



[Zr_{0.72}Y_{0.28}]Al₄C₄: A new member of the homologous series (MC)_l(T₄C₃)_m (M = Zr, Y and Hf, T = Al, Si and Ge)

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ABSTRACT

A new layered carbide, [Zr_{0.72}Y_{0.28}]_lAl₄C₄, has been synthesized and characterized by X-ray powder diffraction, transmission electron microscopy and energy dispersive X-ray spectroscopy (EDX). The atom ratios [Zr:Y] were determined by EDX, and the initial structure model was derived by the direct methods, and further refined by Rietveld method. The crystal is trigonal (space group $P\bar{3}m1$, $Z = 1$) with lattice dimensions of $a = 0.333990(5)$ nm, $c = 1.09942(1)$ nm and $V = 0.106209(2)$ nm³. This compound shows an intergrowth structure with [Zr_{0.72}Y_{0.28}C₂] thin slabs separated by Al₄C₃-type [Al₄C₄] layers. It is a new member with $l = 1$ and $m = 1$ of the homologous series, the general formula of which is (MC)_l(T₄C₃)_m ($l = 1, 2$ and 3 , $m = 1$ and 2 , $M = \text{Zr, Y and Hf}$, $T = \text{Al, Si and Ge}$).

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1. Introduction

Recent efforts in our laboratory have aimed at defining a new homologous series of phases (ZrC)_l(Al₄C₃)_m ($l, m = \text{integers}$) [1–3]. Members of this series that have been confirmed so far include (ZrC)₂Al₄C₃ ($l = 2, m = 1$), (ZrC)₃Al₄C₃ ($l = 3, m = 1$), (ZrC)(Al₄C₃)₂ ($l = 1, m = 2$) and (ZrC)₂(Al₄C₃)₂ ($l = 2, m = 2$). These compounds exhibit a close structural and compositional relationship; the crystal structures can be regarded as intergrowth structures consisting of the Al₄C₃-type [Al_{4m}C_{3m+1}] layers separated by the NaCl-type [Zr_lC_{l+1}] layers. These two types of layers share the two-dimensional networks of carbon atoms at their boundaries (Fig. 1). The C–C distances of the networks, ranging from 0.3318 to 0.3328 nm, are comparable to those of ZrC and Al₄C₃ crystals; the former distance is 0.3319 nm ($= a(\text{ZrC})/\sqrt{2}$) [4] and that of the latter is 0.3335 nm ($= a(\text{Al}_4\text{C}_3)$) [5], where $a(\text{ZrC})$ and $a(\text{Al}_4\text{C}_3)$ represent the a -axis lengths. Fukuda et al. have therefore proposed that the closeness of the C–C distances between ZrC and Al₄C₃ crystals, being expressed by the equation $a(\text{ZrC})/\sqrt{2} \approx a(\text{Al}_4\text{C}_3)$, is the principal reason for the formation of these layered carbides [1–3,6]. However, attempts to synthesize the new members of the homologous series such as “(ZrC)Al₄C₃ ($l = 1, m = 1$)” and “(ZrC)₃(Al₄C₃)₂ ($l = 3, m = 2$)” were unsuccessful. For the NaCl-type compound ZrC, the unit cell content is [Zr₄C₄], indicating that the existence of the homologous phases with $l \geq 4$ is thermodynamically improbable [6]. Actually, the mixture of ZrC

and (ZrC)₃Al₄C₃ was the stable form for the specimens with the bulk chemical compositions of $l \geq 4$ [1,7]. Accordingly, the maximum value of integer l is limited to 3.

The [Al_{4m}C_{3m+1}] layers were incorporated by several amounts of Si [1,7–9] and/or Ge [10] components, whereas considerable amount of Y [11] component dissolved into the [Zr_lC_{l+1}] layers. Therefore the general formula has to be expanded to (Zr_{1-x}Y_xC)_l[(Al_{1-y-z}Si_yGe_z)₄C₃]_m, where the maximum x -, y - and z -values were 0.02, 0.07 and 0.02, respectively [1,7–11]. After the publication of papers on Zr₂(Al₄Si)₄C₅ [8] and Zr₃(Al₄Si)₄C₆ [7], the isomorphous crystal structures were reported in the Hf–Al–C system for Hf₂Al₄C₅ and Hf₃Al₄C₆ [12]. Accordingly, it would be relevant to further expand the solid-solution formula to (MC)_l(T₄C₃)_m, where $M = \text{Zr, Y and Hf}$, $T = \text{Al, Si and Ge}$.

