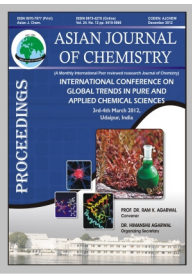
Asian Journal of Chemistry; Vol. 24, No. 12 (2012), 5655-5658

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Elastic and Ultrasonic Properties of XBi (X: B, Cm and U)†

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AJC-11721

The elastic and ultrasonic properties of boron, uranium and curium monobismuthides are reviewed in this article. We present computation of ultrasonic Grüneisen parameters <100>, <110> and <111> directions in the temperature range 100 to 300 K using second and third order elastic constants. The second and third order elastic constants are also calculated using Coulomb and Born-Mayer potential upto second nearest neighbour. The mechanical properties of BBi are better than UBi and CmBi due to its high valued elastic constants. The chosen materials are stable as they satisfied Cauchy's stability criteria. The ultrasonic Grüneisen parameters for CmBi are found highest. Hence CmBi is more sensitive to temperature. Obtained results are discussed with available experimental/theoretical results.

Key Words: Monobismuthides, Elastic constants, Ultrasonic Grüneisen parameters.

INTRODUCTION

The chosen monobismuthides XBi (X: B, Cm and U) have attracted much attention because of their scientific and technological importance. It is of significance to understand their various unusual structural, dynamical, electronic, magnetic, ultrasonic properties. However XBi have received less attention. To the best of our knowledge, XBi has been subject of only a few theoretical works. Recently, different pseudo methods based on the density function theory have been used to study the structural, electronics, lattice dynamics, dielectric properties and phase stability of XBi[1-8]. Like most of the lanthenides, actinides and pnictides, the barium, curium and uranium monobismuthides XBi (X:B, Cm, U) compounds crystallize in NaCl-type structure (B1) at ambient conditions with space group Fm3m (225). In this structure the X-atoms and Bi atoms occupy (0; 0; 0) and (1/2; 1/2; 1/2) positions respectively[7,8].

An investigation into the structural stabilities, electronic and elastic properties of BBi was conducted by Cui *et al*. using *ab initio* calculations[1]. Amara *et al*. reported study and dynamical properties of the BBi over a wide range of temperature using molecular dynamics simulation (MDS)[2]. A structural phase transition from the ground state B_3 phase to B_1 phase at the transition pressure of 31-74 GPa has been studied by Deligoz *et al*.[3]. Bouamana *et al*. reported high pressure effects on the lattice dynamics and dielectrics properties of boron monopnictides using the density functional perturbation theory[4]. The energy dependence of volume for six possible candidate phases of BBi have been investigated by Ferhat and Zaoui using the full potential linearized augmented plane wave (FP-LAPW) method[5]. The elastic constants of BBi in B_3 phase are theoretically obtained at zero pressure[5,6].

At pressures 12 and 5 GPa as it has been shown by X-ray diffraction (XRD) measurements[7]. Rached *et al*. have performed a density function theory (DFT) calculations of the structure, elastic and high pressure properties of cubic XBi (X: Cm, U) compounds using the full potential linear muffin-tin orbital (FP-LMTO) method[8].

To the best of our knowledge, no experiment or theoretical report in literature on ultrasonic Grüneisen parameters (UGP) and other physical properties except few studies on structural and elastic properties[1-8]. But they have used different theories or way to investigate elastic properties. The grounds mentioned above motivate us to choose these monobismuthides for characterization through ultrasonic non-destructive techniques (NDT). For which, we made an attempt to apply computational approach to find the ultrasonic properties of XBi by means of second and third order elastic constants (SOEC and TOEC) along <100>, <110> and <111> directions in the temperature range 100-300 K.

THEORY

The computation of ultrasonic studies will be completed in two parts. In first part we will discuss about temperature

†Presented at International Conference on Global Trends in Pure and Applied Chemical Sciences, 3-4 March, 2012; Udaipur, India

variation of elastic constants (second and third order) of chosen monobismuthides. In second part, the temperature dependent ultrasonic Grüneisen parameter (UGP) have been computed along <100>, <110> and <111> orientations using Mason approach. The whole computation is done starting with nearest neighbour distance or repulsive (hardness) parameter and assuming Coulomb and Born-Mayer type potential in the temperature range 100-300 K.

Computation of elastic constants: Assuming electrostatic potential $\phi(C) = (\pm e^2/r)$ and Born-Mayer type potential $\phi(B) = A \exp(-r/b)$, e, r and b being electronic charge, nearest neighbour distance and hardness parameter and following Brugger's definition[9] of elastic constant at absolute zero.

