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Letter

Single crystal X-ray study of Zr_3NiO

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1. Introduction

A study of the zirconium–nickel–sulfur ternary system currently being carried out in this laboratory has yielded some structurally significant oxides as minor phases. In particular, a single crystal of the Zr_3NiO phase has been isolated and analyzed. This phase has previously been investigated and characterized by X-ray powder diffraction and structurally identified as a filled Re_3B-type structure [1–3]. The single crystal analysis confirms previously reported results.

2. Experimental details

A crystal was selected for the X-ray study from a sample which had undergone a number of experimental treatments. Initially, zirconium, nickel and sulfur in the molar ratios 6:4:5 were heated in an evacuated silica tube at temperatures up to 690 °C. The resulting mixture was arc-melted. Additional zirconium and nickel were added to the sample to bring the final metal ratio to $n(\mathrm{Zr})$: $n(\mathrm{Ni}) = 3{:}1$. The sample was repeatedly crushed, pelletized and inductively heated to temperatures in the range 1050–1230 °C for 12–18 h. The sample was soaked in concentrated HCl for a week to remove a binary sulfide phase, and subsequently heated to 1130 °C for 5 days. The crystal studied here was chosen from this final sample, although the oxide phase, as identified by X-ray diffraction films of the powder, was present before the sample was placed in the acid.

The intensity data for the crystal were collected using a RIGAKU AFC6R single crystal diffractometer and monochromated Mo Kα radiation, employing the ω–2θ scan technique up to 55° (2θ). From a total of 422 reflections ($\pm hkl$), 162 independent reflections with $F^2 > 3\sigma(F_0{}^2)$ were obtained and used for structure analysis. The observed intensities were corrected for Lorentz polarization and absorption effects with the maximum and minimum transmission factors of 1 and 0.768. No significant decay was observed during the data collection.

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3. Results and discussion

The crystal structure was solved using the direct method used in the TEXSAN program. The crystal data, atomic coordinates and thermal parameters for Zr_3NiO are given in Tables 1, 2 and 3 respectively. This phase has been shown to exist with variable oxygen content. The fractional oxygen occupancy ranges from 0.2 to 1.0, and the variation of the lattice parameters as a function of oxygen occupancy has been measured [3]. Full oxygen occupancy in this crystal was indicated by the agreement in lattice parameters (a= 3.33 Å, b=10.99 Å, c=8.77 Å [3] (see Table 1)) as well as by the crystal refinement.

TABLE 1

Crystal data for Zr_3NiO

Space group	*Cmcm*(No. 63)
a (Å)	3.353(1)
b (Å)	11.013(4)
c (Å)	8.755(7)
V (Å^3)	323.3(3)
Z	4
d_{calc} (g cm^{-3})	7.153
Crystal size (mm^3)	0.06×0.03×0.02
μ(Mo Kα) (cm^{-1})	147.71
Data collection instrument	RIGAKU AFC6
Radiation (monochromated in incident beam)	Mo K_α (λ=0.71069 Å)
Temperature (°C)	23
Total number of unique data with $F_o^2 > 3\sigma(F_0^2)$	162
Number of refined parameters	20
Secondary extinction coefficient (10^{-7})	7.8
R^a, R_w^b, GOF^c	0.025, 0.033, 1.149

$^a R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.
$^b R_w = [\Sigma(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; $w = 1/\sigma^2(|F_0|)$.
$^c \mathrm{GOF} = \Sigma((|F_0| - |F_c|)/\sigma_i)/(N_{obs} - N_{parameters})$.

TABLE 2

Atomic positions for Zr_3NiO

Atom	Site	x	y	z
Zr(1)	8f	0	0.3645(1)	0.5601(1)
Zr(2)	4c	0	0.9338(2)	1/4
Ni	4c	0	0.2460(2)	1/4
O	4a	0	0	0

TABLE 3

Thermal parameters for Zr_3NiO

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr(1)	0.0082(7)	0.0071(7)	0.0093(7)	0	0	−0.0016(5)
Zr(2)	0.005(1)	0.012(1)	0.010(1)	0	0	0
Ni	0.022(2)	0.014(1)	0.010(1)	0	0	0
O	0.010(7)	0.018(7)	0.007(6)	0	0	0.006(6)

