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Rb_4YbI_6 Synthesis and Crystal Structure

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The divalent rare earth compound-Rb_4YbI_6 was prepared by a one-step method. Using X-ray powder diffraction data, its crystal structure has been determined and refined by the Rietveld technique to R_{WP}=11.1 by isotype with compound Cs_4PbBr_6. The crystal symmetry is trigonal, a=14.150(1) Å, c=17.463(3) Å, space group $R\bar{3}c$ (167), Z=6. The Yb and I atoms form isolated, slightly distorted $[YbI_6]^{4-}$ octahedra, which are linked via Rb^+ to form chains along the c-axis. The other three Rb^+ hold these chains together to form the crystal structure. © 1997 Academic Press

INTRODUCTION

In ternary systems with divalent rare earth iodides, many compounds have been formed in the process of studying the phase diagrams of REI_2–AI (A: Na^+, K^+, Rb^+, Cs^+; RE: Sm^{2+}, Eu^{2+}, Yb^{2+}) systems (1). The compound Rb_4YbI_6 has been reported to exist in the phase diagram RbI–YbI_2 (2).

In the present work, we used a one-step procedure to synthesize Rb_4YbI_6 directly and determined and refined its crystal structure by X-ray powder diffraction.

EXPERIMENTAL

1. Synthesis

Rb_4YbI_6 was prepared in a one-step procedure (3) from RbI (purity 99.9%), HgI_2 (purity 99.5), and ytterbium metal (purity 99.9%). RbI was dried by heating at 400°C for 4 h in a vacuum of 2.8×10^{-4} Pa and HgI_2 was purified by sublimation in high vacuum . All reactant and product manipulations were carried out in an argon-filled glove box whose atmosphere was continuously purged of H_2O and oxygen.

The reactants RbI, HgI_2, and ytterbium were placed in a previously dried quartz tube in a molar ratio of 4 : 1 : 1. The tube was evacuated to 2.8×10^{-4} Pa, sealed, and heated at 300°C for several days. Then it was put into a tube furnace at above 580°C for 3–4 days. After that the temperature was decreased to 500°C and maintained for 7 days. Finally, the mercury by-product was separated from the product Rb_4YbI_6 by sublimation at 300°C.

2. X-ray Diffraction

Since the divalent ytterbium iodide is very sensitive to moisture, and oxygen, the X-ray diffraction analysis was carried out in an evacuated Guinier camera with Cu$K\alpha_1$ radiation ($\lambda = 1.54051$ Å) and SiO_2 ($a = 4.91323(1)$ Å, $c = 5.40485(3)$ Å) as an internal standard. The diffraction data were corrected with the program SOS I (4) and were indexed by the program TREOR (5) to a hexagonal unit cell ($a = 14.150(1)$ Å, $c = 17.463(3)$ Å) with a figure of merit $M(20)$ (6) of 18. The lattice parameters were refined by the program SOS II (4).

The intensity data were collected with a Rigaku 2400 diffractometer. The extremely moisture- and oxygen-sensitive specimen was covered in the sample holder with a protective tape. The whole diffractometer was flushed continuously with nitrogen gas. The step length was 0.02° and the 2θ range 10–82° was covered.

3. Structure Determination and Refinement

The cell dimensions $a = 14.150(1)$ Å, $c = 17.463(3)$ Å were obtained from Guinier data. From these results, relationships isostructural with Cs_4PbBr_6 (7), have been detected; the trigonal structure space group is $R\bar{3}c$(167). Thus, the starting coordinates of the refinement were taken from Cs_4PbBr_6. Since the products contain tiny amounts of unreacted RbI, the refinement was carried out in two phases (Rb_4YbI_6 and RbI).

The protection tape affected the intensity of diffraction data at 2θ below 20° very strongly. Good pattern fitting results cannot be obtained over the entire 2θ range 10°–82°. Fortunately, the main diffraction data appear above 20°. Finally, in the Rietveld refinement calculation, we used diffraction data between 23° and 82°.

RESULTS AND DISCUSSIONS

1. Synthesis

From the phase diagram of RbI–YbI_2, we know as the reaction system gradually cooled the RbI first

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crystallized and then a peritectic reaction took place:

$$RbI + L = Rb_4YbI_6.$$

This kind of reaction usually occurs very slowly and it is difficult to reach balance. So it is not surprising to find some RbI in the products. The quantity of unreacted RbI was tiny and the other phase ($RbYbI_3$) shows no effect on the X-ray diffraction pattern. Thus the refinement of crystal structure is possible.

