

Band structure calculations on the monoclinic bulk and nano-SrAl₂O₄ crystals

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Received 21 October 2004; received in revised form 27 November 2004; accepted 28 November 2004

Abstract

The electronic structure of SrAl₂O₄ is calculated by density functional method and exchange and correlation have been treated by the generalized gradient approximation within the scheme due to Perdew–Burke–Ernzerhof. The bond length and bond covalency are also calculated by chemical bond method. Compared with the SrAl₂O₄ bulk crystal, the bond covalency of nanocrystal has an increasing trend; its band gap also is wider; the bond lengths of SrAl₂O₄ nanocrystal become shorter, which is responsible for the change of the covalency and band gap.

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Keywords: Electronic structure; Nano-SrAl₂O₄ crystal; Lattice parameters

1. Introduction

Nanocrystals have been investigated widely in recent years because their significant properties differ from the bulk [1–4]. Most of the research efforts are devoted to optical properties induced by quantum confinement and it is expected that they can act as a potential kind of luminescent material both in fundamental research and application [5]. SrAl₂O₄ is a good host material because it has a very wide band gap (experimental value 6.5 eV). Many researchers have reported more optical properties of rare-earth (e.g., Eu and Dy) doped SrAl₂O₄ and solid-state method is major. However, we prepared nanocrystal SrAl₂O₄:Eu²⁺ by combustion synthesis (the bulk material was prepared by solid-state reaction). In the present work, we focus our attention on their structural and electronic properties and report the calculated results by chemical bond method [6,7] and density functional method (generalized gradient approximation

(GGA) with exchange-correlation functional Perdew–Burke–Ernzerhof (PBE) [8]).

This paper is organized as follow. Section 2 briefly describes the method and relevant computational parameters used in the calculations. In Section 3, we introduce the crystal structure of SrAl₂O₄ and experimental cell parameters. In Section 4, we discuss the calculated results in terms of band structure and density of states (DOS). Finally, we give summary of the work in Section 5.

2. Calculation details

The first-principles band calculations have been performed using CASTEP code [9], and exchange and correlation have been treated by the GGA within the scheme due to PBE. The Kohn–Sham wave functions of valence electrons were expanded to a basis set of plane waves within specified cutoff energy ($E_{\text{cut}} = 300$ eV). The Brillouin zone is sampled by a $1 \times 1 \times 1$ Monkhorst–Pack [10] mesh of K points. Valence electrons were

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described by Vanderbilt-type nonlocal ultrasoft pseudo-potentials while tightly bound core electrons were ignored [11]. The bond length and bond covalency of Sr–O and Al–O bonds were calculated by use of chemical bond method.

3. Structure

SrAl_2O_4 has a monoclinic structure of which the space is $P2_1$ and contains four formula units for a total of 28 atoms. Fig. 1 shows a unit cell of SrAl_2O_4 . All of the constituent atoms occupy $2a$ sites according to the Wyckoff notation [12]. The monoclinic structure is composed of corner-sheared AlO_4^{2-} tetrahedrons forming zigzag strings, and Sr ions penetrate the opening of

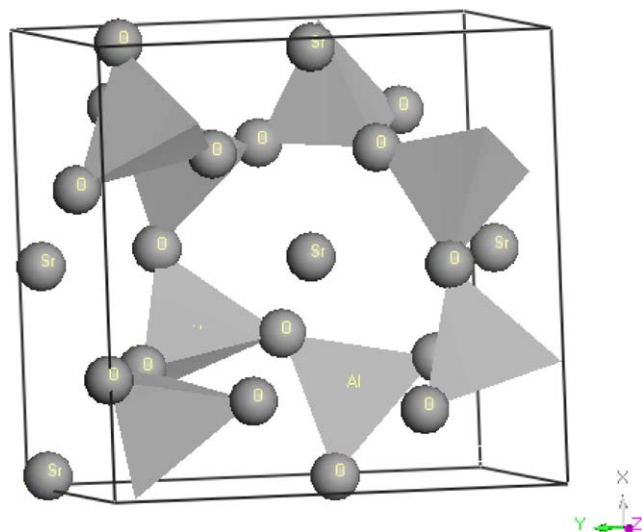


Fig. 1. Crystal structure of SrAl_2O_4 .

the structure to compensate the electric charge of AlO_4^{2-} . In electronic-structure calculations, we have firstly determined more accurate unit-cell parameters of SrAl_2O_4 crystal from a pattern-fitting analysis software.

