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Bulk moduli of Cr_2GaC and Ti_2GaN up to 50 GPa

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ABSTRACT

Using a synchrotron radiation source and a diamond anvil cell, we measured the pressure dependencies of the lattice parameters of two Ga-containing polycrystalline MAX phases: Ti_2GaN and Cr_2GaC. The bulk moduli were calculated to be 189 ± 4 and 188 ± 5 GPa, respectively. Up to a pressure of about 50 GPa, no phase transformations were observed. Ti_2GaN compresses more easily along the *c*-axis, while Cr_2GaC compresses equally in both directions.

1. Introduction

At this time it is fairly well established that the layered ternary carbides and nitrides, the so-called MAX phases, combine some unusual and sometimes unique set of properties [1–12]. The general chemistry of the MAX phases is $M_{n+1}AX_n$, where $n = 1$, 2 or 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element, and X is C or N. Based on the value of n in each formula unit, this class of materials forms three groups known as 211, 312 and 413 materials. These compounds are hexagonal (space group $P6_3/mmc$) with two formula units per unit cell. The structure consists of near close-packed M layers interleaved with layers of pure A, with the carbon/nitrogen atoms filling the octahedral sites between the former.

Like their respective binary *stoichiometric* MX carbides, the MAX phases are elastically stiff, electrically and thermally conductive. Mechanically they cannot be more different, however. Because of their layered nature – where every basal plane is a potential slip and or delamination plane – they are readily machinable and relatively soft. Some of them are exceptionally thermal shock and damage tolerant. Some of them also maintain their strengths to high temperatures, are oxidation, corrosion and creep resistant [10–12].

Over the last few years a concerted effort has been made to understand the relationship between MAX phase chemistries and their mechanical and elastic properties. Most germane to this paper are the bulk moduli. Over the past half dozen years, Manoun et al. [13–22] reported on the bulk moduli – directly measured using a diamond anvil cell and X-ray diffraction – of M_2AlC (M = Ti, V, Cr, Nb and Ta) [13], $Ti_3Si_{0.5}Ge_{0.5}C_2$ [14], Ti_4AlN_3 [15], Ta_4AlC_3 [16], Ti_3AlCN [17], $Ti_3(Al,Sn_{0.2})C_2$ [17], TiVAlC and TiNbAlC [18], Cr_2GeC and V_2GeC [19], Ti_3GeC_2 [20] and Ti_2AlN [21]. More recently, the bulk moduli of Ti_2GeC [22], Ti_2SC [23], Zr_2InC [24], Ti_2InC, $(Ti_{0.5},Zr_{0.5})_2InC$, and M_2SnC (M = Ti, Nb, Hf) [25] were also measured. In all cases, like in Ti_3SiC_2 [26], no phase transitions were observed up to pressures of the order of 50 GPa. The isothermal bulk moduli, K_o, of these compounds, varied from a high of 261 GPa for Ta_4AlC_3 [16], to a low of 127 GPa for Zr_2InC [24]. For the most part, the relative shrinkage along the *c*-direction with pressure was greater than along the *a*-direction. The exceptions were Cr_2AlC [13], Nb_2AsC [27] and Nb_2AlC [13]. The Ta-containing phases were unique in that the shrinkages along both directions were quite comparable [13,16].

Apart from the practical reasons for knowing the bulk moduli of the MAX phases for various potential applications, the study of K_o of the MAX phases has been useful for a number of reasons. First they allow theory to be compared with experiment; an exercise that is more than academic because the agreement or lack thereof is quite informative. In general, the discrepancy between theory and experiment is an important signal indicating problems with the theoretical models and/or more commonly the fact that what

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is modeled is not necessarily what is measured. Theory typically models exact stoichiometries at a temperature of absolute zero; experiments are typically not as clear-cut. For example, the fact that the bulk modulus of Ti_2AlN was significantly lower than it should have been based on its unit cell volume [28,29], led to the conclusion that vacancies were responsible for the discrepancy. In another paper, the fact that the bulk modulus of $(Ti_{0.5},Nb_{0.5})_2AlC$ [18] was lower than the end members despite the fact that its unit cell volume fell in between the end members indirectly confirmed that the Nb/Ti layers in the solid solution were puckered [30]. More recently [25], we showed that in some cases, an inverse correlation exists between the bulk moduli and the unit cell volumes since it is reasonable to assume that the larger the unit cell the longer, and thus weaker the bonds.

