High pressure structural behavior and synthesis of Zr$_2$SC

# High pressure structural behavior and synthesis of $Zr_2SC$

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**Abstract**
A high pressure study of $Zr_2SC$ using synchrotron x-ray diffraction and a Mao–Bell type diamond anvil cell has been performed up to a pressure of 46 GPa at room temperature. No phase transformation has been observed up to this pressure. It is found that the compression along the two axes is almost identical up to 15 GPa, thereafter the $c$-axis shows a slightly higher compressibility. The third order Birch–Murnaghan equation of state was used to fit the experimental pressure–volume data, from which the isothermal bulk modulus was obtained as $K_T = 186(4)$ GPa with a pressure derivative $K'_T = 4.0$. The sample was synthesized using the piston cylinder technique and was found to be predominantly single phase after it was characterized by scanning electron microscopy equipped with an energy dispersive spectrometer and by synchrotron x-ray diffraction. The lattice parameters calculated from the x-ray diffraction were $a_0 = 3.406(2)$ and $c_0 = 12.138(4)$.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Materials, known as $M_{n+1}AX_n$ phases, where $n$ is 1, 2, or 3, and M represents an early transition metal, A an A-group element, and X is either carbon and/or nitrogen [1], have witnessed a surge of interest because of the interesting combination of unique properties. Like ceramics, they are elastically stiff, oxidation resistant, and show high temperature stability, and like metals they are excellent electrical and thermal conductors, and are thermal shock resistant and damage tolerant, which is attributed to two independent basal slip systems. However, one of the most striking features of these materials is their ease of machinability despite being elastically stiff. These materials crystallize in hexagonal crystal symmetry with $P6_3/mmc$ space group in which the edge shared $XM_6$ octahedra are weakly bonded with the interleaved planar close packed A-group element layers [2–4].

Zr₂SC was synthesized by Kudeilka *et al* [5] in powder form, where the lattice parameters were $a = 3.389$ Å and $c = 12.09$ Å, respectively. $Zr_2SC$ also occurs in steels in which Zr is added as a sulfur getter element. These steels exhibit good machinability in both turning and drilling, which interestingly may be in part due to the presence of $Zr_2SC$ [6]. In a recent study on a very closely related compound, $Ti_2SC$, it was found that this material exhibited exceptionally high hardness [7] and high thermal conductivity [8]. The reason for this behavior, according to the *ab initio* calculations by Hug [9], was that since sulfur has the most filled 'p' states of any of the A elements present in these phases, the M–A bonds were as strong as the M–C bonds which increased the overall strength of this compound. Moreover, a transition to a more ceramic like behavior was observed in these phases when sulfur was present as an A element. One of the motivations of this study is thus to find out whether $Zr_2SC$ also displays any of the above characteristics, especially in the bond strength.

The high pressure response of these materials has been studied, both theoretically and experimentally, over the last

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few years in order to find out their structural stability. It is now well known that these materials are structurally stable up to pressures as high as 55 GPa and that the bulk modulus lies in the range of 120–270 GPa [10–15]. Moreover, it is also known that in most of these materials the *c*-axis shows higher compressibility than the *a*-axis as the M–A bonds are weaker than the M–C bonds.

In this study we report on the synthesis of predominantly single phase $Zr_2SC$ and its high pressure behavior up to 46 GPa for the first time. The results include micro-structural characterization with SEM/EDS analysis and x-ray diffraction, determination of isothermal bulk modulus, and its derivative with respect to pressure. These, high pressure results are compared with those of $Ti_2SC$ and $Zr_2SnC$, the former, in addition to being a 211 MAX compound, has a different M element while the latter has a different A element. Thus, this comparison will further aid in understanding the high pressure behavior of these compounds with different M and A elements.