Thus, we obtain elastic constants (SOEC and TOEC) at 0 K. Leibfried and Haln[10] and Leibfried and Ludwing[11] have developed the theory of anharmonic properties in lattice dynamics of crystals and states that the changes in elastic constants occur due to change in vibrational energy of the crystal.

These changes contribute as follows:

$$C_{IJ} = C^0_{IJ} + C^{Vib}_{IJ} \quad \text{and} \quad C_{IJK} = C^0_{IJK} + C^{Vib}_{IJK}$$

The formulation of the temperature dependent SOEC and TOEC is given in our previous papers[12-15].

Orientation dependence of ultrasonic Grüneisen parametres: A number of anharmonic properties of solids are frequently expressed in terms of Grüneisen parameters, which are expressed, in quasiharmonic approximation, as diverse weighted averages of Grüneisen tensor of the first order: $\gamma^j_{\alpha\beta} = -\omega_i^{-1}\partial\omega_i(q)/\partial\eta_{\alpha\beta}$. For example, the thermal expansivity is relative to the specific heat weighted $<\gamma_{\alpha\beta}> = \sum_{q,i} C_{q,i}\gamma^j_{\alpha\beta} / \sum_{q,i} C_{q,i}$, which is thermal Grüneisen parameters γ; and the (shear) ultrasonic attenuation's Grüneisen parameter can be suitably expressed by thermal conductivity weighted averages of the product $\gamma^j_{\alpha\beta}\gamma^j_{\gamma\delta}$. Brugger derived expressions for the components of Grüneisen tensor in terms of second- and third- order elastic constants of an anisotropic elastic continuum. The Grüneisen parameter and elastic constants are related to each other along different crystallographic directions as given in literature[16-19].

RESULTS AND DISCUSSION

The second and third order elastic constants (SOEC and TOEC) give information about mechanical behaviour of solids, about the nature of force operating and provide information about stiffness of materials. The higher order elastic constants strongly related to other anharmonic properties; such as thermal expansion, thermoelastic constants and thermal conductivity. The second and third order elastic constants play an important role in condensed matter physics. They allow an evaluation of first order anharmonic terms of the interatomic potential or generalized Grüneisen parameter, which enter the theories of all anharmonic phenomena, such as the interaction of acoustic and thermal phonons and the equation of state. There are three second order elastic constants (C_{11}, C_{12} and C_{44}) and six third order elastic constants (C_{111}, C_{112}, C_{123}, C_{144}, C_{111}, C_{466} and C_{456}) for boron, curium and uranium monobismuthides has shown in Table-1.

TABLE-1
TEMPERATURE DEPENDENT SOEC AND TOEC OF XBi (10^{10} N/m^2)

Materials		0 K	100 K	200 K	300 K
BBi	C_{11}	6.20	6.61	6.74	6.93
	C_{12}	2.10	2.01	1.92	1.83
	C_{44}	2.10	2.11	2.12	2.13
	C_{111}	-99.9	-102.81	-103.11	-103.84
	C_{112}	-8.58	-8.23	-7.93	-7.60
	C_{123}	3.43	2.92	2.42	1.92
	C_{144}	3.43	3.46	3.48	3.50
	C_{166}	-8.58	-8.65	-8.67	-8.70
	C_{456}	3.43	3.43	3.43	3.43
UBi	C_{11}	3.70	3.87	4.02	4.18
	C_{12}	0.88	0.87	0.75	0.68
	C_{44}	0.88	0.88	0.89	0.90
	C_{111}	-64.66	-65.66	-66.49	-67.35
	C_{112}	-3.56	-3.27	-2.99	-2.70
	C_{123}	1.53	1.08	0.63	0.18
	C_{144}	1.53	1.54	1.55	1.56
	C_{166}	-3.56	-3.57	-3.59	-3.61
	C_{456}	1.53	1.53	1.53	1.53
CmBi	C_{11}	3.96	4.18	4.31	4.48
	C_{12}	0.89	0.82	0.74	0.67
	C_{44}	0.89	0.89	0.90	0.90
	C_{111}	-70.54	-71.64	-72.54	-73.49
	C_{112}	-3.57	-3.26	-2.94	-2.63
	C_{123}	1.56	1.06	0.56	0.06
	C_{144}	1.56	1.56	1.58	1.59
	C_{166}	-3.57	-3.59	-3.60	-3.62
	C_{456}	1.56	1.56	1.56	1.56

