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Theoretical study of structural, electronic, lattice dynamical and dielectric properties of $SrAl_2O_4$

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ABSTRACT

We investigate the structural, electronic, lattice dynamical, and dielectric properties of $SrAl_2O_4$ within density-function theory. The crystal structure is fully relaxed, and the structural parameters are found to be well consistent with the experimental data. The first pressure derivatives of the bulk modulus are predicted to be 2.5 and 4.3 for local density approximation (LDA) and generalized gradient approximation (GGA), respectively. The electronic band structure shows that the valence band maximum is comprised of O 2p states and a small amount of Al 3s and 3p states, and the conduction band minimum is comprised of Sr 5s and a small amount of O 2p, Al 3s and Al 3p states. The phonon frequencies at the center of the Brillouin zone and the dielectric permittivity tensors are calculated using density-function perturbation theory. The electronic (ε_∞) and static (ε_0) dielectric permittivity tensors are theoretically predicted by the calculations with both LDA and GGA formalisms. The results show that the electronic dielectric permittivity is isotropic, while the static dielectric permittivity exhibits to be somewhat anisotropic due to the dominant ionic contributions in static dielectric permittivity.

1. Introduction

Alkaline-earth aluminates are important luminescent host materials [1–3] due to their high quantum efficiency, excellent physical and chemical properties and the easy preparation. For instance, rare-earth ions doped $SrAl_2O_4$ as long-lasting phosphors have been extensively studied in recent years [4–7]. $SrAl_2O_4$:Eu^{2+} phosphor has also attracted considerable attention for its mechanoluminescence behavior arising from the strain field induced by the application of an external stress [8–10]. However, only a few theoretical calculations on $SrAl_2O_4$ can be found in literatures. The electronic structure of $SrAl_2O_4$ was calculated by using the scalar-relativistic full potential linearized augmented plane wave method [11]. The theoretical calculations of elastic coefficients revealed that $SrAl_2O_4$ stuffed tridymite could be a relatively soft oxide [12]. The electronic properties of $SrAl_2O_4$:Eu^{2+} were investigated by using UV–VUV synchrotron radiation spectra and density functional theory calculations, which confirmed that the electrons were the main charge carriers mostly influencing the persistent luminescence process in this material [13].

Electronic property is fundamentally critical for the luminescent properties of solids. The electronic structure of host lattice could give rise to the fundamental absorption of excitation energy which may then be transferred to the luminescent centers (i.e. rare-earth ions) resulting in effective luminescence. Furthermore, lattice vibration (phonon) can also severely affect the luminescent quantum efficiency through the nonradiative transitions of multiphonon orbit–lattice relaxation of excited states in rare-earth ions doped crystals. For instance, the effective phonon energy with 283 cm^{-1} was estimated by the study of electron-vibrational interaction in persistent phosphors $Mg_xSr_{1-x}Al_2O_4$:Eu, Dy [14]. The present work provides a thorough investigation of structural, electronic, lattice dynamical, and dielectric properties of $SrAl_2O_4$ by using first-principles calculations. We also give the analysis and comparisons of the calculated results with the experiments available in literatures.

2. Calculation details

All calculations were performed using the ABINIT package [15,16], which is based on pseudopotentials and plane-waves. Exchange and correlation were treated in the local density approximation (LDA) and generalized gradient approximation (GGA) using density-functional theory (DFT) [17,18]. It relies on an efficient fast Fourier transform algorithm for the conversion of wave functions between real and reciprocal space on the adaptation to a fixed potential of the band-by-band conjugate gradient method and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential. The Teter parametrization fitting the Ceperley–Alder exchange-correlation data [19] was

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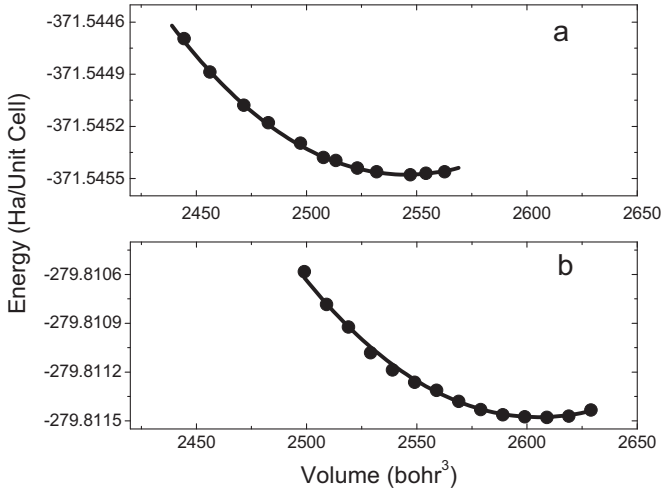

Fig. 1. Calculated total energies with LDA (a) and GGA (b) for $SrAl_2O_4$ as a function of volume. Dots represent calculated values and the solid lines are fitting results by using third-order Birch–Murnaghan equation of state.

applied for LDA calculations, and the Perdew–Burke–Ernzerhof (PBE) [20] functional was applied for GGA calculations. Relaxation of the lattice parameters and interatomic positions within the unit cell was performed using the Broyden–Fletcher–Goldfarb–Shanno algorithm [21] until the maximum component of force acting on any atoms is less than 1 mhartree/bohr.

