Synthesis and characterization of double solid solution $(Zr,Ti)_2(Al,Sn)C$ MAX phase ceramics

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Supporting information

Table S1. Experimental *a*, *c* and z_M data for the $(Zr_{1-x},Ti_x)_2(Al_{0.5},Sn_{0.5})C$ MAX phases. Uncertainties are of the 10^{-3} Å order of magnitude.

Method	Ti (x)	*a* (Å)	*c* (Å)	z_M (Å)
RHP6/30	0.00	3.344	14.568	0.088
	0.30	3.284	14.350	0.085
	0.50	3.234	14.184	0.085
	0.70	3.190	14.014	0.083
	1.00	3.115	13.714	0.082
RHP30	0.00	3.350	14.581	0.086
	0.30	3.278	14.347	0.089
	0.50	3.228	14.153	0.085
	0.70	3.187	14.007	0.083
	1.00	3.114	13.715	0.083
RHP0	0.00	3.345	14.563	0.086
	0.10	3.326	14.503	0.086
	0.30	3.279	14.343	0.087
	0.50	3.232	14.174	0.085
	0.70	3.188	13.996	0.084
	0.90	3.139	13.806	0.083
	1.00	3.115	13.707	0.082
CIP/RHP/0	0.00	3.350	14.573	0.088
	0.10	3.330	14.504	0.085
	0.30	3.283	14.341	0.090
	0.50	3.242	14.175	0.084
	0.70	3.194	13.998	0.085
	0.90	3.141	13.806	0.083
	1.00	3.116	13.709	0.080
CIP/Ar/0	0.00	3.347	14.555	0.091
	0.10	3.330	14.511	0.090
	0.30	3.299	14.360	0.085
	0.50	3.258	14.165	0.086
	0.70	3.203	14.010	0.083
	0.90	3.144	13.808	0.083
	1.00	3.108	13.713	0.081

Table S2. Tabulated CTE data, measured between RT and 1500 °C for the $(Zr,Ti)_2(Al,Sn)C$ MAX phases and reported in literature for Ti_2AlC[1-4], and Ti_2SnC and Zr_2SnC[5].

MAX Phase	Linear Fit (Å)	R^2	α ($\times 10^{-6}$ K^{-1})	α_{av} ($\times 10^{-6}$ K^{-1})	α_c / α_a	Method
$Zr_2(Al_{0.5},Sn_{0.5})C$	$a = 2.38861 \times 10^{-5} \times T(K) + 3.31194$	0.98061	*7.2(3)*	7.3(4)	1.06	XRD
	$\boldsymbol{c = 1.1008 \times 10^{-4} \times T(K) + 14.42827}$	0.99337	**7.6(2)**			
$(Zr_{0.7},Ti_{0.3})_2(Al_{0.5},Sn_{0.5})C$	$a = 2.15898 \times 10^{-5} \times T(K) + 3.25486$	0.99427	*6.6(1)*	6.9(2)	1.13	XRD
	$\boldsymbol{c = 1.06602 \times 10^{-4} \times T(K) + 14.23171}$	0.99849	**7.5(1)**			
$(Zr_{0.3},Ti_{0.7})_2(Al_{0.5},Sn_{0.5})C$	$a = 2.20922 \times 10^{-5} \times T(K) + 3.17773$	0.99427	*6.9(1)*	7.2(3)	1.09	XRD
	$\boldsymbol{c = 1.05682 \times 10^{-4} \times T(K) + 13.91558}$	0.99502	**7.6(1)**			
$Ti_2(Al_{0.5},Sn_{0.5})C$	$a = 2.55248 \times 10^{-5} \times T(K) + 3.09115$	0.99142	*8.2(2)*	8.4(3)	1.05	XRD
	$\boldsymbol{c = 1.17615 \times 10^{-4} \times T(K) + 13.60349}$	0.99805	**8.6(1)**			

