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STRUCTURE STUDY OF SOME LANTHANIDE'S OXIDES BY X-RAY DIFFRACTION AND PAIR POTENTIAL MODELING

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Abstract

A number of $Ln_x O_y$ rare-earth oxides where Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, Dy and Er, x=1, 2, 4, 6 and y=2, 3, 7, 11 have been studied by powder diffractometry and pycnometry coupled with the simulation of their lattice dimensions by empirically derived pair potentials using the GULP code. Crystallographic analysis showed the oxides exist in the tri, tetra and mixed tri-tetra valency with Bravias lattices: hexagonal- *P*, cubic- *I* and cubic- *F* as a result of the oxidation state assumed by the Ln element that may be caused by the nature of the oxide or preparation process involved. Unit cell volumes of the oxides that exhibit identical Bravias lattices reflect a behavior that can be correlated with the atomic number of the Ln element whereby it decreases linearly by uncertainty not exceeding ca. 3%. The average bond lengths of Ln - O polyhedra in the sesquioxides ($Ln_2 O_3$) space group *Ia*3 also follow suit. The behavior is interpreted on a phenomenon known as lanthanide contraction.
Keywords: Rare earth oxides, Crystal structure, Lattice constants.

دراسة تركيب بعض اكاسيد اللنثينات بواسطة حيود الأشعة السينية وأنموذج جهد الزوج

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خلاصة

تم دراسة عدد من اكاسيد اللنثينات (الترابيات النادرة) بالصيغة $Ln_x O_y$ حيث Ln = La ، Ce ، Pr ، Nd ، Sm ، Eu ، Tb ، Dy و Er و x = 1 ، 2 ، 4 ، 6 و y = 2 ، 3 ، 7 ، 11 بواسطة قياس حيود المسحوق والكثافة مقترنة بمحاكات أبعاد الشبيكة من خلال جهـد الـزوج المشـتق تجريبيـا باستخدام الحزمة البرمجية GULP . يبين التحليل البلوري تواجد الأكاسيد بتكافؤ ثلاثي، رباعي و خلـيط من ثلاثي- رباعي و شبائك برافي من النوع : السداسي البدائي P، المكعبي ممركز الجسم I و المكعبـي ممركز الوجه F نتيجة لحالة الاكسدة المأخوذة للعنصر اللنثيني Ln المتسببة من طبيعة الأوكسيد او عمليات التحضير المرتبطة. تعكس حجوم خلية الوحدة للاكاسيد الممتلكة لشبائك متشابه سلوك من الممكن ربطه مع العدد الذري للعنصر اللنثيني حيث يقل الحجم خطيا مع العدد الذري بتغير لايتجاوز حوالي 3%. ويظهـر نفس السلوك على معدل أطوال الآصرة Ln - O في المجسم المتعدد الأوجه للصيغة الأوكسيدية نـوع $Ln_2 O_3$ بالزمرة الفضائية Ia3. يفسر السلوك على ضوء الظاهرة المعروفة بالانكماش اللنثيني.
الكلمات الدالة: اكاسيد الترابيات النادرة ، التركيب البلوري ، ثوابت الشبيكة.

Introduction

The lanthanide series are a group of oxides of particular importance as a catalyst for the synthesis of many other 4f materials [1-3]. It has been suggested that some of studied material properties exhibit periodicity [4]. The crystal structure of the trivalent sesquioxides ($Ln_2 O_3$) fall into three distinct polymorphic forms cubic *Ia*3, hexagonal *P*-3m1 and monoclinic *C*2/m, while the tetravalent fall into cubic *F*m3m [5]. Interestingly, some of the elements in the $Ln_x O_y$ series like La, Pr, Nd, Sm, Gd when converted to nitride and synthesized with 4,4'-bipyridyl, more than one crystal structure namely triclinic *P*-1, monoclinic *P*2/m or orthorhombic $P2_1 2_1 2_1$ is formed depending on the preparation procedures[6 - 8].

Work is currently devoted by the author's group to follow up the effect of addition of $Ln_x O_y$ series on the decomposition of various salts to oxides, which will be given elsewhere, it became evident that structural identification of the chemical formula of each oxide in the series is of particular importance in the subsequent interpretation of its impact on decomposition.