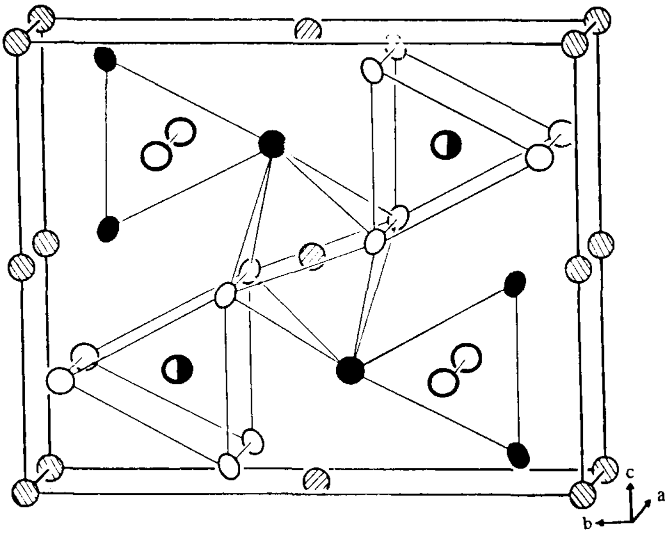

Fig. 1. Unit cell of Zr_3NiO showing octahedral coordination of oxygen and trigonal prismatic coordination of nickel. ○, Zr($x=0$); ○, Ni($x=0$); ◍, O($x=0$); ●, Zr($x=\frac{1}{2}$); ◑, Ni($x=\frac{1}{2}$); ⊘, O($x=\frac{1}{2}$).

The interatomic distances less than 3.4 Å are listed in Table 4. The structure may be seen (Fig. 1) as consisting of chains of trigonal prisms of zirconium atoms sharing triangular faces. Each prism is centered by a nickel atom. The adjacent chains are offset from each other by $x=\frac{1}{2}$. Oxygen atoms occupy the interstitial octahedral site formed by the zirconium atoms from adjacent chains. The shorter zirconium–zirconium distances indicate stronger interactions between the zirconium atoms in adjacent trigonal prisms compared to those within the prism. All the zirconium–zirconium distances in the trigonal prism are greater than 3.3 Å. In fact, the Zr(1)–Zr(2) distance on the triangular face of the prism is 3.68 Å. This is significantly larger than the 3.23 Å separation in elemental zirconium, as well as the other zirconium–zirconium separations in this oxide (Table 4). Although the zirconium–zirconium linkages around the prism are outlined in Fig. 1, the important interactions within the prism are between the nickel and zirconium atoms.

TABLE 4

Interatomic distances for Zr_3NiO (Å)

Zr(1)	–2 O	2.305(1)	Zr(2)	–2 O	2.307(2)
	–2 Ni	2.657(2)		–2 Ni	2.662(3)
	–1 Ni	3.012(3)		–1 Ni	3.439(4)
	–1 Zr(1)	3.165(3)		–2 Zr(1)	3.242(2)
	–2 Zr(1)	3.206(2)		–2 Zr(1)	3.281(2)
	–2 Zr(2)	3.242(2)		–2 Zr(2)	3.3529(4)
	–2 Zr(2)	3.281(2)			
	–1 Zr(1)	3.325(4)	Ni	–4 Zr(1)	2.657(2)
	–2 Zr(1)	3.3529(4)		–2 Zr(2)	2.662(3)
	–2 Zr(1)	3.012(3)			
O	–4 Zr(1)	2.305(1)			
	–2 Zr(2)	2.307(2)			

The zirconium–nickel separation here is 2.66 Å. This is shorter than *d*(Zr–Ni) in ZrNi ($d = 2.68$–2.77 Å) and Zr_2Ni ($d = 2.76$ Å) [4].

References

1 M. V. Nevitt and J. W. Downey, *Trans. Met. Soc. AIME, 221* (1961) 1014.
2 P. Rogl, H. Nowotny and F. Benesovsky, *Monatsh. Chem., 104* (1973) 182.
3 H. Boller, *Monatsh. Chem., 104* (1973) 545.
4 P. Villars and L. D. Calvert (eds.), *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd edn., American Society for Metals, Materials Park, OH, 1991.