## 2. Experimental details

The synthesis of the sample was performed in an end-loaded piston–cylinder apparatus with 1/2 inch-diameter pistons. A talc–pyrex–graphite assembly was used as a furnace, which contained the powder mixture. Two graphite discs were placed on either side of this mixture in order to get a tight packing and also to prevent the contamination by the thermocouple junction. This thermocouple, made of a $W_5Re_{95}$–$W_{26}Re_{74}$ junction and sheathed in an $Al_2O_3$ tube, was rested on the top of one of the graphite discs so that the temperature gradient (between the sample and the thermocouple) was <5 °C. The applied pressure was measured by Heise gages, which accounted for the 10% friction from the pressure medium. The mixture was prepared by mixing Zr (3 $\mu$m, Sigma-Aldrich), S (>99.98%, Sigma-Aldrich), and C (>99.997%, Goodfellow) powders in stoichiometric (2:1:1) proportions followed by ball milling in a hardened steel vial and a hardened steel ball on the Wig–L–bug (Crescent Dental Manufacturing Co., Lyons, IL USA) machine. This mixing process consisted of ten one minute cycles. A 5 min interval was kept between each cycle to avoid excessive heating of the vial from the heat generated during high energy mixing and also to prevent pre-reaction between Zr and S.

The experiments were conducted by first increasing the sample pressure to 1 GPa and then the temperature was increased to 1300 °C at a rate of 50 °C min$^{-1}$. Such a high pressure was necessary to squeeze out any oxygen in the sample chamber and to eliminate any voids that would be present. This condition was maintained for 10 h, after which, the sample was quenched by cutting the power to the apparatus. The $Zr_2SC$ sample obtained subsequently was 6.5 mm in diameter and 2.4 mm in thickness and had a very thin brittle layer around the circumference. This impurity was easily removed by polishing the sample with 600 mesh SiC polishing paper.

Field-emission scanning electron microscopy (SEM) (JEOL JSM 6330 F) was used to investigate the microstructure of the sample coupled with energy dispersive spectroscopy (EDS) for quantitative analysis. The samples were polished with alumina suspension down to 1 $\mu$m, followed by a final surface finish with a colloidal silica suspension. For performing the quantitative analysis, the chemical compositions from seven different areas of the samples were averaged. A small piece of sample was cut out and powdered by grinding in an agate mortar for x-ray diffraction (XRD) analysis. It was noticed that there was not much difficulty while cutting this piece. This powdered sample was used to collect a synchrotron XRD pattern at the ambient condition for its characterization.

The powdered sample, loaded in the stainless steel gasket, was pressurized using a diamond anvil cell. The diamonds had 400 $\mu$m flat culet faces. The gasket of 250 $\mu$m initial thickness was indented to 50 $\mu$m and a hole of 200 $\mu$m was drilled, by electric discharge machining, at the center of this indentation. A mixture of (4:1) methanol:ethanol was used as a pressure medium and platinum (Alfa Aesar, −325 mesh, >99.9% metal basis purity) was used as an internal pressure marker.

The high pressure XRD experiments were conducted at the X17C beam line at the National Synchrotron Light Source situated at Brookhaven National Laboratory. The beam line was setup for angle dispersive x-ray diffraction, wherein, the monochromatic x-rays had a wavelength of 0.4066 Å and were focused to 20 $\mu$m spot size. The cell parameters were determined using least squares refinement of individually fitted peaks, which were assigned to a hexagonal structure with the space group $P6_3/mmc$.

## 3. Results and discussions

The XRD pattern (figure 1) of the sample shows that it is mainly single phase with a small amount of $ZrO_2$ as a second phase, which was estimated from the Rietveld analysis to be $\approx$6±3 wt%. Besides these, no other phases were identified. All of the reflections of this sample were indexed in a hexagonal crystal system belonging to the space group $P6_3/mmc$. The *a* and *c* lattice parameters calculated from the above XRD pattern are 3.406(2) and 12.138(4), respectively.

The SEM analysis of the sample (figure 2) confirmed the above results. This figure indicates that the sample is fully dense and consists mainly of two regions: the dark and the bright regions corresponding, respectively, to the sample and the impurity phase ($ZrO_2$). The most probable reason for the presence of $ZrO_2$ in the final product is the contamination of the original zirconium powder by oxygen. From the EDS analysis of the sample, the concentrations of Zr(64.1(3)) and S(31.2(6)) obtained were consistent with the ratio of 2:1, within experimental errors. The average grain size of the sample was measured to be $\approx$4 $\mu$m. The density measured by the Archimedes principle in the ambient temperature water is 5.99 g cm$^{-3}$, which is 96% of the theoretical density.