Table 1
Bond lengths (Å) in SrAl_2O_4 crystals

	Distance in bulk (Å)	Distance in nano (Å)
Sr(1)–O(1)	2.6672	2.6539
Sr(1)–O(2)	2.6769	2.6639
Sr(1)–O(3)	3.5221	3.5020
Sr(1)–O(3)	2.5206	2.5135
Sr(1)–O(4)	2.5594	2.5521
Sr(1)–O(6)	3.1136	3.0978
Sr(1)–O(7)	2.5721	2.5639
Sr(1)–O(7)	2.7321	2.7220
Sr(2)–O(1)	2.7729	2.7642
Sr(2)–O(2)	2.6972	2.6886
Sr(2)–O(4)	2.6096	2.5936
Sr(2)–O(5)	2.5081	2.4998
Sr(2)–O(5)	3.2818	3.2684
Sr(2)–O(6)	2.5566	2.5474
Sr(2)–O(8)	2.5358	2.5242
Sr(2)–O(8)	2.9909	2.9793
Al(1)–O(2)	1.7347	1.7252
Al(1)–O(4)	1.7407	1.7355
Al(1)–O(6)	1.7370	1.7312
Al(1)–O(8)	1.7702	1.7630
Al(2)–O(1)	1.7586	1.7533
Al(2)–O(3)	1.7537	1.7478
Al(2)–O(5)	1.7720	1.7651
Al(2)–O(8)	1.7336	1.7243
Al(3)–O(1)	1.7589	1.7520
Al(3)–O(4)	1.7623	1.7563
Al(3)–O(5)	1.7440	1.7356
Al(3)–O(7)	1.7589	1.7523
Al(4)–O(2)	1.7539	1.7465
Al(4)–O(3)	1.7304	1.7248
Al(4)–O(6)	1.7555	1.7504
Al(4)–O(7)	1.7628	1.7533

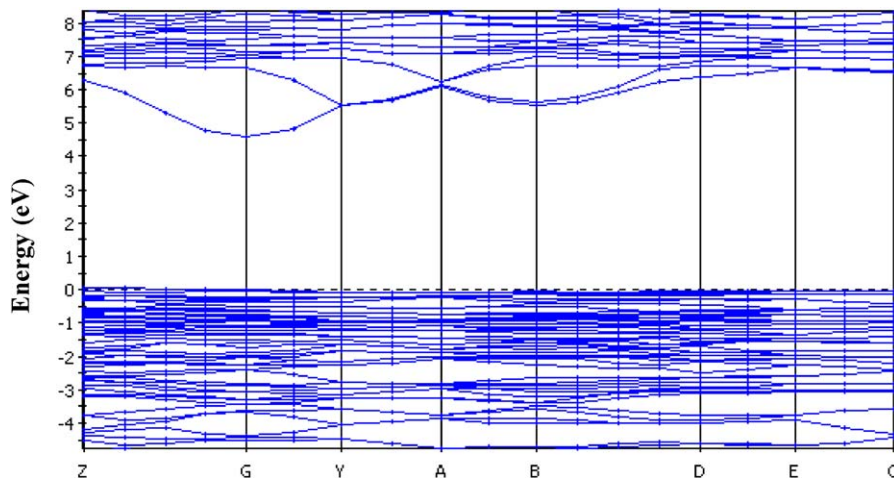


Fig. 2. Band structure of nano- SrAl_2O_4 along the principal high-symmetry directions in the Brillouin zone.

The values of both samples are roughly matched with SrAl_2O_4 standard values given in JCPDS (No. 34-379). It is indexed on a monoclinic lattice with cell parameters $a = 8.443 \pm 0.0007 \text{ \AA}$, $b = 8.810 \pm 0.0009 \text{ \AA}$, $c = 5.151 \pm 0.0008 \text{ \AA}$, $\beta = 93.41 \pm 0.0093^\circ$ for bulk material, and $a = 8.406 \pm 0.0007 \text{ \AA}$, $b = 8.789 \pm 0.0008 \text{ \AA}$, $c = 5.141 \pm 0.0120 \text{ \AA}$, $\beta = 93.24 \pm 0.0020^\circ$ for nanocrystal. Compared to the bulk material, the reduction in unit-cell volume was observed, showing the distortion of the monoclinic lattice in nanocrystal.

