Polish J. Chem., **75**, 153–156 (2001) **COMMUNICATION**

Rietveld Refinement of the Structure of $Nd_2Zn_{15}Ge_2$

by P. Demchenko* and O. Bodak

Department of Inorganic Chemistry, L'viv National University, Kyryla i Mefodiya str., 6, 79005 L'viv, Ukraine

(Received July 11th, 2000; revised manuscript September 5th, 2000)

Current investigation has been undertaken in a continuation of our systematic study of alloying behavior of the neodymium and zinc with IVa group elements. Recently, we reported on the isothermal sections of the Nd–Zn–Si(Ge) systems at 600°C [1], Nd–Zn–Sn(Pb) systems at the same temperature [2] and crystal structures of the ternary compounds [3]. In this communication we present the results of the crystal structure refinement for the $Nd_2Zn_{15}Ge_2$ ternary compound.

The sample with a total mass of 1 g was prepared by compacting a well blended mixture of weighted quantities of Nd filing (99.9%) and powders of Zn and Ge (> 99.99%). The pellet was sealed in an evacuated quartz tube and heated slowly during one week from room temperature to 600°C and kept at 600°C for 150 h. For further homogenization the pellet was pulverized under cyclohexane, recompacted and annealed at 600°C for 250 h in an evacuated silica capsule. After heat treatment the sample was quenched by submerging the silica capsule in cold water.

X-ray powder diffraction data were collected using HZG-4a automatic powder diffractometer (Cu K_α radiation) in the range $20° \le 2\vartheta \le 120°$ with a step size of 0.05° 2ϑ and counting time of 10 s per data point. The data were corrected for absorption and evaluated by the DBW3.2s program [4] using the pseudoVoigt profile function. The refinement procedure was begun with the zero correction, scale factor and mixing parameters. The lattice and profile parameters were included next in the refinement. After that, atomic coordinates and isotropic temperature parameters were included. Finally, all of the parameters were refined together. No obvious preferred orientation effect was observed.

Using data of the previously determined crystal structure [3], the rhombohedral Th_2Zn_{17} structure type was used as trial structure for the refinement with the assumption of a statistical distribution of the Ge and Zn atoms over the 6c, 9d, 18f and 18h sites. However, the best results of the calculation (residual factors, temperature parameters, interatomic distances, standard deviations, *etc.*) were obtained using the model of the $Ce_2Co_{15}Al_2$ structure type [5] – an ordered substitution derivative of the Th_2Zn_{17} structure type. Experimental results are collected in Table 1, atomic coordinates and isotropic temperature parameters are given in Table 2. Interatomic dis-

* Corresponding author.

tances and coordination numbers of the atoms are listed in Table 3. Results of the Rietveld refinement of the $Nd_2Zn_{15}Ge_2$ compound (observed, calculated and difference profiles) are shown in Fig. 1.

Table 1. Crystallographic data of the $Nd_2Zn_{15}Ge_2$ compound.

Compound	$Nd_2Zn_{15}Ge_2$
Structure type	$Ce_2Co_{15}Al_2$
Pearson symbol	hR57
Space group	$R\bar{3}m$ (No. 166)
Unit cell dimensions	a = 0.9057(2) nm
	c = 1.3262(2) nm
	V = 0.9421(3) nm^3
Calculated density	7.478 g/cm^3
Reliability factors (%):	
R_p	2.14
R_{wp}	2.67
Goodness of fit	1.35

Table 2. Atomic coordinates and isotropic temperature parameters for the $Nd_2Zn_{15}Ge_2$ compound.

Atom	Position	x	y	z	$B_{iso} \times 10^2$ (nm^2)
Nd	*6c*	0	0	0.342(1)	0.2(2)
Ge	*6c*	0	0	0.094(2)	1.9(6)
Zn1	*9d*	1/2	0	1/2	0.8(5)
Zn2	*18f*	0.295(2)	0	0	1.8(4)
Zn3	*18h*	0.498(2)	0.502(2)	0.151(2)	1.4(4)

Table 3. Interatomic distances (δ, nm) and coordination numbers of the atoms (CN) for the $Nd_2Zn_{15}Ge_2$ compound.