2. Structure Description

The structure refinement used the program FULLPROF (8). The details of the refinement are presented in Table 1. Figure 1 shows agreement between calculated and observed intensities. Because of the influence of the protection tape, the value of the R_{WP} factor appears comparatively high. The final atomic parameters and selected bond distances are given in Tables 2 and 3, respectively.

The crystal structure contains isolated, slightly distorted $[YbI_6]^{4-}$ octahedra, which are linked via Rb^+ forming chains along *c*-axis. It is also reasonable to think that chains are formed by face-sharing $[YbI_6]^{4-}$ octahedra and $[RbI_6]^{5-}$ distorted trigonal prisms in turn; see Fig. 2. There are two kinds of Rb^+ in this structure. One Rb^+ exists in the chains and is coordinated by 6 I^-; the other three Rb^+ are surrounded by 8 I^- with Rb–I distances ranging from 3.77(1) to 3.94(2) Å. That shows that the $[RbYbI_6]_n^{3-}$ chains are held together by the rubidium.

After we finished this work, we found that G. Meyer obtained a single crystal of the same compound by another method (the metallothermic reduction method) and determined its structure in 1992 (9). His result is concordant with ours.

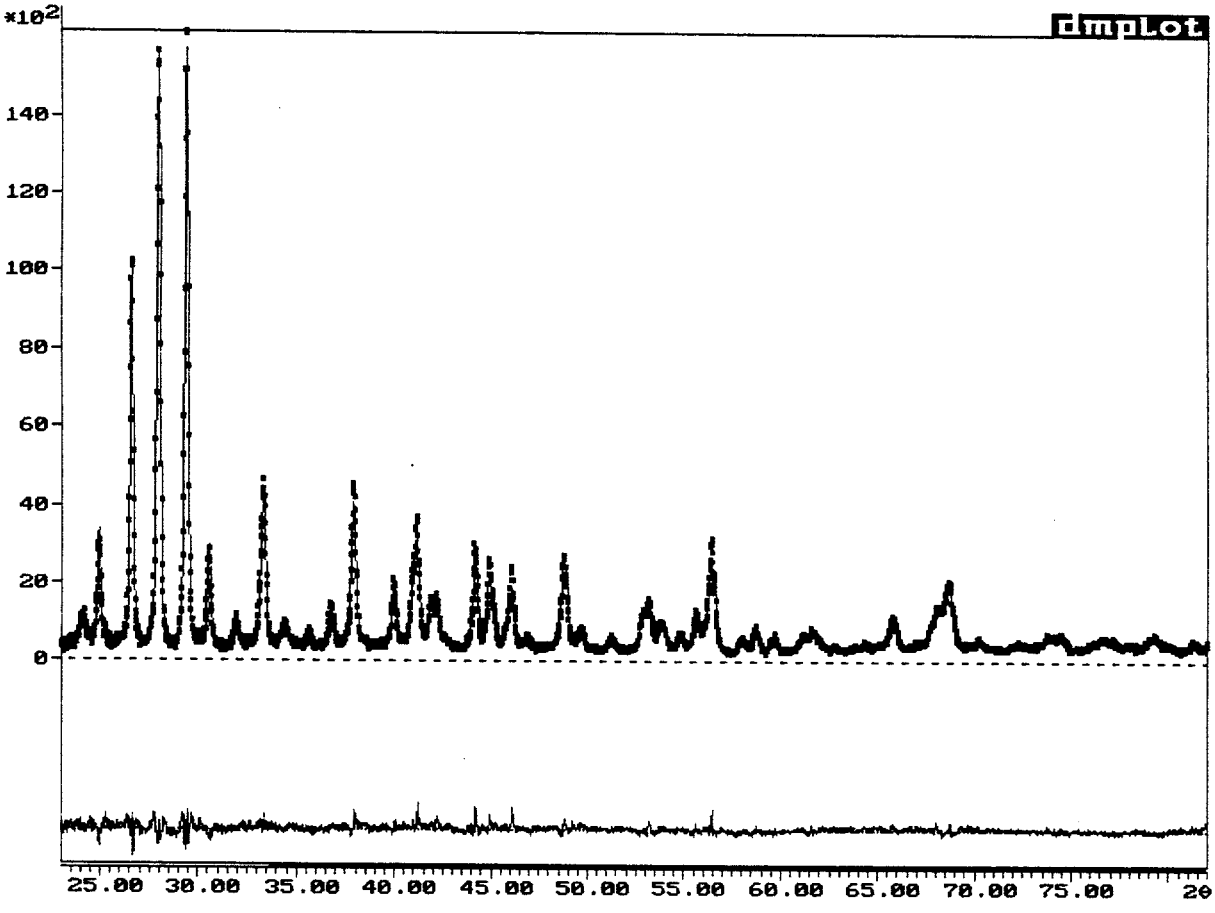

FIG. 1. Observed and calculated diffraction pattern with a difference plot indicated at the base of the figure.

TABLE 1
Crystallographic and Rietveld Refinement Data for Rb_4YbI_6

