

Crystal structure of $\text{Ho}_6\text{Pb}_2\text{Se}_{11}$ and magnetic properties of $\text{R}_6\text{Pb}_2\text{Se}_{11}$ ($\text{R} = \text{Y}, \text{Dy}$ and Ho)

L.D. Gulay^a, D. Kaczorowski^{b,*}, V.Ya. Shemet^a, A. Pietraszko^b

^a Department of General and Inorganic Chemistry, Volyn State University, Voli Ave 13, 43009 Lutsk, Ukraine

^b Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

Received 20 October 2005; accepted 9 November 2005

Available online 18 January 2006

Abstract

Single phase samples of the $\text{R}_6\text{Pb}_2\text{Se}_{11}$ ($\text{R} = \text{Y}, \text{Dy}$ and Ho) compounds were obtained using high temperature synthesis. Crystal structure of $\text{Ho}_6\text{Pb}_2\text{Se}_{11}$ ($\text{Y}_6\text{Pb}_2\text{Se}_{11}$ type, space group $Cmcm$, Pearson symbol $oC76$, lattice parameters: $a = 0.40603(7)$ nm, $b = 1.3397(3)$ nm, $c = 3.7542(5)$ nm) was reinvestigated by means of X-ray single crystal diffraction and refined down to $R1 = 0.0572$. Magnetic properties of the $\text{R}_6\text{Pb}_2\text{Se}_{11}$ compounds were studied in wide ranges of temperature and magnetic field. $\text{Dy}_6\text{Pb}_2\text{Se}_{11}$ and $\text{Ho}_6\text{Pb}_2\text{Se}_{11}$ were found to order antiferromagnetically at $T_N = 2.2$ and 2.4 K, respectively, whereas weak diamagnetism was established for $\text{Y}_6\text{Pb}_2\text{Se}_{11}$.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Rare earth compounds; Chalcogenides; Crystal structures; X-ray single crystal diffraction; Magnetic properties

1. Introduction

The formation and the crystal structure of new ternary compounds $\text{R}_6\text{Pb}_2\text{Se}_{11}$ ($\text{R} = \text{Y}, \text{Dy}$ and Ho) have been reported recently in Ref. [1]. Complete crystal structure investigations have been performed for $\text{Y}_6\text{Pb}_2\text{Se}_{11}$ and $\text{Ho}_6\text{Pb}_2\text{Se}_{11}$ by means of X-ray single crystal and powder diffraction, respectively, whereas for $\text{Dy}_6\text{Pb}_2\text{Se}_{11}$ only the lattice parameters have been determined from the X-ray powder diffractogram. In this paper we present the results of new refinements of the crystal structure of $\text{Ho}_6\text{Pb}_2\text{Se}_{11}$ from the single crystal X-ray diffraction data. Moreover, we report here for the first time on the magnetic properties of the complete series of the $\text{R}_6\text{Pb}_2\text{Se}_{11}$ phases.

2. Experimental details

Powder samples with the nominal compositions $\text{R}_6\text{Pb}_2\text{Se}_{11}$ ($\text{R} = \text{Y}, \text{Dy}$ and Ho) were prepared by sintering the elemental constituents of purity better than 99.9 wt.% in an evacuated quartz ampoule. The synthesis was carried out in a tube resistance furnace. The ampoules were first heated with a rate of $30^\circ\text{C}/\text{h}$ up to 1150°C , and then kept at this temperature for 3 h. Afterwards, the samples were cooled slowly ($10^\circ\text{C}/\text{h}$) down to 600°C and annealed at this temperature for 240 h. Finally the ampoules were quenched in cold water.

The products were checked by X-ray powder diffraction using a DRON-4-13 powder diffractometer (Cu $K\alpha$ radiation, $10^\circ \leq 2\theta \leq 80^\circ$, step scan mode with a step size of 0.05° and counting time of 1 s per data point). All the samples were proved to be single phase with the lattice parameters as reported in Ref. [1].

