First-principles study of the structural, mechanical and electronic properties of ZnX_2O_4 (X=Al, Cr and Ga)*

Zhang Liang(张 良)[a)b)], Ji Guang-Fu(姬广富)[b)†], Zhao Feng(赵 峰)[a)], and Gong Zi-Zheng(龚自正)[c)]

[a)] *Science and Technology of Shock Wave and Detonation Physics Laboratory, Institute of Fluid Physics, Chinese Academy of Engineering Physics, Mianyang* 621900, *China*

[b)] *College of Physical Science and Technology, Sichuan University, Chengdu* 610065, *China*

[c)] *Beijing Institute of Spacecraft Environment Engineering, Beijing* 100094, *China*

(Received 25 September 2010; revised manuscript received 4 November 2010)

This paper performs first-principles calculations to study the structural, mechanical and electronic properties of the spinels $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$, using density functional theory with the plane-wave pseudopotential method. Our calculations are in good agreement with previous theoretical calculations and the available experimental data. The studies in this paper focus on the evolution of the mechanical properties of $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$ under hydrostatic pressure. The results show that the cubic phases of $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$ become unstable at about 50 GPa, 40 GPa and 25 GPa, respectively. From analysis of the band structure of the three compounds at equilibrium volume, it obtains a direct band gap of 4.35 eV for $ZnAl_2O_4$ and 0.89 eV for $ZnCr_2O_4$, while $ZnGa_2O_4$ has an indirect band gap of 2.73 eV.

Keywords: first-principles calculation, phase transition, elastic constants, bandstructure

PACS: 71.15.Mb, 64.60.A–, 62.20.D–, 71.20.–B **DOI:** 10.1088/1674-1056/20/4/047102

1. Introduction

Oxide spinel compounds are an important component of the Earth's crust and mantle, as well as that of lunar rocks and meteorites. These compounds are promising ceramics and exhibit many different and interesting optical, electronic, mechanical, elastic, structural and magnetic properties. Spinels have a general chemical formula, AB_2O_4, and crystallize in a cubic structure. They have cubic symmetry, with a space group $Fd3m$ and 8 formula units per unit cell. The unit cell contains 32 oxygen atoms in cubic close packing and 24 cations (A and B). The A cations are divalent while the B cations are trivalent. The spinels comprise of a rich variety of compounds.[1,2] which are commonly divided into two kinds of structures: 'normal' and 'inverse' structures.

In a 'normal' spinel structure, the divalent A cations fill one eighth of the tetrahedral sites and the trivalent B cations enter one half of the octahedral sites; in an 'inverse' structure all the A cations and half of the B cations occupy the octahedral positions, while the other half of the B cations fill the tetrahedral sites. Intermediate atomic distributions often occur and are characterized by the degree of inversion. While many cubic oxide spinels show a varying extent of cation disorder,[1−3] ZnX_2O_4 (X = Al, Ga, and Cr) show only small departures from the cation distribution of an ideal spinel structure.[4,5] These three compounds can be used to describe similar spinels with a small degree of cation disorder. Therefore, many experiments and theories have attempted to obtain a better understanding of their properties. The cubic spinel $ZnAl_2O_4$ structure was characterized experimentally by Levy *et al.* up to 43 GPa with no observation of a phase transition.[4] Reichmann and Jacobsen investigated the single-crystal elastic constants and sound velocities of $ZnAl_2O_4$ by gigahertz ultrasonic interferometer in a diamond anvil cell.[6] Joo and Jung studied the stability of a $ZnAl_2O_4$ catalyst for reverse-water-gas-shift reactions at temperatures ranging from 673 K to 873 K.[7] Ha *et al.* discussed some physical properties of $ZnAl_2O_4$ when the samples were annealed at various temperatures.[8]

*Project supported by the Open Research Fund of the State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology (Grant No. GCTKF2010017) and the National Basic Research Program of China (Grant No. 2010CB731600).

†Corresponding author. E-mail: cyfjkf@caep.ac.cn

© 2011 Chinese Physical Society and IOP Publishing Ltd

Ciupina *et al.* characterized the structure of synthesized $ZnAl_2O_4$ using x-ray diffraction (XRD) analysis and electronic microscopy.[9] Errandonea *et al.* studied post-spinel transformations and the equation of state by means of room-temperature angle-dispersive XRD measurement of spinel $ZnGa_2O_4$ up to 56 GPa.[10] Goncalves *et al.* observed the formation of $ZnGa_2O_4$ in ZnO: Ga powders by XRD.[11] Krishna *et al.* investigated crystalline zinc gallate ($ZnGa_2O_4$) thin films by employing the pulsed laser deposition technique at room temperature.[12] Wang *et al.* reported a pressure-induced phase transition at 17.5 GPa in $ZnCr_2O_4$ by means of an *in situ* Raman spectroscope.[13] Levy *et al.* studied P–V the equation of state and thermal expansion of synthetic zinc chromium ($ZnCr_2O_4$) using a diamond anvil cell.[14]