4. Band structure and density of state

The calculated band structure along the various symmetry lines is given in Fig. 2 only for nano- SrAl_2O_4 crystal since the band structure of bulk material is very similar. We notice that the minimum forbidden gap of nanocrystal is 4.519 eV, while that of bulk material is 4.479 eV. The band gap of nano- SrAl_2O_4 increases by 0.040 eV than that of bulk SrAl_2O_4 . However, it should be recalled that theoretically derived band gaps in

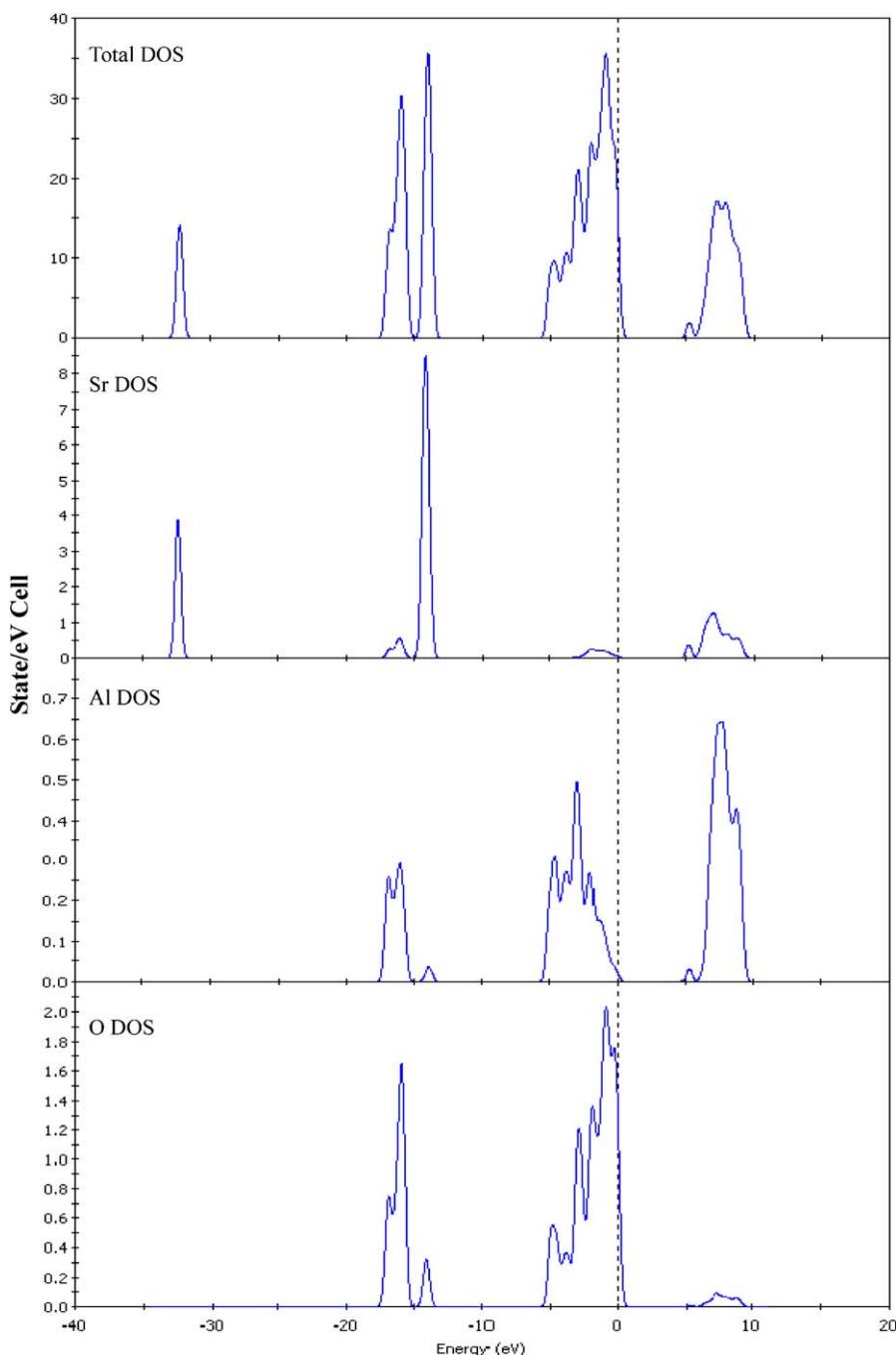


Fig. 3. Calculated DOS of nano- SrAl_2O_4 crystal.