Single crystal of $\text{Ho}_6\text{Pb}_2\text{Se}_{11}$ suitable for structural investigations was selected from the powder sample. The X-ray data were collected on a KUMA Diffraction KM-4 four-circle diffractometer equipped with a CCD camera, using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm).

Magnetic measurements were performed on powder specimens of $\text{R}_6\text{Pb}_2\text{Se}_{11}$ ($\text{R} = \text{Y}, \text{Dy}$ and Ho) in the temperature range 1.9–400 K and in magnetic fields up to 5 T employing a Quantum Design MPMS-5 SQUID magnetometer.

3. Results and discussion

The single crystal X-ray intensities of the Bragg reflections were corrected for Lorentz and polarisation factors. Semiempirical absorption correction was applied. The extinctions were found to be consistent with the space group $Cmcm$. The crystal structure was solved by Patterson methods [2] and refined by a full-matrix least-squares method using SHELX-97 program [3]. The crystal data and the structure refinement details are summarized in Table 1. The refined atomic coordinates and the anisotropic temperature factors are given in Table 2, and the relevant interatomic distances and the coordination numbers of the atoms are listed in Table 3. As many as three positions of

* Corresponding author.

E-mail address: D.Kaczorowski@int.pan.wroc.pl (D. Kaczorowski).

Table 1
Crystal data and structure refinement details of the Ho₆Pb₂Se₁₁ compound

Empirical formula	Ho ₆ Pb ₂ Se ₁₁
Formula weight	2272.52
Space group	<i>Cmcm</i> (No. 63)
Unit cell dimensions	<i>a</i> = 0.40603(7) nm <i>b</i> = 1.3397(3) nm <i>c</i> = 3.7542(5) nm
Volume	2.0421(6) nm ³
Number of formula units per unit cell	4
Calculated density	7.392 g/cm ³
Absorption coefficient	58.960 mm ⁻¹
<i>F</i> (0 0 0)	3760
Crystal size	0.11 mm × 0.06 mm × 0.02 mm
θ range for data collection	3.04–26.37
Index ranges	−5 ≤ <i>h</i> ≤ 5 −16 ≤ <i>k</i> ≤ 13 −46 ≤ <i>l</i> ≤ 46
Reflections collected	10824
Independent reflections	1205 [<i>R</i> (int.) = 0.1390]
Refinement method	Full-matrix least-square on <i>F</i> ²
Data/restraints/parameters	1205/0/62
Goodness-of-fit on <i>F</i> ²	1.063
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0572, <i>wR</i> 2 = 0.0763
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1059, <i>wR</i> 2 = 0.0904
Extinction coefficient	0.000016(8)
Largest diff. peak and hole × 10 ⁻³	2.787 and −2.275 e/nm ³

the Ho atoms, one position of the atoms of the statistical mixture M of the Ho and Pb atoms, one position of the Pb atoms and six positions of the Se atoms were determined. Refining the site occupancy factor for the atoms of the statistical mixture M as a free parameter gets it to a numerical value close to 0.50Ho + 0.50Pb, which satisfies charge balance requirements. The interatomic distances agree well with the sum of the respective ionic radii [4]. Octahedral surrounding exists for the Ho atoms, whereas the atoms M and the Pb atoms are surrounded by trigonal prisms with one and two additional atoms, respectively. In turn, the Se1 and Se6 atoms have tetrahedral coordinations, while the Se2, Se3, Se4 and Se5 atoms have five cations in their neighborhoods. In general, the results of the present single crystal studies of the crystal structure of Ho₆Pb₂Se₁₁ agree well with those derived from the X-ray powder data. Thus, for