From the theoretical point of view, Lopez and Romero performed first-principles calculations to study high-pressure phase transitions in $ZnAl_2O_4$ and $ZnGa_2O_4$.[15] Fang *et al.* investigated the phonon spectrum of a $ZnAl_2O_4$ spinel by both inelastic neutron-scatter and first-principles calculations.[16] Catti *et al.* predicted that $ZnCr_2O_4$ would be decomposed into oxides at 34 GPa by *ab initio* methods.[17]

As far as we know, only Ref. [15] investigated the high-pressure properties of ZnX_2O_4 (X=Al, Ga). However, reference [15] mainly focused on a discussion of the phase transitions of two compounds. In order to shed more light on the understanding of the high-pressure properties of ZnX_2O_4 (X=Al, Ga and Cr) cubic spinels, we report a comparison of the high-pressure structural, elastic and electronic properties of $ZnAl_2O_4$, $ZnCr_2O_4$, and $ZnGa_2O_4$ up to 50 GPa in detail by means of first-principles calculations. The present research work contributes to a fuller understanding of the high-pressure behaviour of oxide spinels.

2. Model and method

In this paper, we focus on the structural, elastic and electronic properties under high pressure by plane-wave pseudopotential density functional theory (DFT) through the Cambridge Serial Total Energy Package (CASTEP) program.[18,19] In the electronic structure calculations, an ultrasoft pseudopotential[20] is employed for all the ion-electron interactions. The exchange–correlation interaction for $ZnAl_2O_4$ and $ZnGa_2O_4$ is treated within the local density approximation (LDA) from the Ceperley–Alder scheme parameterized by Perdew and Zunger,[21,22] while for $ZnCr_2O_4$ using the generalized gradient approximation (GGA) with revised Perdew–Burke–Ernzerhof (RPBE) functions.[23] The Broyden-Fletcher–Groldfarb–Shanno (BFGS) scheme[24] is used to perform the cell optimization. A plane-wave basis set with an energy cut-off of 340 eV is applied. The k integrations over the Brillouin zone are performed up to 6×6×6 Monkhorst–Pack mesh,[25,26] where the self-consistent calculations are considered to be converged when the total energy is within 10^{-6} eV/atom.

3. Results and discussion

3.1. Structural properties

At ambient pressure zinc gallate ($ZnGa_2O_4$), zinc chromium ($ZnCr_2O_4$) and gahnite ($ZnAl_2O_4$) crystallize in a cubic spinel structure with space group $Fd3m$ (227). The Zn atoms are located at the Wyckoff positions, 8a (1/8, 1/8, 1/8) tetrahedral sites, while the Ga, Cr or Al atoms are located at the 16d (1/2, 1/2, 1/2) octahedral sites and the oxygen atoms at 32e (u, u, u), where u is approximately 1/4. The spinel crystal structure is only characterized by the lattice parameter a and the internal parameter u.

In this work, compared with $ZnAl_2O_4$ and $ZnGa_2O_4$ within the LDA, the calculation presents a better result for $ZnCr_2O_4$ within the GGA. In Table 1, we list our calculated results of the lattice constant a_0, the internal parameter u, the bulk modulus B_0 and the bond distances (d_{Zn-O} and d_{X-O}) of these compounds together with the available experimental and theoretical data.

We know that the use of the GGA exchange–correlation functional in theoretical calculations overestimates the lattice parameters and underestimates the bulk modulus, whereas LDA presents the opposite behaviour. Taking the external factor and purity of the material into account, we suppose that our calculated results are in good agreement with the experimental models[4,5,33] and other available experimental data and calculations. Our calculated results of $ZnAl_2O_4$, $ZnCr_2O_4$ and $ZnGa_2O_4$ offer argumentation for experiments and supplementation for theoretical studies.