Recently some work in the field of MAX phase has been published in Journal of Alloys and Compounds, Phatak et al. reported on the synthesis and structural stability of Ti_2GeC [31] and $(Cr_{0.5}V_{0.5})_2GeC$ [32], both phases are stable to the highest pressure studied. Because of the importance of these types of material researchers started to find new ways to prepare MAX phases: Yeh and co-worker are preparing MAX phases by combustion synthesis in the mode of self-propagating high-temperature synthesis which has the potential of low energy requirement, short processing time, simplicity of facilities, and formation of high-purity products [33]; Tian et al. synthesized nearly dense $(Cr_{1-x}V_x)_2AlC$ solid solutions by pulse discharge sintering (PDS) using Cr, V, Al and C powders as starting materials [34].

Of special interest to this work are the two ternaries: Cr_2GaC and Ti_2GaN. As far as we are aware the latter has never been synthesized in fully dense, bulk polycrystalline form and thus little is known about its properties. And while the former was first fabricated in 2005 [35], none of its properties are known. Very recently, Etzkorn et al. [36] grew single crystals from metallic melts generated by an excess of Ga, of a number of Ga MAX phases including, among others, Ti_2GaC, Cr_2GaC and Ti_4GaC_3. The latter is the first Ga-containing representative of the 413 phases. Because the single crystals were small, however, there were no reports on their properties.

Recently Sun et al. [35] reported on the room-temperature spontaneous growth of Ga freestanding nano-ribbons from Cr_2GaC surfaces. The production of these Ga nanostructures could be the first step in the manufacture of gallium arsenide or nitride devices with enhanced characteristics for photonic, electronic, and catalytic applications.

The paper is a continuation of our, and others', efforts to synthesize and characterize the MAX phases and their myriad solid solutions. Herein we report, for the first time, on the bulk moduli – measured using a diamond anvil cell and synchrotron X-rays – of two Ga-containing ternaries: Cr_2GaC and Ti_2GaN up to pressures of the order of 50 GPa.

2. Experimental details

2.1. Synthesis

The processing details of the Cr_2GaC can be found elsewhere [35]. In short, commercial Ga pellets (99.99%, 3 mm), Cr (99.99%, −325 mesh), graphite (99%, −300 mesh) powders (Alpha Aesar, Ward Hill, MA) were mixed in stoichiometric proportions, ball milled for 1 h, and sealed in borosilicate glass tubes under a mechanical vacuum. The tubes were heated to 650 °C for 10 h, which resulted in their collapse and allowed the powders to pre-react. The tubes were then placed in a hot isostatic press heated at 10 °C/min to 650 °C, followed by heating at 2 °C/min to 750 °C. The chamber was pressurized with Ar gas to 70 MPa, further heated at 10 °C/min to 1200 °C, and held at temperature for 12 h.

The starting powders for the fabrication of Ti_2GaN were Ti and GaN. The powders were ball milled for 2 h, poured into a graphite mold and hot pressed. The hot press was heated from room temperature to 675 °C at 500 °C/h and held at that temperature for 1.5 h, after which the temperature was again ramped at the same heating rate to 1150 °C and held at this temperature for 6 h, before furnace cooling. A load that corresponded to a stress of 45 MPa, was applied when the temperature reached 675 °C and held at that temperature for the duration of the run.

2.2. High-pressure experiments

The high-pressure experiments were carried out in a Mao Bell diamond anvil cell, DAC. To conduct these studies two sets of experiments were performed. Powdered samples were pressurized using a gasketed DAC with a 400 μm culet. A 250 μm, in initial thickness, rhenium gasket, indented to about 60 μm, had a 150 μm diameter hole. The X-ray diffraction, XRD, patterns for Cr_2GaC and Ti_2GaN were collected at the high-pressure collaborative access team (HPCAT) beam line at the advanced photon source (Argonne National Laboratory, Chicago). A monochromatic beam – with a wavelength, $\lambda = 0.4066$ Å – was focused to a 10 μm spot size on the sample. Diffraction rings were recorded between $2\theta = 1^\circ$ and 35° using an image plate.

