

## Hydrothermal phase equilibria in $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$ systems

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**Abstract.** Hydrothermal phase equilibria studies have been carried out in the  $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$  systems ( $\text{Ln} = \text{La, Pr, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb}$  and  $\text{Lu}$ ) and the stability fields of the phases  $\text{Ln}(\text{OH})_3$ ,  $\text{LnOOH}$  and  $\text{Ln}_2\text{O}_3\text{-C}$  have been established in the pressure-temperature range of 25000 psi and  $900^\circ\text{C}$ . The sesquioxides  $\text{Ln}_2\text{O}_3\text{-C}$  are stable only in the last four systems of Er to Lu along with the  $\text{Ln}(\text{OH})_3$  and  $\text{LnOOH}$ . The systems from Nd to Ho have only  $\text{Ln}(\text{OH})_3$  and  $\text{LnOOH}$  as stable phases and those from La to Pr have only  $\text{Ln}(\text{OH})_3$  as the stable phase. The unit cell parameters of trihydroxides deviate from the values reported in the literature and this is attributed to the contamination of  $\text{CO}_2$  in the starting material.

**Keywords.** Hydrothermal phase equilibria; lanthanide hydroxide; lanthanide oxyhydroxide; lanthanide oxide.

### 1. Introduction

The electrical and magnetic properties were reported for pure lanthanide oxides (Eyring 1970, 1974) and trihydroxides (Wolf *et al* 1968; Meissner and Wolf 1969; Scott *et al* 1969a, b) at low temperatures. It is expected that mixed lanthanide oxides would prove to be interesting materials with properties ranging from semiconductors to even fast ionic conductors (like  $\text{Ln}^{3+}$  in  $\text{CeO}_2$ ); the latter in analogy to  $\text{ThO}_2\text{-Y}_2\text{O}_3$  solid solution compound reported by Wimmer *et al* (1967) and Patterson *et al* (1967). The synthesis and single crystal growth of the pure and mixed lanthanide oxides is difficult by normal high temperature techniques because of the high melting temperatures of these oxides ( $> 2400^\circ\text{C}$ ). Hydrothermal technique is one of the most promising alternative methods for stabilising such lanthanide oxides and growing single crystals for characterisation, and the knowledge of phase equilibria in the  $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$  systems is an essential prerequisite for any work on synthesis and crystal growth.

Phase diagrams for  $\text{La}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Nd}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Sm}_2\text{O}_3\text{-H}_2\text{O}$  systems were reported by Shaffer and Roy (1959), but these diagrams have been subsequently disputed by Haschke and Eyring (1971). Viswanathiah *et al* (1976) revised the phase diagram for systems  $\text{Nd}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Sm}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Yb}_2\text{O}_3\text{-H}_2\text{O}$  and  $\text{Y}_2\text{O}_3\text{-H}_2\text{O}$

and demonstrated the effect of contamination of  $\text{CO}_2$ ,  $\text{Na}^+$  and  $\text{NO}_3^-$  in these systems in reducing the temperature of the stability of the different phases and also explained the differences in the results of earlier workers. The  $\text{Yb}_2\text{O}_3\text{-H}_2\text{O}$  system reported earlier was not complete and the completed diagram is given again after reinvestigation. The present paper is a continuation of the previous report and the complete phase diagrams for rest of lanthanide oxide-water system (except  $\text{Ce}_2\text{O}_3\text{-H}_2\text{O}$ ) are given.

