

Letter

Structure refinement of two cadmium rare earth selenospinel, CdTm_2Se_4 and CdHo_2Se_4

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1. Introduction

The cadmium rare earth thio- and selenospinel have attracted some interest in recent years because of their magnetic and electrical properties [1–7]. Surprisingly enough, however, no detailed structural data can be found in the literature for the selenospinel. In particular, conclusions regarding the cation distribution have been drawn only from X-ray powder data, which are rather inconclusive. Suchow and Stemple [1], Holtzberg [2] and Bendor and Shilo [3] favour a normal cation distribution, whereas the results of Fujii and coworkers [4, 5] and Pawlak *et al.* [6] indicate at least some degree of inversion.

The present letter describes the results of a structure refinement for CdTm_2Se_4 and CdHo_2Se_4 using single-crystal X-ray data.

2. Experimental details

Several attempts to prepare homogeneous selenospinel by a high temperature reaction of stoichiometric mixtures of the binary components (CdSe , Ho_2Se_3 , Tm_2Se_3) have been unsuccessful. The best results were obtained by a direct reaction of the elements in evacuated sealed quartz ampoules. The reaction needed 2 weeks or even longer at 900 °C for completion. At higher temperatures some decomposition of the rare earth selenospinel was observed. The addition of carefully dried potassium bromide as flux material improved crystal growth.

From the reaction products in the systems Cd–Ho–Se and Cd–Tm–Se small single crystals could be isolated which were suitable for a crystal structure analysis. With energy-dispersive X-ray (EDX) analyses not even traces of potassium or bromine could be detected. The stoichiometric com-

TABLE 1

Crystallographic data and details of the crystal structure analysis for CdTm_2Se_4 and CdHo_2Se_4

	CdTm_2Se_4	CdHo_2Se_4
Crystal system		Cubic
Space group		$Fd\bar{3}m$
a (Å)	11.560(1)	11.631(2)
V (Å ³)	1544.8	1573.4
Z	8	8
D_x (g cm ⁻³)	6.59	6.40
Crystal size (mm ³)	$0.03 \times 0.03 \times 0.03$	$0.12 \times 0.06 \times 0.04$
Diffractometer	Enraf-Nonius CAD-4	
Radiation, monochromator	Mo $K\alpha$ ($\lambda = 0.71073$ Å), graphite	
Scan mode	$\omega-2\theta$	
Range of intensity measurement	$2^\circ \leq \theta \leq 30^\circ$	$2^\circ \leq \theta \leq 40^\circ$
Intensities measured	651	1353
Unique reflections	136	270
Final R , wR	0.045, 0.023	0.037, 0.023

position of the selenospinels was eventually confirmed by the structure refinement.

Weissenberg photographs showed CdHo_2Se_4 and CdTm_2Se_4 to be cubic, Laue class $m\bar{3}m$. Following the observed reflection conditions, the only possible space group was $Fd\bar{3}m$.

Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (Mo $K\alpha$, graphite monochromator in incident beam). Cell parameters have been refined from 25 carefully centred reflections. Intensities were measured in the $\omega-2\theta$ scan mode. Details of the structure analysis can be taken from Table 1. The programme system SHELX-76 [8] was used for all calculations. Atomic scattering factors and f' and f'' values were taken from ref. 9. Bond distances and angles have been calculated using the programme SADIAN [10].

3. Structure analysis

The structure was solved by standard direct methods, followed by successive difference Fourier syntheses and by comparison with data already published for the spinel structure. In the least-squares refinement $|F|$ values were used to refine an overall scale factor, positional parameters and isotropic displacement factors. Refinement of the occupation factors for cadmium, holmium and thulium confirmed the stoichiometry CdLn_2Se_4 within two standard deviations. Consequently, the site occupancy factors (SOFs) were fixed again at 100% before applying a numerical correction for the serious absorption (programme DIFABS [11]) to the original data. Final atomic

TABLE 2

Atomic and displacement parameters, distances and angles for CdTm₂Se₄ and CdHo₂Se₄^a

Atomic coordinates ^b and equivalent isotropic displacement parameters (Å ²) ^c					
CdTm ₂ Se ₄			CdHo ₂ Se ₄		
	<i>U</i> _{eq}			<i>U</i> _{eq}	
Cd in 8 <i>a</i>	0.015		Cd in 8 <i>a</i>	0.016	
Tm in 16 <i>d</i>	0.011		Ho in 16 <i>d</i>	0.012	
Se in 32 <i>e</i>	0.012		Se in 32 <i>e</i>	0.011	
with <i>x</i> = 0.3819(1)			with <i>x</i> = 0.3810(1)		
Atomic distances (Å) and angles (deg)					
CdTm ₂ Se ₄			CdHo ₂ Se ₄		
Cd–Se	2.641(1)	4 ×	Cd–Se	2.639(1)	4 ×
Tm–Se	2.812(1)	6 ×	Ho–Se	2.839(1)	6 ×
Se–Se	3.861(2)	12 ×	Se–Se	3.914(1)	12 ×
Se–Tm–Se	86.70(3)		Se–Ho–Se	87.15(3)	
	93.30(3)			92.85(3)	
Tm–Se–Tm	93.20(4)		Ho–Se–Ho	92.78(4)	
Cd–Se–Tm	122.97(4)		Cd–Se–Ho	123.27(4)	

^aThe estimated standard deviations of the least significant figures are given in parentheses.^bOrigin at centre ($\bar{3}$).^c U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

coordinates and equivalent isotropic displacement factors, selected atomic distances and bond angles are given in Table 2*.

4. Discussion

In both compounds the cadmium ions occupy the tetrahedral sites of the spinel structure. This normal cation distribution was expected, because (i) the Cd²⁺ ion with a d¹⁰ configuration has a pronounced preference for the tetrahedral site,

(ii) the x parameter of the anions is $x > 0.379$; if this happens, the normal cation distribution in 2, 3-spinels is energetically favoured [12].

The Cd–Se distance in both compounds (2.64 Å) agrees with the sum of the tetrahedral covalent radii (2.62 Å) as well as with the Cd–Se distance in a spinel-type high pressure modification of CdIn₂Se₄ (2.61 Å) [13].

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*Lists of observed and calculated structure factors, anisotropic displacement factors, bond distances and angles have been prepared and can be obtained from K.-J. R.

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