Linear response properties were obtained as second-order derivatives of the total energy with respect to an external electric field or to atomic displacements within the framework of density functional perturbation theory (DFPT) [22,23]. The electronic wavefunctions were expanded in plane waves up to a kinetic energy cut-off of 40 Ha (1 Ha = 27.211 eV), and it was confirmed that the total energies were converged within 1 meV/atom with respect to that at 45 Ha. The Brillouin zone (BZ) was sampled by a $4 \times 4 \times 4$ Monkhorst-Pack [24] mesh of k points, with the total energies converged within 0.1 meV/atom with respect to that by a $4 \times 4 \times 8$ Monkhorst-Pack. The BZ sampling and the kinetic energy cutoff were sufficient to guarantee an excellent convergence within 1 cm^{-1} for the calculated phonon frequencies.

3. Results and discussion

3.1. Structural properties

$SrAl_2O_4$ belongs to monoclinic structure (space group $P2_1$) containing four formula units (28 atoms). All the atoms occupy 2a sites according to the Wyckoff notation. $SrAl_2O_4$ has a stuffed tridymite-like structure built up of layers of $[AlO_4]^{5-}$ tetrahedra sharing corners that give rise to six corner rings. Sr^{2+} ions are located in the cavities of the framework of $[AlO_4]^{5-}$ tetrahedra, occupying two different sites with low symmetry and coordinated by nine oxygen atoms [25].

Fig. 1 shows the calculated total energies of $SrAl_2O_4$ with LDA (a) and GGA (b) as a function of volume. The calculated equilibrium volumes (V_0), the bulk modulus (B_0) and the first pressure derivative of bulk modulus (B_0') are determined by fitting the total energy as a function of volume to the third-order Birch–Murnaghan equation of state (EOS) [26]. The results are summarized in Table 1. The calculated lattice parameters are found to be in excellent agreement with experimental data [27]. It is found that LDA underestimates the lattice parameters, while GGA overestimates them. The errors on the lattice parameters for LDA and GGA are both less than 1%. The consistency of the calculated lattice parameters with experimental

Table 1
Structure parameters of $SrAl_2O_4$.

	Exp.	LDA	GGA
a (Å)	8.447	8.412	8.482
b (Å)	8.816	8.792	8.836
c (Å)	5.163	5.132	5.203
β (°)	93.420	93.420	93.417
V (Å^3)	383.797	378.878	389.256
B (GPa)	102	90.5	112.6
B'	–	2.5	4.3

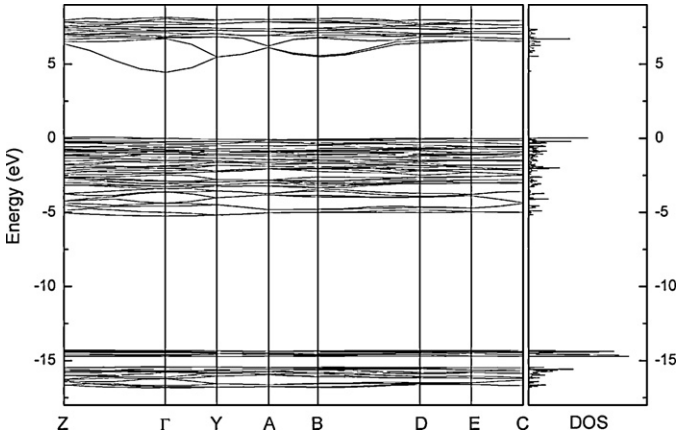

Fig. 2. Electronic band structure of $SrAl_2O_4$ calculated with LDA.

results shows that the theoretical method is valid. The calculated bulk moduli (90.5 and 112.6 GPa for LDA and GGA, respectively) are both close to the experimental value of 102 GPa [28]. The first pressure derivatives of the bulk modulus are 2.5 and 4.3 for LDA and GGA, respectively. Currently, there is no experimental value available for comparison. The large difference of B_0' for LDA and GGA is probably due to the high sensitivity for the derivative of pressure.

3.2. Electronic properties

The electronic band structure and the densities of states (DOS) of $SrAl_2O_4$ are calculated by both LDA and GGA methods. Due to the similar results of LDA and GGA, the calculated band structures and DOS profiles with LDA are presented in Figs. 2 and 3.

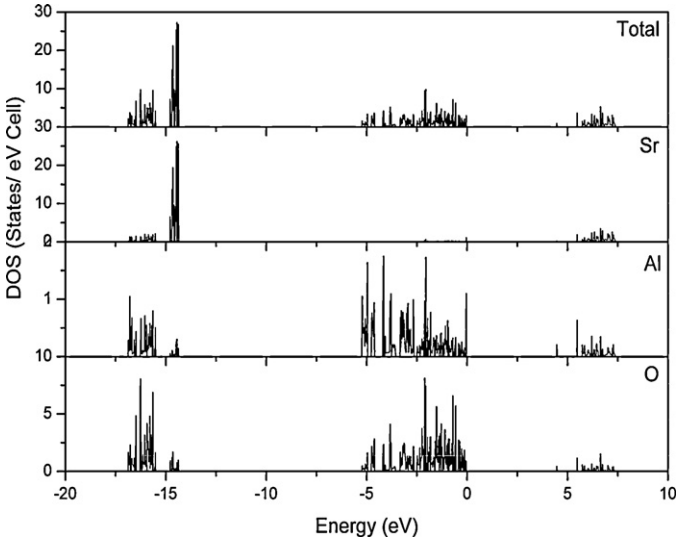

Fig. 3. Electronic density of states $SrAl_2O_4$ calculated with LDA.