



Ab initio study of elasticity, piezoelectricity, and nonlinear optical performance in monoclinic NaAsSe₂



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ARTICLE INFO

Article history:

Received 21 December 2012

Received in revised form 27 February 2013

Accepted 2 March 2013

Available online 25 March 2013

Keywords:

Semiconductors

Electronic properties

Density functional theory

Nonlinear optical properties

Electro-optical properties

Piezoelectricity

ABSTRACT

Monoclinic NaAsSe₂ (γ -NaAsSe₂) has been reported to be a potential IR nonlinear optical material due to the very strong second harmonic generation (SHG). Here, we present a systematic density functional theory (DFT) study on the elasticity, SHG response, linear electro-optical (EO) effect, and piezoelectricity of this compound and analyze the microscopic origins of these properties. We find that γ -NaAsSe₂ has smaller values of elastic moduli than those of AgGaSe₂, and behaves in a ductile manner. The strong SHG response observed experimentally is well predicted by the $2n + 1$ theorem and the “sum over states” expressions based on the DFT. As with the strong SHG response, γ -NaAsSe₂ also presents large linear EO coefficient ($r_{11} = 32.7$ pm/V, as large as that of LiNbO₃), and piezoelectric coefficient ($e_{11} = 1.27$ C/m², about seven times larger than that of α -quartz). The highly distorted structure and the strong hybridizations between As and Se *sp* orbitals are identified as the chief sources of these unique properties. Our results demonstrate the potential applications of γ -NaAsSe₂ in piezoelectric, electro-optical, and nonlinear optical devices.

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1. Introduction

Multifunctional materials that simultaneously possess several outstanding properties are of tremendous fundamental and practical interest. They promise to provide the foundation for a new class of devices in which the electrical, optical, and other properties are coupled to one another. Among the well-known multifunctional materials, the non-centrosymmetric (NCS) crystals are considered as the most important part because of their peculiar symmetry-dependent properties, such as SHG, ferroelectricity, linear EO effect and piezoelectricity [1–7]. Take LiNbO₃ for example, it is a typical multifunctional material with the NCS structure for applications in electro-optical, acousto-optical, piezoelectric and nonlinear optical devices [8]. In searching for new NCS materials, much attentions have been paid to the compounds that contain second-order Jahn-Teller distorted cations such as *d*⁰ transition metal ions [9], *p*-cations with stereochemical activity of a lone pair electrons of *ns*² [10–12], or *d*¹⁰ cations with large polar displacement [5,13,14]. Less attention has been paid to the NCS compounds that contain only main-group elements.

Recently, some NCS alkali-metal chalcogenide compounds, such as NaAsSe₂ [15], KPSe₆ [16], K₂PSe₆ [17], and LiAsS₂ [18] have attracted much attention because of their very strong nonlinear

optical effect compared with the commercially used IR nonlinear optical material, AgGaSe₂. Among them, γ -NaAsSe₂ shows the greatest SHG response, about 75 times stronger than that of AgGaSe₂ in the wavelength range of 700–900 nm [15]. It is suggested to be a very promising nonlinear optical material for IR applications. Song et al. demonstrated that the quasi-one-dimensional structural character of γ -NaAsSe₂ plays an important role in the very large SHG coefficients [19]. In view of such a large SHG response, it will be interesting to see if it has the same or better performance in the piezoelectric and optoelectronic devices for its unique asymmetric structure. In addition, an accurate description of the mechanical properties is urgently needed for a promising nonlinear optical material. First-principles methods provide an accurate and effective way to explore the complex relationship between the structures and the macroscopic properties that are difficult to investigate experimentally [7,20–26]. In this report, we provide a systematic study on the elasticity, SHG response, linear EO effect and piezoelectricity of γ -NaAsSe₂ from first principles and analyze the mechanism of these properties. Due to the lack of experimental data for some properties of γ -NaAsSe₂, α -quartz, GaAs, and AgGaSe₂ are used to assess the accuracy of the computations.

The paper is organized as follows. In Section 2, we describe the crystal structure of γ -NaAsSe₂ and the computational methods. In Section 3, we present and discuss the results we have obtained and compare them with some experimental data. Finally, in Section 4, we present the main conclusions of this work.