Owing to the usefulness of structural analysis of the lanthanide oxides, Hirosaki *et al*. [9] have utilized the density functional theory to make *ab initio* calculation of the crystal structure of $Ln_2 O_3$ sesquioxides. Work on modeling crystal structure and bulk properties of transition metal oxides compounded with the series of rare earth oxides of the formula RE(Ti Ta) O_6 RE = Ce, Pr, Nd, Sm have been studied by atomistic simulation [10]. A model structure of nano – sized ceria (CeO_2) and Gd – doped ceria have been conducted by using interionic-potential and density-functional calculations [11, 12]. In this presentation, structural analysis by x-ray crystallography of a number of rare earth (lanthanide) oxides is utilized and the results are compared with a preliminary simulation of lattice dimensions obtained by pair potential Buckingham model.

Experimental

A number of lanthanide oxides, some from Rare Earth Products, England and others from Ferak Laborat GMBH, Berlin with purity ranging from 99 to 99.9% were used as received. Density of powders was measured by pycnometry. All powders were ball milled and sieved through 45 micron mesh prior to x-ray scan. XRD spectra were obtained from Shimadzu 6000 diffractometer fitted with monochromatic Cu $K\alpha_1$ radiation. Peak positions of Bravias lattice were refined be Firestar code [13].

The lanthanide – oxygen bond was calculated from atomic positions given in [9].

Classical simulation of lattice parameters

The general utility lattice program (GULP) has been utilized in the shell modeling of the lanthanide's oxides [14]. In general, a pair potential $V(r_{ij})$ between atoms i and j separated by a distance r_{ij} consists of a short range interaction $\varphi(r_{ij})$ and a Coulombic term for the long range electrostatic interaction:

$$V(r_{ij}) = \varphi(r_{ij}) + q_i q_j / r_{ij} \qquad (1)$$

The short range interaction describes the Pauli repulsion at short distances and the van der Waal's attraction at larger distances. One of the common and effective functional form for (r ij) is the Buckingham potential of the form:

$$\varphi(r_{ij}) = A_{ij} \exp(-r_{ij} / \rho_{ij}) - C_{ij} / r_{ij}^6 \qquad \ldots\ldots(2)$$

A_{ij}, ρ_{ij} and C_{ij} in Eq. (2) are parameters of the model, and q_i and q_j in Eq. (1) are the ionic charges on atoms i and j respectively.

The short range interaction $\varphi(r_{ij})$ is limited to within a cutoff range (R_{cutoff} = 10 Å) and the long range Coulomb interaction is evaluated by the Ewald summation technique. The Buckingham parameters listed in (Table 1) were used in the calculations of lattice energy by GULP code. Lattice dimensions were determined by minimizing the lattice enthalpy in the constant pressure regime.

Table 1: Buckingham pair potential parameters for the interaction between the lanthanide cation cores and oxygen shells [15]

Element		A (eV)	ρ (Å)	C (eV / Å^6)
La core	O shell	1439.7	0.3651	0
Ce core	O shell	1017.4	0.3949	0
Nd core	O shell	1379.9	0.3601	0
Eu core	O shell	1358.0	0.3556	0
Gd core	O shell	1336.8	0.3551	0

Results and discussion

(Figure 1) shows a typical XRD scans that represent the three Bravias lattices (*P-3m1*, *Ia3* and *Fm3m*) obtained from particular oxides investigated.

