toxic and not environmentally friendly. Therefore, multiple ways are attempted to develop new eco-friendly deep-UV NLO crystals that overcome the demerits of KBBF. One traditional and effective way is to design and synthesize new borate crystals that preserve the structural merits of KBBF while enhance the interlayer interactions. For example, Li₄Sr(BO₃)₂¹⁷ and Rb₃Al₃B₃O₁₀F¹⁸ exhibit relatively strong interlayer bonding strength which are about 4.7 and 9.5 times as large as that of KBBF, respectively. Another novel and promising way is to develop non-boron phosphates featured PO₄ tetrahedral building blocks which are transparent down to the deep-UV region.¹⁹ Admittedly, the SiO₄ and AlO₄ building blocks can also satisfy the deep-UV transparency requirement,^{16a,18,20} thus the extension of this promising pathway is expected to obtain more candidates for deep-UV applications.

Moreover, the combination of different anionic units in a same compound properly has been proved to be a very effective synthetic route for developing new NLO crystal because of its significant

^a Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Xinjiang Key Laboratory of Electronic Information Materials and Devices, No. 40-1, South Beijing Road, Urumqi 830011, China. E-mails: ffzhang@ms.xjb.ac.cn, zhyang@ms.xjb.ac.cn, slpan@ms.xjb.ac.cn Fax: (86)-991-3838957; Tel: (86)-991-3674558.

^b University of Chinese Academy of Sciences, Beijing 100049, China.

^c Xinjiang Products Quality Supervision & Inspection Institute of Technology, Urumqi 830011, China

† Electronic Supplementary Information (ESI) available: CCDC number 1435956 for Li₃AlSiO₅; CIF file; atomic coordinates, isotropic thermal parameters and bond valence sums; selected bond lengths and angles; data of band structure calculations; optical images and theoretical morphology of Li₃AlSiO₅; Thermal ellipsoid plot of the asymmetric unit; the arrangement of [AlSiO₅]³⁻ slabs; UV-Vis-NIR diffuse reflectance spectrum; IR spectrum; the TG-DSC curves; calculated band structure of Li₃AlSiO₅ by DFT and PBE0.

effect to increase compositional flexibility of the compounds.^{21,22} It is this flexibility that allows for the potential to tune the physical properties of the material for applications in nonlinear optics.²³ Guided by this strategy, our group has successfully synthesized a series of new NLO crystals with deep-UV transparency and suitable SHG responses, such as $K_3B_6O_{10}Cl$,²⁴ $Cs_2B_4SiO_9$,^{20b} $Ba_4B_{11}O_{20}F$,²⁵ $Ba_4(BO_3)_3(SiO_4)$ Ba_3Cl and $Ba_4(BO_3)_3(SiO_4)$ Ba_3Br .²⁶

Inspired by the fruitful results achieved by the above strategies, we extend the aforementioned boron-free pathway to the aluminosilicate system. Meanwhile, we choose the alkali metal (Li) as the cations, which have no *d-d* electron transitions that are ideal for the transmission of deep-UV region. Then we thoroughly investigate the $Li_2O-Al_2O_3-SiO_2$ system and discover the first aluminosilicate NLO crystal Li_3AlSiO_5 through the high temperature solution method. In this paper, the synthesis, crystal structure, linear and NLO properties, thermal behaviors as well as theoretical studies of Li_3AlSiO_5 are comprehensively discussed.

Experimental Section

Solid-state Synthesis. High-purity (99.99 %) Li_2CO_3 , Al_2O_3 , SiO_2 and NaF were used as received. The polycrystalline samples of Li_3AlSiO_5 were synthesized by solid-state reaction method. Stoichiometric reagents of Li_2CO_3 (17.734 g, 0.24 mol), Al_2O_3 (4.078 g, 0.02 mol) and SiO_2 (4.806 g, 0.04 mol) were mixed thoroughly and loaded into a corundum crucible. The mixture was preheated at 973 K for 24 h in order to decompose the carbonate. Then the samples were thoroughly ground, gradually heated to 1273 K and held at this temperature for 10 days with several intermediate grindings and mixings. The phase purity of the product was confirmed by the powder X-ray diffraction (XRD) measurement (shown in Fig. 1).

Powder XRD. Powder XRD were carried out using a Bruker D2 ADVANCE X-ray diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The 2θ range was $10-70^\circ$ with a scan step width of 0.02° and a fixed counting time of 1 s per step.

Single-crystal Growth. Single crystals of Li_3AlSiO_5 were grown from the high-temperature solution through spontaneous crystallization using NaF as the flux. The solution was prepared in a platinum crucible by melting a mixture of polycrystalline samples of Li_3AlSiO_5 and NaF at a molar ratio of 1 : 2. Then the platinum crucible was placed in the center of a programmable temperature furnace and gradually heated to 1223 K, held at this temperature for

3 days. The temperature was decreased to 1023 K at a rate of 1 K/h. Then the platinum crucible was allowed to cool to room temperature at a rate of 10 K/h. Thus colorless and transparent crystals with sizes of submillimeter scale were obtained (Fig. S1a, ESI†). These crystals are stable in air and moisture conditions. The theoretical morphology of Li_3AlSiO_5 was simulated by the Mercury program²⁷ according to the Bravais-Friedel and Donnay-Harker (BFDH) theory²⁸ (Fig. S1b, ESI†). We can see that the as-grown crystals are in principle consistent with the theoretical morphology despite their small sizes.

X-ray Crystallographic Studies. The high-quality single crystal of Li_3AlSiO_5 was selected for the structure determination. It was determined by single-crystal XRD on an APEX II CCD diffractometer using graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K and integrated with the SAINT program.²⁹ Numerical absorption corrections were carried out using the SCALE program for area detector.²⁹ All calculations were performed with programs from the SHELXTL crystallographic software package.³⁰ All atoms were refined using full-matrix least-squares techniques. The final difference Fourier synthesis map showed the maximum and minimum peaks at 0.290 and $-0.329 \text{ e \AA}^{-3}$, respectively. The structure was checked with PLATON³¹ and no higher symmetries were found. Crystal data and structure refinement information are given in Table 1. The final refined atomic coordinates and isotropic thermal parameters, as well as selected bond lengths and angles for

Table 1 Crystal data and structure refinement for Li_3AlSiO_5 .