## 2. Experimental

The starting material was a freshly ignited oxide (99.9% pure-Fluka AG Switzerland and Leico Industries, New York) and double-distilled freshly boiled water. About 50–60 mg of oxide powder was charged in a platinum ampoule (5 cm long) along with 5–6 drops of water and sealed by welding the open end. The duration of the experiment was 90–100 hr and all the experiments were done with stellite

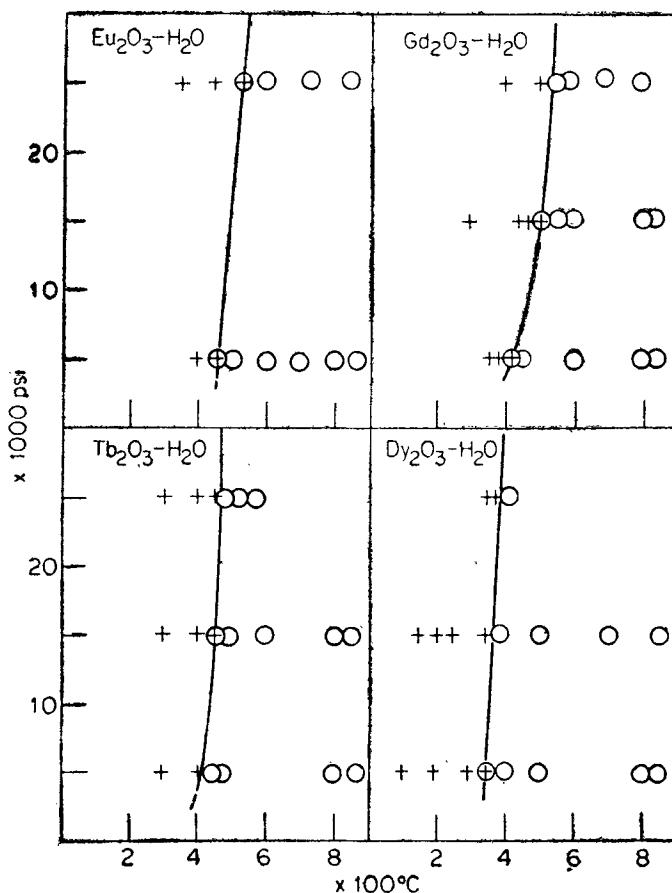


Figure 1. Phase diagrams for  $\text{Eu}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Gd}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Tb}_2\text{O}_3\text{-H}_2\text{O}$  and  $\text{Dy}_2\text{O}_3\text{-H}_2\text{O}$  systems.

test tube vessels and tempress unit HR-IB-4. The other experimental details are similar to those described earlier (Viswanathiah *et al* 1976; Kutty *et al* 1978).

### 3. Results and discussions

Phase diagrams for all the  $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$  systems presently studied are given in figures 1 and 2, except for  $\text{La}_2\text{O}_3\text{-H}_2\text{O}$  and  $\text{Pr}_2\text{O}_3\text{-H}_2\text{O}$  systems. In both these systems the only stable phase within the present PT limits is  $\text{Ln}(\text{OH})_3$  hexagonal and therefore the phase diagram is not given. In the system  $\text{Lu}_2\text{O}_3\text{-H}_2\text{O}$  experiments were made at 5000 psi only to locate the oxide-oxyhydroxide and trihydroxide boundary. The  $\text{Lu}(\text{OH})_3\text{-LuOOH}$  boundary lies at  $60^\circ\text{C}$  and the  $\text{LnOOH-Ln}_2\text{O}_3\text{-C}$  lies at  $160^\circ\text{C}$ . The trihydroxide and oxyhydroxide are the only two stable phases from Nd to Ho. The cubic  $\text{Ln}_2\text{O}_3$  phase is stable from Er to Lu, along with the  $\text{LnOOH}$  and  $\text{Ln}(\text{OH})_3$  phase. The other polymorphic forms of sesquioxides namely the B-type (monoclinic) reported earlier to be the stable