Table 1. Calculated lattice constant a_0 in (Å, 1 Å=0.1 nm), bulk modulus B_0 (in GPa), internal parameter u, bond distances (d_{Zn-O} and d_{X-O}) in (Å) compared to the available experimental results and the other calculations of ZnX_2O_4 (X=Al, Ga, and Cr).

		a_0/Å	u	B_0/GPa	d_{Zn-O}/Å	d_{X-O}/Å
$ZnAl_2O_4$	this work	7.98 (LDA)	0.26	202.20	1.92	1.89
	Experimental model[4]	8.09	0.27	201.70	1.97	1.91
	expt.	8.02[13]	0.26[13]	219.65[13]	1.93[13]	1.90[13]
		8.00[14]	0.39[14]	218[14]	1.93[14]	1.89[14]
		8.09[32]	0.26[32]		1.94[32]	1.92[32]
	calc.	8.05[27]	0.27[27]	183[27]]	8.02[31]	1.90[31]
		8.09[28]	0.26[31]	206.91[30]	1.93[31]	
		8.02[31]		219.65[31]		
$ZnGa_2O_4$	This work	8.28 (LDA)	0.26	192.87	1.95	1.98
	Experimental model[5]	8.33	0.26		1.98	1.99
	expt.	8.34[10]	0.26[10]	233[10]	1.95[10]	2.00 [10]
		8.29[13]	0.26[13]	218.93[13]	1.95[13]	1.99[13]
		8.33[32]	0.26[32]		1.97[32]	1.99[32]
	calc.	8.41[27]	0.26[27]	156[27]	1.97[5]	1.99[5]
		8.25[29]	0.26[29]	207.52[30]	1.94[29]	1.98[29]
		7.98[30]	0.27[30]	218.93[31]	1.97[30]	1.87[30]
		8.29[31]	0.26[31]		1.95[31]	1.99[31]
$ZnCr_2O_4$	This work	8.34 (GGA)	0.26	173.34	1.95	2.00
	Experimental model[34]	8.33	0.262		1.95	2.00
	expt.	8.33[34]		183.10[14]		
		8.33[35]				
	Calc.	8.33[14]		215[17]	1.95[17]	1.97[17]

In order to show the structural properties of these compounds under high pressure, the unit cells of ZnX_2O_4 compounds at the ground state have been applied at hydrostatic pressures ranging from 0 to 50 GPa, in steps of about 5 GPa. Optimization of the internal coordinates at each pressure is performed. The pressure dependence of the lattice parameter (a) and the internal parameter (u) is presented in Figs. 1 and 2.

The calculated equilibrium lattice constants (a_0) 7.98 Å and 8.275 Å are in good agreement with the experimental results of 8.091 Å[4] and 8.334 Å[5] for $ZnAl_2O_4$ and $ZnGa_2O_4$, respectively. Recently, CASTEP has been proven to be accurate by many calculations applied to understanding the structural properties.[36−46] We also performed a similar study for $ZnCr_2O_4$ using GGA in the RPBE functions.[23] We have obtained a similar result with an overestimation of the experimental lattice constant 8.327 Å of 0.19 %. There is a good agreement between our calculated results for these spinels and previous experimental data[4,14] and theoretical calculations[15,27] in Fig. 1. In Fig. 1, we can note that the lattice parameter a increases with the atomic number of X (Al, Cr and Ga). The lattice constants of $ZnCr_2O_4$ and $ZnGa_2O_4$ are almost the same while they are larger than that of $ZnAl_2O_4$. It seems that the variation of the lattice constants with the different electronic shells is larger than that with the same electron shells.

The values of the internal parameter u are found to be u = 0.264, 0.261 and 0.26, which agree with those of the experimental models, 0.265,[4] 0.262[5] and 0.262[33] for $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$, respectively. In Fig. 2, the results in this work for $ZnAl_2O_4$ and $ZnGa_2O_4$ are in good agreement with other calculations.[15,27] However, there is no other theoretical or experimental data for $ZnCr_2O_4$ to compare. As expected, the internal parameter u changes with pressure because of the differences between the Al^{+3}, Ga^{+3} and Cr^{+3}. Given that the divalent cations are located at the same sites in the three compounds, u should decrease with the increase of the size of the trivalent cation.[47] Moreover, all three compounds show negative slopes. It indicates that these spinels try to reach the ideal structure ($u = 0.25$) under pres-

sure.

