Crystal structure and compressibility of a high-pressure Ti-rich oxide, $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$, isomorphous with cubic zirconia

Hexiong Yang [a,*], Jürgen Konzett [b], Robert T. Downs [a]

[a] Department of Geosciences, University of Arizona, Tucson, AZ 85721-0077, USA
[b] Institut für Mineralogie und Petrographie, Universität Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

ABSTRACT

A Ti-rich oxide, $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})_{\sum = 1.0}O_{1.81}$, was synthesized at 8.8 GPa and 1600 °C using a multi-anvil apparatus. Its crystal structure at ambient conditions and compressibility up to 10.58 GPa were determined with single-crystal X-ray diffraction. This high-pressure phase is isomorphous with cubic zirconia (fluorite-type) with space group $Fm\bar{3}m$ and unit-cell parameters $a = 4.8830(5)$ Å and $V = 116.43(4)$ Å^3. Like stabilized cubic zirconia, the structure of $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$ is also relaxed, with all O atoms displaced from the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position along $\langle 1\,0\,0 \rangle$ by 0.319 Å and all cations from the (0, 0, 0) position along $\langle 1\,1\,1 \rangle$ by 0.203 Å. No phase transformation was detected within the experimental pressure range. Fitting the high-pressure data (V vs. P) to a third-order Birch–Murnaghan EOS yields $K_0 = 164(4)$ GPa, $K' = 4.3(7)$, and $V_0 = 116.38(3)$ Å^3. The bulk modulus of $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$ is significantly lower than that (202 GPa) determined experimentally for cubic TiO_2 or that (~210 GPa) estimated for cubic ZrO_2. This study demonstrates that cubic TiO_2 may also be obtained by introducing various dopants, similar to the way cubic zirconia is stabilized below 2370 °C. Furthermore, $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$ has the greatest ratio of Ti^{4+} content vs. vacant O^{2-} sites of all doped cubic zirconia samples reported thus far, making it a more promising candidate for the development of electrolytes in solid oxide fuel cells.

1. Introduction

Cubic zirconia with the fluorite-type structure is an unquenchable high-temperature polymorph of ZrO_2 above 2370 °C. This phase, however, can be stabilized at lower temperatures by adding various dopants, such as Y_2O_3, La_2O_3, Sc_2O_3, CaO, and MgO. When the valency of the dopant cations is lower than that of Zr^{4+}, oxygen vacancies are formed to maintain the overall charge neutrality. Stabilized cubic zirconia (SCZ) is an excellent conductor of O^{2-} ions at temperatures above 700 °C and has numerous technological applications, such as oxygen sensors in the automobile industry, solid electrolytes in high-temperature fuel cells, thermal barrier coatings in engines, and high-toughness ceramics [e.g., 1,2]. Recently, the addition of TiO_2 into SCZ has drawn considerable attention because such a solid solution is not only a remarkable super-plastic ceramic [3–5], but also a potential candidate for solid-oxide-fuel-cell electrolytes, owing to its excellent stability at high temperature, good compatibility with the SCZ electrolytes, mixed (ionic plus electronic) conductivity, and electrocatalytic activity [e.g., 6–12]. For example, Liou and

Worrell [13] found that the electronic contribution to total conductivity in some TiO_2-SCZ solid solutions could be as high as 90% between 800 and 1000 °C. Fagg et al. [14] further noted that the electronic conductivity contribution in the TiO_2-SCZ solid solutions can be optimized with increasing Ti^{4+} content. Nevertheless, the maximum amount of TiO_2 that can be incorporated into Y-SCZ (yttrium-stabilized cubic zirconia) is only about ~20% at 1500 °C [9], though the tetragonal zirconia may contain up to 40 mol% TiO_2 [15]. In this study, we report the high-pressure synthesis of a Ti-rich oxide, $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$, and the determinations of its structure and compressibility with single-crystal X-ray diffraction.