Table-1 depicts that all the SOEC are positive in nature. It is obvious from Table-1 that the values of C_{11} and C_{44} are increasing and value of C_{12} decreasing as temperature increases. It is noted that with increasing temperature bulk modulus decreases. For a cubic crystal, the mechanical stability leads the restriction on elastic constant as follows:

$B_T = C_{11} + 2C_{12})/3 > 0$, $C_{44} > 0$ and $C_S = C_{11} + C_{12})/2 > 0$

The quantities C_{44} and C_S are shear and tetragonal elastic constants of a cubic crystal. These elastic constants B_T, C_{44} and C_S are presented in Table-2.

TABLE-2
BULK MODULI (B_T), ELASTIC CONSTANT (C_{44}) AND TETERGONAL MODULI (Cs) OF XBi (10^{10} N/m^2) AT ROOM TEMPERATURE

Materials	Bulk modulus B_T	C_{44}	C_S
BBi	3.53	2.13	2.55
UBi	1.85	0.90	1.75
CmBi	1.94	0.90	1.91

The elastic constants of XBi under temperature satisfy all these Born-criteria. Hence the chosen monobismuthides are mechanically stable at this temperature range. The calculated second order elastic constants satisfy all these conditions, including the fact that $C_{11} > C_{12}$. Furthermore evaluated SOEC also satisfy all these stability criteria *i.e.* $C_{12} < B_T < C_{11}$. Thus our computed values of SOEC are justified. The elastic constant C_{11} represents elasticity in length, while C_{12} and C_{44} are related to the elasticity in shape, which is a shear constant. The transverse strain causes a change in shape without a change in volume. The thermal contribution to elastic constants is very significant.

The temperature dependent C_{44}/C_{12} ratio is shown in Fig. 1.

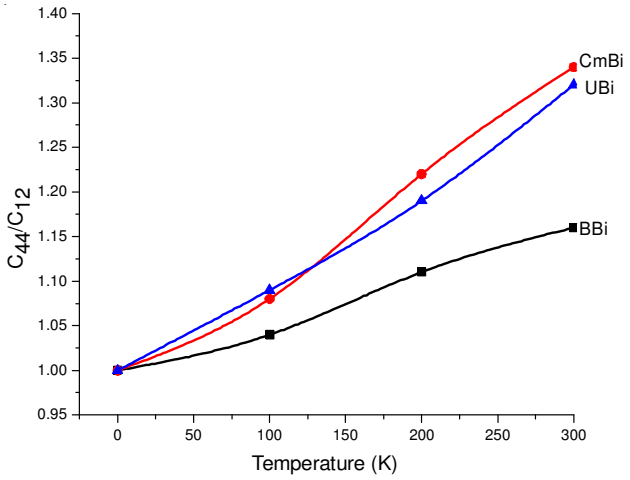

Fig. 1. C_{44}/C_{12} *vs.* temperature of XBi

Fig. 1 depicts that the temperature dependence of C_{44}/C_{12} for XBi, we have deviations from the Cauchy's relation, increases with temperature. Thus the result indicates the dominance of ionic interaction decreases with the temperature. The values of C_{111}, C_{112} and C_{166} are negative in nature, while C_{123}, C_{144} and C_{456} are positive. Among the calculated TOECs of chosen materials, C_{111} are highest valued and order of magnitude larger than that of SOEC. It is depicted from the Table-1, that out of six TOEC, two (C_{111}, C_{144}) are increasing with temperature, while other three (C_{111}, C_{123} and C_{166}) are decreasing with temperature and the value of C_{456} remains constant. The increase or decrease in SOEC and TOEC is due to increase or decrease in atomic interactions with temperature. This type of behaviour of elastic constant is more or less same as previously studied B_1 structured materials like gadolinium monopnictides[12] and intermetallics[20].

Table-1 depicts that BBi has highest valued SOEC and TOEC in contrast to other chosen monobismuthides CmBi and UBi. Hence mechanical properties of BBi is much better than those of CmBi and UBi.

The ultrasonic Grüneisen parameters are tabulated in Table-3.

