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Density functional perturbation theory calculations of vibrational and thermodynamic properties of $Zn_{1-x}Be_xO$ alloys.

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ABSTRACT

The elastic, phonon and thermodynamic properties of $Zn_{1-x}Be_xO$ alloy are investigated by performing density functional theory (DFT) and density functional perturbation theory (DFPT) calculations. The calculated lattice parameters decreases with the increase of Be content that is in good agreement with the available theoretical and experimental data. The effect of Be composition on elastic constants was investigated for $Zn_{1-x}Be_xO$ alloys. Phonon dispersion curves show that $Zn_{1-x}Be_xO$ are dynamically stable. Thermodynamic properties, including Helmholtz free energy, enthalpy, entropy and heat capacity, were evaluated under quasi-harmonic approximation using the calculated phonon density of states. Finally, the results show that $Zn_{1-x}Be_xO$ alloys with lower Be content are more thermodynamically stable. The agreement between the present results and the known data that are available only for ZnO and BeO is generally satisfactory.

1. Introduction

Zinc oxide (ZnO) is an attractive metal oxide because of its applicability for blue and ultraviolet (UV) light emitting diodes (LED) and laser diodes (LD) [1,2]. This interest stems from the electronic properties including a large direct band gap (E_g=3.37 eV at 300 K), a large exciton binding energy (~60 meV), strong spontaneous (P_S=−0.57 C/m^2) and piezoelectric (e_{33}=1.20 C/m^2, e_{31}=−0.56 C/m^2) polarizations, as well as the relative ease of synthesis of ZnO powders, single crystals, thin films, and nanostructures [3,4]. Due to these properties, ZnO is a key enabling material in sensors and actuators, transparent thin-film electronics, and optoelectronic and piezoelectric devices [5,6]. Furthermore, its low material cost, high crystalline quality, and high radiation resistance make it a promising material to compete with GaN-based technologies [7].

Since reliable and stable p-type ZnO semiconductor material can now be grown using arsenic as dopant [8], a critical step for producing high-efficiency ZnO devices is the fabrication of ZnO-based quantum wells and superlattices. Since the electronic properties of ZnO can be readily tuned by doping or alloying, it is possible to expand its applications by designing materials systems for specific conditions and/or restrictions. For example, doping ZnO with Al (1–2%) or Ga (2–7%) results in a solid solution with a high carrier concentration (~10^{21} cm^{-3}) and a commensurate low electric resistivity (~10^{-5} Ω cm) [9,10]. Such materials have already been incorporated in flat panel displays and solar cells as transparent electrodes to replace the relatively expensive In–Sn oxide (ITO) [11].

ZnO-based multiple quantum well structures such as ultra thin ZnO/$Zn_{1-x}Mg_xO$ multi layers may provide better

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Table 1
Calculated lattice constants *a* and*c* of $Zn_{1-x}Be_xO$ after geometric optimization compared with available theoretical and experimental data.

x	*a* (Å)				*c* (Å)		
		This work	Expt.	Other calculations	This work	Expt.	Other calculations
$Zn_{1-x}Be_xO$	0	3.275	3.258[a]	3.283[b], 3.256[c]	5.304	5.220[a]	5.309[b], 5.256[c]
	0.25	3.145		3.134[c]	5.132		5.076[c]
	0.5	2.915		2.972[c]	4.970		4.99[c]
	0.75	2.788		2.889[c]	4.528		4.675[c]
	1	2.714	2.698[d]	2.764[c]	4.412	4.377[d]	4.487[c]

[a] Ref. [31].
[b] Ref. [32].
[c] Ref. [33].
[d] Ref. [15].

Table 2
The calculated elastic constants for $Be_xZn_{1-x}O$compared with both theoretical and experimental data.

