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STRUCTURE REFINEMENT OF B-RE_2O_3 (RE=YB, LU).

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Abstract

The monoclinic B-modification of lutetium and ytterbium sesquioxides was obtained by high pressure high temperature (P=5.0 GPa, T=1000 C, 1300 C) treatment of cubic C-RE_2O_3 (RE=Yb, Lu) in toroid-type high pressure apparatus. X-ray data from materials were collected in Imaging Plate Guinier Camera G670 (Huber). The procedure of full profile Rietveld analysis was performed with the help of GSAS (General Structure Analysis System) to get the structural information, which can be used in structure data base. The unit cell dimensions are as follows: Lu_2O_3, a=13.6903(2), b=3.41261 (5), c=8.4422(1) Å, β=100.171(1)°; Yb_2O_3, a=13.7056(1) , b=3.43146(3), c=8.4730(1) Å , β=100.157(1)°. A new high pressure phase of lutetium and ytterbium sesquioxides was found in the samples after treatment at P=5.0 GPa, T=1000 C.

Key words: *high pressure-high temperature treatment, lutetium sesquioxide, ytterbium sesquioxide, X-ray powder diffraction, full-profile analysis.*

1. INTRODUCTION

Rare-earth elements and their compounds, particularly oxides, are widely used in science and technology due to the unique physical and chemical properties, such as fluorescent, laser and others. The first systematic study of the polymorphism of sesquioxides of rare earth elements was conducted by Goldschmidt with co-authors (Goldschmidt V. M., 1925). Depending on the size of the rare earth atoms sesquioxides are crystallized in three structural types denoted by Goldschmidt as A, B and C. At ambient pressure and temperature La-Pm oxides are crystallized in the hexagonal A-cell (S.G. P-3m, Z = 1), Sm-Gd (Tb) - in the monoclinic B-cell (S.G. C2/m, Z=6) and (Tb) Dy-Lu – in the cubic C-cell (S.G. Ia-3, Z = 16).

Tens of papers devoted to the investigations of transitions between these modifications, depending on the temperature were published for the last more than 80 years (for instance (Warshaw J. and Roy R., 1961, Foex M., Traverse J. P., 1965, Glushkova V.B. and Bogdanov A.G., 1965, Coutures J.P. et al., 1976, Greis O., 1980, Chen G., 1992, Adachi G. Y. and Imanaka N., 1998, Zinkevich M., 2007 etc.)). Influence of high pressure on the phase transitions in the lanthanide sesquioxides was studied in several works (for instance (Hoekstra H. R., 1966, Atou T., 1989, Meyer C., 1995, Tschauner O. et al., 2005, Hongo T. et al., 2007, etc)). The B polymorph is denser than C one on several percents which leads to the C→B transformation under high pressure.

Hoekstra (Hoekstra H. R., 1966) show that the pressure and temperature stabilize B-modification, and already at P> 4.0 GPa oxides from Dy to Lu are crystallized in the monoclinic dense cell. The unit cell parameters of the B phase for RE = Sm-Lu are presented in Hoekstra's work. The structure of obtained at ambient pressure monoclinic phases of Sm_2O_3 (Cromer D.T., 1957), Eu_2O_3 (Yakel H.L.jr., 1979), Gd_2O_3 (Guentert O., 1958) and Tb_2O_3 (Hubbert-Paletta E.and Mueller-Buschbaum H., 1968) was solved, refined and presented in structural databases. Guo with co-authors (Guo Q. Et al., 2007) calculated the unit cell and position parameters for B-Er_2O_3 by using of density functional theory

(DFT). The dependence of the unit cell parameters on the pressure at ambient temperature was obtained for B-Lu_2O_3 (Jiang S. et al., 2010), B-Yb_2O_3 (Meyer C. et al., 1995). The structure of B phase for Dy-Lu was not refined and therefore not represented in structural databases, and that was the main motivation of this work. In the first step we have synthesized and refined the structure of two oxides B-Lu_2O_3 and B-Yb_2O_3. The results of this work are presented below.

