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A convenient low temperature route to the formation of lanthanide oxides

Adrian T. Rowley and Ivan P. Parkin*
Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA (UK)

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Abstract

The formation of oxides of the type Ln_2O_3 (Ln = La, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er) is reported. They have been obtained from the solid state reaction of anhydrous $LnCl_3$ with Li_2O at oven temperatures of 500 °C. DSC studies show the reaction is initiated at 280–310 °C. The sesquioxides have been characterised by X-ray powder diffraction (XRD), SEM/EDAX and magnetic moment measurements.

Introduction

We have been studying new low temperature routes to transition metal and lanthanide nitrides [1, 2] by solution and solid state methods and have extended this study to include oxides of the lanthanide series. Lanthanide nitrides can be prepared at 450 °C by a solid state reaction of the anhydrous lanthanide chloride and lithium nitride, Li_3N. In an extension of this study we have now shown that the lanthanide oxides can be prepared by a similar reaction using lithium oxide, Li_2O.

Lanthanide sesquioxides, Ln_2O_3, are usually prepared by the oxidative ignition of the metals or of their compounds [3]. The exceptions to this are Ce, Pr and Tb, the most stable products of which are CeO_2, Pr_6O_{11} and Tb_4O_7, from which the sesquioxides can be obtained by controlled reduction with hydrogen [4]. More recently, it has been shown that thermal decomposition of complexes of the type $Ln_2(L)(NO_3)_4 \cdot xH_2O$ (where H_2L is the macrocycle obtained by condensation of 2,6-diformyl-4-chlorophenol and 1,8-diamino-3,6-dioxaoctane) can yield the lanthanide sesquioxides at temperatures of approximately 1200 °C [5].

Mixed metal oxides of the type $Ln'Ln''O_3$ ($Ln'Ln''$ = LaSm, LaGd, LaDy, NdGd, DyEu, DyNd) have also been prepared by this method from the corresponding macrocyclic complexes $Ln'Ln''(L)(NO_3)_4 \cdot xH_2O$.

Experimental

All manipulations were carried out in a glove box under an atmosphere of dinitrogen. Lithium oxide was obtained from Aldrich Chemical Co. and used as supplied. Anhydrous lanthanide(III) chlorides were obtained from Strem Chemicals and used as supplied. X-ray diffraction patterns were recorded on a Siemens D5000 diffractometer with nickel filtered Cu Kα radiation, $\lambda = 1.5406$ Å. Differential scanning calorimetry was obtained in aluminium pans on a Polymer Laboratory differential scanning calorimeter under argon flow (10 ml/min) at 5 °C/min ramp rate from 200–625 °C.

Lithium oxide (0.05 g, 1.7 mmol) was combined with $\frac{2}{3}$ equivalence of anhydrous lanthanide chloride in a glass ampoule which was sealed under vacuum. The ampoule was heated at 500 °C for 10 h. The resultant solid was washed with distilled H_2O and dried before being analysed by X-ray powder diffraction (XRD) (Table 1), magnetic moment measurement, FT-IR, SEM and EDAX analysis. The metal oxides formed after washing contained less than 0.5% Li by conventional microanalysis.

Caution. Reaction between hydrated lanthanide halides and Li_2O in sealed tubes has been known to explode on heating.

Results and discussion

Thermal initiation of the reaction between Li_2O and anhydrous lanthanide halides in a conventional oven at 500 °C produces the lanthanide oxide, Ln_2O_3, and additionally, depending on the metal, some LnOCl, eqns. (1) and (2).

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*Author to whom correspondence should be addressed.

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$$2LnCl_3 + 3Li_2O \xrightarrow{500\ ^\circ C} 6LiCl + Ln_2O_3 \qquad (1)$$

(Ln = Tb, Dy, Ho, Er)

$$LnCl_3 + Li_2O \xrightarrow{500\ ^\circ C} xLnOCl + yLn_2O_3 + LiCl \qquad (2)$$

(Ln = La, Pr, Nd, Eu, Gd)

The reactivity of the lanthanide chlorides towards Li_2O appears to increase from left to right across the lanthanide series. From Nd to Gd a mixture of the sesquioxides and oxide chlorides, LnOCl, is obtained initially eqn. (2), however from Tb to Er the sesquioxides are obtained exclusively eqn. (1).