2. Experimental procedures

The high-pressure $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$ phase, abbreviated hereafter as TZMC for simplicity, was first found as a breakdown product of mathiasite, $K(Ti_{13}Cr_4FeZrMg_2)O_{38}$, at 8.8 GPa and 1600 °C in an experimental study on phase relations and stabilities of crichtonite $(AM_{21}O_{38})$ and magnetoplumbite $(AM_{12}O_{19})$ under the Earth's upper-mantle conditions, where A = mostly Ba, Sr, K, and M = mostly Fe, Mg, Cr, Ti, Zr [16]. It was subsequently synthesized at these same pressure and

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* Corresponding author.
  E-mail address: hyang@u.arizona.edu (H. Yang).

temperature conditions using high-purity oxides with a composition (wt%) 52.8 TiO_2, 28.5 ZrO_2, 9.5 Cr_2O_3, 2.1 Fe_2O_3, and 7.1 MgO. The starting material was pre-dried at 150 °C overnight, placed in a 1.18 mm outer diameter Pt_{100} capsule with an inner graphite liner and welded shut immediately. The synthesis was made at the Geophysical Laboratory of the Carnegie Institution of Washington on a 600 t Walker-type multi-anvil apparatus with an 18/11 (18 mm edge-length of octahedron, 11 mm truncation of WC cubes) assembly. The octahedron was cast from an MgO-based ceramic with a rhenium heater. The temperature was measured using a W3%Re–W25%Re thermocouple and both pressure and temperature were computer-controlled during the entire run-duration of 90 min. After the experiment, the recovered Pt-capsule was embedded in epoxy resin and ground to expose the center of the charge for microprobe analysis and extraction of crystals for structure analysis.

The composition of TZMC was analyzed using a JEOL Superprobe electron microprobe at the Geophysical Laboratory. Analytical conditions were 50 nA and 15 kV with a residence time of 30 s on peak and 15 s on backgrounds of the X-ray lines. Raw counts were corrected online with the ZAF procedure. In the absence of information on the Fe^{2+}/Fe^{3+} ratios, all Fe were assumed to be Fe^{3+} as in the starting material. The average composition from analyses of 15 individual crystals is (wt%): 54.6±0.7 TiO_2, 32.2±1.1 ZrO_2, 7.3±0.4 Cr_2O_3, 0.2±0.0 Fe_2O_3, and 5.4±0.2 MgO, which gives a chemical formula $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})_{\sum = 1.0}O_{1.81}$, by analogy with SCZ (see below). In addition to the TZMC crystals, a small amount of an interstitial Ti–Mg-rich phase appeared in the experiment.

On the basis of optical examination and X-ray diffraction peak profiles, a nearly equi-dimensional crystal was selected and mounted on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoK$_\alpha$ radiation. X-ray diffraction data at ambient conditions were collected with frame widths of 0.5° in ω and 30 s counting time per frame. All reflections with $I > 2\sigma(I)$ were indexed based on a cubic unit cell (Table 1). No satellite or super-lattice reflections were observed. The intensity data were corrected for X-ray absorption using the Bruker program SAINT. Observed systematic absences of reflections suggest the possible space group $F432$, $F\bar{4}3m$, or $Fm\bar{3}m$. The structure was solved and refined in space group $Fm\bar{3}m$ using the program SHELX97 [17], as it gave the best refinement statistics.

The determined structure is isomorphous with SCZ. An initial structure refinement with isotropic displacement parameters (U_{iso}) for all atoms was undertaken by assuming all cations ($M = Ti+Zr+Mg+Cr$) at the $4a$ position (0, 0, 0) with a full occupancy and O atoms at the $8c$ position $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ with a partial occupancy, as observed in many SCZ crystals [e.g., 18–26], yielding an R_1 factor of 0.025, the goodness-of-fit of 1.242, and the oxygen site occupancy of 0.856. The U_{iso} parameters, 0.035(1) Å^2 for M and 0.090(4) Å^2 for O, however, appear to be abnormally large compared to those usually expected for such a simple structure [18]. The difference Fourier syntheses at the convergence of the refinement revealed the presence of two noticeable residual peaks, one at the $32f$ position (x, x, x), about 0.3 Å away from the M cation position, and the other at the $48g$ position $(\frac{1}{4}+x, \frac{1}{4}, \frac{1}{4})$, about 0.4 Å away from the O position, indicative of possible site splitting (or relaxations) for both M cation and O atoms from the ideal fluorite-type structure. Thus, considering the differences in the size and valence charge among the four cations (Ti^{4+}, Zr^{4+}, Mg^{2+}, and Cr^{3+}), as well as the previous studies on various SCZ crystals, two site-splitting models were attempted in the subsequent refinements. Model 1 (based on charge consideration) assumed ($Zr^{4+}+Ti^{4+}$) at the $4a$ position (M1 site) and ($Mg^{2+}+Cr^{3+}$) at the $32f$ position (M2 site), with some O atoms occupying the $48g$ position (i.e., displaced along $\langle 1 0 0 \rangle$). Model 2 (based on size consideration) assumed the same site-splitting for O atoms as in model 1, but ($Zr^{4+}+Mg^{2+}$) at M1 and ($Ti^{4+}+Cr^{3+}$) at M2. The refinements for the two models with U_{iso} parameters for both M and O atoms, nonetheless, produced a nearly identical outcome: all O atoms were displaced to the $48g$ position and all cations to the $32f$ position, with the R_1 factor of 0.020 and the goodness-of-fit of 1.084. The U_{iso} parameters for M and O atoms reduced to 0.017(1) and 0.038(4) Å^2, respectively. Consequently, for the final structure model, we assumed all O atoms at the $48g$ position and all cations at the $32f$ position and refined their coordinates with anisotropic displacement parameters. Because of the limited number of observed independent reflections (only 37, even with $2\theta_{max} = 88°$) (Table 1), no occupancy for the M or O site was refined. The occupancies for the M and O sites were fixed to 12.5% and 15.1%, respectively, based on the chemistry determined from electron microprobe analysis, $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})_{\sum = 1.0}O_{1.81}$. The resultant R_1 factor and the goodness-of-fit were 0.016 and 0.970, respectively. Final atomic coordinates and displacement parameters are listed in Table 2 and selected bond distances in Table 3.