2. EXPERIMENTAL

A powders of C (cubic) modifications of Lu_2O_3 and Yb_2O_3 (Fig.1) of 99.9% purity were pressed into pellets 1.5 ÷2 mm in height and 3 mm in diameter. The toroid-type high pressure chamber was used in the experiments (Fig.2). A detailed description of the equipment and the experimental procedure has been given elsewhere (Zibrov I.P. et al., 1998, Filonenko V.P. and Zibrov I.P., 2001). This apparatus allows us to study the kinetics of the transformations because it is possible to use the treatment times from seconds till tens of minutes depending on the temperature.

P-T conditions of treatment corresponded to the stability range of B modification on the phase diagram (Hoekstra H.R., 1966) namely, P = 5.0 GPa, T = 1000 C and 1300 C. The temperature was held for 1-120 sec at 1000 C and 5-120 sec at 1300 C, followed by quenching the sample to room temperature at a rate of ~100 C/s before the pressure was released. Extracted from the high pressure chamber samples were purified mechanically from the hexagonal BN (hBN) and subjected to X-ray phase analysis on a diffractometer AXS with the XY position-sensitive detector (Bruker, Germany). Selected for structural analysis samples were run in the Imaging Plate Guinier Camera G670 (Huber, Germany) (Cu $K\alpha_1$ radiation). The obtained X-ray data were subjected to full-profile analysis procedure using the software package GSAS (Larson A.C. and Von Dreele R.B., 1987, Toby B. H., 2001). The diffraction peak shapes could be described by a symmetric, or nearly symmetric, pseudo-Voigt function. The structure of Sm_2O_3 (Cromer D.T., 1957) was used as starting model in the refinement.

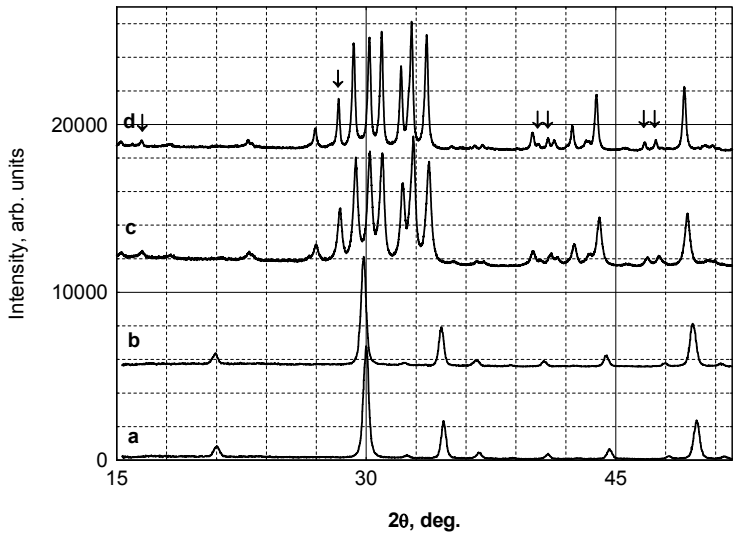


Fig.1. X-ray diffraction patterns of: starting C-Lu_2O_3 – a; starting C-Yb_2O_3 – b; Lu_2O_3 after treatment at P=5.0 GPa, T=1000 C – c; Yb_2O_3 after treatment at P=5.0 GPa, T=1000 C – d. Arrows mark the peaks belonging to unknown phase.