If the material is hard and has low compressibility, the stress state of a sample compressed in a DAC can become highly non-hydrostatic. This potential problem, however, can be minimized by using a large volume of a low shear-strength material as the pressure-transmitting medium. We have repeatedly shown that aluminum, Al – with its low shear modulus and lack of phase transitions – was a good pressure-transmitting medium. Another advantage of Al is the fact that its pressure–volume relationship is established [37]. In this work, the MAX phases, in the form of a fine powder, were carefully loaded between Al foils that were 15 μm in initial thickness.

The diffraction patterns, recorded on an image plate at room temperature, were integrated using FIT2D software. The pressure was determined from the equation of state of Al [37]. The cell parameters were obtained using GSAS and/or a least squares refinement on individually fitted peaks.

3. Results and discussion

The XRD patterns for both compounds were indexed assuming a hexagonal structure with space group $P6_3/mmc$. The lattice parameters at ambient pressures, a_o and c_o for Cr_2GaC were calculated to be 2.884(1) and 12.62(2) Å, respectively; the respective values for Ti_2GaN were 3.003(2) and 13.33(2) Å. Table 1 compares the lattice parameters and unit cell volumes, V_o, of these compounds to those of Cr_2GeC [19] and Cr_2AlC [13]. Clearly, our values are in good agreement with those reported previously [4]. No extra peaks appear in the XRD patterns even at a pressure of 50 GPa. Thus, like the other MAX phases studied to date [13–27] these structures are quite stable.

Least squares fit of the changes in the relative unit cell volume, V/V_o, with pressure, P (Fig. 1) yields:

$$\frac{V}{V_o} = 1 - 0.0045\frac{P}{P_o} + 2 \times 10^{-5}\left(\frac{P}{P_o}\right)^2 \quad (1)$$

where $P_o = 1$ GPa, and V is unit cell volume at pressure P. The values of $V_o = 91.2 \pm 0.1$ Å^3 for Cr_2GaC and $V_o = 104.1 \pm 0.3$ Å^3 for Ti_2GaN (Table 1). Fitting these results to the Birch–Murnaghan equation

Table 1

Ambient pressure lattice parameters and unit cell volumes, V_o, of Ti_2GaN and Cr_2GaC measured herein. Also listed are the corresponding values for Cr_2GeC and Cr_2AlC. The space group adopted for all phases is $P6_3/mmc$.

M_2AlC	Ti_2GaN	Cr_2GaC	Cr_2GeC	Cr_2AlC
a (Å)	3.003 ± 0.002	2.884 ± 0.001	2.950 ± 0.006	2.857 ± 0.002
		2.891 ± 0.022	2.931[e]	2.86[a]
	3.00[a]	2.88[a]	2.95[a]	2.854[b]
		2.9008[d]		2.848[c]
c (Å)	13.33 ± 0.02	12.62 ± 0.02	12.086 ± 0.008	12.81 ± 0.02
		12.63 ± 0.03	12.066[e]	12.8[a]
	13.3[a]	12.61[a]	12.08[a]	12.82[b]
		12.632[d]		12.72[c]
V_o (Å)^3	104.1 ± 0.3	91.2 ± 0.2	91.1 ± 0.8	90.6 ± 0.5

[a] Ref. [39].
[b] Ref. [40].
[c] Ref. [41].
[d] Ref. [36].
[e] Ref. [42].