For the compressibility measurement of TZMC at high pressures, the same crystal used for the structure determination was polished to ~0.04 mm in thickness and loaded into a modified Merrill-Bassett diamond-anvil cell. A mixture of 4:1 methanol:ethanol was used as the pressure medium and three small ruby

Table 1
Summary of crystal data and refinement results for cubic $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$.

	Room temperature
Crystal size (mm)	$0.09 \times 0.09 \times 0.08$
Space group	$Fm\bar{3}m$ (no. 225)
a (Å)	4.8830(5)
V (Å^3)	116.43(4)
Z	4
ρ_{calc} (g/cm^3)	5.399
λ (Å)	0.71069
μ (mm^{-1})	7.29
θ range for data collection	2.23 to 44.0
No. of reflections collected	240
No. of independent reflections	40
No. of reflections with $I > 2\sigma(I)$	37
No. of parameters refined	9
R(int)	0.006
Final R factors [$I > 2\sigma(I)$]	$R_1 = 0.016$, $wR_2 = 0.039$
Final R factors (all data)	$R_1 = 0.018$, $wR_2 = 0.040$
Goodness-of-fit	0.970
$\Delta\rho_{max}$	0.07 e Å^{-3} (0.76 Å from the O site)
$\Delta\rho_{min}$	−0.10 e Å^{-3} (1.70 Å from the O site)

Table 2
Atomic coordinates and displacement parameters in $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
M	0.0240(9)	0.0240(9)	0.0240(9)	0.018(2)	$= U_{11}$	$= U_{11}$	0.0001(5)	$= U_{12}$	$= U_{12}$	0.018(2)
O	0.185(2)	1/4	1/4	0.050(8)	0.042(4)	$= U_{22}$	0	0	−0.007(3)	0.045(5)

Note: M = (Ti+Zr+Mg+Cr). U_{ij} parameters are in unit of Å^2.

chips were included as the internal pressure calibrant [27]. A Picker four-circle diffractometer equipped with an Mo X-ray tube was used for high-pressure X-ray diffraction measurements with the fixed-ϕ mode [28]. Unit-cell parameters were determined from least-squares refinement of 12–18 reflections using an eight-reflection centering technique [29]. No phase transition was detected up to 10.58 GPa. Measured unit-cell parameters as a function of pressure are recorded in Table 4.

Table 3
Possible bond distances (Å) in $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$.

	Distances (Å)	Number of equi-distant bonds/Site multiplicity
M–O	1.747(9)	3/48
M–O	1.864(7)	3/48
M–O	1.904(5)	6/48
M–O	2.012(6)	6/48
M–O	2.048(6)	3/48
M–O	2.112(9)	3/48
M–O	2.149(9)	3/48
M–O	2.243(7)	6/48
M–O	2.276(8)	3/48
M–O	2.367(7)	3/48
M–O	2.398(8)	6/48
M–O	2.515(7)	3/48

Table 4
Unit-cell parameters of cubic $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$ at high pressures.