Empirical formula	Li_3AlSiO_5
Temperature	296(2) K
Crystal system, space group	Orthorhombic, $Pna2_1$
Unit cell dimensions	$a = 5.331(3) \text{ \AA}$ $b = 15.551(9) \text{ \AA}$ $c = 4.782(3) \text{ \AA}$
Volume	$396.4(4) \text{ \AA}^3$
Z, Calculated density	4, 2.612 g cm^{-3}
Absorption coefficient	0.715 mm^{-1}
$F(000)$	304
Crystal size	$0.203 \times 0.119 \times 0.117 \text{ mm}^3$
Theta range for data collection	2.62 to 27.52°
Limiting indices	$-6 \leq h \leq 5$, $-19 \leq k \leq 20$, $-6 \leq l \leq 6$
Reflections collected / unique	2255 / 881 [$R(\text{int}) = 0.0299$]
Completeness to theta = 27.49°	100.0 %
Data / restraints / parameters	881 / 1 / 77
Goodness-of-fit on F^2	1.031
Final R indices [$F_o^2 > 2\sigma(F_o^2)$] ^[a]	$R_1 = 0.0287$, $wR_2 = 0.0667$
R indices (all data) ^[a]	$R_1 = 0.0378$, $wR_2 = 0.0725$
Absolute structure parameter	0.12(19)
Extinction coefficient	0.014(2)
Largest diff. peak and hole	0.290 and $-0.329 \text{ e \AA}^{-3}$

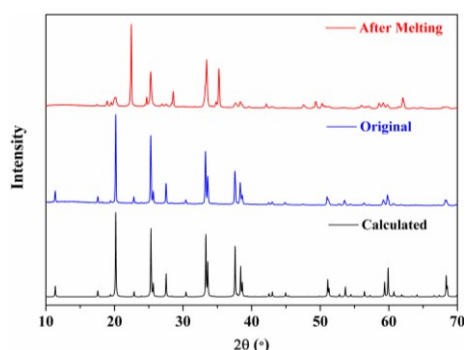


Fig. 1 Experimental and calculated XRD patterns of Li_3AlSiO_5 .

^[a] $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ and $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}}{2\sigma(F_o^2)}$

$\text{Li}_3\text{AlSiO}_5$ are summarized in Tables S1 and S2, ESI†, respectively.

IR Spectroscopy. IR spectrum was recorded on Shimadzu IR Affinity-1 Fourier transform IR spectrometer in the range of 400 - 4000 cm^{-1} with a resolution of 2 cm^{-1} . The sample was mixed thoroughly with dried KBr (4 mg of the sample and 400 mg of KBr).

UV-Vis-NIR Diffuse Reflectance Spectrum. Optical diffuse reflectance spectrum for the $\text{Li}_3\text{AlSiO}_5$ polycrystalline sample was measured in nitrogen atmosphere at room temperature with Shimadzu SolidSpec-3700DUV spectrophotometer. Data were collected in the wavelength range of 190 to 2000 nm.

Second-order NLO Measurements. The SHG intensities of $\text{Li}_3\text{AlSiO}_5$ were evaluated by the Kurtz-Perry method.³² The measurements were carried out with a Nd:YAG pulsed solid-state laser (1064 nm, 10 kHz, 10 ns). The output light intensities emitted from the samples were collected by a photomultiplier tube. For the reason that the SHG efficiency depends strongly on particle size,³³ polycrystalline $\text{Li}_3\text{AlSiO}_5$ samples were ground and sieved into the following particle size ranges: 0-20, 20-38, 38-55, 55-88, 88-105, 105-150, 150-200 μm . The microcrystalline KDP samples with the same particle size ranges were served as the references.

Thermal Analysis. Thermal gravimetric (TG) analysis and differential scanning calorimetry (DSC) of $\text{Li}_3\text{AlSiO}_5$ were carried out on a simultaneous NETZSCH STA 449C thermal analyzer instrument. The sample was enclosed in a platinum crucible and heated with a heating rate of 10 K/min in an atmosphere of flowing nitrogen from room temperature to 1673 K.

Numerical Calculation Details. For the first-principles calculations, the CASTEP package,³⁴ a plane-wave pseudopotential method³⁵ based on density functional theory (DFT), was employed to analyze the electronic structure and the relationship between optical properties and crystal structure. The structure fixed to the experimental crystallographic data was used as the original structure to geometry optimization using the BFGS minimization technique. The converged criterion of the residual forces on the atoms, the displacements of atoms and the energy change were less than 0.01 eV/Å, 5×10^{-4} Å and 5.0×10^{-6} eV per atom, respectively. A series of successful algorithms were executed, and finally, the Ceperley and Alder-Perdew-Zungerof (CA-PZ) functional based on the local density approximation (LDA) and norm-conserving pseudopotential (NCP) were chosen as the exchange-correlation functional and pseudopotential. The optimized valence electronic configurations for NCP are Li $2s^1$, Al $3s^23p^1$, Si $3s^23p^2$, and O $2s^22p^4$ and the plane-waves cut-off energy of 1050 eV was used to ensure a small plane-wave basis set without compromising the accuracy required by our study. The Monkhorst-Pack³⁶ k -point meshes were set with a density of $7 \times 2 \times 7$ with a separation of 0.03 /Å in the Brillouin zone for the electronic structures and band structures. These conditions were further applied to calculate the optical responses. In the calculation of PBE0, the Monkhorst-Pack k -point sampling $3 \times 1 \times 3$ with a separation of 0.07 /Å was adopted. The other calculation parameters and convergent criteria were set as the default values of the CASTEP code.