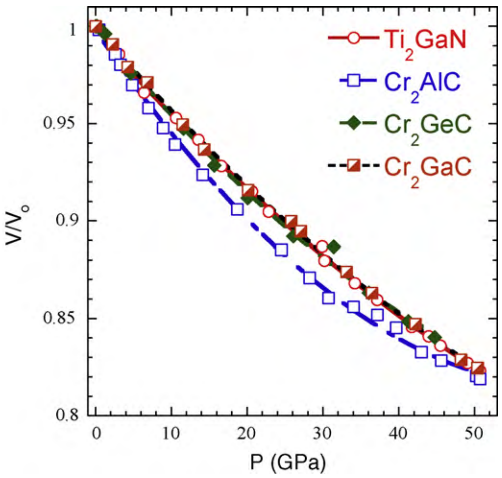

Fig. 1. Pressure dependencies of V/V_o of Ti_2GaN and Cr_2GaC. Also included are the results for Cr_2AlC [13] and Cr_2GeC [19]. The lines are least square fits of the data points. In all cases the square of the correlation coefficient, R^2, values were >0.99.

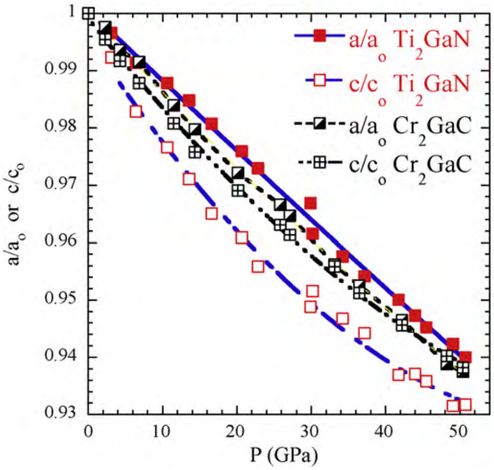

Fig. 2. Pressure dependencies of a/a_o and c/c_o for Ti_2GaN and Cr_2GaC. The lines are least square fits of the data points. In all cases the square of the correlation coefficient, R^2, values, obtained from least squares fitting of the results, were >0.99.

[38] viz.:

$$P = \frac{3}{2}K_o\left[\left(\frac{V}{V_o}\right)^{-7/3} - \left(\frac{V}{V_o}\right)^{-5/3}\right] \times \left[1 + \frac{3}{4}(K'_o - 4)\left[\left(\frac{V}{V_o}\right)^{-2/3} - 1\right]\right] \qquad (2)$$

yields a K_o value of 188 ± 5 GPa, with a derivative, K'_o of 3.6 ± 0.3 for Cr_2GaC and a K_o value of 189 ± 4 GPa, with a derivative, K'_o of 3.5 ± 0.3 for Ti_2GaN. Table 2 compares these values with those of Cr_2GeC and Cr_2AlC from which it is apparent that while the values of K_o of Cr_2GaC, Ti_2GaN and Cr_2GeC are comparable, they are all larger than those of Cr_2AlC.

The results shown in Fig. 2 shed more light on the origins of the differences of K_o between the various compounds. Like most other MAX phases, the compressibility is anisotropic (Fig. 2). A least squares fit of the loading curves for Cr_2GaC, shown in Fig. 2, yield the results listed in Table 3. Also included are the values for Cr_2GeC and Cr_2AlC. In all case, the R^2 values were >0.998. From these results it is clear that while the compressibility of the bonds in the *a*- and *c*-directions are quite comparable in Cr_2GaC, the anisotropy is larger in Ti_2GaN. The averages, however, are comparable (Fig. 1).

The compressibility along the *a*-direction in Cr_2AlC is greater than along the *c*-direction [13]. It is interesting to note that the compression along the *a*-direction in Cr_2AlC is quite similar to that of the *c*-axis in Cr_2GaC. These subtleties must be traceable to the intricacies of bonding and represent a fertile area of research for theoreticians.

In general, for the MAX phases, as for most solids, there is an inverse correlation between V_o and K_o. Fig. 3 plots the relationship for a select number of Ti- and Cr-containing MAX phases for which information is available [25]. From these results it is obvious that while for the Ti-containing MAX phases a decent correlation – with a least squares R^2 value of ≈0.72 – exists, no such relationship exists for the Cr-containing MAX phases. The reason for the latter state of affairs is unclear at this time, but this could be related to the intricacies of bonding in the Cr-containing compounds and/or the presence of point defects. We note in passing that of all the MAX phases, the discrepancy between theory and experiment is highest for Cr_2AlC [13].