Ti_2AlC			*7.1(3)*	8.07	1.41	XRD[1]
			10.0(5)			
			8.2(2)			Dilatometer[2]
Ti_2AlC			*9.0(1)*	9.2	1.07	Neutron diffraction[3]
			9.6(1)			
			8.7			Dilatometer[4]
Ti_2SnC			10.0(2)			Dilatometer[5]
Zr_2SnC			8.3(2)			Dilatometer[5]
Ti_2SnC	$a = 2.62 \times 10^{-5} \times T(K) + 3.1591$	0.9983	*8.3(1)*	8.2(3)	0.99(3)	XRD
	$\boldsymbol{c = 1.12 \times 10^{-4} \times T(K) + 13.665}$	0.9956	**8.2(2)**			XRD

α_a values appear in *italic*, α_c in **bold** and α values measured by dilatometer are underlined. The number in parenthesis indicates the uncertainty in the last digit.

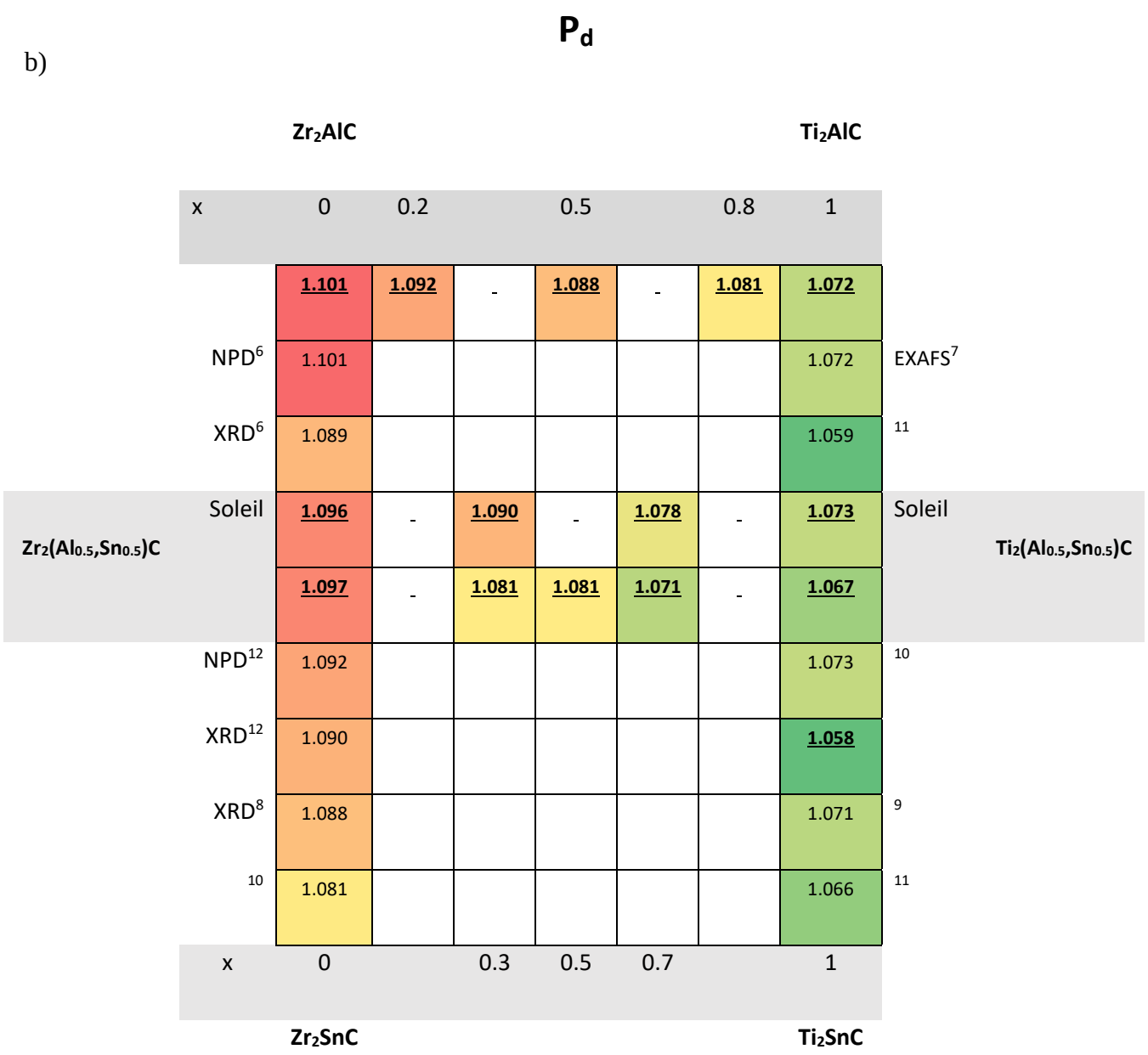
The O_d and P_d values for the $(Zr_{1-x},Ti_x)_2(Al_{0.5},Sn_{0.5})C$ MAX phases, which were calculated in this work using equations (1) and (2), are summarised in **Figure S1a and b** along with the available literature data indicating the measurement method.[6–12] A colour code was used to indicate maximum distortions (>>1) in red and minimum distortion values (≈ 1) in green. O_d/P_d ratio values are tabulated in **Figure S1c**, where any deviations from O_d/P_d = 1 are coloured towards red, and values close to $O_d/P_d \approx 1$ are coloured in green. The Ti_2SnC distortion values found in literature were not experimentally determined, but calculated,[9–11] and were added to **Figure S1** along with the experimentally determined values in this work. If available, the measurement method is also indicated, i.e., X-Ray Diffraction (XRD), Neutron Powder Diffraction (NPD), or Extended X-Ray Absorption Fine Structure (EXAFS). The '*' symbol indicates near phase-pure (≥ 95 wt %) MAX phases, either synthesised in this work or reported in literature. The corners of **Figure S1a to c** are occupied by the ternary carbides (end-members) that are relevant to this study, i.e., Zr_2AlC, Ti_2AlC, Zr_2SnC and Ti_2SnC. Between the ternary end-members, relevant solid solution MAX phases may be found, with compositional changes in the Ti/Zr content shown in the horizontal direction, and changes in the Sn/Al content shown in the vertical direction.