The product of the reactions was often contained as a fused lump and a small amount of white solid was sublimed onto the walls of the ampoule. The white sublimed solid was shown to be lithium chloride by X-ray powder diffraction (XRD), lithium flame test and EDAX analysis. The fused material showed a smooth morphology by SEM and oxygen, metal and chloride by EDAX analysis. These findings are consistent with the formation of lithium chloride with the lanthanide oxide or lanthanide oxide chloride. The lanthanide oxides were purified by trituration with water which not only removed the LiCl but also the LnOCl (no chloride peak remaining in the lanthanide oxide sample as detected by EDAX analysis, and no powder diffraction pattern for LnOCl after trituration).

The SEM profile of the triturated lanthanide oxides showed micron sized particles with sharp angles and faces. The FT-IR spectra of the triturated lanthanide oxides showed absorptions at 500 cm^{-1} consistent with an Ln–O stretching frequency. The magnetic moments [7] for the lanthanide oxides were identical to those recorded previously by 'high temperature' routes, as shown in Table 1. No lithium ($<0.5\%$) was detected in the triturated lanthanide oxide powders by conventional microanalysis.

The lanthanide oxides formed from the solid state reaction of Li_2O and $LnCl_3$ (Ln = Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er) are all cubic with the exception of La_2O_3 and Pr_2O_3 which are hexagonal as determined from their XRD patterns. The reaction of $CeCl_3$ and Li_2O at an oven temperature of 500 °C yields cubic CeO_2 (space group *Fm*3*m* (No. 255)), not the sesquioxide, possibly due to the +4 oxidation state of cerium being more stable than the +3. In general after a reaction time of two hours a crystalline lanthanide oxide was formed, however, the degree of crystallinity as judged by the Scherrer equation [8] varied from crystalline sizes of 150–700 Å.

Figure 1 illustrates the X-ray powder diffraction pattern for Tb_2O_3 and Fig. 2 the mixed patterns for LaOCl and La_2O_3 formed in this study.

Mixed metal oxides have been prepared by Guerriero *et al.* [5] from mixed metal complexes of the type $Ln'Ln''(L)(NO_3)\cdot xH_2O$ as described earlier. Attempts to produce mixed metal oxides by the low temperatures reaction of Li_2O with a mixture of two anhydrous lanthanide chlorides was unsuccessful even when the temperature was raised to 900 °C. From these reactions a mixture of metal oxide and metal oxide chloride was obtained, the metal furthest to the right in the lanthanide series tending to form the metal oxide with the metal furthest to the left in the series forming the metal oxide chloride.

The reactions of $TbCl_3$ and $HoCl_3$ with Li_2O was studied by DSC, which revealed a large exotherm at 290 and 294 °C, respectively (Fig. 3). The energy released (200–300 kJ mol^{-1}) is far too large to be associated with a phase change and corresponds to the expected heat of reaction on forming metal oxide and LiCl as determined by the Hess law [9]. Interestingly, the exotherm takes place over a fifteen minute time period indicating that the reaction is not violently exothermic like reactions involving $MoCl_5/Na_2S$ where the products have cooled to room temperature after a minute [10]. The heat transfer to the reactants is easier in the DSC cell than the glass ampoule reactions and the oven

TABLE 1. Lanthanide sesquioxide, Ln_2O_3, data, formed from reaction of $LnCl_3$ and Li_2O

Ln_2O_3	Crystal system	Lattice parameter, *a* (Å)		Space group [6]	M_B (BM)	
		Calculated	Lit. value [6]		Obs.	Lit. [7]
La_2O_3	hexagonal	3.94	3.93	*P*-3*m*1 (164)		
Pr_2O_3	hexagonal	3.89	3.86	*P*-3*m*1 (164)	4.5	4.6
Nd_2O_3	cubic	11.11	11.08			
Gd_2O_3	cubic	11.08	10.81	*Ia*3 (206)		
Tb_2O_3	cubic	10.75	10.75	*Ia*3 (206)	9.8	9.7
Dy_2O_3	cubic	10.73	10.66	*Ia*3 (206)	10.9	10.6
Ho_2O_3	cubic	10.65	10.61	*Ia*3 (206)	10.8	10.7
Er_2O_3	cubic	10.60	10.55	*Ia*3 (206)		
CeO_2	cubic	10.78	10.82	*Fm*3*m* (255)		