Figure 3 shows XRD patterns of the sample as a function of pressure up to 46 GPa and table 1 summarizes the dependency of lattice parameters, unit cell volume, and their relative changes with pressure. A shift of diffraction peaks to smaller *d*-spacings, which is normal, is observed due to the apparent contraction of the crystal lattice. As the pressure was
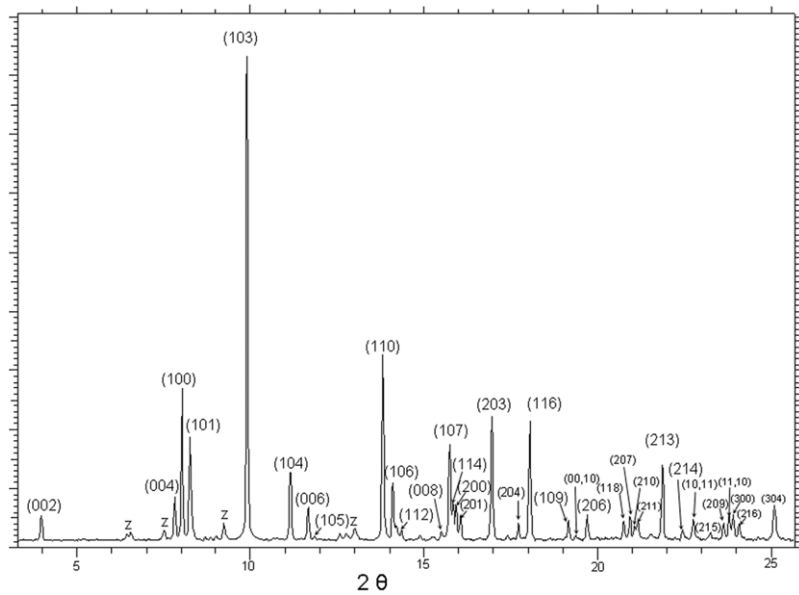
**Figure 1.** X-ray diffraction pattern of the sample collected with monochromatic synchrotron x-rays with a wavelength of 0.4066 Å and a spot size of 20 $\mu$m. The values in the bracket are the indexes of the corresponding peaks. 'z' indicates peaks from $ZrO_2$.
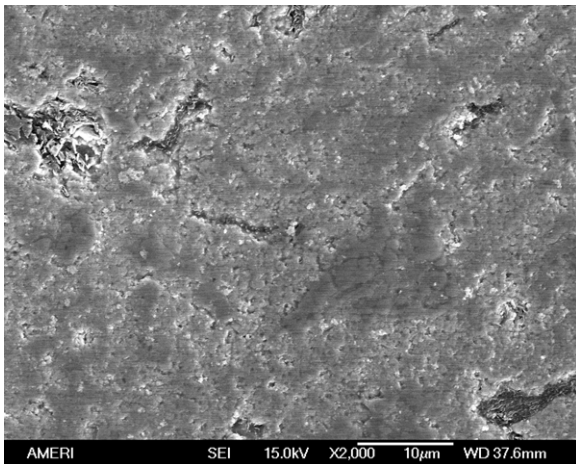


**Figure 2.** SEM image of the polished $Zr_2SC$ sample. The bright region at the top left corner indicates sample pull-out while polishing.