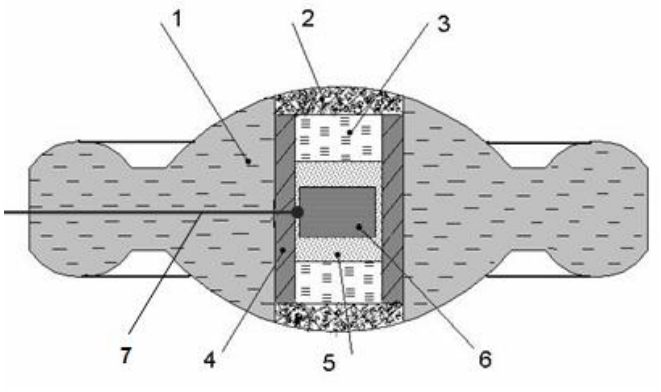
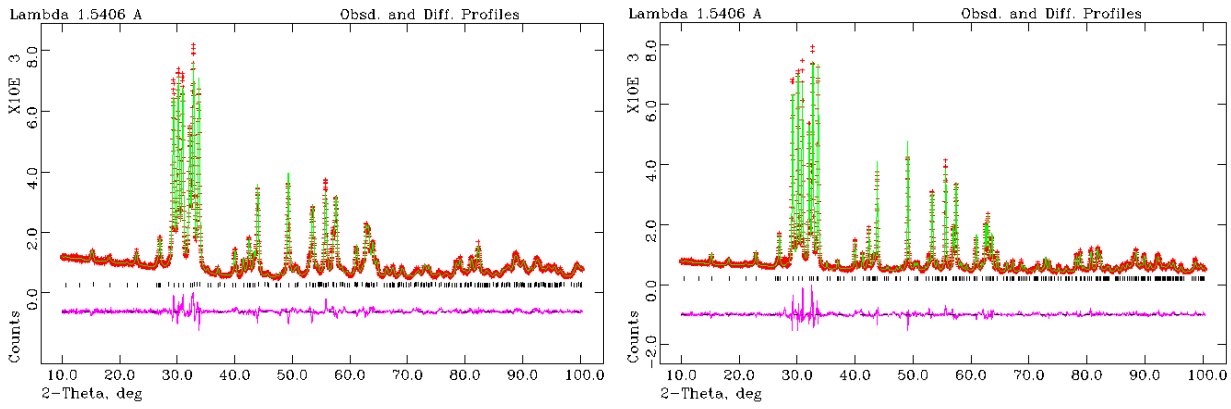


Fig.2. Scheme of the high-pressure cell: 1- lithographic limestone container, 2 - cover from a mixture of hBN and graphitic powders, 3 - cover from a hBN, 4 - graphitic heater, 5 - hBN powder, 6 - sample, 7 - thermo-couple.

3. RESULTS

Experiments have shown that at the pressure 5.0 GPa and T=1000 C samples in addition to B-oxide always contained a second phase (Fig.1). The amount of this phase in the samples was practically independent on the treatment time in the range from 1 to 120 seconds. Indexing gives the tetragonal unit cell parameters *a*=5.4915(8), *c*=5.3450(9) Å which are close to the unit cell parameter of fluorite CaF_2 (*a*=5.463 Å). The similarity of these two phases is confirmed by the fact that strongest peak of the new phase (Fig.1c,d) on 2θ=28.39° has indices (111). Hoekstra (Hoekstra H.R., 1966) has not seen this phase, probably, because of longer time of annealing under pressure: 30 min. at T=1000 C. We are trying to get this phase in pure form for structural studies.

Raising the temperature treatment till 1300 C resulted in obtaining monophasic samples containing pure B-modification. The results of full-profile analysis for sesquioxides of Lu and Yb are shown in Fig.3a,b and presented in the Table 1. Atomic coordinates and isotropic thermal parameters for these compounds are presented in the Table 2 and selected interatomic distances - in the Table 3.



a b

Fig.3. Rietveld refinement of B-Lu_2O_3 (a) and B-Yb_2O_3 (b).

Observed (+), calculated (solid line) and the difference between observed and calculated (bottom curve) X-ray powder diffraction profiles are shown. The positions of all the allowed Bragg reflections are indicated by the row of vertical tick marks.

Table 1. Experimental detailes for B-Lu_2O_3 and B-Yb_2O_3.

Chemical formula	Lu_2O_3	Yb_2O_3
Chemical formula weight	397.93	394.08
Space group	**C 2/m**	**C 2/m**
a (Å)	13.6903(2)	13.7056(1)
b (Å)	3.41261 (5)	3.43146(3)
c (Å)	8.4422(1)	8.4730(1)
β (°)	100.171(1)	100.157(1)
V ($Å^3$)	388.22(1)	392.24(1)
Z	6	6
D_x (Mg m^{-3})	10.213	10.010
R_F	0.030	0.041
R_P	0.041	0.049
R_{WP}	0.053	0.064
d (Durbin-Watson) (Hill R.J. and Flack H.D., 1987)	0.220	0.179
No of parameters used	59	60

Table 2. Fractional atomic coordinates and isotropic displacement parameters U_{iso} ($Å^2$) for B-Lu_2O_3 and B-Yb_2O_3.