There are two other ternary carbides reported so far in the Zr–Al–C system: (ZrC)₂Al₃C₂ and (ZrC)₃Al₃C₂ [6,13]. These carbides also form a homologous series with the general formula of (ZrC)_nAl₃C₂ ($n = 2$ and 3) [1]. The crystals show the intergrowth structures with alternating layers of [Zr_nC_{n+1}] and [Al₃C₃]. In the system U–Al–C, there are two types of ternary carbides (UC)₂Al₃C₂ and (UC)Al₃C₂ [5,13]. The former carbide is isostructural with (ZrC)₂Al₃C₂. The latter carbide, together with (ScC)Al₃C₂ [13] and (YC)Al₃C₂ [14,15], can be regarded as the intergrowth structure consisting of the [RC₂] slabs separated by the Al₄C₃-type [Al₃C₃] layers, where $R = \text{U, Sc and Y}$. Accordingly, these layered carbides are of the members with $n = 1$ for the homologous series (RC)_nAl₃C₂ ($R = \text{Zr, U, Sc and Y}$, $n = 1, 2$ and 3).

In the present study, we have experimentally verified the formation of (Zr,Y)Al₄C₄; a new member of the homologous series (MC)_l(T₄C₃)_m ($l = 1, 2$ and 3 , $m = 1$ and 2 , $M = \text{Zr and Y}$, $T = \text{Al}$).

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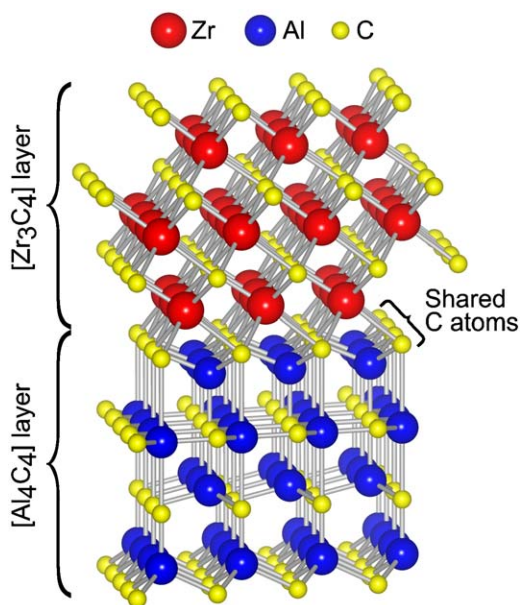


Fig. 1. A part of the layered structure of $(\text{ZrC})_3\text{Al}_4\text{C}_3$, showing the two-dimensional networks of carbon atoms at the boundary between $[\text{Zr}_3\text{C}_4]$ and $[\text{Al}_4\text{C}_4]$ layers.

The new layered carbide consisted of the $[(\text{Zr,Y})\text{C}_2]$ thin slabs (A) separated by the $[\text{Al}_4\text{C}_4]$ layers (B) with a sequence of $\langle \text{ABA-B} \cdots \rangle$ because the thickness of the layers were ~ 0.29 nm for A and ~ 0.81 nm for B, and the thickness of the AB layer was ~ 1.1 nm. The crystal structure has been determined from X-ray powder diffraction (XRPD) data using direct methods, and described in relation to the other layered carbides.