Ultrasonic Grüneisen parameter (UGP) plays a significant role in study of thermoelastic properties of materials. It is used to describe physical properties of the materials as thermal expansion, thermal conductivity and temperature variation of elastic constants. In present case SOEC and TOEC are used to find out the value of UGP. It is obvious that ultrasonic Grüneisen parameter (UGP) is found highest for longitudinal wave along <100> and <110>, while for shear wave along <111> directions for all the materials. These directions are values for thermal purposes for the chosen materials. The values of Grüneisen parameter for CmBi are found highest in contrast to BBi and UBi. So we can say that CmBi may be the best candidate for thermoelastic properties.

Conclusion

Thus, in this study, a simplified model *i.e.* Born-Mayer model is used to find out the elastic constants (SOEC and TOEC) using two basic parameter *i.e.* lattice parameter and hardness parameter. According to the evaluation made from proposed theory, the trend of second order elastic constants are as $C_{11} > C_{44} > C_{12}$ and while trend of the third order elastic constant (TOEC) is $C_{144} > C_{456} > C_{123} > C_{166} > C_{111}$. The obtained value of elastic constants are also fulfilled Born criteria of mechanical stability as these materials obtained positive values of bulk, shear and tetragonal moduli and other important relationship of elastic constant like $C_{11} > C_{12}$, $C_{12} < B_T < C_{11}$. Cauchy's relations are deviated on increment of temperature as visualised by Fig. 1. Hence on increment of temperature, ionic relation between the atoms decreases. The values of elastic constants are found to be highest in case of BBi. Hence BBi is most mechanical promising material in comparision to CmBi and UBi. The values of ultrasonic Grüneisen parameter for CmBi are found highest for all the temperatures. Hence CmBi is most suitable candidate for thermal purposes. Thus obtained results are useful for further physical studies of these materials.

TABLE-3
TEMPERATURE DEPENDENT ULTRASONIC GRUNEISEN PARAMETERS OF XBi

Direction	Material		100 K	200 K	300 K
<100>	BBi	$<\gamma_i^j>_{long}$	0.46	0.44	0.43
		$<(\gamma_i^j)^2>_{long}$	1.81	1.72	1.62
		$<(\gamma_i^j)^2>_{s1}$	0.12	0.12	0.12
	UBi	$<\gamma_i^j>_{long}$	0.46	0.44	0.42
		$<(\gamma_i^j)^2>_{long}$	2.18	2.03	1.92
		$<(\gamma_i^j)^2>_{s1}$	0.12	0.12	0.12
	CmBi	$<\gamma_i^j>_{long}$	0.46	0.44	0.42
		$<(\gamma_i^j)^2>_{long}$	2.27	0.16	1.98
		$<(\gamma_i^j)^2>_{s1}$	0.12	0.12	0.12
<111>	BBi	$<\gamma_i^j>_{long}$	-0.69	-0.66	-0.63
		$<(\gamma_i^j)^2>_{long}$	2.17	1.99	1.83
		$<(\gamma_i^j)^2>_{sh}$	2.04	1.97	1.88
	UBi	$<\gamma_i^j>_{long}$	-0.74	-0.69	-0.66
		$<(\gamma_i^j)^2>_{long}$	2.45	2.18	1.96
		$<(\gamma_i^j)^2>_{sh}$	2.57	2.45	2.35
	CmBi	$<\gamma_i^j>_{long}$	-0.75	-0.71	-0.67
		$<(\gamma_i^j)^2>_{long}$	2.52	2.25	2.02
		$<(\gamma_i^j)^2>_{sh}$	2.68	2.57	2.46
<110>	BBi	$<\gamma_i^j>_{long}$	-0.76	-0.74	-0.71
		$<(\gamma_i^j)^2>_{long}$	2.32	2.18	2.03
		$<(\gamma_i^j)^2>_{sh1}$	0.18	0.12	0.11
		$<(\gamma_i^j)^2>_{sh2}$	2.99	2.88	2.77
	UBi	$<\gamma_i^j>_{long}$	-0.76	-0.72	-0.69
		$<(\gamma_i^j)^2>_{long}$	2.72	2.52	2.34
		$<(\gamma_i^j)^2>_{sh1}$	0.10	0.09	0.09
		$<(\gamma_i^j)^2>_{sh2}$	3.81	3.62	3.45
	CmBi	$<\gamma_i^j>_{long}$	-0.76	-0.72	-0.69
		$<(\gamma_i^j)^2>_{long}$	2.83	2.62	2.44
		$<(\gamma_i^j)^2>_{sh1}$	0.09	0.09	0.09
		$<(\gamma_i^j)^2>_{sh2}$	3.99	3.80	3.62

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