Atom	***Site***	*x*	*y*	*z*	U_{iso}
B-Lu_2O_3					
Lu1	4(i)	0.63614(11)	0	0.48388(13)	0.0265(6)
Lu2	4(i)	0.69091(12)	0	0.13703(14)	0.0099(4)
Lu3	4(i)	0.96750(16)	0	0.18584(19)	0.0299(5)
O1	4(i)	0.1321(8)	0	0.2747(11)	0.025
O2	4(i)	0.8324(9)	0	0.0134(12)	0.025
O3	4(i)	0.7615(10)	0	0.3995(13)	0.025
O4	4(i)	0.4608(9)	0	0.3434(12)	0.025
O5	2(b)	0	0.5	0	0.025
B-Yb_2O_3					
Yb1	4(i)	0.63567(11)	0	0.48590(13)	0.0203(5)

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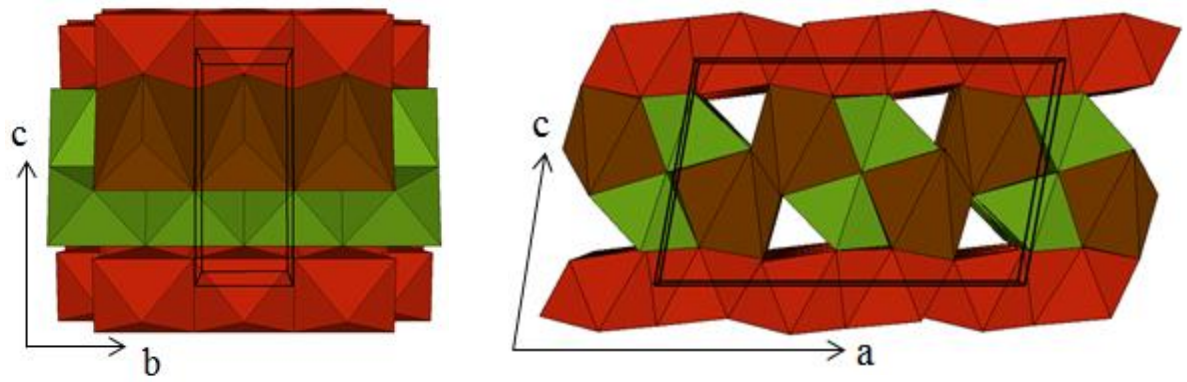
Yb2	4(i)	0.69026(14)	0	0.13656(15)	0.0136(4)
Yb3	4(i)	0.96754(16)	0	0.18760(18)	0.0253(5)
O1	4(i)	0.1298(10)	0	0.2770(13)	0.048(2)
O2	4(i)	0.8201(13)	0	0.0195(15)	0.048(2)
O3	4(i)	0.7615(11)	0	0.3911(15)	0.048(2)
O4	4(i)	0.4687(12)	0	0.3446(15)	0.048(2)
O5	2(b)	0	0.5	0	0.048(2)

Table 3. Selected interatomic distances r_{ij} (Å) with STD's (in brackets) for B-Lu_2O_3 and B-Yb_2O_3 and corresponding bond valences s_{ij} (according to (Brown I.D. and Altermatt D., 1985).

	r_{ij} (B-Lu_2O_3)		r_{ij} (B-Yb_2O_3)	s_{ij}
Lu1-O1	2.449(7) x2	Yb1-O1	2.456(8) x2	0.265
Lu1-O3	2.315(8) x2	Yb1-O3	2.344(10) x2	0.359
Lu1-O3	1.971(12)	Yb1-O3	2.027(15)	0.846
Lu1-O4	2.139(12)	Yb1-O4	2.198(16)	0.533
Lu1-O4	2.482(11)	Yb1-O4	2.389(15)	0.318
Average	2.303	Average	2.316	
			Sum (valence of Yb1)	2.945
Lu2-O1	2.290(7) x2	Yb2-O1	2.322(9) x2	0.381
Lu2-O2	2.118(6) x2	Yb2-O2	2.155(8) x2	0.598
Lu2-O2	2.356(12)	Yb2-O2	2.185(18)	0.552
Lu2-O3	2.255(11)	Yb2-O3	2.205(13)	0.523
Lu2-O5	2.6649(15)	Yb2-O5	2.6598(17)	0.153
Average	2.299	Average	2.286	
			Sum (valence of Yb2)	3.186
Lu3-O1	2.246(11)	Yb3-O1	2.219(13)	0.503
Lu3-O2	2.142(11)	Yb3-O2	2.257(15)	0.454
Lu3-O4	2.175(7) x2	Yb3-O4	2.169(8) x2	0.576
Lu3-O5	2.4119(11) x2	Yb3-O5	2.4326(11) x2	0.283
Average	2.260	Average	2.280	
			Sum (valence of Yb3)	2.674
O1-O2	2.564(13)	O1-O2	2.718(18)	
O1-O3	2.549(12)	O1-O3	2.554(14)	