The results plotted in Fig. 3 indicate that the order in K_o, in column 13 of the periodic table, is $Ti_2GaN > Ti_2AlC > Ti_2InC$. Similarly, K_o for $Cr_2GaC > Cr_2AlC$. Some of the experimental results, however, are not supported by *ab initio* calculations. For example, the experimental K_o for Cr_2AlC, 165 GPa [13], is significantly lower than those predicted for this compound, that range from 193 to 230 GPa [41,44,45].

Lastly, we note that the fact that K_o for Ti_2AlN is significantly lower than that for Ti_2GaN, despite comparable V_o values (Fig. 3), is further evidence that the former reflects the presence of vacancies [28,29]. The presumable lack of vacancies in Ti_2GaN, would account for its higher K_o.

Table 2
Relative unit cell volume changes, V/V_o, with pressure and summary of experimental bulk moduli. The pressure derivative, K'_o, is also given. All the square of the correlation coefficient values were >0.99. Also the bulk modulus from *ab initio* calculations is included for comparison.

Solid	$V/V_o = \alpha + \beta(P/P_o) + \gamma(P/P_o)^2$	K_o (GPa)	K'_o	K_o (GPa) *ab initio*
Ti_2GaN	$1 - 0.0045P/P_o + 2 \times 10^{-5}\ (P/P_o)^2$	189 ± 4 (this work)	3.5 ± 0.3	182 [46]
Cr_2GaC	$1 - 0.0045P/P_o + 2 \times 10^{-5}\ (P/P_o)^2$	188 ± 5 (this work)	3.6 ± 0.3	–
Cr_2GeC	$1 - 0.0049P/P_o + 3 \times 10^{-5}\ (P/P_o)^2$	182 ± 2 [19]	4	214 [47]
Cr_2AlC	$1 - 0.0058P/P_o + 4 \times 10^{-5}\ (P/P_o)^2$	165 ± 2 [13]	4.1 ± 0.1	226 [41]

Table 3
Relative lattice parameter changes with pressure, *P*. P_o defines the units used and is equal to 1 GPa. The square of the correlation coefficient values in all cases were greater than 0.99.

M_2AX	Max pressure (GPa)	$a/a_o = 1 + \beta(P/P_o) + \gamma(P/P_o)^2$	$c/c_o = 1 + \beta(P/P_o) + \gamma(P/P_o)^2$
Ti_2GaN	51	$1 - 0.0012P/P_o + 5 \times 10^{-7}\ (P/P_o)^2$	$1 - 0.0021P/P_o + 2 \times 10^{-5}\ (P/P_o)^2$
Cr_2GaC	50	$1 - 0.0014P/P_o + 4 \times 10^{-6}\ (P/P_o)^2$	$1 - 0.0017P/P_o + 9 \times 10^{-6}\ (P/P_o)^2$
Cr_2AlC	51	$1 - 0.0021P/P_o + 2 \times 10^{-5}\ (P/P_o)^2$	$1 - 0.0017P/P_o + 10^{-5}\ (P/P_o)^2$
Cr_2GeC	45	$1 - 0.0015P/P_o + 4.6 \times 10^{-6}\ (P/P_o)^2$	$1 - 0.0019P/P_o + 1.7 \times 10^{-5}\ (P/P_o)^2$

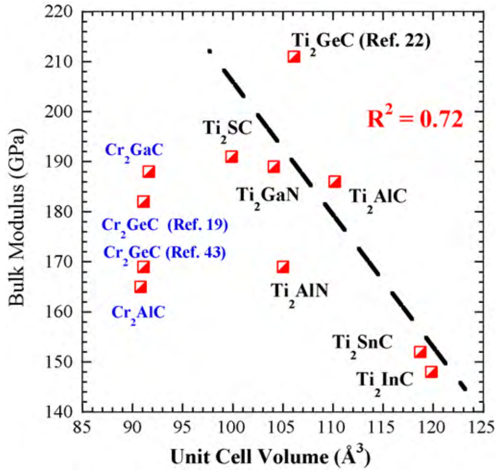

Fig. 3. Effect of unit cell volume on the bulk moduli of Ti- and Cr-containing MAX phases. In addition to the two compounds reported herein, we also plot the results of Ti_2SC [23], Ti_2GeC [22], Ti_2AlC [13], Ti_2SnC [25], Ti_2InC [25] Cr_2AlC [13], and Cr_2GeC [19,43]. And while there is a clear inverse correlation – with a least squares fit correlation coefficient, R^2 of 0.72 – between K_o and V_o for the Ti-containing phases, that correlation is absent for the Cr-containing ones.