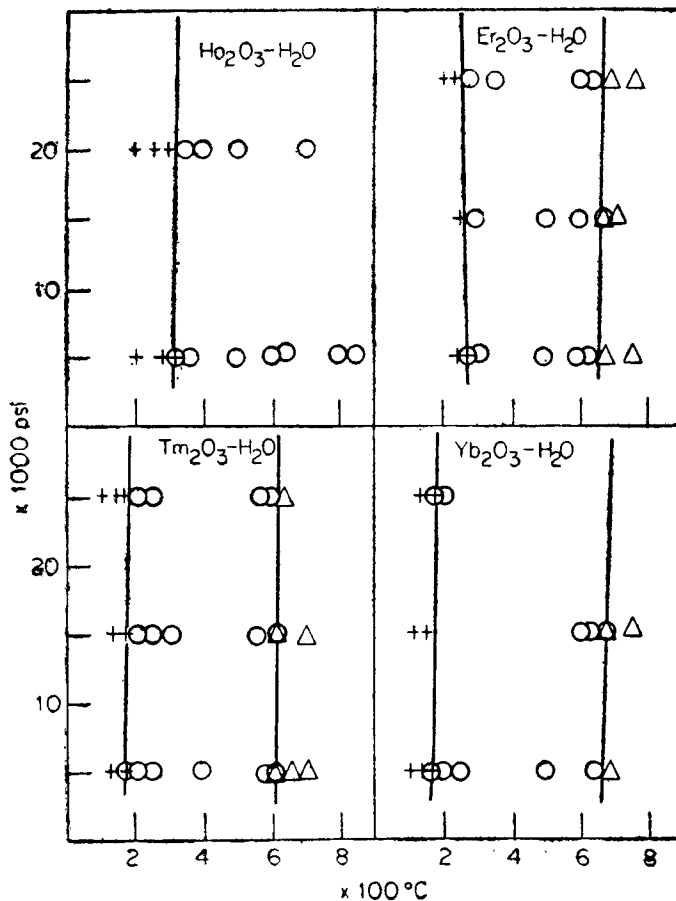


Figure 2. Phase diagrams for  $\text{Ho}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Er}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Tm}_2\text{O}_3\text{-H}_2\text{O}$  and  $\text{Yb}_2\text{O}_3\text{-H}_2\text{O}$ .

phase in  $\text{Nd}_2\text{O}_3\text{-H}_2\text{O}$  and  $\text{Sm}_2\text{O}_3\text{-H}_2\text{O}$  systems, by Shaffer and Roy (1959) could not be stabilised.

The temperature of  $\text{Ln}(\text{OH})_3$  and  $\text{LnOOH}$  phase boundary are plotted against the atomic number (figure 3). The plot is nearly linear, except for deviations at Eu and Yb. The unit cell parameters of the  $\text{Ln}(\text{OH})_3$  have been plotted against the atomic number (figure 4). The unit cell values reported by Dillin and Milligan (1973) are also plotted to show their deviation from the present values. It is found that the cell constants calculated in the present study are larger than those reported in literature. It must be emphasised here that the cell parameter reported by all the previous workers is measured on the trihydroxides prepared by invariably using some mineralisers, particularly NaOH. It is found by the present authors that such mineralisers will undoubtedly have  $\text{CO}_2$  contamination, and the hydroxide so crystallised are bound to have slight substitution of  $\text{CO}_3^{2-}$  for  $\text{OH}^-$ ; this being accompanied by the generation of hydroxyl ion vacancy. Such hydroxides will have the composition  $\text{Ln}(\text{OH})_{3-2x}(\text{CO}_3)_x$  with extremely low  $\text{CO}_2$  concentration and will give an x-ray pattern similar to pure  $\text{Ln}(\text{OH})_3$  but with a lower cell value. Though the extent of such influence on  $\text{Ln}(\text{OH})_3$  structures has not been quantitatively established,  $\text{Nd}(\text{OH})_3$  prepared with