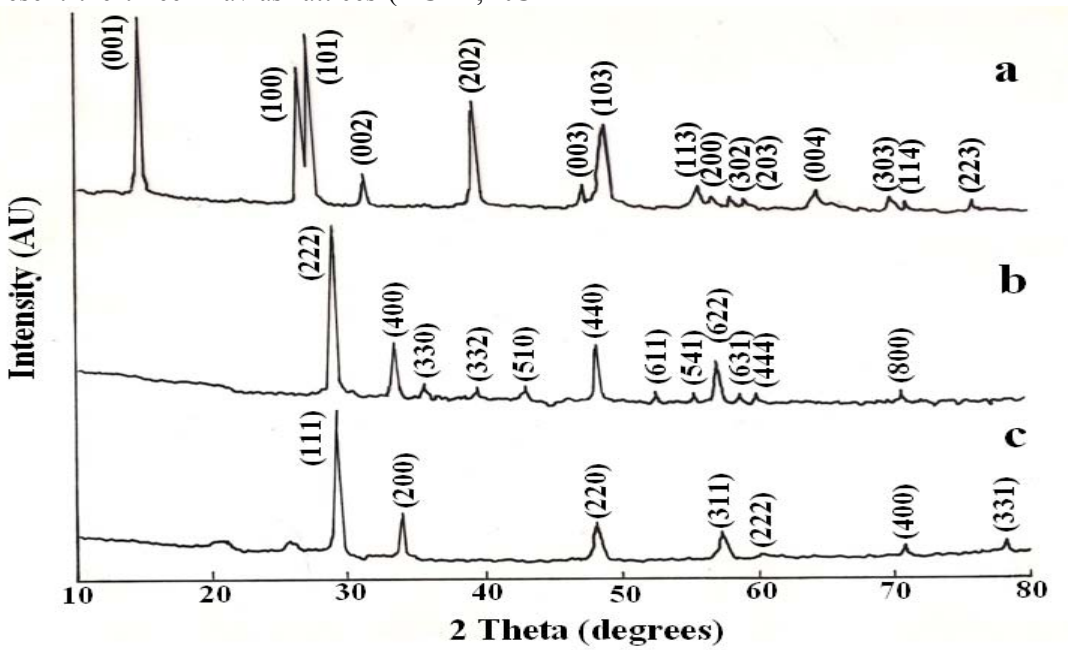

Figure 1: Typical XRD scans representing *three* Bravias lattices with their Miller indices marked: a. Hexagonal *P-3m1* for La_2O_3 b. Cubic *Ia3* for Dy_2O_3 c. Cubic *Fm3m* for Tb_4O_7

(Table 1) shows the lattice constants for the $Ln_x O_y$ series determined from XRD profiles and from GULP potential model simulation. One of the interesting results is the appearance of some lanthanide oxides in a mixed valence (tri – tetra) especially the $Pr_6 O_{11}$ and $Tb_4 O_7$. It is noted from Table 1 that the GULP results are in fair agreement when compared with the XRD and literature results which can be referred to the limited availability of precise potential values in the literature for the lanthanide elements. Moreover, not all the potential values are available in the literature for the lanthanide oxides considered in this work.

Table 1: Lattice constants for hexagonal *P-3m1* and cubic *Ia3* and *Fm3m* of $Ln_x O_y$ rare earth oxides from XRD and GULP with corresponding values from literature. Values in parenthesis are SD.

Rare earth oxide	Space group	Lattice constant (Å)		
		Refined XRD	GULP	Ref. [9,16]
La_2O_3	*P-3m1*	a 3.940(5) c 6.152(8)	3.907 6.119	3.936 6.166
CeO_2	*Fm3m*	a 5.417(3)	5.451	5.413
Pr_6O_{11}	*Fm3m*	a 5.463(4)	NA	5.467
Nd_2O_3	*Ia3*	a 11.043(5)	11.017	11.176
Sm_2O_3	*P-3m1*	a 3.861(5) c 6.169(8)	NA	3.860 6.170
Sm_2O_3	*Ia3*	a 10.921(4)	NA	10.995
Eu_2O_3	*Ia3*	a 10.858(6)	10.895	10.869
Gd_2O_3	*Ia3*	a 10.780(7)	10.843	10.812
Tb_4O_7	*Fm3m*	a 5.301(4)	NA	5.290
Dy_2O_3	*Ia3*	a 10.671(4)	NA	10.670
Er_2O_3	*Ia3*	a 10.549(3)	NA	10.544

The results in (Table 2) show that the volume per molecule of the $Ln_2 O_3$ sesquioxides in the *Ia3* polymorph decreases with increasing atomic number of lanthanide element in accordance with the lanthanide contraction phenomena**.** This behavior can well be seen in (Figure 2), which shows the molecular volume versus lanthanide's atomic number for Ia3 and Fm3m polymorphs.

Table 2: Cell volume per molecule of $Ln_x O_y$ series according to polymorph and densities measured and calculated.