4. Conclusions

A diamond anvil cell and synchrotron radiation were used to measure the pressure dependencies of the lattice parameters of two Ga-containing polycrystalline MAX phases: Ti_2GaN and Cr_2GaC. The bulk moduli were calculated to be 189 ± 4 and 188 ± 5 GPa, respectively. Up to a pressure of about 50 GPa, no phase transformations were observed. Ti_2GaN compresses more easily along the *c*-axis, while Cr_2GaC compresses almost equally in both directions.

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References

[1] M.W. Barsoum, M. Radovic, in: R.W.C.K.H.J. Buschow, M.C. Flemings, E.J. Kramer, S. Mahajan, P. Veyssiere (Eds.), Encyclopedia of Materials Science and Technology, Elsevier, Amsterdam, 2004.
[2] M.W. Barsoum, in: R.W.C.K.H.J. Buschow, M.C. Flemings, E.J. Kramer, S. Mahajan, P. Veyssiere (Eds.), Encyclopedia of Materials Science and Technology, Elsevier, Amsterdam, 2006.
[3] M.W. Barsoum, T. El-Raghy, J. Am. Ceram. Soc. 79 (1996) 1953–1956.
[4] M.W. Barsoum, Prog. Solid State Chem. 28 (2000) 201–281.
[5] M. Radovic, M.W. Barsoum, T. El-Raghy, S.M. Wiederhorn, W.E. Luecke, Acta Mater. 50 (2002) 1297–1306.
[6] M. Radovic, M.W. Barsoum, T. El-Raghy, S.M. Wiederhorn, J. Alloys Compd. 361 (2003) 299–312.
[7] T. El-Raghy, M.W. Barsoum, A. Zavaliangos, S.R. Kalidindi, J. Am. Ceram. Soc. 82 (1999) 2855–2860.
[8] T. Zhen, M.W. Barsoum, S.R. Kalidindi, M. Radovic, Z.M. Sun, T. El- Raghy, Acta Mater. 53 (2005) 4963–4973.
[9] T. Zhen, M.W. Barsoum, S.R. Kalidindi, Acta Mater. 53 (2005) 4163–4171.
[10] J. Travaglini, M.W. Barsoum, V. Jovic, T. El-Raghy, Corros. Sci. 45 (2003) 1313.
[11] M.W. Barsoum, L.H. Ho-Duc, M. Radovic, T. El-Raghy, J. Electrochem. Soc. 150 (2003) B166.
[12] M.W. Barsoum, N. Tzenov, A. Procopio, T. El-Raghy, M. Ali, J. Electrochem. Soc. 148 (2001) C551.
[13] B. Manoun, R.P. Gulve, S.K. Saxena, S. Gupta, M.W. Barsoum, C.S. Zha, Phys. Rev. B 73 (2006) 024110.
[14] B. Manoun, H.P. Liermann, S.K. Saxena, et al., Appl. Phys. Lett. 84 (2004) 2799.
[15] B. Manoun, S.K. Saxena, M.W. Barsoum, Appl. Phys. Lett. 86 (2005) 101906.
[16] B. Manoun, S.K. Saxena, T. El Raghy, M.W. Barsoum, Appl. Phys. Lett. 88 (2006) 201902.
[17] B. Manoun, S.K. Saxena, G. Hug, A. Ganguly, E.N. Hoffman, M.W. Barsoum, J. Appl. Phys. 101 (2007) 113523.
[18] B. Manoun, F. Zhang, S.K. Saxena, S. Gupta, M.W. Barsoum, J. Phys.: Condens. Matter 19 (2007) 246215.
[19] B. Manoun, S. Amini, S. Gupta, K. Surendra, Saxena, W. Michel, Barsoum, J. Phys.: Condens. Matter 19 (2007) 456218.