**Table 1.** Summary of lattice parameters, unit cell volume, and their relative changes with pressure.

| $P$ (GPa) | $a$ (Å) ($\pm 0.002$) | $c$ (Å) ($\pm 0.03$) | Vol (Å$^3$) ($\pm 0.2$) | $a/a_o$ | $c/c_o$ | $v/v_o$ |
|---|---|---|---|---|---|---|
| 0 | 3.406 | 12.14 | 122.0 | 1 | 1 | 1 |
| 2.91 | 3.396 | 12.08 | 120.6 | 0.9967 | 0.9954 | 0.9889 |
| 5.48 | 3.379 | 12.05 | 119.1 | 0.9918 | 0.9925 | 0.9764 |
| 10.94 | 3.347 | 11.94 | 115.8 | 0.9825 | 0.9834 | 0.9494 |
| 14.47 | 3.331 | 11.88 | 114.2 | 0.9778 | 0.9792 | 0.9363 |
| 18.21 | 3.315 | 11.83 | 112.5 | 0.9728 | 0.9745 | 0.9224 |
| 22.54 | 3.305 | 11.73 | 111.0 | 0.9701 | 0.9668 | 0.9100 |
| 24.68 | 3.293 | 11.69 | 109.8 | 0.9666 | 0.9634 | 0.9003 |
| 28.8 | 3.281 | 11.64 | 108.5 | 0.9631 | 0.9592 | 0.8897 |
| 31.02 | 3.269 | 11.60 | 107.3 | 0.9594 | 0.9558 | 0.8799 |
| 35.41 | 3.251 | 11.55 | 105.7 | 0.9541 | 0.9517 | 0.8663 |
| 39.31 | 3.236 | 11.51 | 104.3 | 0.9498 | 0.9480 | 0.8553 |
| 40.94 | 3.233 | 11.49 | 104.0 | 0.9489 | 0.9464 | 0.8523 |
| 44.89 | 3.220 | 11.43 | 102.6 | 0.9450 | 0.9417 | 0.8410 |
| 46.46 | 3.212 | 11.42 | 102.0 | 0.9427 | 0.9405 | 0.8360 |

increased the peaks from the monoclinic zirconia phase started to weaken and at $\approx$6–8 GPa peaks from the orthorhombic structure of zirconia started to become prominent, which is a well documented transformation in the literature [16]. There was one unidentified low intensity peak in the range of 8°–9° $2\theta$ that remained until the end of the experiment. This peak is believed to be from the tetragonal high pressure phase of zirconia; however, peak overlap and very low intensity from this phase made its positive identification rather difficult. Moreover, the sample peaks started to become broader and overlapped each other as the pressure was increased. Other than these observations there were no changes in the relative intensities of the existing peaks, which implies that $Zr_2SC$ maintains its structural integrity up to at least 46 GPa.

The pressure dependency of the $d$-spacings is shown in figure 4, which shows a continuous decrease with the increase in pressure, again indicating that the sample is stable up to 46 GPa. The $d$-spacing of only those reflections that were prominent, non-overlapping, and observable until the end of the experiment are shown. The $d$-spacing of the (002) reflection was divided by three in order to maintain a uniform scale of the figure.

The compressibility along both the $a$ and the $c$ lattice directions of $Zr_2SC$ (figure 5) shows very little anisotropy up to 15 GPa, after which the compressibility along the $c$-direction becomes slightly higher. However, the overall compressibility can be considered to be isotropic as compared to that exhibited by most of the MAX phases [10, 12, 17], except $Ta_2AlC$ [12], which also exhibited a similar behavior. The reason for this may be that the M–A bonds, in $Zr_2SC$, are as strong as the M–C bonds, which according to Hug *et al* [9], based on the *ab initio* calculations, was because the increase in the number
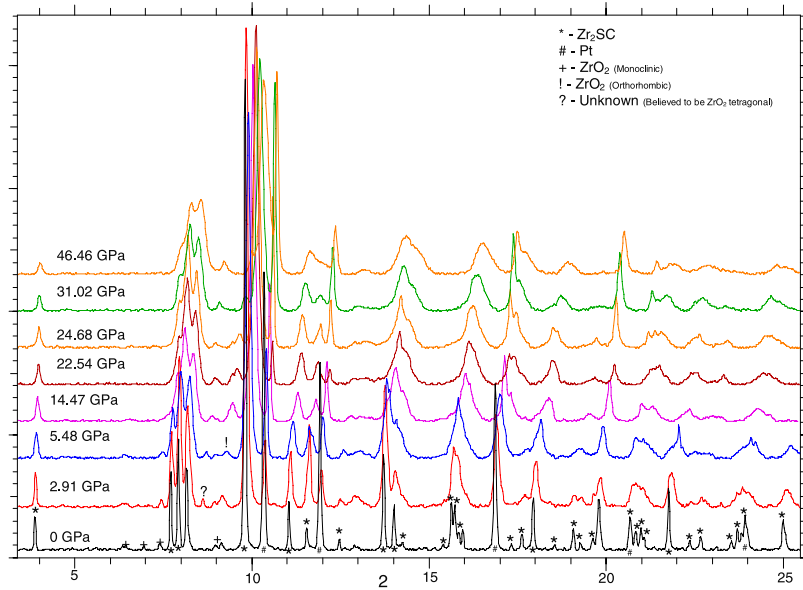
**Figure 3.** X-ray diffraction patterns of $Zr_2SC$ at selected pressures. The symbols represent the following (* = $Zr_2SC$), (# = Pt), (+ = $ZrO_2$ (monoclinic)), (! = $ZrO_2$ (orthorhombic)), (? = unknown).
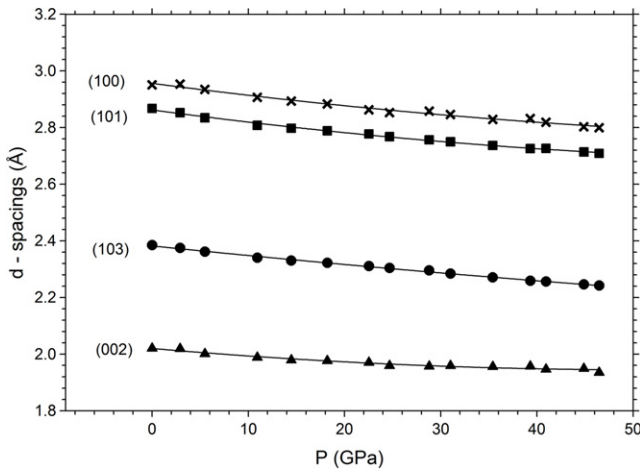