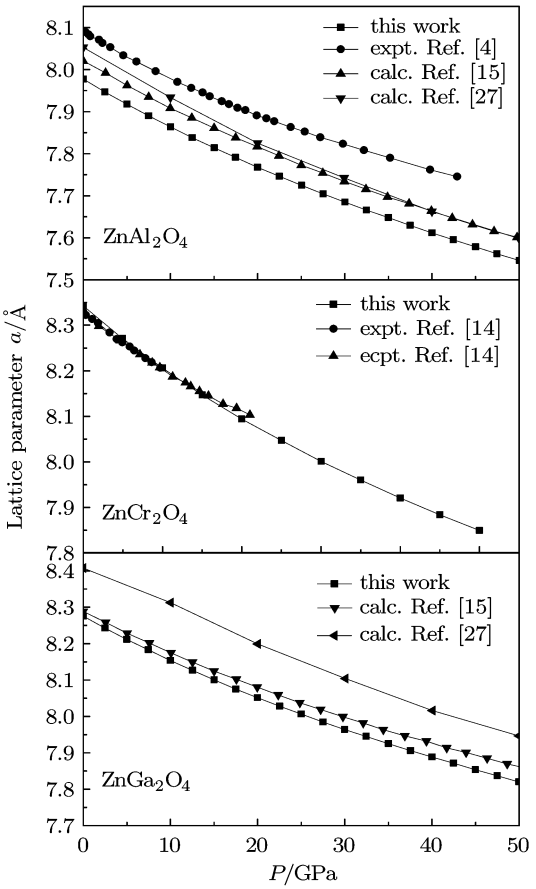


Fig. 1. Calculated pressure dependence of the lattice parameter a (Å) for $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$ compounds.

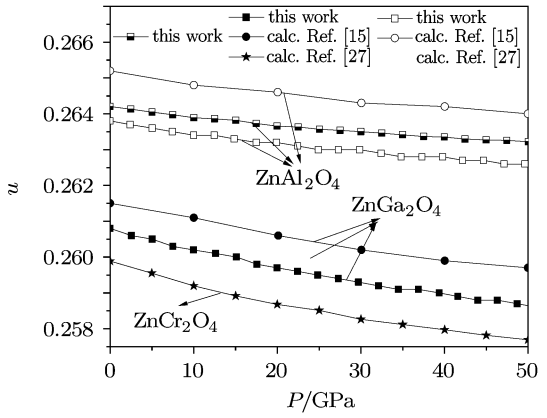


Fig. 2. Pressure dependence of the internal parameter u of the spinels $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$ compounds up to 50 GPa.

3.2. Mechanical properties

We extract the bulk modulus B_0 for $ZnAl_2O_4$ of 202.2 GPa and $ZnGa_2O_4$ of 192.87 GPa within the LDA and for $ZnCr_2O_4$ of 173.34 GPa within the GGA. Our results are in good agreement with previous experiments and theoretical calculations (see Table 1). It is noticed that the calculated bulk modulus values decrease from $ZnAl_2O_4$, $ZnGa_2O_4$ to $ZnCr_2O_4$ compounds. It suggests that $ZnCr_2O_4$ is more compressible than the other oxides. This is due essentially to the ion size differences among Al^{+3}, Ga^{+3} and Cr^{+3}.

The variations in the bulk modulus B (GPa) of the spinels $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$, with respect to pressure, are presented in Fig. 3. We can clearly observe a linear dependence in all curves of these spinels in the considered range of pressure. We also yield the pressure derivatives B': 3.73, 4.12, and 4.25 for $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$, respectively. Our calculated pressure derivatives B' for $ZnAl_2O_4$ and $ZnGa_2O_4$ are in good agreement with other calculations: 4.02,[15] 3.826,[27] 3.4,[48] 4.43[49] for $ZnAl_2O_4$ and 4.35,[15] 3.717,[27] 3.77,[30] 3.5[48] for $ZnGa_2O_4$. As far as we know, there is no literature with which to make a comparison with $ZnCr_2O_4$. It is found that the compressibility of the bulk modulus for these spinels increases from $ZnCr_2O_4$, $ZnGa_2O_4$ to $ZnAl_2O_4$ compounds. This is mainly because the material is easier to compress when the radius of the ion is longer. The sequences of the sizes of the ions are Al^{+3} <Ga^{+3} <Cr^{+3}.

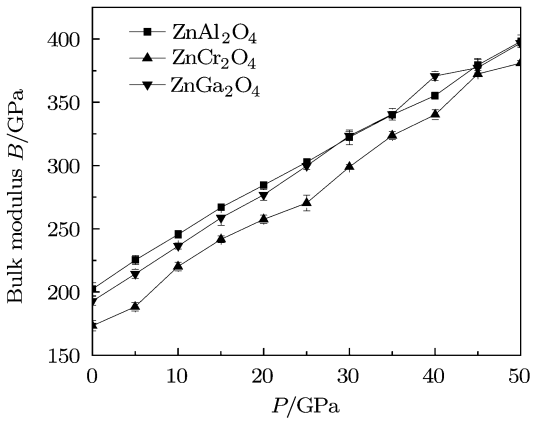


Fig. 3. Calculated pressure dependence of the bulk modulus B of the spinels $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$.