[20] B. Manoun, F.X. Zhang, S.K. Saxena, M.W. Barsoum, T. El-Raghy, J. Phys. Chem. Solids 67 (2006) 2091.
[21] B. Manoun, H. Yang, S.K. Saxena, A. Ganguly, M.W. Barsoum, B. El Bali, Z.X. Liu, M. Lachkar, J. Alloys Compd. 433 (2007) 265–268.
[22] N.A. Phatak, S.K. Saxena, Y. Fei, J. Hu, J. Alloys Compd. 474 (2009) 174.
[23] S.R. Kulkarni, R.S. Vennila, N.A. Phatak, S.K. Saxena, C.S. Zha, T. El-Raghy, M.W. Barsoum, W. Luo, R. Ahuja, J. Alloys Compd. 448 (2008) L1–L4.
[24] B. Manoun, S.K. Saxena, H.P. Liermann, R. Gulve, E. Hoffman, M.W. Barsoum, G. Hug, C.S. Zha, Appl. Phys. Lett. 85 (2004) 1514.
[25] B. Manoun, O. Leaffer, S. Gupta, E.N. Hoffman, S.K. Saxena, J.E. Spanier, M.W. Barsoum, Solid State Commun. 149 (2009) 1978.
[26] A. Onodera, H. Hirano, T. Yuasa, et al., Appl. Phys. Lett. 74 (1999) 3782.
[27] R.S. Kumar, S. Rekhi, A.L. Cornelius, M.W. Barsoum, App. Phys. Lett. 86 (2005) 111904.
[28] M. Radovic, A. Ganguly, M.W. Barsoum, J. Mater. Res. 23 (2008) 1517.
[29] T. Scabarozi, A.A. Ganguly, J.D. Hettinger, et al., J. Appl. Phys. 104 (2008) 073713.
[30] G. Hug, M. Jaoun, M.W. Barsoum, Phys. Rev. B 71 (2005) 24105.
[31] N.A. Phatak, S.K. Saxena, Y. Fei, J. Hu, J. Alloys Compd. 474 (2009) 174–179.
[32] N.A. Phatak, S.K. Saxena, Y. Fei, J. Hu, J. Alloys Compd. 475 (2009) 629–634.
[33] C.L. Yeh, Y.G. Shen, J. Alloys Compd. 482 (2009) 219–223.
[34] W.B. Tian, Z.M. Sun, H. Hashimoto, Y.L. Du, J. Alloys Compd. 484 (2009) 130–133.
[35] Z.-M. Sun, S. Gupta, H. Ye, M.W. Barsoum, J. Mater. Res. 20 (2005) 2618–2621.
[36] J. Etzkorn, M. Ade, D. Kotzott, M. Kleczek, H. Hillebrecht, J. Solid State Chem. 182 (2009) 995–1002.
[37] R.G. Greene, H. Luo, A.L. Ruoff, Phys. Rev. Lett. 73 (1994) 2075–2078.
[38] F. Birch, Phys. Rev. 71 (1947) 809.
[39] H. Nowotny, in: H. Reiss (Ed.), Prog. Solid State Chem. 2 (1970) 27.
[40] J.C. Schuster, H. Nowotny, C. Vaccaro, J. Solid State Chem. 32 (1980) 213.
[41] Z. Sun, et al., Appl. Phys. Lett. 83 (2003) 899.
[42] O.D. Leaffer, S. Gupta, M.W. Barsoum, J.E. Spanier, J. Mater. Res. 22 (2007) 2651.
[43] N.A. Phatak, S.R. Kulkarni, V. Drozd, S.K. Saxena, L. Deng, Y. Fei, J. Hu, W. Luo, R. Ahuja, J. Alloys Compd. 463 (2008) 220.
[44] J.M. Schneider, Z. Sun, R. Mertens, F. Uestel, R. Ahuja, Solid State Commun. 130 (2004) 445.
[45] J. Wang, Y. Zhou, Phys. Rev. B 69 (2004) 214111.
[46] A. Bouhemadou, Solid State Sci. 11 (2009) 1875–1881.
[47] A. Bouhemadou, Appl. Phys. A 96 (2009) 959–967.