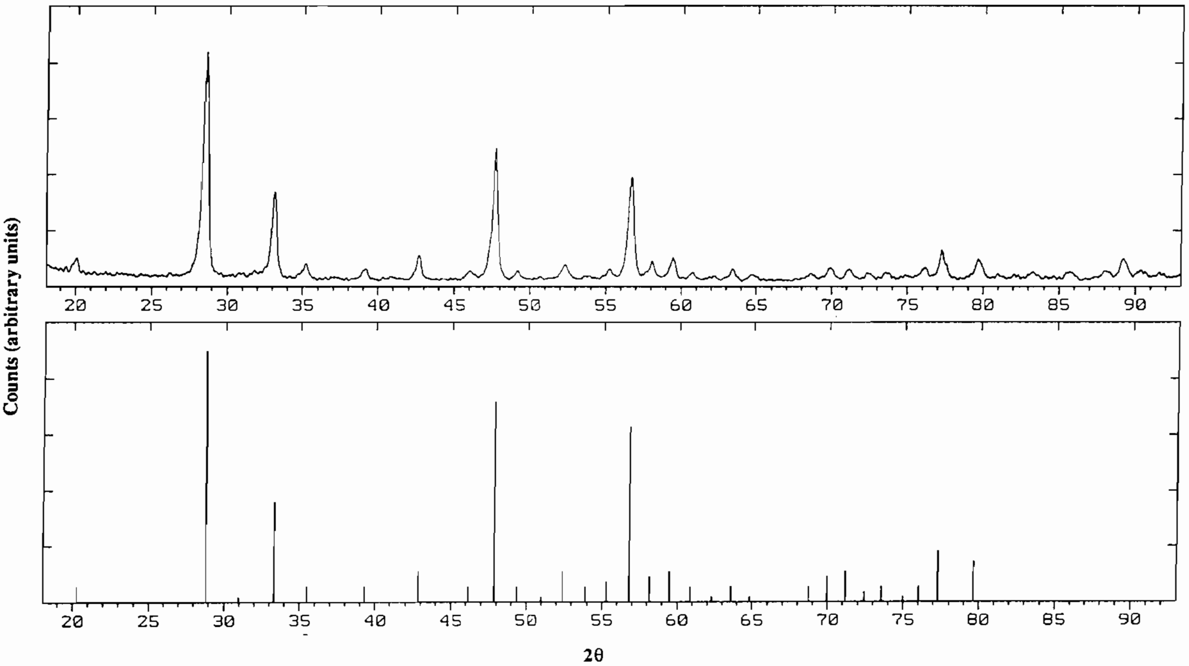

Fig. 1. Upper trace X-ray powder diffraction pattern obtained from reaction of Li_2O and $TbCl_3$; lower trace standard X-ray powder diffraction pattern from Tb_2O_3.