For the cubic phase, there are three independent symmetric elements (C_{11}, C_{12}, and C_{44}). In Fig. 4, we present the variation of the elastic constants (C_{11}, C_{12} and C_{44}) of $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$ with respect to the variation of pressure. Our calculated values of the elastic constants of $ZnAl_2O_4$ are in good agreement with the other calculation.[27] We also find that the corresponding elastic constants C_{11}, C_{12} and

C_{44} increase from $ZnCr_2O_4$, $ZnGa_2O_4$ to $ZnAl_2O_4$. As we know, for a cubic crystal, mechanical stability is judged from the following condition under isotropic pressure:[50]

$$\tilde{C}_{44} > 0, \quad \tilde{C}_{11} > |\tilde{C}_{12}|, \quad \tilde{C}_{11} + 2\tilde{C}_{12} > 0, \qquad (1)$$

where $\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P(\alpha = 1, 4)$, $\tilde{C}_{12} = C_{12} + P$. From the equation mentioned above, the medium condition can be rewritten as

$$C_{11} > C_{12} + 2P. \qquad (2)$$

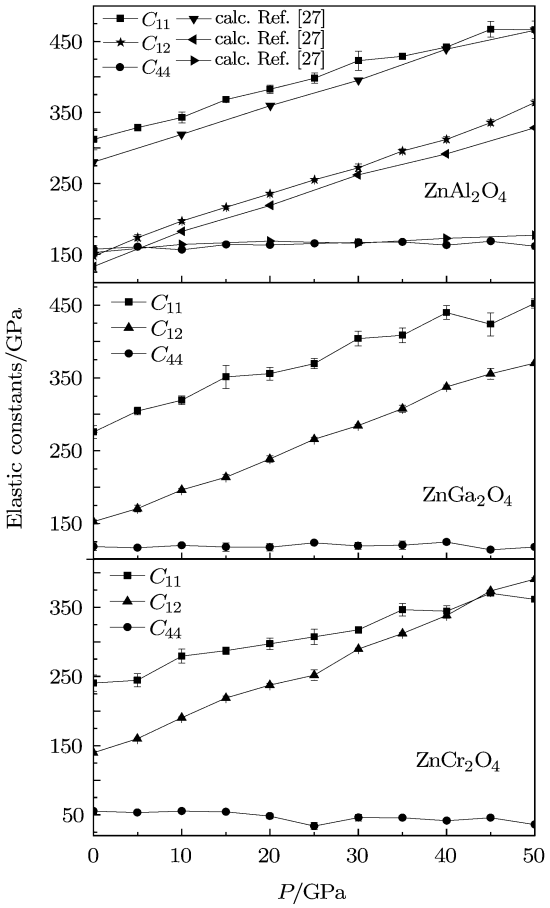


Fig. 4. Calculated pressure dependence of elastic constants (C_{11}, C_{12}, and C_{44}) of $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$.

Considering Eq. (2), we find that in fact for $ZnAl_2O_4$ the term $C_{12}+2P$ is equal to C_{11} at 50 GPa. So the cubic structure is unstable beyond 50 GPa, i.e. there is a phase transition at 50 GPa for $ZnAl_2O_4$. This is a small deviation from the other theoretical result 38.5 GPa.[15] However, experimentally, Levy *et al.* did not observe any phase transition up to 43 GPa by XRD at room temperature.[4] From the results of the experiment and our calculations mentioned above, we think that the phase transition may occur between 43 GPa and 50 GPa.[4] For $ZnGa_2O_4$, it is found that there is a phase transition at about 40 GPa. Our calculated result is in agreement with the experimental data 31.2 GPa[10] and the other theoretical calculation 33.44 GPa;[15] and for $ZnCr_2O_4$, our calculated pressure of the phase transition is 25 GPa, which corresponds to the experimental result of 17.5 GPa.[13] Our calculated pressures of the phase transition for $ZnCr_2O_4$, $ZnGa_2O_4$ and $ZnAl_2O_4$ are 25 GPa, 40 GPa and 50 GPa, respectively. We also note that the corresponding pressures increase from $ZnCr_2O_4$, $ZnGa_2O_4$ to $ZnAl_2O_4$. There are no other differences among $ZnCr_2O_4$, $ZnGa_2O_4$ and $ZnAl_2O_4$ except X (X=Cr, Ga, and Al) atoms. So we infer that the corresponding pressure-induced phase transition occurs at lower pressures with the decrease of the ion size in the similar compounds.

