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Chemical bonding and elastic properties of quaternary arsenide oxides YZnAsO and LaZnAsO investigated by first principles

SHI Yi-ming[1], YE Shao-long[2]

1. Department of Basic Teaching, Hunan Institute of Technology, Hengyang 421000, China;
2. School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

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Abstract: The structural parameters, chemical bonding and elastic properties of the tetragonal phase quaternary arsenide oxides YZnAsO and LaZnAsO were investigated by using density-functional theory (DFT) within generalized gradient approximation (GGA). The GGA calculated structural parameters are in agreement with the experimental results. Population analysis suggests that the chemical bonding in YZnAsO and LaZnAsO can be classified as a mixture of ionic and covalent characteristic. Single-crystal elastic constants were calculated and the polycrystalline elastic modules were estimated according to Voigt, Reuss and Hill's approximations (VRH). The result shows that both YZnAsO and LaZnAsO are relatively soft materials exhibiting ductile behavior. The calculated polycrystalline elastic anisotropy result shows that LaZnAsO is more anisotropy in compressibility and YZnAsO is more anisotropy in shear.

Key words: YZnAsO; LaZnAsO; chemical bonding; elastic properties; density-functional theory; generalized gradient approximation; Voigt, Reuss and Hill's approximations

1 Introduction

The quaternary oxypnictide layered compounds REZnPO (RE=Y, La−Nd, Sm, Gd, Dy, Ho) and REZnAsO (RE=Y, La−Nd, Sm, Gd−Er) with the ZrCuSiAs-type structure have received considerable attention [1−6] because of the discovery of superconductivity in LaOFeP, LaNiOP and LaFeAsO(F)[7−11]. They have similar layered structures with alternating [ReO] and [ZnPn] (Pn=As, P) layers, and exhibit a wide variety of interesting electrical, optical, and magnetic properties. YZnAsO and LaZnAsO, which are isostructural to the layered rare-earth oxypnictides REZnAsO (RE=Y, La−Nd, Sm, Gd, Er), are semiconductor compounds with band gap of 1.5−2.3 eV in experimental investigation [2, 5] or 0.65−1.3 eV in theoretical calculation [6]. KAYANUMA et al [2] have successfully grown LaZnAsO thin films on MgO substrates with an epitaxial relationship of (001) LaZnAsO ‖ (001) MgO and [110] LaZnAsO ‖ [110] MgO. The electrical conductivity of the undoped LaZnAsO epitaxial films was 0.2 S/cm at room temperature. The positive Seebeck coefficients of the epitaxial film indicated a p-type semiconductor. The optical bandgap of LaZnAsO was estimated to be about 1.5 eV. It is expected that LaZnAsO may be a promising matrix for diluted magnetic semiconductors if Zn^{2+} is partially replaced by a divalent transition metal, such as Mn^{2+}. LINCKE et al [5] have synthesized well crystallized form REZnAsO (RE = Y, La) from the ingots of rare earth elements, arsenic, and ZnO in NaCl/KCl fluxes in sealed silica ampoules. The REZnAsO structures consist of alternate stacks of ($RE^{3+}O^{2-}$) and ($Zn^{2+}As^{3-}$) layers with covalent RE—O and Zn—As intralayer and weak ionic interlayer bonding. LaZnAsO and YZnAsO show an optical bandgap of E_g≈2.3 eV and E_g≈1.9 eV respectively. BANNIKOV et al [6] investigated the electronic properties and chemical bonding picture of LaZnAsO and YZnAsO. The band structures result showed that both of them are semiconductors with the band gaps of about 0.65 eV for LaZnAsO and 1.3 eV for YZnAsO. The bonding can be classified as a mixture of ionic and covalent contributions. To the best of our knowledge, there are no reports on the elastic properties of YZnAsO and

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Corresponding author: SHI Yi-min; Tel: +86-15111157635; E-mail: hn_syb@126.com
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LaZnAsO. However, elastic properties are very important for materials because they provide information on interatomic potentials and relate to various fundamental solid state phenomena such as interatomic bonding, equations of state, phonon spectra as well as specific heat capacity, thermal expansion, Debye temperature [12]. Most importantly, elastic properties are essential for many practical applications related to the mechanical properties of solid: load deflection, internal strain, thermoelastic stress, sound velocities and fracture toughness [12].