The length-gauge formalism method³⁷ was used to estimate the SHG coefficients. At a zero frequency, the static second-order nonlinear susceptibilities can be ascribed to Virtual-Hole (VH) and Virtual-Electron (VE) processes,³⁸

$$\chi_{\alpha\beta\gamma}^{(2)} = \chi_{\alpha\beta\gamma}^{(2)}(\text{VE}) + \chi_{\alpha\beta\gamma}^{(2)}(\text{VH}) \quad (1)$$

where $\chi_{\alpha\beta\gamma}^{(2)}(\text{VE})$, $\chi_{\alpha\beta\gamma}^{(2)}(\text{VH})$, and $\chi_{\alpha\beta\gamma}^{(2)}$ (two bands) are computed with the formulas as follows:

$$\chi_{\alpha\beta\gamma}^{(2)}(\text{VE}) = \frac{e^3}{2\hbar m^3} \sum_{vc'} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im} \left[P_{cv}^\alpha P_{cc'}^\beta P_{c'v}^\gamma \left(\frac{1}{\omega_{cv}^3 \omega_{vc'}^2} + \frac{2}{\omega_{vc}^4 \omega_{c'v}} \right) \right] \quad (2)$$

$$\chi_{\alpha\beta\gamma}^{(2)}(\text{VH}) = \frac{e^3}{2\hbar m^3} \sum_{v'c'} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im} \left[P_{v'v}^\alpha P_{cv}^\beta P_{c'v}^\gamma \left(\frac{1}{\omega_{cv}^3 \omega_{v'c'}^2} + \frac{2}{\omega_{vc}^4 \omega_{c'v}} \right) \right] \quad (3)$$

α, β, γ are Cartesian components, v and v' , c and c' denote valence bands and conduction bands, respectively. $P(\alpha\beta\gamma)$, $\hbar\omega_{ij}$ and p_{ij}^α refer to full permutation, the band energy difference and momentum matrix elements, respectively.

Results and Discussion

Crystal Structure. $\text{Li}_3\text{AlSiO}_5$ crystallizes in orthorhombic crystal system with a polar space group of $Pna2_1$ (no. 33). The asymmetric unit of $\text{Li}_3\text{AlSiO}_5$ consists of three crystallographically independent Li atoms, one Al atom, one Si atom and five O atoms, all of which reside on general positions (Fig. S2, ESI†). All cations are four-coordinated forming LiO_4 , AlO_4 and SiO_4 tetrahedra.

Detailed investigation on the structure has shown that the SiO_4 units are isolated from each other and each Si atom locates at the joint of a pseudo-skeleton which exhibits 6-membered ring tunnels viewing down the a -axis, (Fig. 2a) where the $[\text{AlO}_3]_\infty$ chains that formed by corner shared AlO_4 tetrahedra reside (Fig. 2b). The connection of the SiO_4 units and the $[\text{AlO}_3]_\infty$ chains leads to the anionic $[\text{AlSiO}_5]^{3-}$ slabs as shown in Fig. 2b and Fig. S3, ESI†. In the structure, $\text{Li}(1)\text{O}_4$ tetrahedra connect with each other by vertical O atoms to form 1 D $[\text{Li}(1)\text{O}_3]_\infty$ chains along the a -axis, and the $\text{Li}(2)\text{O}_4$ tetrahedra also make up $[\text{Li}(2)\text{O}_3]_\infty$ chains by corner-sharing along the c -axis; however, the $\text{Li}(3)\text{O}_4$ tetrahedra keep isolated from each other (Fig. 3). The connection of these Li-O groups and the $[\text{AlSiO}_5]^{3-}$ slabs via sharing oxygen atoms results in the final structure of $\text{Li}_3\text{AlSiO}_5$ (Fig. 3).

In the structure of $\text{Li}_3\text{AlSiO}_5$, the Li-O bond lengths vary from 1.892(5) to 2.086(6) Å, the Al-O bond lengths vary from 1.749(2) to 1.776(3) Å and the Si-O bond lengths range from 1.597(2) to 1.672(2) Å. All of the bond lengths and angles for the title compound are consistent with other Li, Al or Si containing compounds reported previously.³⁹ The bond valence sum analyses⁴⁰

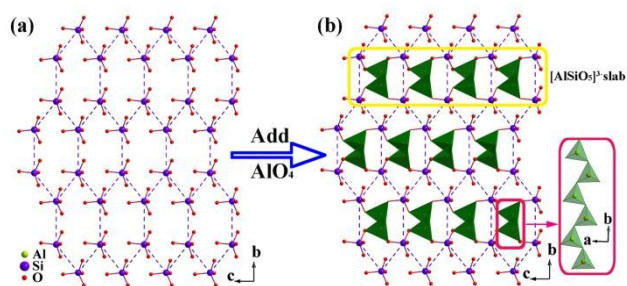


Fig. 2 (a) The arrangement of SiO_4 groups in the crystal structure of $\text{Li}_3\text{AlSiO}_5$, dotted lines are drawn to guide the eye; (b) Formation of $[\text{AlSiO}_5]^{3-}$ anion groups.

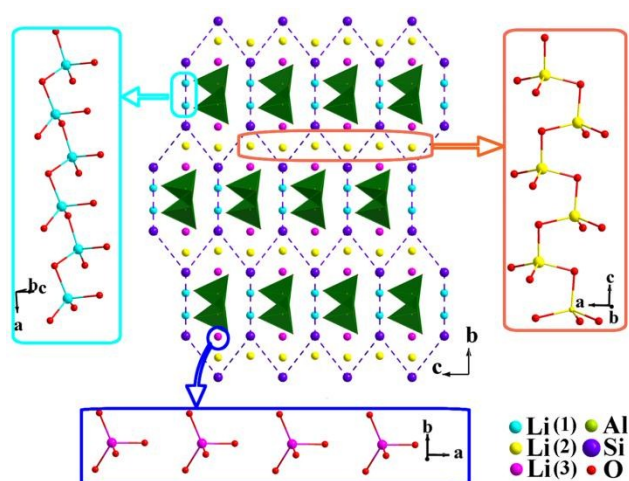


Fig. 3 Schematic diagram of $\text{Li}_3\text{AlSiO}_5$ structure. (All the O atoms connected with Li, Si atoms have been omitted for clarity)

of each atom in $\text{Li}_3\text{AlSiO}_5$ (Li, 0.93 ~ 1.01; Al, 2.75; Si, 3.93; O, -1.91 ~ -2.04) indicate that the Li, Al, Si and O atoms are in oxidation states of + 1, + 3, + 4 and - 2, respectively (Table S1, ESI†). The results of bond valence calculations further prove that the coordination of all atoms are reasonable.

$\text{Li}_3\text{AlSiO}_5$ have structure that resemble hexagonal diamond (lonsdaleite) and many famous natural and synthetic compounds also crystalline in diamond-like structures, for example, binary compound wurtzite ($\alpha\text{-ZnS}$) and ternary compounds AgGaS_2 (Fig. 4). In addition, numerous quaternary diamond-like semiconductors (DLSs) have been discovered (e.g., $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnSnSe}_4$,⁴¹ $\text{Cu}_2\text{ZnGeS}_4$,⁴² $\text{Ag}_2\text{CdGeS}_4$)⁴³ and widely used in the areas of nonlinear optics,⁴⁴ thermoelectrics⁴⁵ and photovoltaics,⁴⁶ etc. The wide application of these quaternary compounds comes from their increased chemical and structural freedom, which make their physical properties more flexible relative to binary and ternary compounds.⁴⁷ The title compound, however, represent a quaternary diamond-like structure of insulator. So its physical properties are worthy of study. The crystal structure has been predicted to be isostructural with $\text{Li}_3\text{AlGeO}_5$,⁴⁸ but the detail information of $\text{Li}_3\text{AlSiO}_5$ has not been reported.

