High Temperatures-High Pressures, Vol. 41, pp. 235–239
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Temperature dependence of the bulk modulus of MgB_2

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Received: December 27, 2011. Accepted: March 31, 2012.

There are contradictory data in the literature for the temperature dependencies of the isothermal bulk modulus (K_T) of magnesium diboride (MgB_2). Recently; the present author has calculated the K_T of zircon ($ZrSiO_4$) and titanium diboride (TiB_2) above room temperature by using the Anderson-Grüneisen equation, the pressure derivative of the bulk modulus and the thermal expansion coefficients (Özkan H, J Eur Ceram Soc **28**, 3091 (2008); Intermetallics **19**, 596 (2011)). The results obtained for $ZrSiO_4$ and TiB_2 verified the method to be a practical way to predict the bulk moduli of materials at high temperatures. In this study the method was extended to calculate the K_T of MgB_2 above room temperature. The results show that the bulk moduli of MgB_2 decrease with increase of temperature from 150.0 GPa at 300 K to 132.2 GPa at 1000 K leading to the temperature derivatives $(\partial K_T/\partial T)_P$ of -0.015 GPa/K near 300 K and -0.028 GPa/K near 1000 K. The present results are in good agreements with the corresponding results from the recent first-principle calculations of the elastic constants.

Keywords: Elastic constants, temperature dependence of bulk modulus, pressure dependence of bulk modulus, Anderson-Grüneisen parameter, first-principle calculations, ceramic superconductors.

1 INTRODUCTION

Magnesium diboride (MgB_2) is an interesting and technologically important superconductor. It has a hexagonal structure and simple composition without copper and oxygen atoms. It is rather inert, not very sensitive to

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contaminations and quite suitable for making superconducting composites. The electrical carrier densities and the critical current densities of MgB_2 may be quite high. MgB_2 is a member of the intermetallic diborides important for high-temperature applications.

The elastic constants of solids are important for technological applications. They describe responses of materials to stress components and give information about the inter-atomic forces. It is interesting to note that no experimental data exist in the literature for the single crystal elastic constants of MgB_2 and their temperature dependencies. Only limited data are available for the polycrystalline elastic moduli below room temperature [1]. However, several first-principles density functional (*DFT*) calculations of the elastic constants of MgB_2 were published [2]. Depending on the method and approximations used different *DFT* calculations appear to lead to quite different values for the elastic constants [2]. In recent years the first-principle calculations of the elastic constants have been extended to high temperatures and high pressures. Guo et al. [3] reported the first-principle calculations of the elastic constants of MgB_2 and the variations of the bulk modulus (K_T) with temperature and pressure up to 300 K and 110 GPa, respectively. The $(\partial K_T/\partial T)_P$ value for MgB_2 near 300 K calculated from the K_T vs T plot of Ref [3] (-0.036 GPa/K) contradicts with the experimental value of Ref. [1] (-0.010 GPa/K) near 300 K by a factor of 3,6. On the other hand, the $(\partial K_T/\partial T)_P$ value for MgB_2 near 300 K obtained from the recent first-principle calculations of the elastic constants and their temperature dependencies is about -0.015 GPa/K [4]. This value is quite different than the earlier experimental and the theoretical values [1,3].

Aside from the assumptions and approximations of the first-principle calculations, what would be the criteria to clarify such large contradictions of the theoretical values if accurate experimental data are not available for the temperature dependencies of the bulk moduli? One answer to this question may lie on the correlations of the pressure and temperature dependencies of the bulk moduli [5,6]. In our previous studies we have used a new method to evaluate the temperature dependencies of the isothermal bulk modulus of zircon ($ZrSiO_4$) and titanium diboride (TiB_2) by using the equation for the Anderson-Grüneisen parameter (δ_T), the pressure derivative of the bulk modulus (K') and the coefficients thermal expansion (α_V) [5,6]. The results obtained for $ZrSiO_4$ and TiB_2 agree well with the corresponding experimental temperature dependencies of the bulk moduli [5–8]. The method presented in our previous studies [5,6] is based on the accurate experimental parameters and give reliable results to substantiate the theoretical calculations of the bulk moduli of materials at high temperatures.

2 MATERIALS AND METHODS

The Anderson-Grüneisen equation and its solution used to compute the temperature dependencies of the isothermal bulk modulus are given below [5–8].

$$\left(\partial K_T / \partial T\right)_P / K_T = -\alpha_V \delta_T \tag{1}$$

$$K_T = K_{T_0} e^{-\int_{T_0}^{T} \alpha_V(T)\delta(T)dT} . \tag{2}$$

Here, K_T is the isothermal bulk modulus at temperature T and K_{T0} is the isothermal bulk modulus at the reference temperature T_0. The thermodynamic basis of these equations, the equivalence of δ_T and K' and the quasi-harmonic model were discussed in the references [5–8].

3 RESULTS AND DISCUSSIONS

The isothermal bulk moduli of MgB_2 were calculated up to 1000 K with small temperature intervals using Equations 1 and 2. The parameters used are: $K_{T_0} = 150 \pm 5$ GPa, at 300 K the reference temperature, $K' = 4.0$ as δ_T obtained from the high pressure compression studies [9,10]. The coefficients of thermal expansion (α_V) from Ref [11] were used for the computations above room temperature. The computations were extended below room temperature by using the high resolution thermal expansion data of MgB_2 [12].