In this study, the chemical bonding and elastic properties of the tetragonal phase of YZnAsO and LaZnAsO are investigated using first principles calculations based on DFT.

2 Calculation details and models

The first principle calculations were based on DFT using a plan-wave expansion of the wave function implanted in CASTEP code [13]. The exchange correlation energy was calculated by the GGA with the Perdew-Burke-Ernzerhof (PBE) function [14]. The ionic cores were represented by norm-conserving pseudo-potentials [15−17] for Y, La, O, Zn and As atoms. The Y $4d^1 5s^2$ electrons, La $5d^1 6s^2$ electrons, O $2s^2 2p^4$ electrons, Zn $3d^{10} 4s^2$ electrons, and As $4s^2 4p^3$ electrons were explicitly treated as valence electrons. The Monkhorst and Pack scheme of k-point sampling was used for integration over the first Brillouin zone [18]. The cutoff energy was chosen to be 900 eV, and the Brillouin-zone sampling k-point set mesh parameters were 12×12×6. This set of parameters assure the total energy convergence of 5.0×10^{-6} eV/atom, the maximum force of 0.01 eV/Å, the maximum stress of 0.02 GPa and the maximum displacement of 5.0×10^{-4} Å.

3 Results and discussion

3.1 Geometry and structure properties

The crystal structure of the tetragonal phase of YZnAsO and LaZnAsO belongs to the space group *P*4/*nmm*, *Z*=2 (ZrCuSiAs type), where blocks [YO/LaO] are sandwiched with [ZnAs] blocks as depicted in Fig. 1. There are four inequivalent atomic positions: Y/La at 2*c* site (1/4, 1/4, $z_{Y/La}$), O at 2*a* site (3/4, 1/4, 0), Zn at 2*b* site (3/4, 1/4, 1/2), and As at 2*c* site (1/4, 1/4, z_{As}) [2, 5−6], in which $z_{Y/La}$ and z_{As} are the internal coordinates of Y/La and As, respectively. The experimental lattice parameters are $a=b$=0.394 2 nm and c=0.884 0 nm for YZnAsO, and $a=b$=0.409 6 nm and c=0.907 0 nm for LaZnAsO; and the internal coordinates of Y/La and As are reported as $z_{Y/La}$=0.121 7 and z_{As}=0.682 5 for YZnAsO and $z_{Y/La}$=0.133 7 and z_{As}=0.671 1 for LaZnAsO [2, 5−6], respectively.

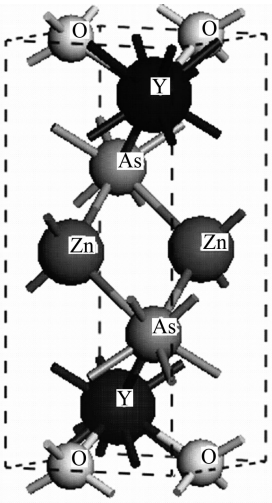

Fig. 1 Crystal structure sketch of YZnAsO

At the first stage the full structural optimization of this phase was performed both over the lattice parameters and the atomic positions including the internal coordinate $z_{Y/La}$ and z_{As}. The calculated optimization lattice parameters a, c, V and atomic coordinates compared with available experimental data [2, 5] for YZnAsO and LaZnAsO are summarized in Table 1, which show that the calculated structural parameters are in agreement with the experimental data.

3.2 Chemical bonding

The Mulliken bond population is useful for evaluating the bonding character in a material. A high value of the bond population indicates a covalent bond, and a low value indicates an ionic bond. Positive and negative values indicate bonding and anti-bonding states, respectively [17, 19]. The Mulliken atomic

Table 1 Calculated lattice parameters and atomic internal coordinate compared with experimental data [2, 5] for YZnAsO and LaZnAsO

Compound	Method	a/nm	c/nm	V/nm^3	$z_{Y/La}$	z_{As}
YZnAsO	Experiment	0.394 2	0.884 0	0.137 4	0.121 7	0.682 5
	Calculation	0.396 3	0.885 8	0.139 1	0.119 5	0.693 4
LaZnAsO	Experiment	0.409 6	0.907 0	0.152 1	0.133 7	0.671 1
	Calculation	0.400 1	0.899 0	0.143 9	0.123 0	0.683 0

population analyses of YZnAsO and LaZnAsO listed in Tables 2 and 3 show a charge transfer from [YO/LaO] block to [ZnAs] block, indicating that the internal of [YO/LaO] block and the [ZnAs] block is ionic character; and the bond population shows the intra-block of Y—O/La—O and Zn—As are covalent character. The chemical bondings in YZnAsO and LaZnAsO have a mixture of ionic and covalent characteristic, which is in agreement with the results of Refs. [5−6].