Table 2
Calculated bond covalency (%) of SrAl₂O₄ crystals

	Covalency in bulk	Covalency in nano
Sr(1)–O(1)	0.0504	0.0509
Sr(1)–O(2)	0.0504	0.0508
Sr(1)–O(3)	0.0476	0.0480
Sr(1)–O(3)	0.0516	0.0521
Sr(1)–O(4)	0.0513	0.0517
Sr(1)–O(6)	0.0482	0.0486
Sr(1)–O(7)	0.0511	0.0516
Sr(1)–O(7)	0.0499	0.0504
Sr(2)–O(1)	0.0497	0.0501
Sr(2)–O(2)	0.0501	0.0506
Sr(2)–O(4)	0.0508	0.0513
Sr(2)–O(5)	0.0478	0.0482
Sr(2)–O(5)	0.0517	0.0521
Sr(2)–O(6)	0.0512	0.0517
Sr(2)–O(8)	0.0514	0.0519
Sr(2)–O(8)	0.0486	0.0490
Al(1)–O(2)	0.1846	0.1862
Al(1)–O(4)	0.1844	0.1858
Al(1)–O(6)	0.1845	0.1859
Al(1)–O(8)	0.1832	0.1846
Al(2)–O(1)	0.1836	0.1849
Al(2)–O(3)	0.1837	0.1852
Al(2)–O(5)	0.1830	0.1844
Al(2)–O(8)	0.1846	0.1862
Al(3)–O(1)	0.1835	0.1849
Al(3)–O(4)	0.1833	0.1848
Al(3)–O(5)	0.1841	0.1856
Al(3)–O(7)	0.1834	0.1849
Al(4)–O(2)	0.1836	0.1851
Al(4)–O(3)	0.1846	0.1860
Al(4)–O(6)	0.1835	0.1849
Al(4)–O(7)	0.1832	0.1848

semiconductors and insulators may be underestimated using first-principle methods. This does not affect the accuracy of the description of the total energy and related properties of crystals and molecules. Using the determined unit-cell parameters of SrAl₂O₄ crystal and the structural study of polycrystalline SrAl₂O₄ by Schulze et al. [12], we were able to identify Sr²⁺ in two different sites with low symmetry and coordinated by eight oxygens and Al³⁺ by four oxygens. The bond length of Sr–O and Al–O is shown in Table 1, which is calculated by chemical bond method. The bond length of nanocrystal is shorter than that of bulk material, which is responsible for band gap change in bulk and nanocrystal according to the chemical bond theory.

The DOS for bulk and nano-SrAl₂O₄ crystal also shows close similarities, so we only present the plots of the DOS in nanocrystal. Since the partial DOS (PDOS) is a useful tool to analyze the nature of the chemical bonding in solids, we display PDOS plots for nano-SrAl₂O₄ crystal in Fig. 3. In general, the polyatomic oxide has a finite energy gap between the valence and

conduction bands. The O 2*p* orbital has the major contribution to the valence band, while the conduction band is mainly constructed from the Sr 5*s* orbital, with a few contributions of Al 3*s*, Al 3*p* and O 2*p*. Although a small overlapping is also observed between Sr 5*s*, Sr 5*p* and O 2*p* orbitals, the contribution is less than that between Al 3*s*, Al 3*p* and O 2*p* orbitals. This indicates a stronger interaction or higher bond covalency of Al–O than that of Sr–O. This is also confirmed by the quantitative bond covalency calculation (Table 2). In addition, compared with the bulk crystal, the bond covalency of nanocrystal has an increasing trend, which is related to the change of the bond length.

5. Conclusions

In this paper, the band structures of monoclinic bulk and nano-SrAl₂O₄ crystals are calculated using density functional method (GGA with exchange-correlation functional PBE). The bond length and bond covalency are also calculated by chemical bond method. The calculated results show that the band gap of nano-SrAl₂O₄ crystal becomes wide compared with the bulk crystal. In addition, the bond lengths of nano-SrAl₂O₄ crystal are shorter than that of the bulk counterpart and the bond covalency of nano-SrAl₂O₄ crystal also has an increasing trend. It is suggested that the change of the structural and optical properties in nanocrystal is related to the change of the lattice parameters.

Acknowledgments

The authors are indebted to Yanshan University for computing time.

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