2. Experimental

2.1. Synthesis

The new carbide was initially recognized as unidentifiable diffraction lines in the XRPD patterns of the reacted $\text{ZrC}-\text{YC}_2-\text{Al}_4\text{C}_3$ mixtures. The XRPD pattern exhibited the characteristic diffraction peak at $2\theta \approx 8.04^\circ$ for $\text{CuK}\alpha_1$ radiation ($d \approx 1.1$ nm), strongly suggesting that the unknown phase is $(\text{Zr,Y})\text{Al}_4\text{C}_4$. We obtained the powder specimen that was mainly consisting of the new carbide together with small amounts of $(\text{ZrC})(\text{Al}_4\text{C}_3)_2$, $(\text{YC})\text{Al}_3\text{C}_2$ and YAlO_3 by the following procedures. The reagent-grade chemicals of zirconium carbide (99.9%, KCL Co., Ltd, Saitama, Japan), yttrium carbide (KCL, 99.9%) and aluminum carbide (KCL, 99.9%) were mixed in molar ratios of $[\text{ZrC}:\text{YC}_2:\text{Al}_4\text{C}_3] = [5:5:11]$, which is equivalent to $[\text{Zr}:\text{Y}:\text{Al}:\text{C}] = [5:5:44:43]$. Because the latter two reagents are highly hygroscopic, they were treated in a dry box to prevent the hydrolysis as much as possible. The mixture was pressed into pellets ($\varnothing 13$ mm \times 10 mm), heated at 2273 K for 30 min in inert gas atmosphere of Ar, followed by cooling to ambient temperature by cutting furnace power off. The reaction product was a slightly sintered polycrystalline material. It was finely ground to obtain powder specimen. The yttrium aluminum oxide was most probably formed because the hydrolysis occurred to some extent for the starting materials during weighing and mixing.

2.2. Characterization

XRPD intensities of the powder specimen were collected on a diffractometer (X'Pert PRO Alpha-1, PANalytical B.V., Almelo, the

Netherlands) equipped with a high speed detector in Bragg–Brentano geometry using monochromatized $\text{CuK}\alpha_1$ radiation (45 kV, 40 mA) in a 2θ range from 5.0137° to 148.9311° (an accuracy in 2θ of $\pm 0.0001^\circ$). The automatic divergence slit was employed to maintain an illumination length of 5 mm on the sample. Thus, the quantitative profile intensities were collected over the whole 2θ range. Other experimental conditions were: continuous scan, total of 8614 datapoints and total experimental time of 1.9 h. The structural data were standardized using the computer program STRUCTURE TIDY [16]. The crystal-structure models were visualized with the computer program VESTA [17].

The powder specimen was also examined using a transmission electron microscope (JEM 3000F, JEOL Ltd., Tokyo, Japan) operated at 300 kV and equipped with an energy dispersive X-ray analyzer (EDX; VOYAGER III, NORAN Instruments, Middleton, WI, USA). The powder particles were deposited with ethyl alcohol on a copper grid. A selected area electron diffraction (SAED) pattern and corresponding lattice image were obtained. A chemical analysis was made for nine crystal fragments to determine the heavy atom ratios $[\text{Zr}:\text{Y}]$. The correction was made by the ZAF routines.

3. Results and discussion

3.1. Structure determination and refinement

The SAED pattern [Fig. 2(a)] was successfully indexed with a hexagonal unit cell with dimensions of $a \approx 0.33$ nm and $c \approx 1.1$ nm. The corresponding lattice image [Fig. 2(b)] strongly suggests that the crystal structure is built up from stacking combinations of two basic sheets. The heavy atom ratios $[\text{Zr}:\text{Y}]$ were determined to be $[0.72(3):0.28(3)]$, where the numbers in parentheses indicate standard deviations. Accordingly, the chemical formula of the new carbide is most probably $[\text{Zr}_{0.72(3)}\text{Y}_{0.28(3)}]\text{Al}_4\text{C}_4$.

The XRPD pattern in Fig. 3 showed the presence of weak diffraction intensities peculiar to $(\text{ZrC})(\text{Al}_4\text{C}_3)_2$, $(\text{YC})\text{Al}_3\text{C}_2$ and YAlO_3 . All of the other diffraction peaks belonging to the new carbide were successfully indexed with the hexagonal unit cell.