P(GPa)	a(Å)	V(Å^3)
0.00	4.8820(5)	116.36(4)
0.60	4.8765(5)	115.96(4)
1.26	4.8693(5)	115.45(4)
1.93	4.8635(5)	115.05(4)
2.91	4.8537(6)	114.34(4)
3.80	4.8464(5)	113.83(4)
4.95	4.8354(6)	113.06(4)
6.09	4.8263(5)	112.42(4)
6.72	4.8208(6)	112.04(4)
7.42	4.8155(5)	111.67(4)
8.28	4.8086(5)	111.19(4)
8.93	4.8037(6)	110.85(4)
9.52	4.7984(5)	110.48(3)
10.02	4.7942(5)	110.19(4)
10.58	4.7800(5)	109.90(4)

3. Results and discussion

3.1. Crystal structure of TZMC

The crystal structure of TZMC exhibits a common feature observed in numerous SCZ crystals—the displacements (or relaxations) of atoms from the ideal fluorite model (Table 5). Such a phenomenon in SCZ, especially the positions of O atoms, has been a central subject of extensive investigations, because it is the key to understanding the oxygen motion in SCZ as fuel-cell electrolytes at high temperatures. It is generally agreed that the relaxation of atoms in SCZ from the ideal fluorite model results from the need to achieve the best bonding environment for Zr^{4+}, which is too small to fully occupy the site coordinated cubically by eight O^{2-} ions at ambient conditions. According to Argyriou [30], this relaxation is principally a consequence of static, rather than dynamic, disorder of atoms. However, the reported positions and site occupancies of atoms in SCZs vary remarkably (Table 5), due partly to the variety of compositions examined and different thermal histories of samples.

Previous studies have shown that, on the one hand, the O atoms may occupy three possible sites in SCZ, namely the 8c ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), 32f ($\frac{1}{4}+x$, $\frac{1}{4}+x$, $\frac{1}{4}+x$), and/or 48g ($\frac{1}{4}+x$, $\frac{1}{4}$, $\frac{1}{4}$) positions, with a preference for the last position (Table 5). This is also the case for TZMC, in which all O atoms are displaced by 0.319 Å from the 8c position along $\langle 1\,0\,0 \rangle$ to the 48g position. On the other hand, cations in most SCZ samples have been found at the 4a position. Possible cation relaxation in SCZ from the ideal fluorite model has been suggested by Steele and Fender [19], Argyriou et al. [26], and Welberry et al. [31], but it has only been confirmed recently by Ishizawa et al. [18] using the combined results of single-crystal synchrotron radiation diffraction and EXAFS measurements on a $(Zr_{0.76}Y_{0.24})O_{1.88}$ sample. In that sample, the small Zr^{4+} is displaced along $\langle 1\,1\,1 \rangle$ to the 32f (x, x, x) position, whereas the large Y^{3+} remains at the 4a position (Table 5). The M cations in TZMC are also displaced in the same direction as Zr^{4+} in $(Zr_{0.76}Y_{0.24})O_{1.88}$ studied by Ishizawa et al. [18], providing another substantiated example for the cation relaxation. The displaced distance of the M cations in TZMC from the 4a position is 0.203 Å, which is slightly longer than that (0.188 Å) of Zr^{4+} in $(Zr_{0.76}Y_{0.24})O_{1.88}$ [18]. This observation is likely to be a result of the difference between the mean cation size in the two samples, as the larger relaxation of the SCZ structure has been found to be correlated with the smaller cation size [19]. In fact, TZMC has the smallest mean

Table 5
Summary of average structure refinements of stabilized cubic zirconia-type materials.