O_d

a)

		Zr_2AlC						Ti_2AlC	
	x	0	0.2		0.5		0.8	1	
		1.034	**1.044**	-	**1.047**	-	**1.059**	**1.067**	
	NPD[6]	1.034						1.067	EXAFs[7]
	XRD[6]	1.061						1.081	11
$Zr_2(Al_{0.5},Sn_{0.5})C$	Soleil	**1.020**	-	**1.027**	-	**1.054**	-	**1.057**	Soleil
		1.057	-	**1.090**	**1.080**	**1.105**	-	**1.109**	$Ti_2(Al_{0.5},Sn_{0.5})C$
	NPD[12]	1.082						1.129	10
	XRD[12]	1.085						**1.192**	
	XRD[8]	1.078						1.184	9
	10	1.084						1.136	11
	x	0		0.3	0.5	0.7		1	
		Zr_2SnC						Ti_2SnC	

b)


P_d
Zr_2AlC
Ti_2AlC
x 0 0.2 0.5 0.8 1
1.101 1.092 - 1.088 - 1.081 1.072
NPD[6] 1.101 1.072 EXAFS[7]
XRD[6] 1.089 1.059 11
Soleil 1.096 - 1.090 - 1.078 - 1.073 Soleil
$Zr_2(Al_{0.5},Sn_{0.5})C$
1.097 - 1.081 1.081 1.071 - 1.067 $Ti_2(Al_{0.5},Sn_{0.5})C$
NPD[12] 1.092 1.073 10
XRD[12] 1.090 1.058
XRD[8] 1.088 1.071 9
10 1.081 1.066 11
x 0 0.3 0.5 0.7 1
Zr_2SnC
Ti_2SnC