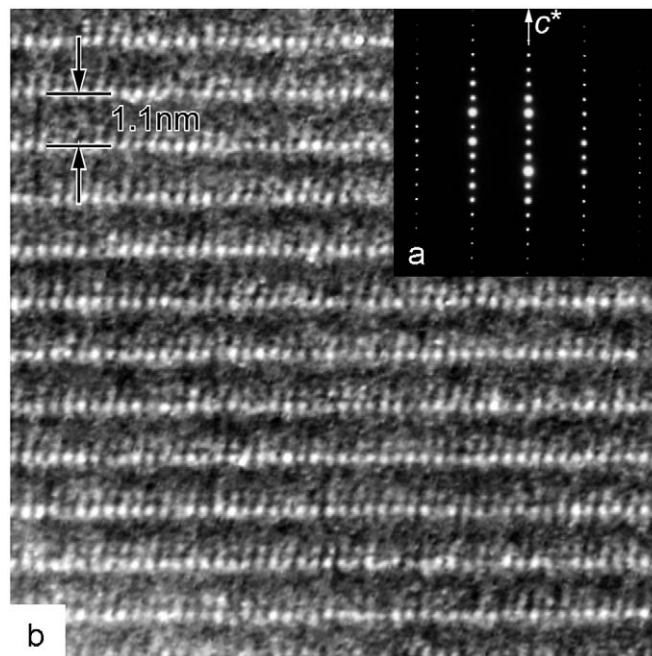


Fig. 2. (a) Selected-area electron diffraction pattern and (b) corresponding lattice image. Incident beam perpendicular to the c -axis.

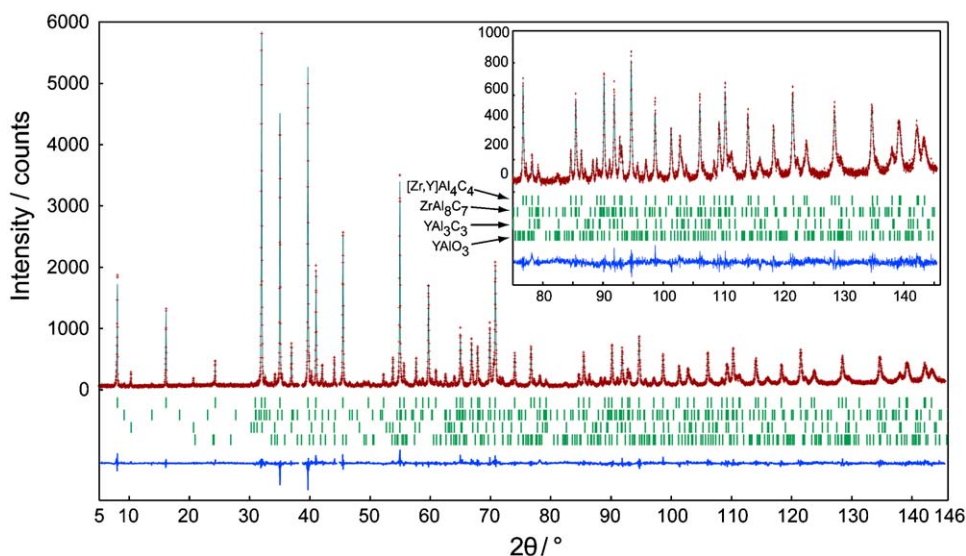


Fig. 3. Comparison of the observed diffraction pattern (symbol: +) with the corresponding calculated pattern (upper solid lines). The difference curve is shown in the lower part of the diagram. Upper vertical bars indicate the positions of possible Bragg reflections.

The unit-cell parameters and integrated intensities were selectively refined by the Le Bail method [18], using the computer program RIETAN-FP [19]. The refined unit-cell dimensions were $a = 0.333929(5)$ nm, $c = 1.09923(1)$ nm and $V = 0.106152(4)$ nm³. The integrated intensities were examined to confirm the presence or absence of reflections. There were no systematic absences for hkl reflections, implying that the possible space groups are $P3$, $P\bar{3}$, $P321$, $P3m1$, $P\bar{3}m1$, $P312$, $P31m$ and $P\bar{3}1m$.