IR Measurement. In order to further confirm the coordination environments of anionic groups in the $\text{Li}_3\text{AlSiO}_5$ structure, IR spectroscopic measurement was carried out and the result is shown

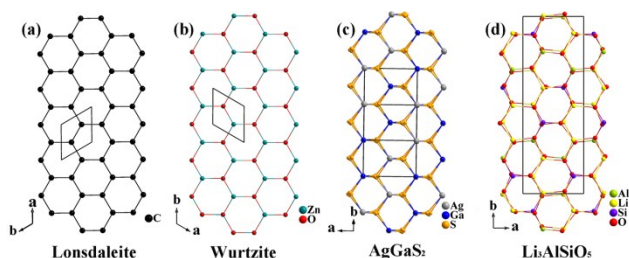


Fig. 4 The diamond-like structures from unitary to quaternary system: (a) The structure of hexagonal diamond (Lonsdaleite); (b) The structure of wurtzite ($\alpha\text{-ZnS}$); (c) The structure of AgGaS_2 ; (d) The structure of $\text{Li}_3\text{AlSiO}_5$.

in Fig. S4, ESI†. The IR spectrum of $\text{Li}_3\text{AlSiO}_5$ shows high transmittance in the range of 4000–1300 cm^{-1} (2.50–7.69 μm) and displays a series of strong absorption bands with frequencies below 1300 cm^{-1} . According to previous work, the absorption bands at 1127, 1064, 1029, 950 cm^{-1} can be assigned as the O-Si-O stretching vibrations of the SiO_4 groups. The bands at 878, 835, 457, 441 cm^{-1} originate from the symmetric and asymmetric stretching vibrations of the Al-O bonds in the AlO_4 tetrahedra. The bands around 702 and 623 cm^{-1} are characteristic for the Si-O-Al bridges. The band around 531 cm^{-1} is signed to the bending of the Si-O-Li bridges. The peaks observed in the IR spectrum are in agreement with other compounds containing SiO_4 , AlO_4 and LiO_4 groups.^{40b,40c,49}

The UV-Vis-NIR Diffuse Reflectance Spectrum. The UV-Vis-NIR diffuse reflectance spectra of polycrystalline $\text{Li}_3\text{AlSiO}_5$ are displayed in Fig. 5a and Fig. S5, ESI†. Absorption (K/S) data were calculated from the following Kubelka–Munk function: $F(R) = (1 - R)^2/2R = K/S$, where R is the reflectance, K is the absorption, and S is the scattering.⁵⁰ As shown in Fig. 5a and Fig. S5, ESI†, although there exists a relatively small absorption beginning from about 4.3 eV which is most probably caused by the inescapably tiny impurity in the polycrystalline powder,⁵¹ the sample has a large reflectance (> 80%) in the range of 190 – 2000 nm (corresponding to 6.53 – 0.62 eV) and the reflectance at 190 nm is ~ 90%. The results indicate that the experimental band gap value of $\text{Li}_3\text{AlSiO}_5$ is greater than 6.53 eV; that is to say that the UV cut-off edge is below 190 nm. This value is comparable to those of Al or Si-containing deep-UV NLO crystals such as $\text{Rb}_3\text{Al}_3\text{B}_3\text{O}_{10}\text{F}^{18}$ (< 200 nm), $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (180 nm)^{20a} and $\text{Cs}_2\text{B}_4\text{SiO}_9$ ^{20b} (< 190 nm). This suggests that the crystal may have potential applications in the deep-UV region.

NLO Properties. $\text{Li}_3\text{AlSiO}_5$ crystallizes in the polar space group, therefore, it is expected to possess NLO properties. The curve of SHG signal as a function of particle size are shown in Fig. 5b. It is clear that the SHG intensities become larger with increasing particle sizes of the $\text{Li}_3\text{AlSiO}_5$ powders before they attain the maximization independent of the particle sizes. The result is consistent with phase-matching behavior according to the rule proposed by Kurtz and Perry.³² It is also found that $\text{Li}_3\text{AlSiO}_5$ exhibits SHG responses approximately 0.8 times that of KDP in the same particle size range of 150–200 μm . Such a powder SHG efficiency is comparable to some recently reported deep-UV NLO crystals, for example $\beta\text{-KBe}_2\text{B}_3\text{O}_7$ (0.75 \times KDP), $\gamma\text{-KBe}_2\text{B}_3\text{O}_7$ (0.68 \times KDP), $\text{RbBe}_2\text{B}_3\text{O}_7$ (0.79 \times KDP),¹³ $\text{Ba}_3\text{P}_3\text{O}_{10}\text{Cl}$ (0.6 \times KDP), $\text{Ba}_3\text{P}_3\text{O}_{10}\text{Br}$ (0.5 \times KDP)^{19a} and $\text{Ba}_5\text{P}_6\text{O}_{20}$ (0.8 \times KDP).^{19c}

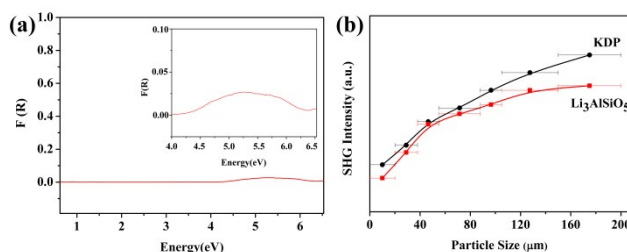


Fig. 5 (a) UV-Vis-NIR diffuse reflectance spectrum of $\text{Li}_3\text{AlSiO}_5$; (b) SHG intensity vs particle size curve at 1064 nm for $\text{Li}_3\text{AlSiO}_5$, KDP samples serve as the references (The solid curves are drawn to guide the eyes and are not fits to the data).