The present K_T vs T values for MgB_2 and the corresponding experimental and theoretical data [1,3,4] are listed in Table 1 and plotted in Figure 1. The uncertainties in the α_V, K_{T0} and K' values are estimated to be less than 5 %.

TABLE 1
The values for the bulk modulus (- GPa) of MgB_2 at different temperatures obtained in the present study and the theoretical and experimental data in the literature.

T (K)/ K_T	Present study	Frst-prsp. Ref [4]	Frst-prsp. Ref [3]	Experiment Ref [1]
0	154.2	146.4	156.8	145.0
100	153.2	145.8	156.6	144.9
200	151.7	144.8	155.0	144.4
220	151.1		154.5	144.2
240	150.8		153.9	144.0
260	150.6		153.2	143.9
280	150.3		152.5	143.7
300	150.0	143.8	151.8	143.5
400	148.0	142.8		
500	145.8	140.2		
600	143.4	138.6		
700	140.6	136.3		
800	137.9	134.6		
900	135.1	133.0		
1000	132.2	129.4		

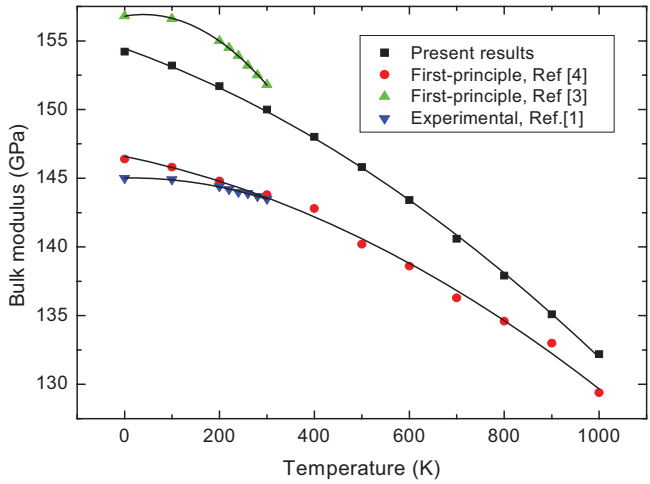

FIGURE 1
The bulk moduli vs. temperature graphs for MgB_2. The present values of the bulk moduli agree well with the corresponding values obtained from the recent first-principle calculations [4].

The essential features of the present results and the related data in the literature are as follows. The present $(\partial K_T/\partial T)_P$ values for MgB_2 change from about, -0.015 GPa/K near 300 K to -0.028 GPa/K near 1000 K. The α_V and the product $\alpha_V K_T$ approach constant values of about 53.0×10^{-6}/K and 6.9 MPa/K, respectively as temperature increases to 1000 K. The $(\partial K_T/\partial T)_P$ values obtained from the ultrasound spectroscopy study of a dense, polycrystalline MgB_2 near 300 K are about -0.010 GPa/K [1] in reasonable agreements with the present results. The $(\partial K_T/\partial T)_P$ values obtained from the earlier first-principle calculation of the elastic constants of MgB_2 near 300 K are about -0.036 GPa/K [3], that is 2.4 times larger in magnitude than the present value near 300 K.

In a recent first principle calculations of the structural and thermodynamic properties of the compounds in the Mg-B-C system the single crystal elastic constants (C_{11}, C_{33}, C_{44}, C_{12} and C_{13}) of MgB_2 and their temperature dependencies were reported [4]. Using the C_{ij} vs T data and the Voigt formula for the hexagonal system [5], for which, $C_{66} = (C_{11} - C_{12})/2$, we calculated the Voigt bulk (K_{TV}) and shear moduli (G_{TV}) of MgB_2 up to 1000 K.

$$K_{TV} = \left(2C_{11} + C_{33} + 2C_{12} + 4C_{13}\right)/9, \tag{3}$$

$$G_{TV} = \left(7C_{11} + 2C33 + 12C_{44} - 5C_{12} - 4C_{13}\right)/30 \tag{4}$$

The calculated temperature derivatives of the Voigt K_{TV} in 300 K $-$ 1000 K range vary from about -0.015 GPa/K near 300 K to about -0.027 GPa/K near 1000 K. It is remarkable to note that these values are about same as the values obtained in the present study. If the present calculations would be

repeated by taking K_{T_0} to be 143.8 GPa (at 300 K) as in Ref [4] the present data would exactly match with the data of Ref [4].

We have compared the $(\partial K_T/\partial T)_P$ values of MgB_2 and magnesium oxide (MgO) because their bulk moduli are quite close to each other. It is interesting to note that the $(\partial K_T/\partial T)_P$ values of MgO is about, -0.030 GPa/K near 1000 K [14] quite close to the value for MgB_2 obtained in this study. Such similarities of the physical properties make MgO a suitable substrate material for making MgB_2 thin films [13].

4 CONCLUSIONS

The temperature dependencies of the isothermal bulk modulus of MgB_2 were computed by using the Anderson-Grüneisen equation, the pressure derivative of the bulk modulus and the coefficients of thermal expansion. The values found for the temperature dependencies of the isothermal bulk modulus of MgB_2 agree well with the corresponding values obtained from the recent first-principle calculations of the temperature dependencies of the elastic constants. This study not only presents new data for the bulk moduli of MgB_2 but also it provides further evidence for the practical method to predict the bulk moduli of materials at high temperatures.

ACKNOWLEDGEMENTS

The author thanks to Dr. E. Kilit and Ö. Kahraman for computer help.

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