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2. Model and computational details

γ -NaAsSe₂ crystallizes in the NCS space group *Pc*, in which densely packed parallel AsSe₂¹⁻ polymeric anionic chains are formed by corner sharing of [AsSe₃]³⁻ pyramids, and the alkali-metal ions Na⁺ are located in the chains [15], as shown in Fig. 1. It could be briefly described as a highly distorted α -NaAsSe₂ [15,27] by shifting Na, As and Se ions from their regular positions.

We first perform the structural relaxation carefully by using different exchange and correlation functionals, including the local-density approximation (LDA) [28,29] implemented in the ABINIT package [30,31], the projector-augmented wave (PAW) [32] method with the LDA and the Perdew–Burke–Ernzerhof (PBE) [33] exchange and correlation functionals implemented in the VASP package [34]. Among these functionals, the LDA in the ABINIT code yields the closest lattice parameters and bond distances to experiment. The calculated equilibrium lattice parameters of γ -NaAsSe₂ crystal are $a = 11.39$ Å, $b = 5.78$ Å, $c = 11.60$ Å, and $\beta = 89.15^\circ$, which are well within the theoretical uncertainties, almost two percent deviation with respect to the experimental ones: $a = 11.68$ Å, $b = 5.90$ Å, $c = 11.82$ Å, and $\beta = 90.45^\circ$. Therefore, all the other studies on the elasticity, SHG, linear EO effect and piezoelectricity are based on this optimized structure. The self-consistent norm conserving pseudopotentials are generated by using the Troullier–Martins scheme [35]. For Na, 3s electron, and for As and Se, 4s and 4p electrons are treated as the true valence. A high plane-wave energy cutoff of 45 Hartree and Monkhorst–Pack [36] *k*-point meshes of $4 \times 6 \times 4$ are found to be sufficient to reach convergence for the lattice relaxation and the properties calculations. The method of density-function perturbation theory (DFPT) implemented in ABINIT code is used to calculate the response properties [37]. Three kinds of perturbations, including strain, electric-field, and atomic-displacement, are combined selectively to obtain the elastic constants, SHG coefficients, linear EO tensor, and piezoelectric tensor [38–41].

The static SHG coefficients are calculated by two methods in this work [42]. The one, as described above, is the $2n + 1$ theorem based on the DFPT without the scissor correction [5,40]. In this scheme, the nonlinear optical susceptibility is calculated by a third-order derivative of the energy with respect to low-frequency electric fields,

$$\chi_{ijl}^{(2)} = -\frac{3}{\Omega} E^{e_i} e_j e_l. \quad (1)$$

According to the $2n + 1$ theorem, the evaluation of third-order energy derivatives requires no higher-order derivatives of the wave functions than the first one. The first-order wave functions can be obtained from linear response. For more details of this scheme, see Ref. [40].

The other method is using the “sum over states” (SOS) expressions carried out by Rashkeev and co-workers based on the plane-wave code VASP [43–45]. In the static case, the imaginary part of the static second-order optical susceptibility can be expressed as:

$$\begin{aligned} \chi_{ijl}^{abc} = & \frac{e^3}{\hbar^2 \Omega} \sum_{nmlk} \frac{r_{nm}^a (r_{ml}^b r_{ln}^c + r_{ml}^c r_{ln}^b)}{2\omega_{nm}\omega_{ml}\omega_{ln}} (\omega_n f_{ml} + \omega_m f_{ln} + \omega_l f_{nm}) \\ & + \frac{ie^3}{4\hbar^2 \Omega} \sum_{nmlk} \frac{f_{mn}}{\omega_{nm}^2} [r_{nm}^a (r_{mn,c}^b + r_{mn,b}^c) + r_{nm}^b (r_{mn,c}^a + r_{mn,a}^c) + r_{nm}^c (r_{mn,b}^a + r_{mn,a}^b)], \end{aligned} \quad (2)$$

where r is the position operator, $\hbar\omega_{nm} = \hbar\omega_n - \hbar\omega_m$ is the energy difference for the bands m and n , $f_{mn} = f_m - f_n$ is the difference of the Fermi distribution functions, subscripts a , b , and c are Cartesian indices, and $r_{mn,a}^b$ is the so-called generalized derivative of the coordinate operator in k space,