According to the anionic group theory,⁵² the SHG response of a crystal mainly comes from the contribution of anionic groups and the orientations of anionic groups in the structure affect their total NLO contribution. Considering the arrangement of anionic groups in $\text{Li}_3\text{AlSiO}_5$, it is found that all the tetrahedra groups pointing in the same direction along the c -axis is helpful for the crystal to generate relatively large SHG response (see Fig. S3a). Therefore, the alignment of the anionic tetrahedra groups in $\text{Li}_3\text{AlSiO}_5$ leads to its moderate SHG response.

Thermal Properties. The TG-DSC curves of $\text{Li}_3\text{AlSiO}_5$ crystal are shown in Fig. S6, ESI†. TG study shows that there is no obvious weight loss in the temperature up to 1673 K. Meanwhile, two sharp endothermic peaks are observed in the DSC curve at about 1473 K and 1492 K, respectively. It is expected that $\text{Li}_3\text{AlSiO}_5$ is stable until heated to ~ 1473 K. In addition, polycrystalline $\text{Li}_3\text{AlSiO}_5$ was placed in a platinum crucible and heated to 1673 K, and then slowly cooled to room temperature. Powder XRD data of the solidified melt shows a diffraction pattern different from that of the original $\text{Li}_3\text{AlSiO}_5$ powder (shown in Fig. 1). These results demonstrate that $\text{Li}_3\text{AlSiO}_5$ is an incongruently melting compound. Thus, large crystal of $\text{Li}_3\text{AlSiO}_5$ can be grown using the flux method.

Theoretical Studies. In order to explore the intrinsic relationship between the electronic structure and optical properties, the first-principles studies were made. Firstly, DFT⁵³ was adopted to evaluate the band gap of $\text{Li}_3\text{AlSiO}_5$. The calculated band structure along high symmetry points in the first Brillouin zone is plotted in Fig. S7a, ESI† and the state energies along special points are listed in Table S3a. The results show that the highest energy of the valence band (VB) is located at the U point, and the lowest energy of the conduction band (CB) is located at the G point. Accordingly, $\text{Li}_3\text{AlSiO}_5$ is an indirect band gap crystal and the value of the band gap is 6.05 eV, which is less than the experimental value (> 6.53 eV). The DFT usually underestimates the band gap because the insufficient description of the eigenvalues of the electronic states. Then we adopted hybridization functional PBE0 to accurately predict the value of band gap. The band structure is plotted in Fig. S7b, ESI† and the state energies along special points are listed in Table S3b. From the results we can see that the calculated band gap is 7.29 eV (corresponding to 170 nm). Therefore, the cut-off edge of $\text{Li}_3\text{AlSiO}_5$ should be down to 170 nm which is consistent with the experimental observation. It further confirms the deep-UV transparency of the $\text{Li}_3\text{AlSiO}_5$ crystal.

Fig. 6 displays the density of states (DOS) and partial DOS (PDOS) projected on the constitutional atoms of $\text{Li}_3\text{AlSiO}_5$ in the vicinity of the band gap. They can be sorted into four major distinct regions: (1) The peaks in the range of -19.0 to -15.0 eV of VB are composed of O 2s, Li 2s, Si 3s3p and Al 3s3p states. (2) The upper part of the VB from -7.0 to 0 eV mainly arises from O 2p states, mixing with small amounts of Li 2s, Si 3s3p and Al 3s3p states. (3) The CB between 6.1 to 7.5 eV are contributed by Li 2s, and Al 3s3p states, while Li 2s states accounts for a major contribution. (4) 7.5 to 15.0 eV in the CB, O 2p, Li 2s, Si 3s3p, and Al 3s3p states, are all involved and overlap fully among them, indicating the strong interactions of Al-O, Si-O and Li-O bonds in the system. It should be emphasized that in the vicinity of the Fermi level, O 2p and Li 2s states play a dominant role implying the interaction between Li and O may determine the band gap of $\text{Li}_3\text{AlSiO}_5$.

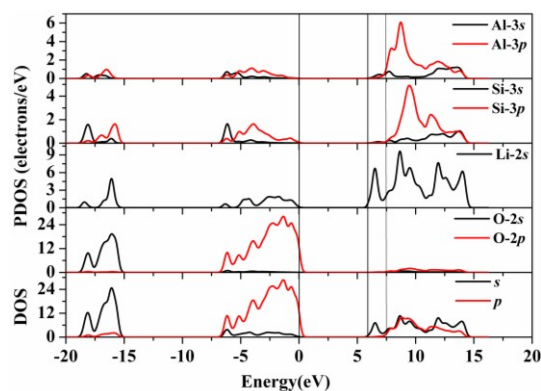


Fig. 6 The DOS and PDOS of $\text{Li}_3\text{AlSiO}_5$.

The SHG coefficients (d_{ij}) were calculated by Equations (1) – (3). $\text{Li}_3\text{AlSiO}_5$ crystal allows for five nonzero SHG coefficients (d_{ij}), d_{31} , d_{32} , d_{33} , d_{24} , and d_{15} owing to its $Pna2_1$ space group. Under the restriction of Kleinman symmetry,⁵⁴ d_{31} is equal to d_{15} and d_{32} is equal to d_{24} . Therefore, there are only three independent nonzero d_{ij} coefficients, namely, d_{15} , d_{24} , and d_{33} , the values of which need to be determined. The calculated results are $d_{15} = 0.091$ pm/V, $d_{24} = 0.247$ pm/V and $d_{33} = 1.41$ pm/V, respectively. However, according to the symmetry of the title compound, only d_{24} is effective and it is about 0.63 times that of KDP ($d_{36} = 0.39$ pm/V).⁵⁵ This value is in agreement with the experiment result.

To gain further insight into the origin of SHG effect, the SHG-density method⁵⁶ was employed to analyze the electrons states response in the atoms. As for $\text{Li}_3\text{AlSiO}_5$, the virtual-electron makes a significant contribution (80%), therefore we will just exhibit the virtual-electron process in SHG effect of occupied and unoccupied states (shown in Fig. 7). As shown in Fig. 7, the 2p orbitals of O atoms and the σ anti-bonding orbital of AlO_4 and SiO_4 play the dominant role in occupied and unoccupied states, respectively, while the SHG-density of AlO_4 and that of SiO_4 are almost equal. Thus we can deduce that the SHG effect of $\text{Li}_3\text{AlSiO}_5$ mainly originates from the cooperation of AlO_4 and SiO_4 anionic groups. The results are consistent with the anionic group theory proposed by Chen et al for the UV and deep-UV NLO crystals.⁵²

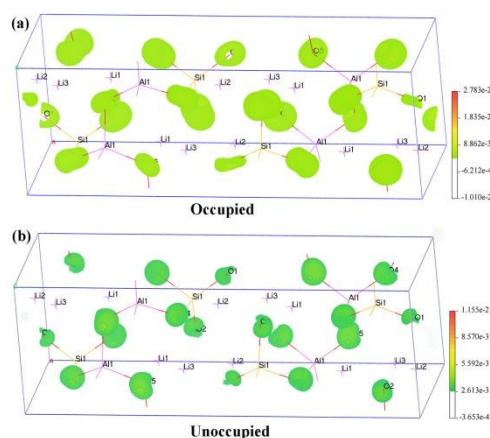


Fig. 7 The virtual-electron process of the SHG tensors for occupied states (a) and unoccupied states (b).