In general, the number of formula units in the unit cell (Z) is determined from the unit-cell volume V (nm³), true density D_t (Mg m⁻³) and molecular weight M (g) as follows:

$$Z = VD_t / (M \times 1.660 \times 10^{-3}). \quad (1)$$

The molar ratios of [Zr:Y:Al:C] are [0.72:0.28:4:4] for the new carbide, and hence the M value (g) is equal to 246.5. Because the densities (Mg m⁻³) are 2.98 for Al₄C₃ [5] and 4.46 for (ZrC)₂Al₄C₃ [1], the D_t -value of [Zr_{0.72}Y_{0.28}]Al₄C₄ must be around 3.72 [= (2.98+4.46)/2]. Substituting 246.5 g, 0.10615 nm³ and 3.72 Mg m⁻³ for, respectively, M -, V - and D_t -values in Eq. (1) yields 0.97 for an approximate value of Z . Thus, the Z -value must be equal to 1, which indicates that the unit cell content is [0.72Zr 0.28Y 4Al 4C]. Because the atomic scattering factors for Zr and Y are nearly the same, a unit-cell content with [Zr 4Al 4C] was used as input data for the search of an initial structure model. All of the possible space groups were tested using the EXPO2004 package for crystal structure determination [20]. The individual integrated intensities that were refined by the Le Bail method were used for the direct methods. A promising structural model was successfully obtained for the space group $P\bar{3}m1$ (centrosymmetric). There are 5 independent atoms in the unit cell; one Zr atom (Zr/Y site located on Wyckoff position 1a), two Al atoms (Al(1) and Al(2) sites on 2d) and two C atoms (C(1) and C(2) sites on 2d).

Structural parameters were subsequently refined by the Rietveld method [21] using the computer program RIETAN-FP [19] (Fig. 3). A Legendre polynomial was fitted to background intensities with 12 adjustable parameters. The split Pearson VII function [22] was used to fit the peak profile. The isotropic atomic displacement parameters (B) of the C sites were constrained to have the same value. Reliability indices [23] for a final result were $R_{wp} = 9.36\%$, $S = 1.19$ and $R_p = 7.19\%$ ($R_B = 3.89\%$ and $R_F = 2.43\%$ for [Zr_{0.72}Y_{0.28}]Al₄C₄). Crystal data are given in Table 1, and the

Table 1

Crystal data for (Zr_{0.72}Y_{0.28}C)Al₄C₃.

Chemical composition	Zr _{0.72(3)} Y _{0.28(3)} Al ₄ C ₄
Space group	$P\bar{3}m1$
a (nm)	0.333990(5)
c (nm)	1.09942(1)
V (nm ³)	0.106209(2)
Z	1
D_x /Mg m ⁻³	3.85

Table 2

Structural parameters for (Zr_{0.72}Y_{0.28}C)Al₄C₃.

Site	Wyckoff position	x	y	z	$100 \times B$ (nm ²)
Zr/Y	1a	0	0	0	0.82(4)
Al(1)	2d	1/3	2/3	0.4135(2)	1.08(6)
Al(2)	2d	1/3	2/3	0.7914(2)	0.72(5)
C(1)	2d	1/3	2/3	0.1335(5)	0.25(8)
C(2)	2d	1/3	2/3	0.6217(5)	0.25

Table 3

Interatomic distances (nm) in (Zr_{0.72}Y_{0.28}C)Al₄C₃^a.

Zr/Y–C(1)	0.2423(3) × 6
Zr/Y–Al(2)	0.2997(2) × 6
Al(1)–C(2)	0.1967(1) × 3
Al(1)–C(2)	0.2289(6)
Al(1)–Al(2)	0.2965(3) × 3
Al(1)–C(1)	0.3079(6)
Al(2)–C(2)	0.1866(6)
Al(2)–C(1)	0.2098(2) × 3

^a All distances shorter than 0.30 nm (metal–metal) and 0.31 nm (metal–carbon) are given.

final atomic positional and B parameters are given in Table 2. The selected interatomic distances, together with their standard deviations, are given in Table 3. Quantitative X-ray analysis with correction for microabsorption according to Brindley's procedure [24] was implemented in the program RIETAN-FP. The phase composition of the sample was found to be 84.4 mass%

$[\text{Zr}_{0.72}\text{Y}_{0.28}]\text{Al}_4\text{C}_4$, 4.1 mass% $(\text{ZrC})(\text{Al}_4\text{C}_3)_2$, 9.0 mass% $(\text{YC})\text{Al}_3\text{C}_2$ and 2.5 mass% YAlO_3 . We in turn determined from calculation the average composition (molar ratio) of the sample to be $[\text{Zr}:\text{Y}:\text{Al}:\text{C}] = [5:3.0:31.1:30.6]$. The deviation from the initial composition is most probably caused by the preferential evaporation of Al_4C_3 component during heating [2,25] as well as the incorporation of Y component into $(\text{ZrC})(\text{Al}_4\text{C}_3)_2$.

