Product Prediction: Intermediates Formed During Rare Earth Reactions

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Abstract. Thermal analyses, X-ray diffraction (XRD), and HR-XRD (High Resolution XRD) were used to identify thermal behavior products in a family of solid-state reactions involving rare earth (REE) reagents. REE where sorted in light and heavy groups. The general reactions under study were: REE(OH)3 + Fe2O3 + As2O3 → 2REEFeO3 + As2O3↑ and 2REE(OH)3 + Fe2O3 + As2O3 → 2REEFeO3 + As2O3↑ + 3H2O↑, REE= La, Ce, Nd, Sm, Gd, Dy, Ho, Er, and Yb. Based on the experimental results, it is possible to predict the different compounds of REE products in a series of reactions analyzing only three of the reactions, two for light REE and one for heavy REE.

Key words: Rare-earth, XRD, TG-DSC, solid-state reaction, thermal stability

Introduction

Rare earth orthoferrites, REEFeO3 present interesting properties when iron is substituted [1, 2] with another transition metal. For example, a partial Fe substitution with Mn in the yttrium orthoferrite, YFe1-xMnxO3, changes its magnetic behavior dramatically [1]. The substitution induces a spin-reorientation transition from the low-temperature antiferromagnetic state to a high-temperature weak ferromagnetic state. As far as we know, there are no studies around the substitution of arsenic in rare earth orthoferrites. Trivalent arsenic (As3+) in an octahedral site, is the same size as Mn3+, roughly 72 pm. It is interesting to research that cation substitution.

There is a lack of literature on the formation of rare earth orthoferrites. One of the few available reference found was that of Parida. Parida et al. [3] studied the thermodynamic properties of LaFeO3 and determined its enthalpy increments and standard molar Gibbs energy of formation; but the thermal stability and reactions expected phases that precede the main product remain unknown.

On our study, rare earth elements were separated into two groups sorted by molecular weight using the classification by Barret and Dhesi [4]: a) light rare earth, from lanthanum to samarium, and b) heavy rare earth, from gadolinium to lutetium. Within each group, the chemical properties of the elements are very similar. The advantage of studying the REE as light and heavy is that the chemical behavior of each group is expected to be the same. The reactions selected were REE2O3 + Fe2O3 + As2O3 → 2REEFeO3 + As2O3↑ and 2REE(OH)3 + Fe2O3 + As2O3 → 2REEFeO3 + As2O3↑ + 3H2O↑. The reagents used were: La2O3, La(OH)3, Gd2O3, CeO2, Pr2O3, and the corresponding oxides of Nd, Sm, Dy, Ho, Er, and Yb (REE2O3).

Only La2O3, La(OH)3, and Gd2O3 were treated to guarantee their chemical form, all the other rare earth reagents were used as were stored, some of the reagents were in hydroxide form. Thermal analyses (thermogravimetric analysis, TG, and differential scanning calorimetry, DSC) were used to determine the thermal stability of the compounds and temperatures at which thermal events occur. To understand the reactions process, three reactions, that are representative of the light and heavy REE groups, were fully studied to determine the intermediate products at selected temperatures; two with light REE, La2O3 + As2O3 + Fe2O3, and La(OH)3 + As2O3 + Fe2O3, and one with a heavy REE, Gd2O3 + As2O3 + Fe2O3. Light REE oxides can absorb water easily and transform to hydroxides, which is why the analysis contemplate both forms. Temperatures between thermal events were chosen for each of the three reactions to determine their behavior at each temperature. Using the first derivative of the DSC (Fig. 1 and 2) the thermal events between 25 to 700 °C can be determine, in the middle of two thermal events a temperature was chosen. At the selected temperatures, a sample of reactants was heated and then cooled gradually (C) inside the furnace and quenched in ice (Q) in a platinum pan. Cooling gradually allows the reactions to form stable compounds. Quenching in ice permits the identification of metastable compounds. X-ray diffraction (XRD) was used to identify reagents, products, and intermediate products between thermal events for the reactions with La2O3 and Gd2O3, while HR-XRD (High Resolution X-Ray Diffraction) was performed for the La(OH)3 reaction. The use of HR-XRD allowed to identify the intermediate products clearly.