Table 2 Mulliken atomic population analysis of YZnAsO and LaZnAsO

Compound	Species	Population				Charge/e
		s	p	d	Total	
YZnAsO	Y	0.41	0.26	1.47	2.14	0.86
	O	1.84	4.89	0.00	6.72	−0.72
	Zn	0.67	1.34	9.96	11.98	0.02
	As	1.35	3.80	0.00	5.15	−0.15
LaZnAsO	La	0.22	0.12	1.46	1.79	1.21
	O	1.87	4.91	0.00	6.78	−0.78
	Zn	0.73	1.38	9.96	12.08	−0.08
	As	1.49	3.87	0.00	5.35	−0.35

Table 3 Mulliken bond population analysis of YZnAsO and LaZnAsO

Compound	Bond	Population	Length/nm
YZnAsO	Y—O	0.77	0.224 623
	Zn—AS	0.33	0.261 935
	Zn—Zn	0.88	0.280 202
	O—O	−0.10	0.280 202
LaZnAsO	La—O	0.54	0.226 381
	Zn—As	0.39	0.260 921
	Zn—Zn	0.75	0.282 911
	O—O	−0.08	0.282 911

3.3 Elastic properties

Elastic constants are defined by means of a Taylor expansion of the total energy, namely, the derivative of the energy as a function of a lattice strain [13]. The tetragonal phase YZnAsO and LaZnAsO crystals have six independent elastic constants C_{11}, C_{33}, C_{44}, C_{66}, C_{12} and C_{13} [20−21] which are presented in Table 4. For the tetragonal crystal, its mechanical stability requires that its independent elastic constants should satisfy the Born's stability criteria [20−21]:

$$C_{ii}>0\ (i=1, 3, 4, 6),$$
$$C_{11}-C_{12}>0,\ C_{11}+C_{33}-2C_{13}>0,$$
$$2(C_{11}+C_{12})+C_{33}+4C_{13}>0 \quad (1)$$

Table 4 Calculated single crystal elastic constants C_{ij}, bulk modulus B and compressibility coefficient β of YZnAsO and LaZnAsO

Compound	C_{11}	C_{33}	C_{44}	C_{66}
YZnAsO	189.96	116.55	13.86	37.42
LaZnAsO	227.57	112.33	35.05	50.32
Compound	C_{12}	C_{13}	B/GPa	β
YZnAsO	36.91	41.79	78.38	0.012 76
LaZnAsO	37.18	53.10	87.00	0.011 49

From Table 4, it can be seen that these criteria are all satisfied, which indicates that YZnAsO and LaZnAsO are mechanically stable. The single crystal bulk moduli B are 78.38 and 87.00 GPa for YZnAsO and LaZnAsO, respectively, which means that YZnAsO and LaZnAsO are soft materials. The polycrystal bulk modulus B and shear modulus G are estimated using the VRH approach in the following forms [20−23]:

$$B_V=(2C_{11}+2C_{12}+C_{33}+4C_{13})/9,$$
$$G_V=(M+3C_{11}-3C_{12}+12C_{44}+6C_{66})/30,$$
$$B_R=C^2/M,$$
$$G_R=15/[18B_V/C^2+6/(C_{11}-C_{12})+6/C_{44})+3/C_{66}],$$
$$C^2=(C_{11}+C_{12})C_{33}-2C_{13}^2,$$
$$M=C_{11}+C_{12}+2C_{33}-4C_{13},$$
$$B_H=(B_R+B_V)/2,$$
$$G_H=(G_R+G_V)/2 \quad (2)$$

The elastic modulus E and Poisson ratio ν are estimated by [20−21]

$$E=9BG/(3B+G),$$
$$\nu=(3B-E)/6B=(3B-2G)/(6B+2G) \quad (3)$$

All the calculated results are presented in Table 5. It can be seen that the value of B_H/G_H ratio for YZnAsO is 2.57 and for LaZnAsO is 1.87, which are larger than the critical value (1.75) separating ductile and brittle materials [20−21], indicating that both YZnAsO and LaZnAsO behave in a ductile manner, and YZnAsO is more ductile than LaZnAsO. It is known that the values of the Poisson ratio (ν) are minimal for covalent materials (ν=0.1), and increase for ionic systems [20−21]. In our case, the calculated Poisson ratios (ν) are 0.327 7 for YZnAsO and 0.272 9 for LaZnAsO, which means a sizable ionic contribution in intra-bonding.