Composition	Cation positions		O positions & occupancy (%)			Method	Reference
	M1	M2$_{\langle 111 \rangle}$	O1	O2$_{\langle 100 \rangle}$	O3$_{\langle 111 \rangle}$		
$Zr_{0.74}Y_{0.26}O_{1.87}$	M		44	47	9	P-N	[19]
$Zr_{0.74}Yb_{0.26}O_{1.87}$	M		47	47	6		[19]
$Zr_{0.82}Y_{0.18}O_{1.91}$	M			Major	Small	S-N	[20]
$Zr_{0.85}Ca_{0.15}O_{1.85}$	M			Major	Small		[20]
$Zr_{0.87}Ca_{0.13}O_{1.87}$	M		9	91		S-X	[21]
$Zr_{0.79}Y_{0.21}O_{1.89}$	M		39	61			[21]
$Zr_{0.72}Y_{0.28}O_{1.86}$	M				100	S-tof-N	[22]
$Zr_{0.82}Y_{0.18}O_{1.91}$	M			Major	Small	E	[23,24]
$Zr_{0.875}Mg_{0.125}O_{1.875}$	M			100		P-N	[25]
$Zr_{0.818}Y_{0.182}O_{1.909}$	M		35	55	10	P-N	[26]
$Zr_{0.695}Y_{0.306}O_{1.847}$	M		37	53	10		[26]
$Zr_{0.610}Y_{0.390}O_{1.805}$	M		25	59	16		[26]
$Zr_{0.76}Y_{0.24}O_{1.88}$	Y	Zr	45	55		S-synchrotron	[18]
$Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10}O_{1.81}$		M		100		S-X	This study

E = electron diffraction and microscopy; P = powder; S = single crystal; X = X-ray diffraction; N = neutron diffraction; tof = time-of-flight; M = (Zr+Y+Ca+Yb+Ti+Zr+Mg+Cr); Major = major amount; Small = small amount; Coordinates of atomic sites: M1 at (0, 0, 0), M2 at (x, x, x), O1 at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), O2 at ($\frac{1}{4}+x$, $\frac{1}{4}$, $\frac{1}{4}$), O3 at (($\frac{1}{4}+x$, $\frac{1}{4}+x$, $\frac{1}{4}+x$).

cation size of all materials listed in Table 5. Yet, we cannot rule out the possible effects of different synthesis conditions, since TZMC is the only high-pressure synthesized material in Table 5.

Because of various relaxation models (Table 5), the exact coordination of Zr^{4+} in SCZ has been a matter of discussion. A number of studies propose that Zr^{4+} in SCZ is seven-coordinated, resembling that in monoclinic ($P2_1/c$) baddeleyite, the stable form of ZrO_2 at ambient conditions. This is consistent with the conclusions derived from studies of Raman spectra [32] and EXAFS [18]. For TZMC, it may not be realistic to assume that all cations (Zr^{4+}, Mg^{2+}, Ti^{4+}, and Cr^{3+}) are seven-coordinated, since small Cr^{3+} and Ti^{4+} (relative to Zr^{4+} and Mg^{2+}) normally prefer a six-coordinated environment. In other words, Cr^{3+} and Ti^{4+} in TZMC may occupy a local environment that is different from the one for Zr^{4+} and Mg^{2+}. If this is indeed the case, then it may help to explain the large U_{iso} values we observed for both O and M atoms.

3.2. High-pressure properties of TZMC

The unit-cell volumes of TZMC as a function of pressure are plotted in Fig. 1. Fitting the weighted unit-cell volume and pressure data to a third-order Birch–Murnaghan equation of state yields $V_0 = 116.38(3)\,\text{Å}^3$, $K_0 = 164(4)\,\text{GPa}$, and $K' = 4.3(7)$. The bulk modulus of our sample can be compared to that (202 GPa) for the pure cubic TiO_2 polymorph determined by Mattesini et al. [33] or that (190–210 GPa) for pure or yttria-stabilized (8–20 mol% Y_2O_3) cubic ZrO_2 [e.g., 34–40]. The significantly smaller K_0 value of our sample is probably due to the substitution of cations with lower valency (Mg^{2+} and Cr^{3+}) for Ti^{4+} and Zr^{4+}.

It should be pointed out that there have been considerable efforts to understand the structure and stability of cubic TiO_2, as this material may possess certain physical and chemical properties superior to those of cubic ZrO_2 [33,41–43]. In nature, TiO_2 is commonly found in the tetragonal (rutile) or orthorhombic (anatase and brookite) structure. The cubic polymorph, either with the pyrite ($Pa\bar{3}$) or the fluorite structure ($Fm\bar{3}m$), has been proposed to form only at high pressures, by analog to various rutile-type metal dioxides, such as SnO_2, PbO_2, HfO_2, and RuO_2