The reactions REE2O3 + Fe2O3 + As2O3 → 2REEFeO3 + As2O3↑ and 2REE(OH)3 + Fe2O3 + As2O3 → 2REEFeO3 + As2O3↑ + 3H2O↑ were selected to study the substitution of arsenic in the
iron site of orthoferrites. The thermal characterization was necessary to understand step by step the reaction process. After analyzing the TG and DSC curves it was decided to do the identification of phases between thermal events because of the similarities in the thermal (TG and DSC) behavior of all the reactions.

**Results and Discussion**

The investigation consisted of two main procedures: the thermal characterization of the reactions and the identification of phases in the reactions. For the thermal characterization of the reactions, TG and DSC were selected. The thermal analyses for each of the eleven reactions between 25 and 700 °C were done. The second procedure consisted of the identification of phases formed at different temperatures in a range from 25 to 700 °C for the reactions with La$_2$O$_3$, Ce, Pr, Nd, and Sm using two cooling methods; gradually cooled (C) in air until ambient temperature was reached and quenched in ice (Q) at about 1 °C.

**Thermal characterization**

TG and DSC analyses are compared in Figs. 1 and 2, TG (dotted line), DSC (solid black) and the first derivative of DSC (solid gray). There was weight loss between 28% for the reaction with Er, and 37% for La(OH)$_3$. The weight loss took place with two distinct patterns. The first pattern had one slope, for the reactions with La$_2$O$_3$, Ce, Gd$_2$O$_3$, Dy, Ho, Er, and Yb, that started approximately at 190 °C and ended around 270 °C. The second pattern had two slopes for reactions with La(OH)$_3$, Pr, Nd, and Sm; the first slope behaved similarly to the one in the first pattern with same start and end temperatures. The second slope started approximately at 270 °C and ended at 350 °C. There was a clear relation between the reactions with the same behavior.

Neumann *et al.* [5] studied the decomposition of pure La(OH)$_3$ where TG presented two slopes, similar to the present case. They found for pure La(OH)$_3$ that the total weight loss was 15% and the first slope started at 320 °C and ended at 400 °C. The second slope started at 400 °C and ended at 550 °C. The reported reactions for the decomposition of pure La(OH)$_3$ are: 2La(OH)$_3$ → 2LaOOH + 2H$_2$O↑ → La$_2$O$_3$ + H$_2$O↑. The decomposition of pure La(OH)$_3$ shed light in the possible intermediates that could be found. In the case of our reaction, 2La(OH)$_3$ + Fe$_2$O$_3$ + As$_2$O$_3$ → 2REEFeO$_3$ + As$_2$O$_3$↑ + 3H$_2$O↑; the weight loss was 37% and the first slope started at 190 °C. There is a shift in temperature, comparing the decomposition of pure La(OH)$_3$ with our reaction with La(OH)$_3$, caused by the
mixture of compounds and the presence of As$_2$O$_3$. The weight loss posed a more sophisticated process to explain.

Weight loss cannot be superficial water; all reagents were dried at 120 °C for 24 h prior synthesis. A theoretical analysis of the maximum amount of water that these reactions could lose if the REE reagent was RE(OH)$_3$ was done. The loss weight due to water would be between 12% for reaction with yttrium hydroxide and 14% for reaction with lanthanum hydroxide. Table 1 portrays the theoretical weight loss of the reactions assuming all rare earth reagents were in their hydroxide form. Other factors for the loss weight are the reagents in question: Fe$_2$O$_3$ has a melting point of 1565 °C [6], while REE oxides have a melting point between 2230 °C for Ce$_2$O$_3$ to 2435 °C for Yb$_2$O$_3$ [7]. The melting points of As$_2$O$_3$ polymorphs are 272 – 315 °C for arsenolite [8, 9, 10, and 11], 193 – 314 °C [9, 10, and 12] for claudetite, and the boiling point for both compounds are 460 °C [9]. The weight loss was because the As$_2$O$_3$, which represented between 26% for the reaction with Yb$_2$O$_3$ and 36% for the reaction with La(OH)$_3$, evaporated. The evaporation of arsenic oxide was complete, the weight loss was higher for every reaction that the As$_2$O$_3$ could be accounted for.