c) **O_d/P_d**

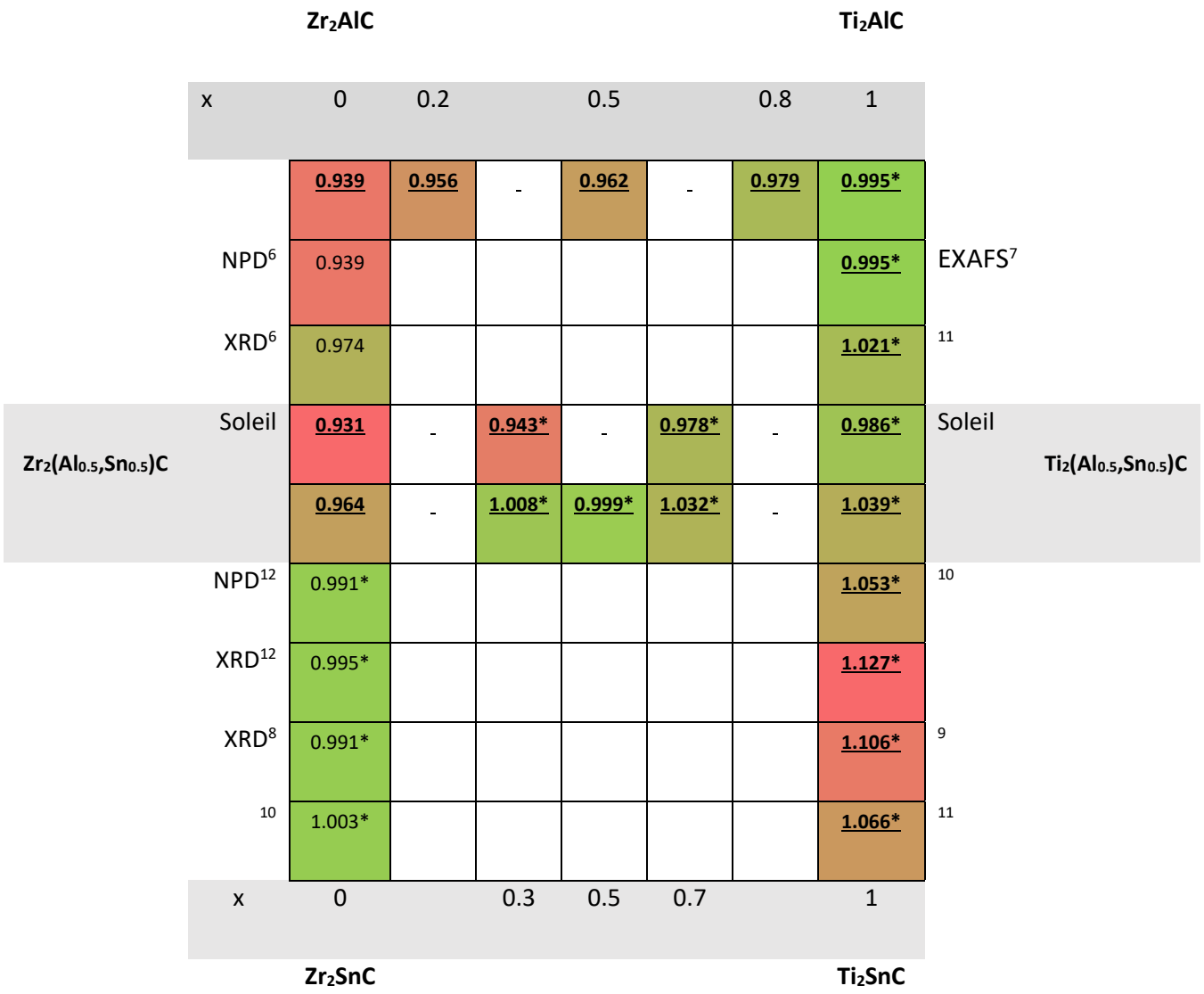


Figure S1. Calculated O_d (a), P_d (b) and O_d/P_d (c) values for the $(Zr_{1-x},Ti_x)_2(Al_{0.5},Sn_{0.5})C$ phases synthesized by RHP6/30 in this work, along with the available literature data[6-12] and measurement methods. The '*****' symbol indicates the produced ceramics with ≥95 wt % phase purity. The horizontal axis is the Ti content, x. The colour scale used in (a) and (b) associates the "high" values with red, and the "low" values with green. In (c), O_d/P_d values that are close to 1 are indicated in green, and those deviating from that value are coloured progressively towards red.

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