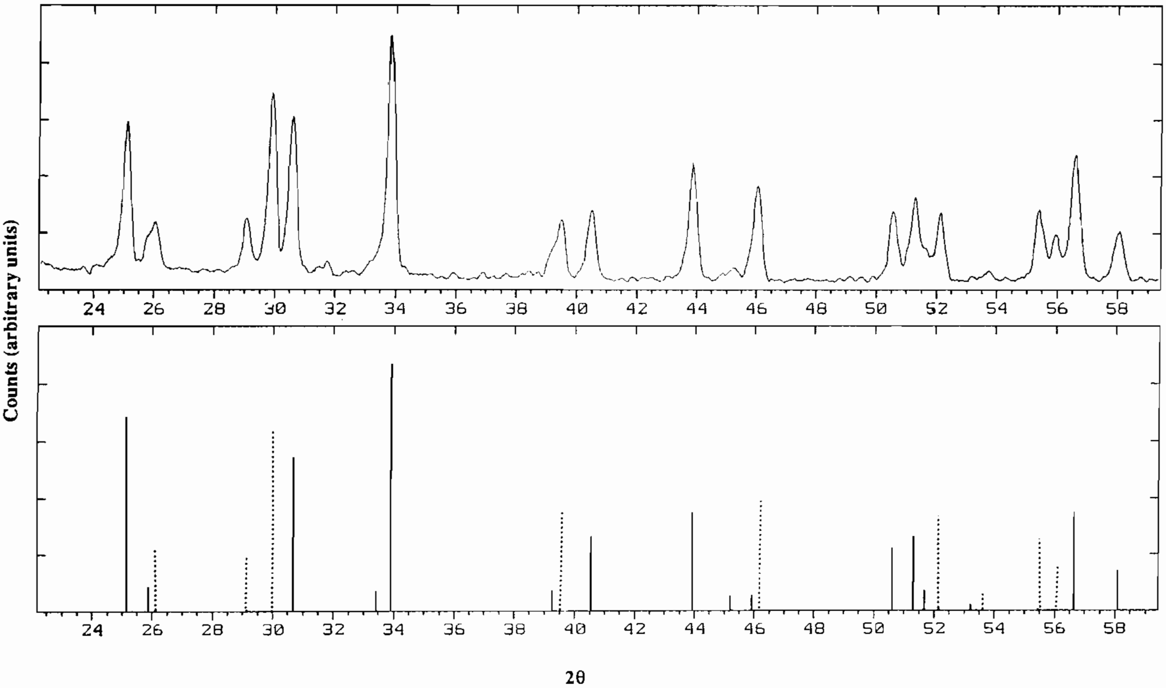

Fig. 2. Upper trace X-ray powder diffraction pattern obtained from reaction of $LaCl_3$ and Li_2O; lower trace standard X-ray powder diffraction patterns for LaOCl (——) and La_2O_3 (·····).

initiation temperature of 500 °C probably corresponds to *c.* 300 °C at the sample surface after the effects of thermal gradients within the oven are taken into account. Blank runs of Li_2O, $TbCl_3$ or $HoCl_3$ revealed no phase changes or reactions in the DSC cell from 200 to 450 °C.

Lanthanide halides react with Li_3N to form lanthanide nitrides via a spontaneous exothermic reaction, typically with a red glow emanating from a sealed ampoule and the whole reaction required only 2–3 s for completion. The differences between the reactions of Li_3N and Li_2O with lanthanide chlorides may be due to the

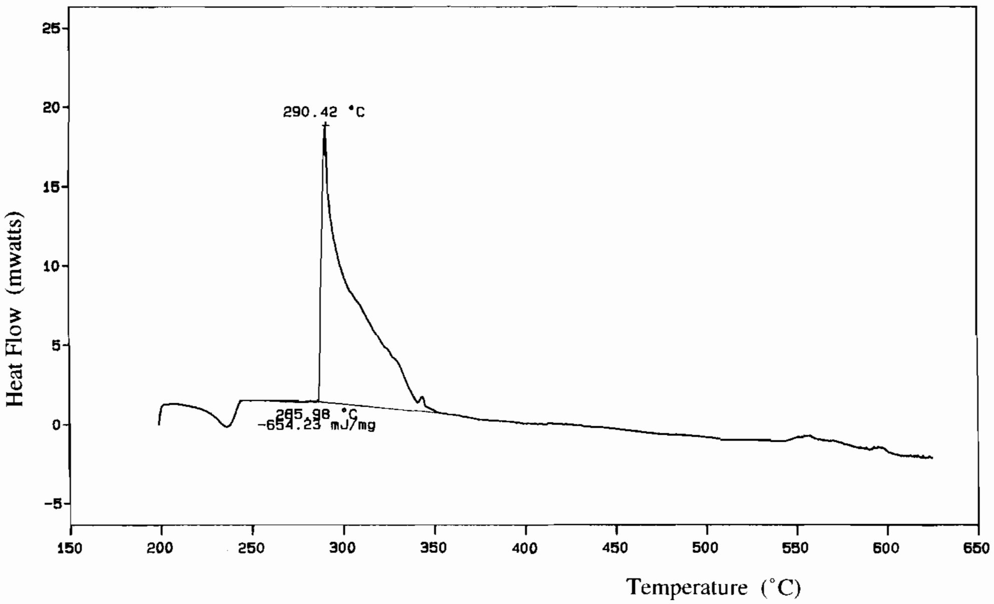

Fig. 3. Differential scanning calorimeter trace for the reaction of $TbCl_3$ and Li_2O.

intimate surface area contact between the reagents. Lithium oxide (m.p. > 1700 °C) is more thermally stable than lithium nitride (m.p. = 555 °C dec.) and thermally initiated decomposition of the lithium nitride may increase contact between the solids and propagate an explosive exothermic reaction through the whole solid. In the Li_2O case this does not happen although a fused product and sublimed LiCl (b.p. > 1300 °C at atmospheric pressure) indicates that the reaction is indeed exothermic, possibly, with a series of propagations that fail to spread through the bulk of the material. This is confirmed by the DSC studies which show the exotherm for the reaction covers a fifteen minute period.

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