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Letter

New Zr_6CoAs_2-type R_6MnSb_2 and R_6MnBi_2 compounds (R=Y, Lu, Dy, Ho)

A.V. Morozkin

Department of Chemistry, Moscow State University, Leninskie Gory, House 1, Building 3, GSP-2, Moscow 119992, Russia

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Abstract

A powder X-ray diffraction investigation of the new ternary compounds Zr_6CoAs_2-type R_6MnSb_2 and R_6MnBi_2 (R=Y, Lu, Dy, Ho) is reported. The compounds Ho_6MnSb_2 (a=0.8070(2) nm, c=0.4230(1) nm), Lu_6MnSb_2 (a=0.7930(1) nm, c=0.4173(1) nm), Y_6MnBi_2 (a=0.8242(1) nm, c=0.4292(1) nm), Dy_6MnBi_2 (a=0.8211(1) nm, c=0.4286(1) nm), Ho_6MnBi_2 (a=0.8164(1) nm, c=0.4250(1) nm) and Lu_6MnBi_2 (a=0.8019(2) nm, c=0.4185(1) nm) crystallize in the hexagonal Zr_6CoAs_2-type structure (space group *P6b2m* No. 189). The Zr_6CoAs_2-type structure is a superstructure of the Fe_2P-type structure.

Keywords: Rare earth compounds; Crystal structure; X-ray diffraction

During the course of a systematic investigation of ternary rare-earth compounds we have detected new Zr_6CoAs_2-type R_6MnSb_2 and R_6MnBi_2 compounds. The Zr_6CoAs_2-type is a superstructure of the Fe_2P-type structure (space group *P6b2m* No. 189) [1]. In the Zr_6CoAs_2-type structure the rare earth atoms occupy the 3(g) site (X_{R1}, 0, 1/2) and the 3(f) site (X_{R2}, 0, 0). The manganese atoms occupy the special position l(b) (0, 0, 1/2) and the antimony (bismuth) atoms occupy the special position 2(c) (1/3, 2/3, 0) [2].

In the present investigation the compounds were prepared in an electric arc furnace under an argon atmosphere using a non-consumable tungsten electrode and a water-cooled copper tray. Antimony, bismuth, rare earths and manganese (purity of all components 99.99%) were used as the starting components. Zirconium was used as a getter during melting. Subsequently, the compounds were annealed at 1170 K for 170 h in an argon atmosphere and quenched in ice-cold water.

X-ray powder diffraction patterns were obtained on a DRON-3.0 diffractometer (Cu Kα radiation, 2θ=20–70°, step 0.05°, for 5 s/step). The obtained diffractograms were identified and intensity calculations were made in the isotropic approximation using the Rietan programs [3,4].

Table 1
Lattice parameters a and c (nm), c/a, unit cell volume V (nm^3) and atomic position parameters of R_6MnX_2 (R=Y, Lu, Dy, Ho; X=Sb, Bi) of the Zr_6CoAs_2-type structure (space group *P6b2m* No. 189)[a]

Compound	a	c	c/a	V	X_{R1}	X_{R2}	R_F
Ho_6MnSb_2	0.8070(2)	0.4230(1)	0.52416	0.23857	0.599(2)	0.235(2)	3.2
Lu_6MnSb_2	0.7930(1)	0.4173(1)	0.52623	0.22726	0.602(1)	0.239(2)	6.4
Y_6MnBi_2	0.8242(1)	0.4292(1)	0.52075	0.25250	0.601(2)	0.238(2)	5.5
Dy_6MnBi_2	0.8211(1)	0.4286(1)	0.52198	0.25025	0.605(2)	0.238(2)	5.6
Ho_6MnBi_2	0.8164(1)	0.4250(1)	0.52058	0.24532	0.604(1)	0.238(1)	5.0
Lu_6MnBi_2	0.8019(2)	0.4185(1)	0.52189	0.23306	0.607(2)	0.234(3)	6.8

[a] The R factors are given in percent ($R_F = 100 \cdot (\Sigma_k |(I_k^{obs})^{1/2} - (I_k^{cal})^{1/2}| / \Sigma_k |(I_k^{obs})^{1/2}|)$%, I_k^{obs} is the integrated intensity evaluated from summation of contribution of the kth peaks to net observed intensity, I_k^{cal} is the integrated intensity calculated from refined structural parameters).

E-mail address: morozkin@general.chem.msu.ru (A.V. Morozkin).

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Six new compounds have been detected: Ho_6MnSb_2, Lu_6MnSb_2, Y_6MnBi_2, Dy_6MnBi_2, Ho_6MnBi_2 and Lu_6MnBi_2. Analysis of the powder X-ray diffractograms shows unambiguously that the rare-earth compounds crystallize in the hexagonal Zr_6CoAs_2-type structure (space group *P6b2m* No. 189). The lattice parameters of the compounds, refined at room temperature, the reliability factor R_F and the atomic position parameters resulting from the refinements are given in Table 1. Interatomic distances for the Dy_6MnBi_2 compound are given in Table 2.