**Figure 4.** The pressure dependence of $d$-spacings of $Zr_2SC$.



**Figure 5.** The pressure dependence of relative cell parameters ($a/a_0$ and $c/c_0$) and the equation of state of $Zr_2SC$ with the curve fitted to the third order Birch–Murnaghan equation of state.

of electrons of S atoms as compared to the other A (Al, Ge, In) elements lowered the energy of the M–A bonds as compared to that of M–C bonds, thus making the M–A bonds stronger than the latter. Based on this result, it is reasonable to assume that the M–A bonds are as strong as the M–C bonds in $Zr_2SC$, due to which the $c$-direction is becoming stiffer and thus exhibits compressibility similar to that of the $a$-direction. Moreover, it is thought that, in the case of $Zr_2SC$, the increase in pressure forces some of the electrons from the bonding states to transfer into the anti-bonding states, thereby making the $c$-direction weaker and more compressible than the $a$-direction after $\approx 15$ GPa.

A least squares fit to the results shown in (figure 5) yields the following relations

$$\frac{a}{a_0} = 1 - 1.534(6) \times 10^{-3} P + 6.85(1) \times 10^{-6} P^2$$
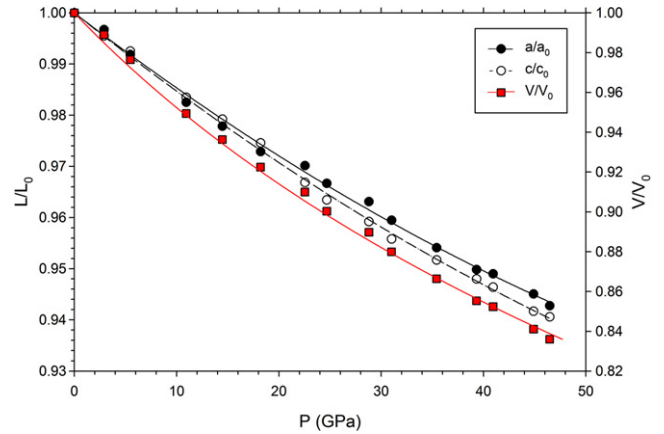
$$R^2 = 0.9973 \tag{1}$$

$$\frac{c}{c_0} = 1 - 1.599(5) \times 10^{-3} P + 6.75(1) \times 10^{-6} P^2$$

$$R^2 = 0.9987 \tag{2}$$

where $P$ is the pressure in GPa and $R$ is the correlation coefficient. These results again indicate that the anisotropy in the compressibility along the two directions is much less. After fitting the pressure dependence of the volume of $Zr_2SC$ (figure 5) with the third order Birch–Murnaghan [18] equation of state, the bulk modulus is obtained as $K_T = 186(4)$ with its pressure derivative $K'_T = 4.0$ (fixed).