3.2. Structure description

The crystal structure of the quaternary carbide $(\text{Zr}_{0.72}\text{Y}_{0.28}\text{C})\text{Al}_4\text{C}_3$ has been confirmed to be of a new one, consisting of $[\text{Zr}_{0.72}\text{Y}_{0.28}\text{C}_2]$ layers (thickness of 0.294 nm) separated by the Al_4C_3 -type $[\text{Al}_4\text{C}_4]$ layers with 0.806 nm thickness (Fig. 4). The mean interatomic distances in $(\text{Zr}_{0.72}\text{Y}_{0.28}\text{C})\text{Al}_4\text{C}_3$ compared well with those of ZrC , Al_4C_3 , $(\text{ZrC})_n\text{Al}_3\text{C}_2$ and $(\text{ZrC})\text{Al}_4\text{C}_3$ [1–3,5,6,13]. The Zr/Y site is octahedrally coordinated by C atoms with the distance of 0.242 nm, which is comparable to those of the ZrC_8 polyhedra in ZrC (0.235 nm), $(\text{ZrC})_2\text{Al}_3\text{C}_2$ (0.241 nm), $(\text{ZrC})_3\text{Al}_3\text{C}_2$ (0.239 nm), $(\text{ZrC})_2\text{Al}_4\text{C}_3$ (0.237 nm) and $(\text{ZrC})_3\text{Al}_4\text{C}_3$ (0.236 nm). The Zr/Y–Al distance of 0.300 nm is comparable to the Zr–Al distances of $(\text{ZrC})_2\text{Al}_3\text{C}_2$ (0.297 nm), $(\text{ZrC})_3\text{Al}_3\text{C}_2$ (0.297 nm), $(\text{ZrC})_2\text{Al}_4\text{C}_3$ (0.299 nm) and $(\text{ZrC})_3\text{Al}_4\text{C}_3$ (0.302 nm). The Al atoms are tetrahedrally coordinated with the mean distance of 0.204 nm. These Al–C distances are comparable to those of the AlC_4 tetrahedra in Al_4C_3 ranging from 0.194 to 0.218 nm (the mean = 0.206 nm) [5], which implies that the $[\text{Al}_4\text{C}_4]$ layer is structurally comparable to the compound Al_4C_3 .

With $(\text{YC})\text{Al}_3\text{C}_2$, the C–C distance of the carbon network at the interlayer boundary between $[\text{YC}_2]$ and $[\text{Al}_3\text{C}_3]$ is 0.3422 nm [14], which is longer than those of $(\text{ZrC})(\text{Al}_4\text{C}_3)_m$ ($l = 2$ and 3 , and $m = 1$ and 2) ranging from 0.3318 to 0.3328 nm. Hence the incorporation of Y component into the $[\text{Zr}_l\text{C}_{l+1}]$ layers would increase the C–C distances. Actually, the C–C distance in $[\text{Zr}_{0.72}\text{Y}_{0.28}\text{C}_2]$ slab is 0.3340 nm, which is very close to that of Al_4C_3 crystal (0.3335 nm). Accordingly, the replacement of Zr by 28 mol% Y in the $[\text{ZrC}_2]$ layer would effectively reduce the misfit degree at the interlayer boundary between $[(\text{Zr,Y})\text{C}_2]$ and $[\text{Al}_4\text{C}_4]$,

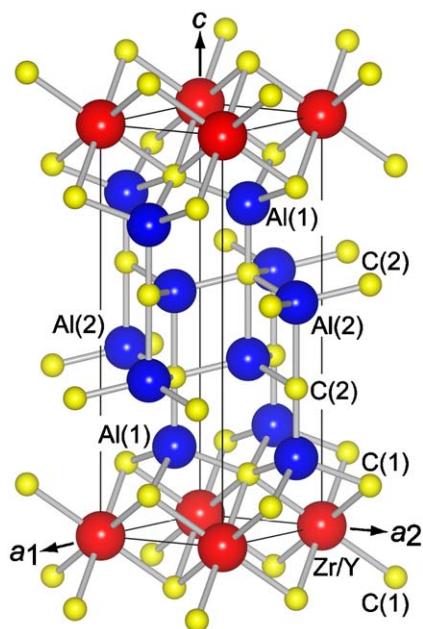


Fig. 4. Crystal structure of $(\text{Zr}_{0.72}\text{Y}_{0.28}\text{C})\text{Al}_4\text{C}_3$.