Atoms		δ, nm	CN	Atoms		δ, nm	CN
Nd	– 3Zn3	0.3199(8)	20	Zn2	– 2Zn1	0.260(1)	13
	– 6Zn2	0.3209(7)			– 3Zn2	0.268(1)	
	– 1Ge	0.329(1)			– 2Zn3	0.273(2)	
	– 3Zn3	0.339(2)			– 2Zn3	0.278(1)	
	– 3Zn3	0.346(2)			– 2Ge	0.295(1)	
	– 3Zn1	0.3499(6)			– 2Nd	0.3209(7)	
	– 1Nd	0.419(1)		Zn3	– 2Zn3	0.262(2)	12
Ge	– 1Ge	0.249(1)	14		– 2Zn1	0.264(2)	
	– 3Zn1	0.2787(8)			– 2Zn2	0.273(2)	

	– 3Zn3	0.289(2)		– 2Zn2	0.278(1)
	– 6Zn2	0.295(1)		– Ge	0.289(2)
	– 1Nd	0.329(1)		– Nd	0.3199(8)
Zn1	– 4Zn2	0.260(1)	12	– Nd	0.339(2)
	– 4Zn3	0.264(2)		– Nd	0.346(2)
	– 2Ge	0.2787(8)			
	– 2Nd	0.3499(6)			

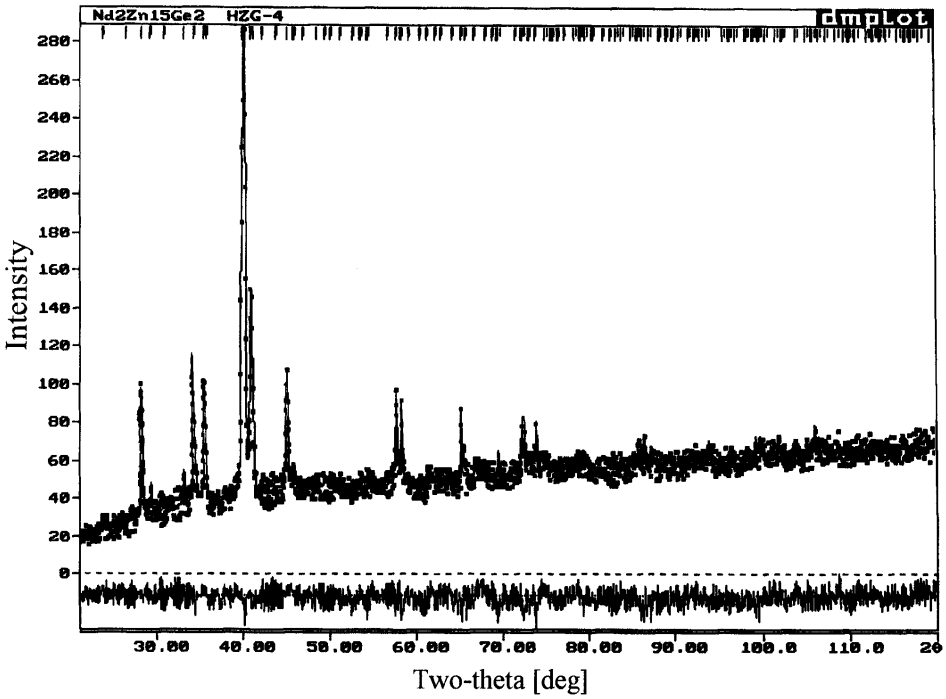

Figure 1. Results of the Rietveld refinement of the $Nd_2Zn_{15}Ge_2$ (observed, calculated and difference profiles).

According to Borzone *et al*. [6], the binary Nd_2Zn_{17}-compound has two polymorphic modifications: a low-temperature phase with the Th_2Ni_{17} structure type and a high-temperature phase with the Th_2Zn_{17} structure type. As we reported earlier [1], the compound Nd_2Zn_{17} with the Th_2Ni_{17} structure type was found to exist at 600°C. A small admixture of germanium (~10%) to the binary compound Nd_2Zn_{17} leads to a structure change from hexagonal Th_2Ni_{17} structure type (space group $P6_3/mmc$) for the binary compound to rhombohedral $Ce_2Co_{15}Al_2$ structure type (space group $R\bar{3}m$)

for the ternary compound, which has an ordered structure of the high-temperature modification of the binary Nd_2Zn_{17} compound (Th_2Zn_{17} structure type). An analogous transformation takes place in the ternary Ce–Co–Al system: according to Zarechnyuk *et al*. [5] the binary Ce_2Co_{17} compound crystallizes in the Th_2Ni_{17} structure type at 500°C and ternary $Ce_2Co_{15}Al_2$ compound has an ordered structure of the Th_2Zn_{17} structure type. The phases with the composition 2:15:2 are formed also with Ce at 200°C: the $Ce_2Zn_{15}Ge_2$ compound crystallizes in the $Ce_2Co_{15}Al_2$ structure type, but refinement of the crystal structure has not been performed in view on a non-single phase sample [7].

Finally, it is worthwhile to emphasize that single crystal data are desirable for the $Nd_2Zn_{15}Ge_2$ compound in order to clarify the complete ordering in occupancy of the Ge and Zn atoms over the 6c, 9d, 18f and 18h sites.

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