O1-O4	3.037(12)	O1-O4	2.932(16)	
O1-O5	3.175(8)	O1-O5	3.185(9)	
O2-O2	2.805(20)	O2-O2	2.554(26)	
O2-O5	2.878(10)	O2-O5	3.032(15)	
O3-O3	2.466(15)	O3-O3	2.579(19)	
O4-O4	2.673(20)	O4-O4	2.622(25)	
O4-O5	3.040(11)	O4-O5	3.025(13)	



a b

Fig.4. The structure of Yb_2O_3 along *a* axis (a) and along *b* axis (b).
Red and brown polyhedra are seven coordinated Yb [YbO7], green-six coordinated Yb [YbO6].
This figure was drawn with the help of ATOMS program (Dowty E., 1989).

4. DISCUSSION

As it is seen from the Table 3 Lu1,Yb1, Lu2 and Yb2 are seven-fold coordinated [REO7] whereas Lu3 and Yb3 are six-fold coordinated [REO6]. [REO7] polyhedra have a shape of capped trigonal prism: six oxygen atoms form distorted trigonal prism and the seventh is placed in front of one of the three rectangular faces (red and brown polyhedra in Fig.4). The shape of [REO6] polyhedron is distorted octahedron (green polyhedra in Fig.4).

We could not calculate valence of Lu atoms because r_0 value is not presented in the Brown's paper (Brown I.D. and Altermatt D., 1985). The valence of Yb3 2.674 (Table 3) is rather far from 3 in comparison with Yb1 and Yb2. It is due to the small contribution of two bonds Yb3-O5 because of their large bond lengths. The same situation is in [LuO6] octahedron (Table 3). The average RE-O bond lengths are close to each other (Table 3) and within the standard deviations practically. The average Lu-O bond lengths in C-Lu_2O_3 are less and correspond Lu1-O *r*=2.247 Å and Lu2-O *r*=2.235 Å (Saiki A. et al. 1985) and the average Yb-O bond lengths in C-Yb_2O_3 are less too and correspond Yb1-O *r*=2.252 Å and Yb2-O *r*=2.244 Å (Ishibashi H. et al., 1994). It is in a good agreement with

bond valence calculations because C.N. of RE in C-RE_2O_3 is six (octahedra) and the more C.N., the more bond lengths.

The positional parameters of metal atoms are practically the same as in Sm sesquioxide (Cromer D.T., 1957) but oxygen positional parameters differ, especially O3 and O4. The most probable reason of oxygen sublattice rearrangement is the big difference between ionic radii of Lu^{3+}, Yb^{3+} (0.848 Å, 0.858 Å, C.N. 6, respectively) and Sm^{3+} (0.964 Å, C.N. 6) (Shannon R.D. and Prewitt C.T., 1969).

The B-Lu_2O_3 sample is crystallized worse in comparison with B-Yb_2O_3 as evidenced by the values of FWHM (in Fig.1c diffraction peaks are broader than in Fig.1d). This made it impossible to refine displacement parameters of oxygen atoms in B-Lu_2O_3 and they were fixed during refinement.

5. CONCLUSIONS

The monoclinic modification of Lu and Yb sesquioxides were obtained by treatment of C-Lu_2O_3 and C-Yb_2O_3 at P=5.0 GPa and T=1300 C. The structure of these compounds was refined and compared with the structure of B-Sm_2O_3. The structural parameters are sent to the database ICSD (Inorganic Crystal Structure Data). A new sesquioxides of Lu and Yb were obtained after treatment of starting cubic phases at lower temperature (around 1000 C). The structure solution of this new compound is under way now.

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