The elastic anisotropy in compressibility (A_B) and shear (A_G) using the model in Ref. [24] for polycrystalline materials is

Table 5 Calculated polycrystalline elastic constants, elastic modulus E, Poisson ratio v and B_H/G_H of YZnAsO and LaZnAsO

Compound	B_V	B_R	B_H	G_V	G_R
YZnAsO	81.94	78.38	80.16	38.09	24.33
LaZnAsO	94.91	87.00	90.96	52.36	45.02
Compound	G_H	B_H/G_H	E/GPa	v	
YZnAsO	31.21	2.57	82.87	0.327 7	
LaZnAsO	48.69	1.87	123.95	0.272 9	

$$A_B = (B_V - B_R)/(B_V + B_R),$$
$$A_G = (G_V - G_R)/(G_V + G_R) \quad (4)$$

A value of zero represents elastic isotropy and a value of 100% is the largest possible anisotropy. The calculated polycrystalline elastic anisotropy in bulk modulus A_B and shear modulus A_G are listed in Table 6. It shows that the shear modulus anisotropy A_G is larger than the bulk modulus anisotropy A_B for both YZnAsO and LaZnAsO. And LaZnAsO is more anisotropy in compressibility (4.35%) and YZnAsO is more anisotropy in shear (22.04%). The larger anisotropy may produce cracking propagation during sample preparing and using. Utilization of very small YZnAsO and LaZnAsO particles would be a way of minimizing cracking.

Table 6 Calculated polycrystalline elastic anisotropy for bulk modulus A_B and shear modulus A_G of YZnAsO and LaZnAsO

Compound	A_B/%	A_G/%
YZnAsO	2.22	22.04
LaZnAsO	4.35	7.54

4 Conclusions

1) The structural parameters, chemical bonding and elastic properties of YZnAsO and LaZnAsO were investigated by first principles. The GGA calculated structural parameters are in agreement with the available experimental data.

2) The chemical bonding was analyzed. The results show that YZnAsO and LaZnAsO are a mixture of ionic and covalent characteristic.

3) The single crystal elastic constants were calculated, and the polycrystal bulks and shear modulus, elastic modulus, Poisson ratios and B_H/G_H were derived. The results show that both YZnAsO and LaZnAsO are mechanically stable and relatively soft materials behaving in a ductile manner.

4) The calculated polycrystalline elastic anisotropy in bulk modulus and anisotropy in shear modulus show that LaZnAsO is more anisotropy in compressibility and YZnAsO is more anisotropy in shear.

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四元砷氧化物 YZnAsO 和 LaZnAsO 的化学键和弹性性质的第一性原理研究

施毅敏[1], 叶绍龙[2]

1. 湖南工学院 基础教学部，衡阳 421000；
2. 中南大学 冶金科学与工程学院，长沙 410083

摘　要：利用基于密度泛函理论(DFT)的广义梯度近似(GGA)研究四方相四元砷氧化物 YZnAsO 和 LaZnAsO 的结构参数、化学键和弹性性质。结果表明，GGA 计算的结构参数与实验值吻合较好。布居分析显示 YZnAsO 和 LaZnAsO 中的化学键具有混合的离子−共价特征。计算得到了单晶的弹性常数，由 Voigt, Reuss 和 Hill (VRH)近似导出了多晶弹性模量，结果表明 YZnAsO 和 LaZnAsO 为具有一定延展性、相对较软的材料。多晶的弹性各向异性结果显示，LaZnAsO 的体模量各向异性相对较大，而 YZnAsO 的剪切模量各向异性相对较大。

关键词：YZnAsO；LaZnAsO；化学键；弹性性质；密度泛函理论；广义梯度近似；VRH 近似

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