		C_{11} (GPa)	C_{12} (GPa)	C_{13}(GPa)	C_{33}(GPa)	C_{44}(GPa)
ZnO	This work	**209.52**	**127.65**	**117.50**	**213.00**	**42.95**
	Experiments	206.217[a]	118.117[a]	118[a]	211[a]	44.50[a]
	Calculations	227[b]; 217[c]	55[b]; 117[c]	93[b]; 121[c]	206[b]; 225[c]	49[b] ; 50[c]
		215.7[d]; 191.16[e]	136.1[d]; 111.96[e]	122.7[d]; 85.63[e]	249.6[d]; 190.57[e]	38.6[d]; 36.89[e]
$Zn_{0.75}Be_{0.25}O$	This work	**225.12**	**127.11**	**115.3**	**282.33**	**51.66**
$Zn_{0.5}Be_{0.5}O$	This work	**243.20**	**126.28**	**108.61**	**353.18**	**72.08**
$Zn_{0.25}Be_{0.75}O$	This work	**324.17**	**126.05**	**104.38**	**399.31**	**89.34**
BeO	This work	**462.55**	**124.55**	**83.58**	**495.39**	**135.70**
	Experiments	460.6[f]	126.5[f]	88.5[f]	491.6[f]	147.7[f]
	Calculations	432.5[d]	135.8[d]	99.0[d]	474.1[d]	131.3[d]

[a] Ref. [37].
[b] Ref. [38].
[c] Ref. [39].
[d] Ref. [40].
[e] Ref. [41].
[f] Ref. [42].

oscillation strength and enhanced exciton binding energy in blue and ultraviolet (UV) light emitting devices [12]. However, if ZnO-based solid solutions could be developed, they would work in this range; this would significantly reduce cost since ZnO is compatible with integrated circuit (IC) and can be synthesized with good stoichiometric control via a number of deposition methods [13].

Band-gap engineering of ZnO can be achieved by alloying with MgO (E_g=7.70 eV) for UV applications and such alloy can also be used as barrier layers in ZnO/(Zn,Mg)O superlattices for quantum well devices [14,15]. However, the phase separation occurs in $Zn_{1-x}Mg_xO$ solid solutions when the Mg composition exceeds 33% [15]. This is due to the differences in the crystal structures of ZnO [wurtzite, *P*63*mc*] and MgO (cubic, rocksalt). As such, the UV absorption range is limited to 3.37–3.90 eV in the $Zn_{1-x}Mg_xO$ system for $x < 0.33$ [16].

Therefore BeO (E_g= 10.60 eV) which also crystallizes in the wurtzite structure has been considered as an alloying system of ZnO for UV optoelectronic devices and sensors. It was shown that $Zn_{1-x}Be_xO$ thin films can be deposited using hybrid beam deposition [17] with no phase separation over the entire composition range [15]. Furthermore, as the band gap in $Zn_{1-x}Be_xO$ can theoretically be tuned from 3.37 to 10.60 eV, this materials system may replace $Zn_{1-x}Mg_xO$ solid solutions which are being considered in applications such as polymer-oxide hybrid solar cells, field effect transistors, high-*k* films on Si, quantum Hall effect devices, acoustic resonators and large electromechanical coupling [18–21].

The literature on $Zn_{1-x}Be_xO$ is limited to a few experimental and theoretical studies that concentrate on the electronic structure, band gap energies, and optical properties [15,16,22–25]. To the best of our knowledge, the phononic and thermodynamic properties of this alloy are less studied. The knowledge of phonon and thermodynamic properties of $Zn_{1-x}Be_xO$ alloy are required in the development of high quality optoelectronic devices. The potential applications of $Zn_{1-x}Be_xO$ alloy system for applications described above have not been fully explored. In this work, we examine the elastic, phononic and thermodynamic properties of the $Be_xZn_{1-x}O$ alloy by the first principle theoretical method.

The paper is organized as follows: in the next section we give a brief description of the computational details. In Section 3, the results and discussions of structural and elastic properties of $Zn_{1-x}Be_xO$ are studied. Then the phonon properties of the $Zn_{1-x}Be_xO$ including phonon dispersion relations and partial phonon densities of states (PDOS) are studied using the density functional perturbation theory (DFPT) method. Temperature dependence of thermal properties such as free energy, specific heat, enthalpy, entropy and Debye temperature are predicted in the last part. Finally, we present our conclusions.