Conclusions

In summary, we have successfully developed the first aluminosilicate NLO crystal $\text{Li}_3\text{AlSiO}_5$ by the high temperature solution method. It is eco-friendly with all the containing elements nontoxic. Interestingly, the crystal possesses a quaternary diamond-like structure which is constructed only by tetrahedral building units with all the LiO_4 , AlO_4 and SiO_4 pointing in the same direction, so the compound could be an ideal candidate for the study of structure-property relationship about tetrahedron-containing compounds. Moreover, the experimental cut-off edge of $\text{Li}_3\text{AlSiO}_5$ is below 190 nm and further band gap calculation by PBE0 shows that the cut-off edge of $\text{Li}_3\text{AlSiO}_5$ can be down to 170 nm. The compound is phase matchable at the 1064 nm fundamental wavelength with moderate powder SHG efficiency (about $0.8 \times \text{KDP}$). In addition, the crystal is nonhygroscopic and thermally stable up to 1472 K. These attributes suggest that $\text{Li}_3\text{AlSiO}_5$ is a potential deep-UV NLO crystal. Future efforts will be devoted to the growth of large high-quality single crystal and relevant physical properties studies.

Acknowledgements

The authors gratefully acknowledge the financial support of this work by National Natural Science Foundation of China (Grant Nos. 21301189, 51425206, U1129301, 21461026), the Xinjiang International Science & Technology Cooperation Program (20146001), the Funds for Creative Cross & Cooperation Teams of CAS, Xinjiang Key Laboratory Foundation (Grant No. 2014KL009), and the Science and Technology Project of Urumqi (Grant 51425206), the Foundation of the Youth Innovation Promotion Association of CAS.