Rare earth oxide	V (Å³)			ρ_m (g/cm³)	ρ_c (g/cm³)
	P-3m1	*Ia3*	*Fm3m*		
$La_2 O_3$	82.71			6.510	6.539
CeO_2			158.98	7.135	7.189
$Pr_6 O_{11}$			163.05	6.902	6.936
$Nd_2 O_3$		84.16		6.605	6.637
$Sm_2 O_3$	79.63	81.42		6.975	7.111
$Eu_2 O_3$		79.99		7.253	7.303
$Gd_2 O_3$		78.72		7.607	7.644
$Tb_4 O_7$			148.93	8.308	8.334
$Dy_2 O_3$		75.94		8.117	8.154
$Er_2 O_3$		73.37		8.615	8.655

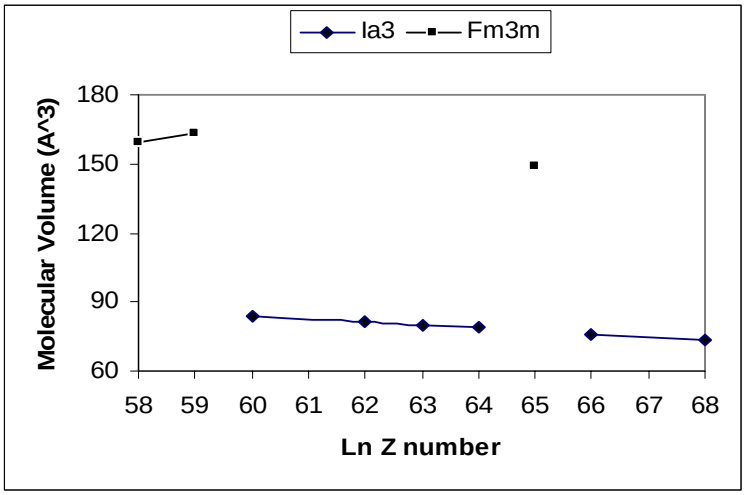

Figure 2: Volume per molecule of $Ln_x O_y$ versus atomic number of Ln element.

Polymorph quantification

$Sm_2 O_3$ is the exception among the oxides considered whereby it shows two polymorphs in a single XRD spectrum - the cubic and hexagonal. Weight composition of these polymorphs was done by direct comparison method [17] using the formula:

$$W_C = 1 / (1 + 1/k (I_H / I_C)) \% \qquad (3)$$

where W_C is the wt% of cubic polymorph, k is a constant, I_H and I_C are the intensities of hexagonal and cubic Bragg's lines.

The weight composition of each of the cubic and hexagonal polymorphs were found to be 61% and 39% respectively. Presence of these polymorphs indicate incomplete phase transformation toward the cubic polymorph.

Lanthanide – Oxygen bond

(Table 3) shows bond lengths of lanthanide to oxygen calculated from atomic positions and space group symmetry. The Ln – O bond lengths in the sesquioxides show similar behavior with that of unit cell and volume and lie nicely with the sum of ionic radii taken from [18] for trivalent lanthanide. The bond lengths in the oxides containing possible mixed valency

appear to be less certain due to competing influence of the valence states.

Table 3: Ln – O bond lengths for hexagonal *P-3m* and cubic *Ia3* and *Fm3m* polymorphs.

Rare earth oxide	Bond length (Å)			Sum of ionic radii(Å)
	P-3m	*Ia3*	*Fm3m*	
La_2O_3	2.452			2.55
CeO_2			2.526	2.41
Pr_6O_{11}			2.549	2.49
Nd_2o3		2.476		2.48
Sm_2O_3	2.446	2.452		2.44
Eu_2O_3		2.432		2.43
Gd_2O_3		2.426		2.42
Tb_4O_7			2.473	2.40
Dy_2O_3		2.399		2.39
Er_2O_3		2.369		2.36

Conclusion

XRD and pycnometry have proved to be effective in obtaining crystallographic data that are particularly important in determining the chemical formula of the lanthanide oxide whether sesquioxide (Ln_2O_3) or non-sesquioxide. This would be very useful step in the research application as these oxides are used as a catalysts.

Crystallographic data also serve to distinguish between different structural symmetries present in one particular oxide.

Employing pair potential in the calculation of crystal lattice dimensions need to be reviewed since precise and comprehensive empirical potential data for lanthanides are needed. However, this approach is a useful numerical technique for modeling structure and bulk properties in macro and nano-sized materials.

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