By comparing the results of this study with those of $Ti_2SC$ [10] and $Zr_2InC$ [13], as shown in (figures 6(a)–(c)) the effect of changes in the 'A' and 'M' element on the high pressure behavior of these phases is intended. It is seen that (figure 6(a)) $Zr_2InC$ has the highest volume compressibility of all the three phases. It also shows higher compressibility
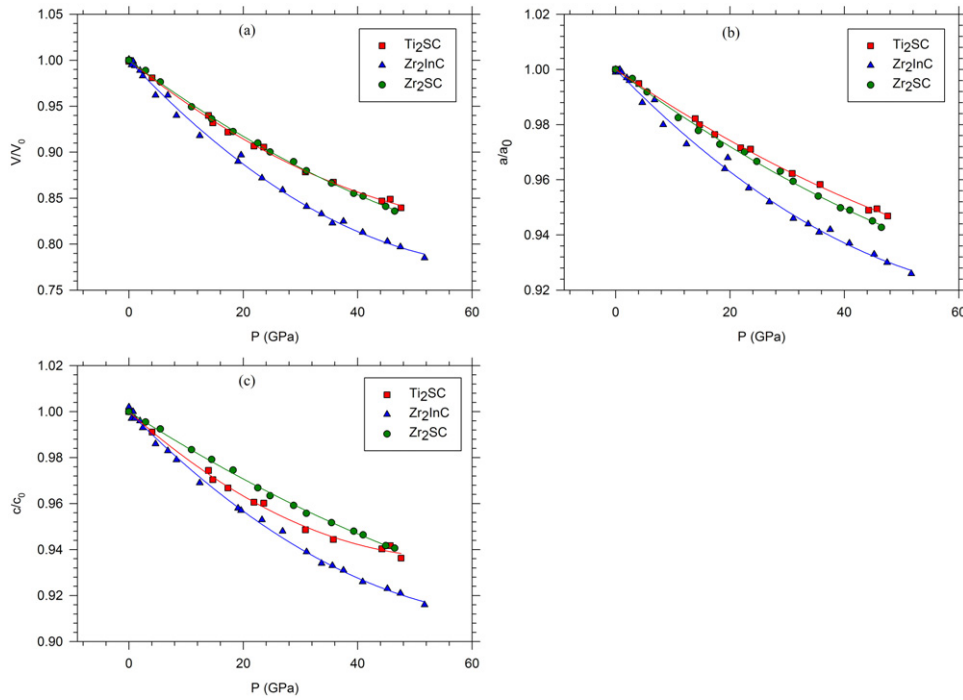
**Figure 6.** Comparison of the pressure dependence of (a) the unit cell volumes, (b) the '*a*' lattice parameters, and (c) the '*c*' lattice parameters, of $Zr_2SC$ with those of $Ti_2SC$ [10] and $Zr_2InC$ [13].

along both the *a*-and the *c*-directions (figures 6(b) and (c)) and therefore has the lowest bulk modulus (130 GPa). $Zr_2SC$ has higher compressibility than $Ti_2SC$ along the *a*-direction (figure 6(b)), however, it has a lower compressibility along the *c*-direction (figure 6(c)), thus the overall effect is that both $Zr_2SC$ and $Ti_2SC$ show almost identical pressure–volume behavior (figure 6(a)) and therefore have bulk moduli that are very close to each other; 191 and 186 GPa for $Ti_2SC$ and $Zr_2SC$, respectively. From this comparison, the following can be deduced: (a) changing of 'A' element changes the bulk modulus significantly (43% for $Zr_2AC$) and (b) the changes in the 'M' element, however, produce no significant difference in the bulk modulus (2.5% for $M_2SC$). It is thus strongly believed that either the sulfur bearing MAX phases behave differently than the rest, which was also observed by Hug *et al* [9] and recently by Amini *et al* [7], or that the discrimination of the MAX phases based on the bulk modulus should also include some additional criteria besides the individual elements involved. These comments not withstanding, it is hereby acknowledged that more work needs to done in order to validate the above comments.