References

- P. A. Franken, A. E. Hill, C. W. Peters and G. Weinreich, *Phys. Rev. Lett.*, 1961, **7**, 118-119.
- (a) C. T. Chen, T. Sasaki, R. K. Li, Y. C. Wu, Z. S. Lin, Y. Mori, Z. G. Hu, J. Y. Wang, S. Uda, M. Yoshimura and Y. Kaneda, *Nonlinear Optical Borate Crystals: Principles and Applications*, Wiley-VCH, Weinheim, 2012; (b) T. Sasaki, Y. Mori, M. Yoshimura, Y. K. Yap and T. Kamimura, *Mater. Sci. Eng. R.*, 2000, **30**, 1-54; (c) D. A. Keszler, *Curr. Opin. Solid. State Mater. Sci.*, 1996, **1**, 204-208; (d) D. A. Keszler, *Curr. Opin. Solid. State Mater. Sci.*, 1999, **4**, 155-162; (e) P. S. Halasyamani and K. R. Poeppelmeier, *Chem. Mater.*, 1998, **10**, 2753-2769.
- (a) D. M. Burland, R. D. Miller, and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31-75; (b) P. Becker, *Adv. Mater.*, 1998, **10**, 979-992; (c) K. M. Ok, E. O. Chi and P. S. Halasyamani, *Chem. Soc. Rev.* 2006, **35**, 710-717; (d) N. Savage, *Nature Photon.*, 2007, **1**, 83-85; (e) D. Cyranoaki, *Nature*, 2009, **457**, 953-955.
- C. T. Chen, B. C. Wu, A. D. Jiang and G. M. You, *Sci. Sin., Ser. B (Engl. Ed.)*, 1985, **28**, 235-243.
- C. T. Chen, Y. C. Wu, A. D. Jiang, B. C. Wu, G. M. You, R. K. Li and S. J. Lin, *J. Opt. Soc. Am. B*, 1989, **6**, 616-621.
- J. J. De Yoreo, A. K. Burnham and P. K. Whitman, *Int. Mater. Rev.*, 2002, **47**, 113-152.
- T. A. Driscoll, H. J. Hoffman, R. E. Stone and P. E. Perkins, *J. Opt. Soc. Am. B*, 1986, **3**, 683-686.
- (a) A. Harasaki and K. Jpn. Kato, *J. Appl. Phys.*, 1997, **36**, 700-703; (b) A. H. Reshak, *J. Phys.: Condens. Matter*, 2005, **369**, 243-253.
- G. D. Boyd, E. Buehler and F. G. Storz, *Appl. Phys. Lett.*, 1971, **18**, 301-304.
- L. Kang, Z. S. Lin, J. G. Qin and C. T. Chen, *Sci. Rep.*, 2013, **3**, 1366.
- (a) Y. N. Xia, C. T. Chen, D. Y. Tang and B. C. Wu, *Adv. Mater.*, 1995, **7**, 79-81; (b) C. T. Chen, G. L. Wang, X. Y. Wang and Z. Y. Xu, *Appl. Phys. B: Laser Opt.*, 2009, **97**, 9-25.
- C. T. Chen, Y. B. Wang, B. C. Wu, K. C. Wu, W. L. Zeng and L. H. Yu, *Nature*, 1995, **373**, 322-324.
- S. C. Wang, N. Ye, W. Li and D. Zhao, *J. Am. Chem. Soc.*, 2010, **132**, 8779-8786.
- S. C. Wang and N. Ye, *J. Am. Chem. Soc.*, 2011, **133**, 11458-11461.
- H. W. Huang, L. J. Liu, S. F. Jin, W. J. Yao, Y. H. Zhang and C. T. Chen, *J. Am. Chem. Soc.*, 2013, **135**, 18319-18322.
- (a) Z.-G. Hu, M. Yoshimura, Y. Mori and T. Sasaki, *J. Cryst. Growth.*, 2005, **275**, 232-239; (b) C. T. Chen, L. Bai, Z. Z. Wang and R. K. Li, *J. Cryst. Growth.*, 2006, **292**, 169-178.
- S. G. Zhao, P. F. Gong, L. Bai, X. Xu, S. Q. Zhang, Z. H. Sun, Z. S. Lin, M. C. Hong, C. T. Chen and J. H. Luo, *Nat. Commun.*, 2014, **5**, 4019.
- S. G. Zhao, P. F. Gong, S. Y. Luo, S. J. Liu, L. N. Li, M. A. Asghar, T. Khan, M. C. Hong, Z. S. Lin and J. H. Luo, *J. Am. Chem. Soc.*, 2015, **137**, 2207-2210.
- (a) P. Yu, L. -M. Wu, L. -J. Zhou and L. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 480-487; (b) S. G. Zhao, P. F. Gong, S. Y. Luo, L. Bai, Z. S. Lin, C. M. Ji, T. L. Chen, M. C. Hong and J. H. Luo, *J. Am. Chem. Soc.*, 2014, **136**, 8560-8563; (c) S. G. Zhao, P. F. Gong, S. Y. Luo, L. Bai, Z. S. Lin, Y. Y. Tang, Y. L. Zhou, M. C. Hong, and J. H. Luo, *Angew. Chem.*, 2015, **127**, 4291-4295; (d) T. Q. Sun, P. L. Shan, H. Chen, X. W. Liu, H. D. Liu, S. L. Chen, Y. A. Cao, Y. F. Kong and J. J. Xu, *Cryst Eng Comm.*, 2014, **16**, 10497-10504.
- (a) Z. G. Hu, T. Higashiyama, M. Yoshimura, Y. K. Yap, Y. Mori and T. Sasaki, *Jpn. J. Appl. Phys.*, 1998, **37**, L1093-L1094; (b) H. P. Wu, H. W. Yu, S. L. Pan, Z. J. Huang, Z. H. Yang, X. Su and K. R. Poeppelmeier, *Angew. Chem. Int. Ed.*, 2013, **52**, 3406-3410.
- (a) H. Huppertz and Z. Naturforsch, *Can. J. Res., Sect. B*, 2003, **58**, 278-290; (b) G. Sohr, D. M. Toebbens, J. S. auf der Gunne and H. Huppertz, *Chem.-Eur. J.*, 2014, **20**, 17059-17067; (c) S. L. Pan, Y. C. Wu, P. Z. Fu, G. C. Zhang, Z. H. Li, C. X. Du and C. T. Chen, *Chem. Mater.*, 2003, **15**, 2218-2221; (d) G. F. Wang, Y. C. Wu, P. Z. Fu, X. Y. Liang, Z. Y. Xu and C. T. Chen, *Chem. Mater.*, 2002, **14**, 2044-2047; (e) H. W. Yu, H. P. Wu, S. L. Pan, Z. H. Yang, X. L. Hou, X. Su, Q. Jing, K. R. Poeppelmeier and J. M. Rondinelli, *J. Am. Chem. Soc.*, 2014, **136**, 1264-1267.
- (a) E. L. Belokoneva, *Crystallogr. Rev.*, 2005, **11**, 151-198; (b) G. Yuan and D. Xue, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 2007, **63**, 353-362; (c) G.-H. Zou, L. Huang, N. Ye, C. S. Lin, W.-D. Cheng and H. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 18560-18566; (d) J. B. Parise and T. E. Gier, *Chem. Mater.*, 1992, **4**, 1065-1067; (e) Y. Z. Huang, L. M. Wu, X. T. Wu, L. H. Li, L. Chen and Y. F. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 12788-12789; (f) J. -L. Song, C. -L. Hu, X. Xu, F. Kong, and J. -G. Mao, *Angew. Chem. Int. Ed.*, 2015, **54**, 3679-3682.
- J. W. Lekse, M. A. Moreau, K. L. McNerny, J. Yeon, P. S. Halasyamani, and J. A. Aitken, *Inorg. Chem.*, 2009, **48**, 7516-7518.
- H. P. Wu, S. L. Pan, K. R. Poeppelmeier, H. Y. Li, D. Z. Jia, Z. H. Chen, X. Y. Fan and Y. Yang, *J. Am. Chem. Soc.*, 2011, **133**, 7786-7790.