Pattern range 2θ (deg)	23–82
Step size 2θ (deg)	0.02
Space group	$R\bar{3}c$
a (Å)	14.1506(3)[a]
c (Å)	17.4653(5)[a]
Z	6
Number of observations	2951
Number of contributing reflections[b]	229
Number of refined structure parameters[b]	10
Number of refined profile parameters[b]	17
Number of phase	2 (Rb_4YbI_6 and RbI)
Peak shape	Pseudo-Voigt
R_{WP}	11.1
R_P	7.98
R_B[b]	5.60
R_F[b]	5.64

The R factors are defined as

$$R_{WP} = 100[\sum w_i(y_{oi} - y_{ci}/c)^2/\sum w_i y_{oi}^2]^{1/2}$$
$$R_P = 100\sum |y_{oi} - y_{ci}/c|/\sum |y_{oi}|$$
$$R_B = 100\sum |I_o - I_c|/\sum I_o$$
$$R_F = 100\sum |I_o^{1/2} - I_o^{1/2}|/\sum I_o^{1/2}.$$

[a] The internal standard SiO_2 is not used in the X-ray diffraction pattern of Rb_4YbI_6 when the intensity data are collected by Rigaku 2400 diffractometer, Therefore, the cell parameters from the Guinier data should be more accurate.

[b] for Rb_4YbI_6 phase.

TABLE 2
Atomic Coordinates and Isotropic Thermal Parameter

Atom	x	y	z	B (Å^2)
Rb1	0.0	0.0	0.25	2.3(8)
Rb2	0.381(1)	0.0	0.25	2.5(4)
Yb	0.0	0.0	0.0	0.5(2)
I	− 0.0340(6)	0.1612(6)	0.1038(3)	1.1(1)

TABLE 3
Selected Interatomic Distances (Å)

Yb–I	6×				
		3.13(1)	Rb2–I	2×	3.77(1)
Rb1–I	6×	3.61(1)	Rb2–I	2×	3.78(1)
			Rb2–I	2×	3.86(2)
			Rb2–I	2×	3.94(2)

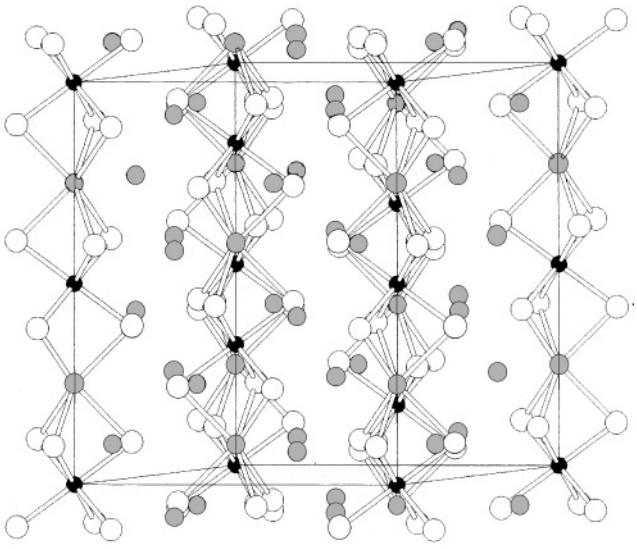

FIG. 2. The structure of Rb_4YbI_6. The black, gray, and white circles represent ytterbium, rubidium and iodide atoms respectively.

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