## 4. Conclusions

By mixing the elemental powders (Zr, S, and C) in stoichiometric (2:1:1) proportions, the 211 MAX phase, $Zr_2SC$, was successfully synthesized in bulk form using the piston cylinder setup. From the synchrotron XRD pattern of the powdered $Zr_2SC$ sample, an impurity in the form of $ZrO_2$ was identified, which was present in the amount of $\approx 6 \pm 3$ wt%. The SEM analysis revealed that the sample was fully dense. From the EDS analysis an Zr:S ratio

of (64.1(3):31.2(6)) was obtained, which is consistent with the 2:1 ratio of this compound. The density measured by the Archimedes principle in the ambient temperature water was 5.99 g cm$^{-3}$, which is 96% of the theoretical density. $Zr_2SC$ showed structural integrity when it was studied under pressure using synchrotron radiation and diamond anvil cell up to 46 GPa. The bulk modulus calculated by fitting the Birch–Murnaghan equation of state to the pressure–volume relationship was $K_T = 186(4)$ GPa with a pressure derivative $K'_T = 4.0$ (fixed). Moreover, the compressibility along the two lattice directions was almost identical up to 15 GPa, after which the *c*-direction became slightly more compressible. However, the overall compressibility was almost isotropic as compared to that of the other 211 MAX phases.

## References

[1] Barsoum M W 2000 *Prog. Solid State Chem.* **28** 201
[2] Barsoum M W 2006 *Encyclopedia of Materials Science and Technology* ed K H J Bischow, R W Cahn, M C Flemings, E J Kramer, S Mahajan and P Veyssiere (Amsterdam: Elsevier)
[3] Barsoum M W and El-Raghy T 1999 *Metall. Mater. Trans.* A **30** 1727
[4] Barsoum M W and El-Raghy T 1996 *J. Am. Ceram. Soc.* **79** 1953
[5] Kudielka H and Rohde H 1960 *Z. Kristallogr. kristallgeom. Kristallphys. Kristallchem.* **114** 447
[6] Masakazu H and Yutaka K 2002 *Eur. Pat. Appl.* US 6,773,661 B2
[7] Amini S, Barsoum M W and El-Raghy T 2008 *J. Am. Ceram. Soc.* at press
[8] Scabarozi T H, Amini S, Finkel P, Leaffer O D, Spanier J E, Barsoum M W, Tambussi W M, Hettinger J D, Lofland S E, Drulis M and Drulis H 2008 submitted
[9] Hug G 2006 *Phys. Rev.* B **74** 184113
[10] Kulkarni S R, Vennila R S, Phatak N A, Saxena S K, Zha C S, El-Raghy T, Barsoum M W, Luo W and Ahuja R 2008 *J. Alloys Compounds* **448** L1
[11] Phatak N A, Kulkarni S R, Drozd V, Saxena S K, Deng L, Fei Y, Hu J, Luo W and Ahuja R 2007 *J. Alloys Compounds* at press doi:10.1016/j.jallcom.2007.09.078
[12] Manoun B, Gulve R P, Saxena S K, Gupta S, Barsoum M W and Zha C S 2006 *Phys. Rev.* B **73** 1
[13] Manoun B, Saxena S K, Liermann H P, Gulve R P, Hoffman E, Barsoum M W, Hug G and Zha C S 2004 *Appl. Phys. Lett.* **85** 1514
[14] Gao N F, Miyamoto Y and Zhang D 2002 *Mater. Lett.* **55** 61
[15] Wang J and Zhou Y 2004 *Phys. Rev.* B **69** 214111
[16] Leger J M, Tomaszeski P E, Atouf A and Pereira A S 1993 *Phys. Rev.* B **47** 14075
[17] Manoun B, Lierman H P, Gulve R P, Saxena S K, Ganguly A, Barsoum M W and Zha C S 2004 *Appl. Phys. Lett.* **84** 2799
[18] Birch F 1978 *J. Geophys. Rev.* **83** 1257