- 25 H. P. Wu, H. W. Yu, Z. H. Yang, X. L. Hou, X. Su, S. L. Pan, X. Su, K. R. Poeppelmeier and J. M. Rondinelli, *J. Am. Chem. Soc.*, 2013, **135**, 4215-4218.
- 26 X. X. Lin, F. F. Zhang, S. L. Pan, H. W. Yu, F. Y. Zhang, X. Y. Dong, S. J. Han, L. Y. Dong, C. Y. Bai and Z. Wang, *J. Mater. Chem. C*, 2014, **2**, 4257-4264.
- 27 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.
- 28 P. Hartman, W. G. Perdok, *Am. Mineral.* 1937, **22**, 463-468.
- 29 SAINT-Plus, version 6.02A; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2000.
- 30 G. M. Sheldrick, SHELXTL, version 6.14; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2003.
- 31 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.
- 32 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798-3813.
- 33 J. P. Dougherty and S. K. Kurtz, *J. Appl. Crystallogr.*, 1976, **9**, 145-158.
- 34 S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.*, 2005, **220**, 567-570.
- 35 M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys.*, 1992, **64**, 1045-1097.
- 36 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* 1976, **13**, 5188-5192.
- 37 C. Aversa and J. E. Sipe, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1995, **52**, 14636-14645.
- 38 (a) J. Lin, M.-H. Lee, Z.-P. Liu, C. Pickard, and C. T. Chen, *J. Phys. Rev. B*, 1999, **60**, 13380; (b) B. Zhang, M.-H. Lee, Z. Yang, Q. Jing, S. Pan, M. Zhang, H. Wu, X. Su and C.-S. Li, *Appl. Phys. Lett.*, 2015, **106**, 031906.
- 39 (a) Y. Yang, S. L. Pan, X. L. Hou, C. Wang, K. R. Poeppelmeier, Z. H. Chen, H. P. Wu and Z. X. Zhou, *J. Mater. Chem.* 2011, **21**, 2890-2894; (b) H. W. Yu, S. L. Pan, H. P. Wu, Z. H. Yang, L. Y. Dong, X. Su, B. B. Zhang, and H. Y. Li, *Cryst. Growth Des.* 2013, **13**, 3514-3521; (c) S. J. Han, S. L. Pan, Z. H. Yang, Y. Wang, B. B. Zhang, M. Zhang, Z. J. Huang, L. Y. Dong, and H. W. Yu, *Z. Anorg. Allg. Chem.*, 2013, **639**, 779-783; (d) F. Liebau, *Structural Chemistry of Silicates*, Springer-Verlag, New York, 1985, p. 12; (e) C. S. Lee, S. L. Wang, Y. H. Chen and K. H. Lii, *Inorg. Chem.* 2009, **48**, 8357-8361; (f) J. D. C. McConnell, A. D. Vita, S. D. Kenny and V. Heine, *Phys. Chem. Minerals.*, 1997, **25**, 15-23; (g) I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 244-247.
- 40 (a) I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 244-247; (b) N. E. Brese and M. O'keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **47**, 192-197.
- 41 C. Persson, *J. Appl. Phys.*, 2010, **107**, 053710.
- 42 O. V. Parasyuka, L. V. Piskacha, Y. E. Romanyukb, I. D. Olekseyuka, V. I. Zarembac and V. I. Pekhnyod, *J. Alloys Compd.*, 2005, **397**, 85-94.
- 43 C. D. Brunetta, W. C. Minsterman, C. H. Lake and J. A. Aitken, *J. Solid State Chem.*, 2012, **187**, 177-185.
- 44 (a) S. Levchenko, D. Dumcenco, Y. S. Huang, E. Arushanov, V. Tezlevan, *J. Alloys Compd.*, 2011, **509**, 7105-7108; (b) Y. Li, W. Fan, H. Sun, X. Cheng, P. Li, and X. Zhao, *J. Phys. Condens. Matter.*, 2011, **23**, 225401; (c) J. A. Brant, D. J. Clark, Y. S. Kim, J. I. Jang, J.-H. Zhang and J. A. Aitken, *Chem. Mater.*, 2014, **26**, 3045-3048.
- 45 (a) X. Y. Shi, F. Q. Huang, M. L. Liu, and L. D. Chen, *Appl. Phys. Lett.*, 2009, **94**, 122103; (b) M.-L. Liu, I.-W. Chen, F.-Q. Huang, and L.-D. Chen, *Adv. Mater.*, 2009, **21**, 3808-3812; (c) C. Sevik and T. Cagin, *Appl. Phys. Lett.*, 2009, **95**, 112105; (d) C. Sevik and T. Cagin, *Phys. Rev. B*, 2010, **82**, 045202.
- 46 (a) Q. Guo, G. M. Ford, W. C. Yang, B. C. Walker, E. A. Stach, H. W. Hillhouse and R. Agrawal, *J. Am. Chem. Soc.*, 2010, **132**, 17384-17386; (b) G. M. Ford, Q. Guo, R. Agrawal and H.W. Hillhouse, *Chem. Mater.*, 2011, **23**, 2626-2629; (c) A. Goetzberger, C. Hebling and H. Schock, *Mater. Sci. Eng.*, 2003, **40**, 1-46.
- 47 S. Y. Chen, A. Walsh, Y. Luo, J.-H. Yang, X. G. Gong, and S.-H. Wei, *Phys. Rev. B*, 2010, **82**, 195203.
- 48 J. M. S. Skakle, J. G. Fletcher, R. A. Howie, C. K. Lee, and A. R. West, *J. Solid State Chem.*, 1992, **98**, 33-39.
- 49 (a) J. K. Song, D. W. Lee, Y.-H. Cho, and K. M. Ok, *Bull. Korean Chem. Soc.*, 2012, **33**, 2423-2426; (b) M. Zhang, H. Xu, E. K. H. Salje and P. J. Heaney, *Phys. Chem. Mineral.*, 2003, **30**, 457-462; (c) W. Lowenstein, *Am. Mineral.*, 1954, **39**, 92-96; (d) P. McMillan, *Am. Mineral.*, 1984, **69**, 622-644; (e) M. Nocun and M. Handke, *J. Mol. Struct.*, 2001, **596**, 145-149; (f) M. Zhang, B. Wruck, A. Graeme-Barbar, E. K. H. Salje and M. A. Carpenter, *Am. Mineral.*, 1996, **81**, 92-104.
- 50 (a) P. Kubelka and F. Z. Munk, *Tech. Phys.*, 1931, **12**, 593-601; (b) J. Tauc, *Mater. Res. Bull.*, 1970, **5**, 721-729.
- 51 (a) L. J. Liu, C. L. Liu, X. Y. Wang, Z. G. Hu, R. K. Li and C. T. Chen, *Solid State Sci.*, 2009, **11**, 841-844; (b) Z. S. Lin, L. F. Xu, L. J. Liu, J. Xu, M. H. Lee, Z. Fang and C. T. Chen, *Phys. Rev. B: Condens. Matter*, 2010, **82**, 035124; (c) Y. G. Wang and R. K. Li, *Opt. Mater.*, 2010, **32**, 1313-1316; (d) I. N. Ogorodnikov, V. A. Pustovarov, S. A. Yakovlev and L. I. Isaenko, *Opt. Mater.*, 2013, **35**, 1173-1178; (e) I. N. Ogorodnikov, V. A. Pustovarov, S. A. Yakovlev, L. I. Isaenko, and S. A. Zhurkov, *J. Lumin.*, 2012, **132**, 1632-1638.
- 52 (a) C. T. Chen; *Sci. Sin.*, 1979, **22**, 756-776; (b) C. T. Chen and G. Z. Liu, *Annu. Rev. Mater. Sci.*, 1986, **16**, 203-243; (c) C. T. Chen, Y. C. Wu and R. K. Li, *Int. Rev. Phys. Chem.*, 1989, **8**, 65-91; (d) C. Chen, Z. Lin and Z. Wang, *Appl. Phys. B: Lasers Opt.* 2005, **80**, 1-25.
- 53 J. P. Perdew and M. Levy, *Phys. Rev. Lett.*, 1983, **50**, 1884.
- 54 D. A. Kleinman, *Phys. Rev.*, 1962, **126**, 1977-1979.
- 55 R. C. Eckardt, H. Masuda, Y. X. Fan, and R. L. Byer, *IEEE J. Quantum Electron.*, 1992, **28**, 2057-2074.
- 56 C.-H. Lo, Master degree thesis, Tamkang University 2005.