In ZnX_2O_4, the Zn cations are located at (1/8, 1/8, 1/8) positions, while the X cations are located at (1/2, 1/2, 1/2) sites and the oxygen at (u, u, u). The bond distances can be expressed as[30]

$$d_{\mathrm{Zn-O}} = \sqrt{3}a\left(u - \frac{1}{8}\right), \qquad (3)$$

$$d_{X-\mathrm{O}} = a\sqrt{\left(u - \frac{1}{2}\right)^2 + 2\left(u - \frac{1}{4}\right)^2}. \qquad (4)$$

We can obtain the bond distances of Zn–O and X–O from Eqs. (3) and (4) for $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$: 1.924 Å and 1.888 Å, 1.949 Å and 1.982 Å, 1.951 Å and 2.006 Å, respectively. The bond distances of ZnX_2O_4 obtained from the equations are almost equal to our calculated results and in excellent agreement with previous experiments and theoretical calculations (see Table 1).

It is shown that the bond distances $d_{\mathrm{Zn-O}}$ and $d_{X-\mathrm{O}}$ have a larger difference in $ZnAl_2O_4$ than in $ZnGa_2O_4$ and $ZnCr_2O_4$ in Fig. 5. Figure 5 shows that $d_{\mathrm{Zn-O}}$ decreases faster with pressure than $d_{\mathrm{Al-O}}$ and evidences that $d_{\mathrm{Zn-O}}$ is longer than $d_{\mathrm{Al-O}}$ in $ZnAl_2O_4$ when the opposite behaviour is true for $ZnGa_2O_4$ and $ZnCr_2O_4$. In this work we also yield the second-order derivatives d'' for $ZnAl_2O_4$, $ZnCr_2O_4$, and $ZnGa_2O_4$, 3.422×10^{-5} for Zn–O and 2.445×10^{-5} for Al–O, 5.278×10^{-5} for Zn–O and 3.032×10^{-5} for Cr–O, 4.074×10^{-5} for Zn–O and 2.680×10^{-5} for Ga–O, respectively. Generally we conclude that, along with the increase of pressure, the bond distances $d_{\mathrm{Zn-O}}$ and $d_{\mathrm{X-O}}$ get closer to each other in $ZnAl_2O_4$

when the opposite behaviour is shown in $ZnGa_2O_4$ and $ZnCr_2O_4$.

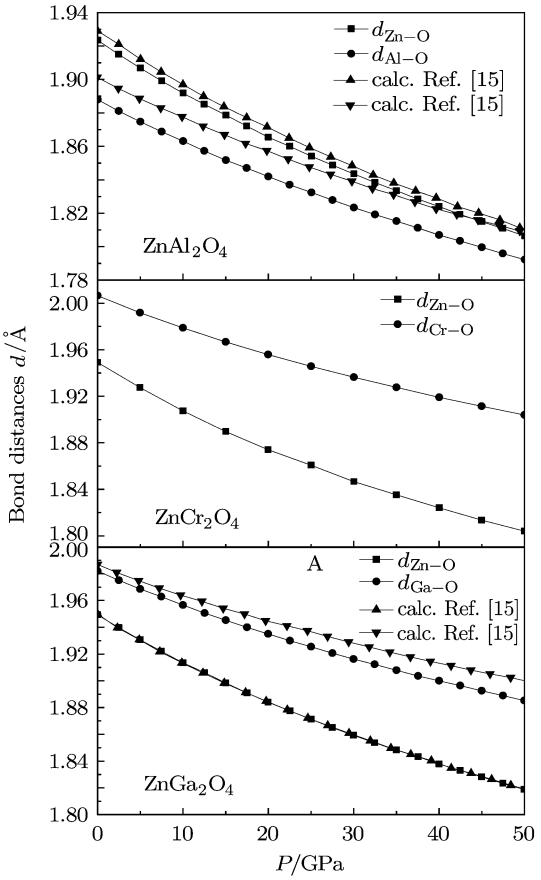


Fig. 5. Pressure dependence of bond distances d_{Zn-O}, d_{X-O} of the spinels up to 50 GPa.

3.3. Electronic properties

In this subsection, we display the band structure of $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$ along the high-symmetry directions. Lopez and Romero predicted that $ZnAl_2O_4$ has a direct band gap of 4.24 eV while $ZnGa_2O_4$ has an indirect band gap of 2.78 eV.[15] Pisani, Maitra, and Valenti reported a band gap of 2.7 eV with no indication whether it is direct or indirect.[29] Sampath, Kanhere, and Pandey obtained a direct band gap of 4.11 eV for $ZnAl_2O_4$ and 2.79 eV for $ZnGa_2O_4$ in tight-binding linear Muffin–Tin orbital (TB-LMTO) calculations.[49] Khenata *et al.* pointed out that $ZnAl_2O_4$ is a direct band gap insulator of about 4.28 eV.[51] Experimentally, the band gap of $ZnAl_2O_4$ is about 3.8 eV–3.9 eV by the reflectance spectroscopy measurements.[52] In Fig. 6, we obtained a direct band gap of 4.35 eV for $ZnAl_2O_4$ and 0.89 eV for $ZnCr_2O_4$ while $ZnGa_2O_4$ has an indirect band gap of 2.73 eV, which is in good agreement with previous calculations[15,29,38,51] and experiment.[52] It indicates that $ZnAl_2O_4$ is a direct band gap insulator and $ZnGa_2O_4$ is an indirect band gap semiconductor. In our calculation, $ZnCr_2O_4$ has a direct band gap of 0.89 eV. However, as far as we know, there is not any literature about the band structure of $ZnCr_2O_4$.