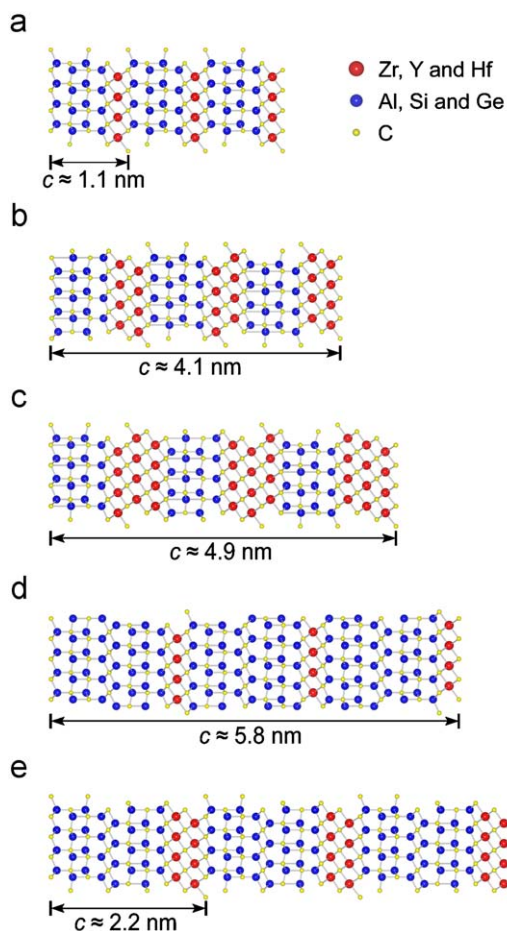


Fig. 5. Atomic configurations in $(\text{MC})(\text{T}_4\text{C}_3)_m$ ($M = \text{Zr, Y and Hf, T} = \text{Al, Si and Ge}$). $(l, m) = (1, 1)$ in (a), $(2, 1)$ in (b), $(3, 1)$ in (c), $(1, 2)$ in (d) and $(2, 2)$ in (e).

leading to the formation of the layered carbide with $l = 1$ and $m = 1$.

The new layered carbide has been found to be a member of the homologous series, the general formula of which is $(\text{MC})(\text{T}_4\text{C}_3)_m$ ($l = 1, 2$ and $3, m = 1$ and $2, M = \text{Zr, Y and Hf, T} = \text{Al, Si and Ge}$). The formula requires two integers l and m that can be changed independently, and hence causes evolution of the structure in two different dimensions (Fig. 5). These layered carbides can be regarded as the natural superlattice quantum-well materials, thus they have prospects for application of thermoelectric power generators [7,8,14,15]. The postulated member with $l = 3$ and $m = 2$ (i.e., $\text{M}_3\text{T}_8\text{C}_9$) must be, although it is still not confirmed yet, composed of the two types of alternately stacking layers of $[\text{M}_3\text{C}_4]$ and $[\text{T}_8\text{C}_7]$. The crystal data must be $a = \sim 0.33$ nm and $c = \sim 4.94$ nm with the space group $\text{P}6_3\text{mc}$.

4. Conclusion

In the Zr–Y–Al–C system, we have successfully synthesized a new layered carbide $(\text{Zr}_{0.72}\text{Y}_{0.28}\text{C})\text{Al}_4\text{C}_3$. The crystal structure was determined from XRPD data and described in relation to the other layered carbides in the system Zr–Al–C. The crystal structure was considered to be composed of the $[\text{Zr}_{0.72}\text{Y}_{0.28}\text{C}_2]$ thin slabs separated by the Al_4C_3 -type $[\text{Al}_4\text{C}_4]$ layers. The carbide has been found to be the first new member with $l = 1$ and $m = 1$ of the homologous series $(\text{MC})(\text{T}_4\text{C}_3)_m$ ($M = \text{Zr and Y, T} = \text{Al}$).

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