[44,45]. Theoretical calculations by Muscat et al. [46] and Ahuja and Dubrovinsky [47] suggest that the pyrite-type TiO_2 may be more stable than the fluorite-type form at high pressures, but neither of them can be stabilized over the rutile structure below 60 GPa. Recently, using a laser-heated diamond-anvil cell, Mattesini et al. [33] reported an in-situ observation of a cubic TiO_2 polymorph at 48 GPa and ~1727 °C, along with the cotunnite-type TiO_2 (orthorhombic *Pbnm* symmetry). The reflections of this cubic phase can be followed on decompression at ambient temperature down to ~9 GPa, but they cannot be assigned indisputably to the fluorite- or pyrite-type structure, as the relatively weak reflections of the pyrite-type structure could be hidden by the reflections from the cotunnite-type phase. Based on the fluorite symmetry and the X-ray diffraction data collected between 10 and 55 GPa, Mattesini et al. [33] obtained a bulk modulus of 202(5) GPa for the cubic TiO_2 phase. However, this value has been questioned by Swamy and Muddle [48] from two aspects: (1) it is only comparable to or even smaller than the bulk moduli for the less dense forms of TiO_2, in which Ti is six-coordinated, such as rutile (211 GPa), brookite (255 GPa), and columbite-type (258 GPa); (2) it is notably smaller than the theoretically-calculated values, which range from 280 to 395 GPa for the fluorite-type TiO_2 and 220 to 318 GPa for the pyrite-type TiO_2 [e.g., 46,48,49].

From the crystal-chemical point of view, an ideal radius ratio for a cation coordinated cubically by 8 anions is between 0.73 and 1.00. However, the ratios R_{Zr}^{4+}/R_O^{2-} and R_{Ti}^{4+}/R_O^{2-} are only 0.61 and 0.54 [50], respectively, indicating that Ti^{4+} and Zr^{4+} cations may be too small to form the ideal fluoride-type structure with O^{2-} at ambient conditions. The less packing efficiency of the cubic TiO_2 structure implies that it should be more compressible than the cubic ZrO_2 phase. Fig. 2 plots the bulk moduli vs. the molar volumes for both pure and doped TiO_2–ZrO_2 systems. Intriguingly, if we connect data for pure cubic TiO_2 and ZrO_2, as well as those for TZMC and doped ZrO_2, we see two roughly parallel lines. This result suggests that pure cubic TiO_2 may indeed be more compressible than pure cubic ZrO_2, lending support to the bulk modulus obtained by Mattesini et al. [33] for the pure cubic TiO_2 phase.
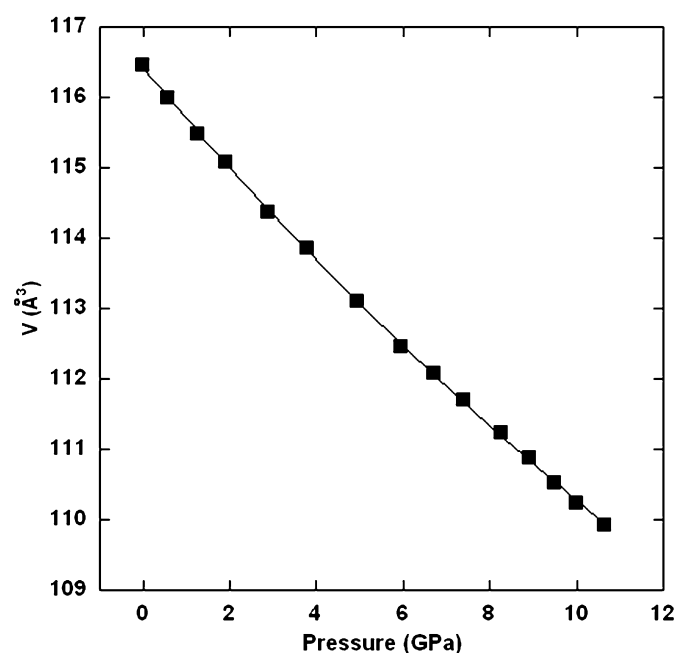