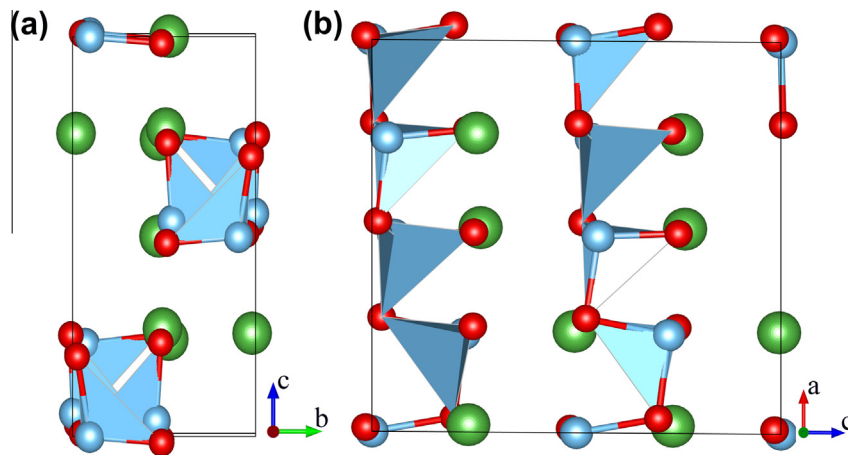


Fig. 1. Perspective view of γ -NaAsSe₂ along the *a*-axis (a), and the *b*-axis (b). The red, cyan, and green particles denote the Se, As, and Na atoms, respectively. The cyan polyhedrons highlight the corner sharing [AsSe₃]³⁻ pyramids. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$r_{nm,a}^b = \frac{r_{nm}^a A_{mn}^b + r_{nm}^b A_{mn}^a}{\omega_{nm}} + \frac{i}{\omega_{nm}} \times \sum_l (\omega_{lm} r_{nl}^a r_{lm}^b - \omega_{nl} r_{ml}^b r_{lm}^a), \quad (3)$$

where $A_{nm}^a = (p_{nm}^a - p_{mnm}^a)/m$ is the difference between the electronic velocities at the bands n and m .

3. Results and discussion

3.1. Elasticity

To study the elasticity of γ -NaAsSe₂, we first obtain the elastic constants including the relaxed ion elastic stiffness tensor and the corresponding compliance tensor by the linear perturbation theory approach [41,46]. These constants are then used to determine some commonly used quantities for identifying the stiffness of a material [47], such as bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν). The orientation-averaged elastic moduli, including B and G are calculated by the Voigt–Reuss–Hill approximation [48,49]. With the values of B and G , we define the average Young's modulus $E = (9BG)/(3B + G)$ and Poisson's ratio $\nu = (3B - 2G)/(6B + 2G)$ [50]. Because of the lack of experimental data on the elasticity of γ -NaAsSe₂, we also calculate these quantities for AgGaSe₂. The results are listed in Table 1.

We find that the calculated ν and B/G of AgGaSe₂ are in good agreement with the experiments, [51] while the predicted B , G and E are somewhat overestimated owing to the underestimation of the lattice constant [52]. The calculated B , G , and E of AgGaSe₂ are about three, two, and two times larger than that of γ -NaAsSe₂, respectively, implying that AgGaSe₂ has stronger abilities to resist volume compression, elastic deformation, and linear compression than γ -NaAsSe₂. These data suggest that γ -NaAsSe₂ is much softer than AgGaSe₂, which can be properly understood from their difference in the bond length. In AgGaSe₂, the Ag–Se bond length is 2.58 Å, and the Ga–Se bond is 2.44 Å [53]. While in γ -NaAsSe₂, the average bond lengths of Na–Se and As–Se bonds are about 2.9 and 2.45 Å, respectively. The shorter average bond lengths in AgGaSe₂ lead it to display stronger bond strength and larger elastic moduli than those of γ -NaAsSe₂. The ratio of B/G is also of interest since it qualitatively reflects the ductility of a material [21]. The critical value of B/G separating brittle from ductile materials is about 1.75 [54]. If $B/G < 1.75$, the material tends to be brittle; otherwise, the material tends to be ductile. The result value of B/G for γ -NaAsSe₂ is 2.85, hence classifying it as ductile. Our works give a quantitative description of the elasticity for γ -NaAsSe₂ for the first time, which is important for its practical applications.

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