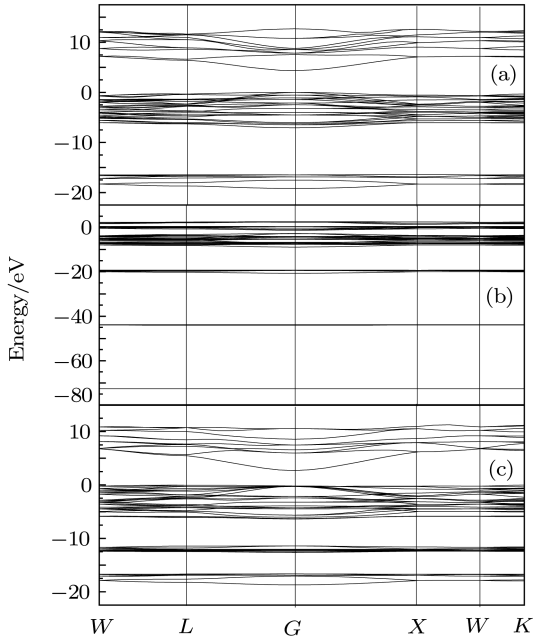


Fig. 6. Calculated band structure of $ZnAl_2O_4$ (a), $ZnCr_2O_4$ (b), and $ZnGa_2O_4$ (c) at equilibrium volume.

4. Conclusions

In this paper, first-principles DFT with the plane-wave pseudopotential methodplane-wave method is employed to study the structural, elastic and electronic properties of the spinels $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$. A summary of our results are listed below.

(i) Our calculated structural parameters of $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$ at zero pressure are in good agreement with previous calculations and the available experiment data.

(ii) Our results for the pressure dependence of the internal parameter u along with the other theoretical investigation shows that the spinels try to reach an ideal structure, which is characterized by $u = 0.25$. We also note that the internal parameter u decreases from $ZnAl_2O_4$, $ZnGa_2O_4$ to $ZnCr_2O_4$.

(iii) The calculated bulk modulus, elastic constants and their pressure derivatives are in good agreement with other calculations and available experimental results. We have found that the cubic structures of the spinels $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$ be-

come unstable at about 50 GPa, 40 GPa and 25 GPa, respectively.

(iv) From the analysis of the band structure of $ZnAl_2O_4$, $ZnGa_2O_4$ and $ZnCr_2O_4$, we infer that $ZnAl_2O_4$ is a wide band-gap insulator, $ZnGa_2O_4$ and $ZnCr_2O_4$ are semiconductors.

References

[1] Wyckoff R W G 1965 *Crystal Structures* (New York: Interscience) p. 821

[2] Sickafus K E and Hughes R 1999 *J. Am. Ceram. Soc.* **82** 3277

[3] Grimes N W 1975 *Phys. Technol.* **6** 22

[4] Levy D, Pavese A, Sani A and Pischedda V 2001 *Phys. Chem. Minerals* **28** 612

[5] Josties M, O'Neill H S C, Bente K and Brey G 1995 *Neues Jahrb. Mineral., Monatsh.* **6** 273

[6] Reichmann H J and Jacobsen S D 2006 *American Mineralogist* **91** 1049

[7] Joo O S and Jung K D 2003 *Bull. Korean Chem. Soc.* **24** 1

[8] Ha L H, Lanh P T, Long N N and Loan T T 2009 *J. Phys.: Conf. Ser.* **187** 012053

[9] Ciupina V, Carazeanu I and Prodan G 2004 *J. Optoelectron. Adv. Mater.* **6** 1317

[10] Errandonea D, Kumar R S, Manjon F J, Ursaki V V and Rusu E V 2009 *Phys. Rev.* B **79** 024103

[11] Goncalves A D S, Lima S A M D, Davolos M R, Antonio S G and Paiva-Santos C D O 2006 *J. Solid State Chem.* **179** 1330