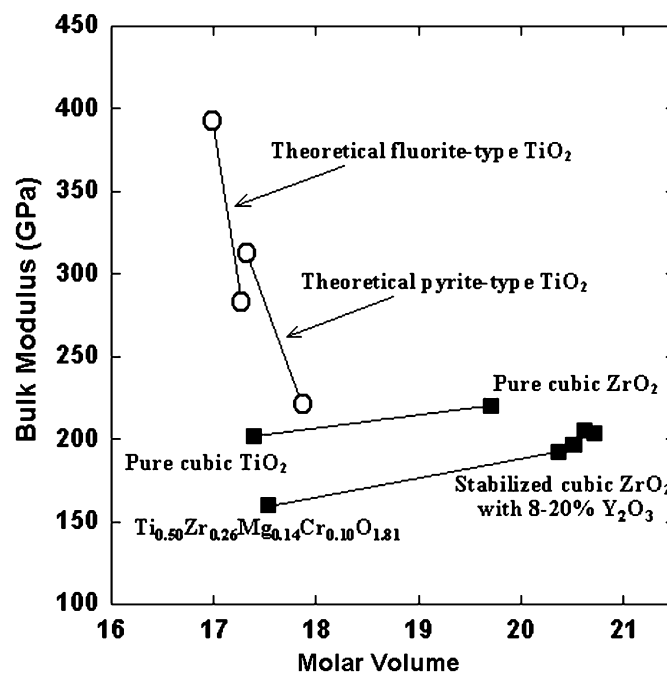**Fig. 1.** Unit-cell volume of $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$ as a function of pressure.

Fig. 2. Bulk modulus vs. molar volume for pure and doped TiO_2 and ZrO_2. Data sources are: pure cubic TiO_2 [33], pure or Y-stabilized cubic ZrO_2 [34–40], and theoretical cubic TiO_2 [46–49].

3.3. Synthesis of TZMC

Previous studies on phase relations in the ZrO_2–Y_2O_3–TiO_2 ternary system have shown that the solubility of Ti^{4+} into the SCZ structure increases with increasing Y^{3+} content [e.g., 7,9,13,51,52]. This observation may be attributed to the fact that the amount of oxygen vacancies in SCZ increases with the addition of Y^{3+}, which facilitates Ti^{4+} to assume its preferred 6-coordinated environment [9]. However, increased oxygen vacancies will augment defect interactions, which will lower ionic conductivity, thus resulting in the reduction in the optimum mixed (electronic and ionic) conductivity in SCZ [12,13]. In other words, the ideal SCZ for the solid-oxide-fuel-cell applications should contain maximum Ti^{4+} and minimum vacant oxygen sites. The solubility of TiO_2 in tetragonal zirconia [53] and SCZ [3] at 1400 °C is as high as 15 mol%. Feighery et al. [9] were able to synthesize an SCZ sample, $Zr_{0.62}Y_{0.20}Ti_{0.18}O_{1.90}$, at 1500 °C, which contains 18 atom% Ti^{4+} with 5% vacancy on the oxygen sites. The ratio of the Ti^{4+} content vs. the vacant O^{2-} sites for that sample is 3.6, which is substantially smaller than that (5.6) for our sample. Hence, TZMC may serve as a more promising material for the development of electrolytes in solid oxide fuel cells. Furthermore, the synthesis of our TZMC sample demonstrates that, although the pure cubic TiO_2 phase is unquenchable from high pressure [33], it is possible to attain a cubic TiO_2 phase by introducing various dopants, similar to the case in stabilizing cubic zirconia. Perhaps, high pressure will also facilitate high content of TiO_2 in SCZ.

4. Conclusion

This work reports the synthesis of a Ti-rich oxide, $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$, at 8.8 GPa and 1600 °C and the determinations of its structure and high-pressure compressibility with single-crystal X-ray diffraction. This high-pressure phase is isomorphous with stabilized cubic zirconia with space group $Fm\overline{3}m$. Like stabilized cubic zirconia, its structure is also relaxed, with all O atoms displaced by 0.319 Å from the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position along $\langle 1\,0\,0 \rangle$ and all cations by 0.203 Å from the $(0, 0, 0)$ position along $\langle 1\,1\,1 \rangle$. This is the second substantiated example for cation relaxation in the ideal fluorite-type cubic zirconia structure. The high-pressure compression experiment on $(Ti_{0.50}Zr_{0.26}Mg_{0.14}Cr_{0.10})O_{1.81}$ revealed no phase transformation up to 10.58 GPa. The determined bulk modulus is 164(4) GPa, significantly lower than that (202 GPa) for cubic TiO_2 or that ($\sim$210 GPa) estimated for cubic ZrO_2, probably due to the substitution of cations with lower valency (Mg^{2+} and Cr^{3+}) for Ti^{4+} and Zr^{4+}. This study demonstrates that cubic TiO_2 may also be obtained by introducing various dopants, similar to the way that cubic zirconia is stabilized below 2370 °C.

Acknowledgements

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