The Zr_6CoAs_2-type R_6MnSb_2 and R_6MnBi_2 compounds can be regarded as having a structure based on Mg-type rare earth solid solutions. We can describe the Mg-type rare earth structure in terms of the Zr_6CoAs_2-type structure as follows: the rare earth atoms occupy the special positions 3(*f*) (1/3, 0, 0) and 3(*g*) (2/3, 0, 1/2), and the occupation factors for the manganese and bismuth atoms are zero. The cell parameters can be represented by $a = a_{Mg}\cdot(3)^{1/2}$ and $c = c_{Mg}$, space group *P6b2m* No. 189. Insertion of the manganese and antimony (bismuth) atoms into the Mg-type rare earth structure leads to a strong distortion of the unit cell and to changes of the interatomic distances. For the Dy and Dy_6MnBi_2 compound one has $(a_{Dy_6MnB_2} - a_{Dy})/a_{Dy} = 0.31867$, $(c_{Dy_6MnBi_2} - c_{Dy})/c_{Dy} = -0.24502$ and $(V_{Dy_6MnBi_2} - V_{Dy})/V_{Dy} = 0.31282$.

The lattice parameters *a*, *c* and the cell volume *V* for the d-elements (Y, Lu) and f-elements (Dy, Ho) are proportional to the atomic radius of the R metals [5]. The *c*/*a* parameter decreases with increasing atomic radius of the R metals, as a rule (Fig. 1).

It is obvious that the strong distortion of the initial Mg-type rare earth unit cell and the insertion of manganese and p-elements in the rare earth unit cell will lead to strong changes in the magnetic properties.

Table 2
Interatomic distances $D \pm 2\times10^{-3}$ nm and coordination number *N* for atoms in Dy_6MnBi_2 compound

Atoms	*D*	*N*
Dy1–1Mn	0.324	17
–4Bi	0.331	
–4Dy2	0.355	
–2Dy2	0.370	
–2Dy1	0.4286	
–4Dy1	0.437	
Dy2–2Mn	0.290	14
–2Bi	0.320	
–2Dy2	0.339	
–4Dy1	0.355	
–2Dy1	0.370	
–2Dy2	0.4286	9
Mn–6Dy2	0.290	
–3Dy1	0.324	
Bi–3Dy2	0.320	11
–6Dy1	0.331	
–2Bi	0.4286	

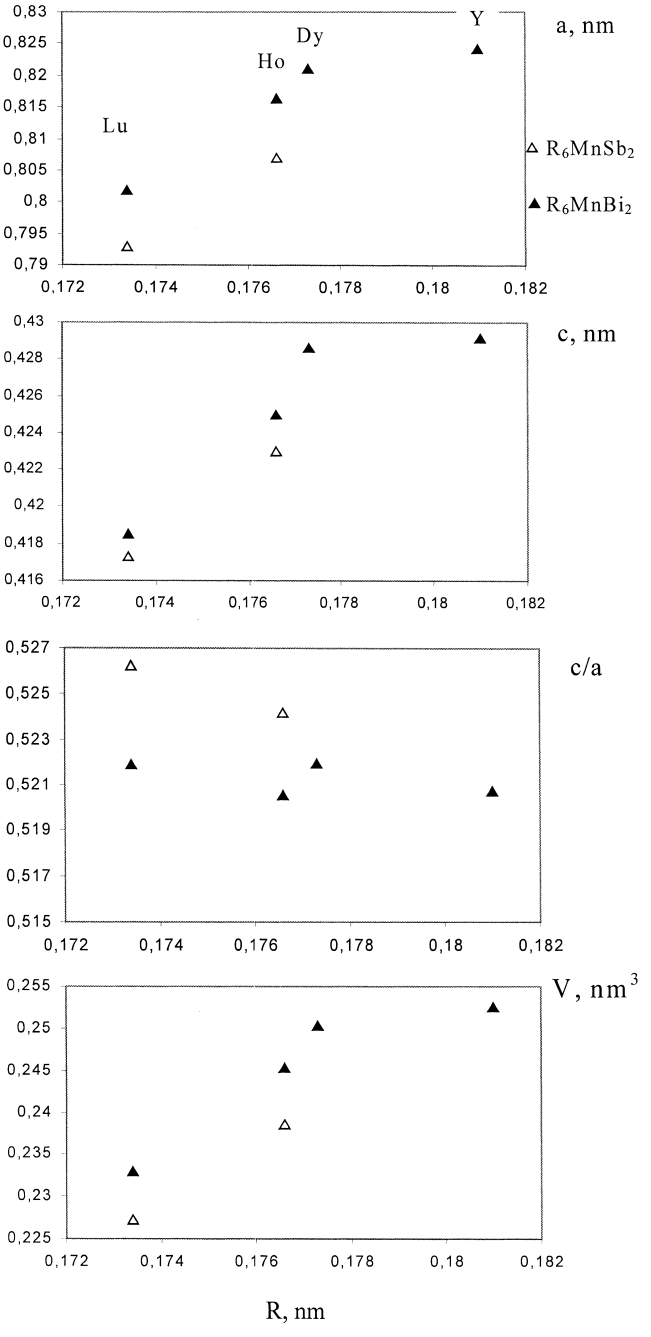

Fig. 1. Cell parameters of R_6MnSb_2 and R_6MnBi_2 compounds versus rare earths atomic radius.

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