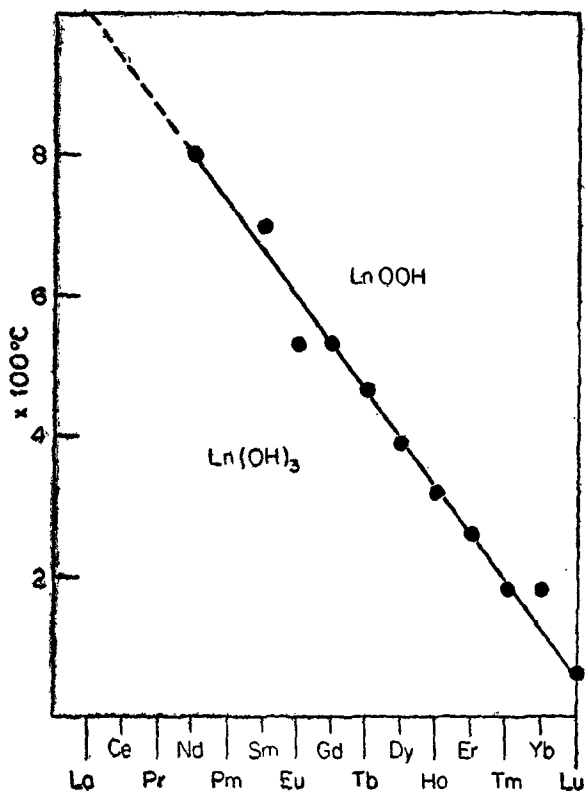


Figure 3. Plot of temperature of  $\text{Ln}(\text{OH})_3\text{-LnOOH}$  boundary against atomic number at 25,000 psi.

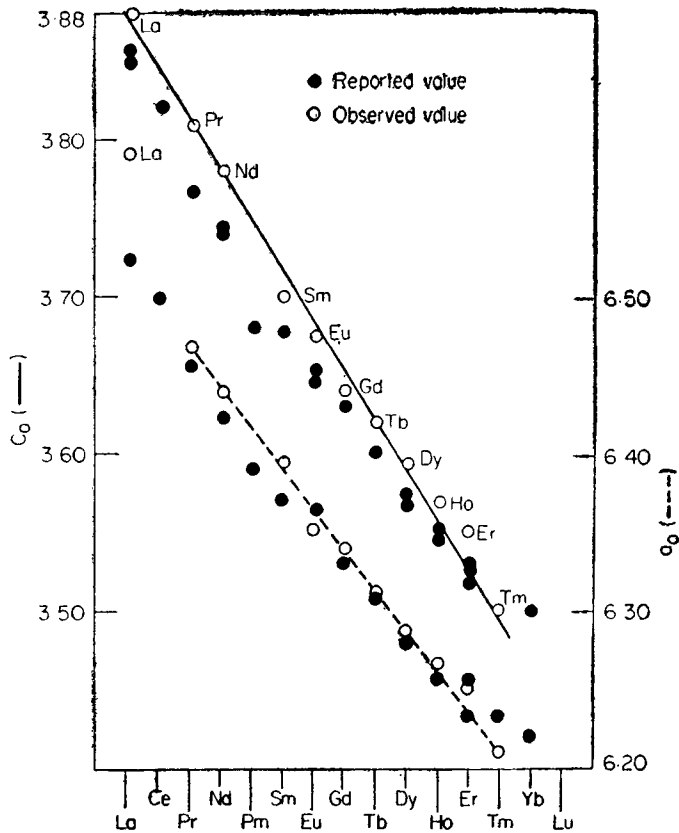


Figure 4.  $a_0$  and  $c_0$  values for  $\text{Ln}(\text{OH})_3$ , plotted against the atomic number. Solid circles are the reported values compiled by Dillin and Milligan (1973).

$\text{NaOH}$  (10 m) solutions has a lower cell value than that prepared from pure  $\text{Nd}_2\text{O}_3\text{-H}_2\text{O}$  systems, and is free from any  $\text{CO}_2$  contamination.

#### 4. Conclusion

In pure  $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$  system, the cubic oxides are stable only from the Er–Lu and none of the other polymorphic forms like B and A type is stable. However, if mineralisers, particularly the oxidising acids like  $\text{HNO}_3$ , are used (Lowenstein *et al* 1972), it is likely that the oxides of lighter lanthanides are also stabilised hydrothermally, within the PT range of normal stellite vessels.

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