[12] Krishna K M, Nisha M, Reshmi R, Manoj R, Asha A S and Jayaraj M K 2005 *Mater. Forum* **29** 243

[13] Wang Z, Lazor P, Saxena S K and Artioli G 2002 *J. Solid State Chem.* **165** 165

[14] Levy D, Diella V, Pavese A, Dapiaggi M and Sani A 2005 *American Mineralogist* **90** 1157

[15] Lopez S and Romero A H 2009 *Phys. Rev.* B **79** 214103

[16] Fang C M, Loong, C K, Wijs G A D and With G D 2002 *Phys. Rev.* B **66** 144301

[17] Catti M, Freyria F F, Zicovich C and Dovesi R 1999 *Phys. Chem. Minerals* **26** 389

[18] Payne M C, Teter M P, Allen D C, Arias T A and Joannopoulous J D 1992 *Rev. Mod. Phys.* **64** 1045

[19] Milman V, Winkler B, White J A, Packard C J, Payne M C, Akhmatskaya E V and Nobes R H 2000 *Int. J. Quantum Chem.* **77** 895

[20] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892

[21] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566

[22] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048

[23] Hammer B, Hansen L B and Norskov J K 1999 *Phys. Rev.* B **59** 7413

[24] Pfrommer B G, Côté M, Louie S G and Cohen M L 1977 *J. Comput. Phys.* **131** 233

[25] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[26] Monkhorst H J and Pack J D 1977 *Phys. Rev.* B **16** 1748

[27] Bouhemadou A and Khenata R 2006 *Phys. Lett.* A **360** 339

[28] Wei S H and Zhang S B 2001 *Phys. Rev.* B **63** 045112

[29] Pisani L, Maitra T and Valenti R 2006 *Phys. Rev.* B **73** 205204

[30] Recio J M, Franco R, Martin Pendas A, Blanco M A, Pueyo L and Pandey R 2001 *Phys. Rev.* B **63** 184101

[31] Lopez-Moreno S, Romero A H, Rodriguez Hernandez P and Munoz A 2009 *High Pressure Research* **29** 573

[32] Hill R J, Craig J R and Gibbs G V 1979 *Phys. Chem. Minerals* **4** 317

[33] Sawada H 1997 *Materials Reserch Bulletin* **32** 873

[34] Klemme S and Van Miltenburg J C 2004 *Mineralogical Magazine* **68** 515

[35] O'Neill H S C and Dollase W A 1994 *Physics and Chemistry of Minerals* **20** 541

[36] Cai Y X and Xu R 2009 *Chin. Phys. Lett.* **26** 113101

[37] Zhang F C, Zhang Z Y, Zhang W H, Yan J F and Yong J N 2009 *Chin. Phys.* B **18** 2508

[38] Yun J N, Zhang Z Y, Yan J F and Deng Z H 2010 *Chin. Phys.* B **19** 017101

[39] Shao X 2010 *Chin. Phys. Lett.* **27** 016101

[40] Tan C L, Cai W and Tian X H 2010 *Chin. Phys.* B **19** 037101

[41] Zhang H, Liu G L, Qi K Z, Zhang G Y, Xiao M Z and Zhu S L 2010 *Chin. Phys.* B **19** 048601

[42] Zuo C Y, Wen J and Bai Y L 2010 *Chin. Phys.* B **19** 047101

[43] Ci Z P, Wang Y H and Zhang J C 2010 *Chin. Phys.* B **19** 057803

[44] Liu J, Chen L, Liu Y, Dong H N and Zheng R L 2010 *Chin. Phys.* B **19** 037103

[45] Sun X W, Chu Y D, Liu Z J, Liu Y X, Wang C W and Liu W M 2005 *Acta Phys. Sin* **54** 5830 (in Chinese)

[46] Liu Z J, Cheng X L, Chen X R, Zhang H and Lu L Y 2004 *Chin. Phys.* **13** 1096

[47] Finger L W, Hazen R M and Hofmeister A M 1986 *Phys. Chem. Minerals* **13** 215

[48] Pandey R, Gale J D, Sampath S K and Recio J M 1999 *J. Am. Ceram. Soc.* **82** 3337

[49] Sampath S K, Kanhere D J and Pandey R 1999 *J. Phys.: Condens. Matter* **11** 3635

[50] Nye J F 1985 *Physical Properties of Crystals* (Oxford: Oxford University Press)

[51] Khenata R, Sahnoun M, Baltache H, Rerat M, Reshak A H, Al-Douri Y and Bouhafs B 2005 *Phys. Lett.* A **344** 271

[52] Sampath S K and Cordaro J F 1998 *J. Am. Ceram. Soc.* **81** 649