Table 2
Atomic coordinates and temperature factors for the Ho₆Pb₂Se₁₁ compound

Atom	Position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Occupation	<i>U</i> _{eq.} × 10 ² (nm ²)	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ho1	8(f)	0	0.0256(1)	0.63326(4)	1.00	0.0133(3)	0.0120(7)	0.0148(7)	0.0133(8)	−0.0006(6)	0	0
Ho2	8(f)	0	0.24622(9)	0.18121(4)	1.00	0.0129(3)	0.0108(7)	0.0151(7)	0.0127(8)	−0.0010(6)	0	0
Ho3	4(a)	0	0	0	1.00	0.0148(5)	0.012(1)	0.015(1)	0.016(1)	−0.0002(9)	0	0
M	8(f)	0	0.2720(1)	0.55714(4)	0.50Ho 0.50Pb	0.0258(4)	0.0144(7)	0.047(1)	0.0160(8)	−0.0004(6)	0	0
Pb	4(c)	0	0.5148(1)	1/4	1.00	0.0369(6)	0.020(1)	0.036(1)	0.053(1)	0	0	0
Se1	8(f)	0	0.0802(3)	0.06906(9)	1.00	0.0260(8)	0.035(2)	0.032(1)	0.010(1)	0.005(1)	0	0
Se2	8(f)	0	0.1206(2)	0.70049(8)	1.00	0.0134(7)	0.012(1)	0.015(1)	0.012(1)	0.001(1)	0	0
Se3	8(f)	0	0.3401(2)	0.11224(8)	1.00	0.0146(7)	0.017(1)	0.015(1)	0.010(1)	0.000(1)	0	0
Se4	8(f)	0	0.3577(2)	0.01515(8)	1.00	0.0143(7)	0.015(1)	0.012(1)	0.015(1)	0.001(1)	0	0
Se5	8(f)	0	0.6047(2)	0.1619(1)	1.00	0.0198(8)	0.009(1)	0.017(1)	0.032(2)	−0.011(1)	0	0
Se6	4(c)	0	0.1653(3)	1/4	1.00	0.018(1)	0.019(2)	0.023(2)	0.011(2)	0	0	0

*U*_{eq.} is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor. The anisotropic temperature factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12}]$.

Table 3
Interatomic distances (δ, nm) and coordination numbers (C.N.) of the atoms in Ho₆Pb₂Se₁₁

Atoms		δ (nm)	C.N.
Ho1	−1Se1	0.2797(4)	6
	−2Se3	0.2824(2)	
	−1Se2	0.2826(3)	
Ho2	−2Se5	0.2886(2)	6
	−2Se2	0.2798(2)	
	−1Se6	0.2801(2)	
	−2Se5	0.2870(2)	
Ho3	−1Se3	0.2879(3)	6
	−2Se1	0.2807(3)	
	−4Se4	0.2843(2)	
M ^a	−2Se1	0.2870(3)	7
	−1Se4	0.2945(3)	
	−2Se4	0.3103(2)	
	−2Se3	0.3265(3)	
Pb	−2Se6	0.2861(3)	8
	−4Se2	0.3297(3)	
Se1	−2Se5	0.3519(6)	4
	−1Ho1	0.2797(4)	
	−1Ho3	0.2807(3)	
Se2	−2M	0.2870(3)	5
	−2Ho2	0.2798(2)	
	−1Ho1	0.2826(3)	
	−2Pb	0.3297(3)	
Se3	−2Ho1	0.2824(2)	5
	−1Ho2	0.2879(3)	
	−2M	0.3265(3)	
Se4	−2Ho3	0.2843(2)	5
	−1M	0.2946(3)	
	−2M	0.3103(2)	
Se5	−2Ho2	0.2870(2)	5
	−2Ho1	0.2886(2)	
	−1Pb	0.3519(6)	
Se6	−2Ho2	0.2801(2)	4
	−2Pb	0.2861(3)	

^a M = 0.50Ho + 0.50Pb.

more detailed description of the structure the interested reader is referred to Ref. [1].

The magnetic properties of Dy₆Pb₂Se₁₁ are presented in Fig. 1. The main panel shows the inverse molar magnetic susceptibility, which behaves in a Curie–Weiss (CW) manner almost

Download English Version:

<https://daneshyari.com/en/article/1626862>

Download Persian Version:

<https://daneshyari.com/article/1626862>

[Daneshyari.com](https://daneshyari.com)