The reactions with La$_2$O$_3$, Ce, Gd$_2$O$_3$, Dy, Ho, Er, and Yb had two principal thermal events, while for the reactions with La(OH)$_3$, Pr, Nd, and Sm there are three main thermal events. Comparing the thermal analyses (TG and DSC) of light REE with La$_2$O$_3$ and La(OH)$_3$, indicated that each different com-

Table 1. Maximum theoretical weight loss in the reactions if all the rare earth reagents were in hydroxide form and the experimental weight loss presented in the reactions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theo. weightloss (%)</th>
<th>Exp. weightloss (%)</th>
<th>Compound</th>
<th>Theo. weightloss (%)</th>
<th>Exp. weightloss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(OH)$_3$</td>
<td>14.2</td>
<td>39</td>
<td>Gd(OH)$_3$</td>
<td>13.0</td>
<td>29</td>
</tr>
<tr>
<td>Ce(OH)$_3$</td>
<td>14.1</td>
<td>31</td>
<td>Dy(OH)$_3$</td>
<td>12.6</td>
<td>36</td>
</tr>
<tr>
<td>Pr(OH)$_3$</td>
<td>14.1</td>
<td>31</td>
<td>Ho(OH)$_3$</td>
<td>12.5</td>
<td>29</td>
</tr>
<tr>
<td>Nd(OH)$_3$</td>
<td>13.8</td>
<td>34</td>
<td>Er(OH)$_3$</td>
<td>12.4</td>
<td>28</td>
</tr>
<tr>
<td>Sm(OH)$_3$</td>
<td>13.4</td>
<td>34</td>
<td>Yb(OH)$_3$</td>
<td>12.0</td>
<td>30</td>
</tr>
</tbody>
</table>

Fig. 2. TG and DSC analysis for Gd$_2$O$_3$, Dy, Ho, Er and Yb reactions. TG (dotted line), DSC (solid black), and DSC first derivative (solid gray).
Table 2. Compounds present at different temperatures cooled with two methods, gradually (C) and by quenching (Q), for La$_2$O$_3$, La(OH)$_3$, and Gd$_2$O$_3$ reactions.

<table>
<thead>
<tr>
<th></th>
<th>La$_2$O$_3$</th>
<th>La(OH)$_3$</th>
<th>Gd$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gradual</strong></td>
<td><strong>Quench</strong></td>
<td><strong>Gradual</strong></td>
<td><strong>Quench</strong></td>
</tr>
<tr>
<td>175°C</td>
<td>La$_2$O$_3$, As$_2$O$_3$, α-Fe$_2$O$_3$</td>
<td>La(OH)$_3$, As$_2$O$_3$, α-Fe$_2$O$_3$</td>
<td>Gd$_2$O$_3$, As$_2$O$_3$, α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>308°C</td>
<td>La$_2$O$_3$, α-Fe$_2$O$_3$</td>
<td>La(OH)$_3$, α-Fe$_2$O$_3$</td>
<td>LaOOH</td>
</tr>
<tr>
<td>380°C</td>
<td>La$_2$O$_3$, α-Fe$_2$O$_3$</td>
<td>La(OH)$_3$, α-Fe$_2$O$_3$, LaOOH</td>
<td>Gd$_2$O$_3$, α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>575°C</td>
<td>La$_2$O$_3$, α-Fe$_2$O$_3$, La(OH)$_3$, LaOOH</td>
<td>α-Fe$_2$O$_3$, La(OH)$_3$, LaOOH</td>
<td>Gd$_2$O$_3$, α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α-Fe$_2$O$_3$, La(OH)$_3$, LaOOH</td>
<td>600°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α-Fe$_2$O$_3$, La(OH)$_3$, LaOOH</td>
<td>Gd$_2$O$_3$, α-Fe$_2$O$_3$</td>
</tr>
</tbody>
</table>

Metastable phases in **bold** and stable phases in plain font.

The reaction with La$_2$O$_3$ and Gd$_2$O$_3$ showed, as was presented earlier, the evaporation of arsenic oxide, As$_2$O$_3$, as the principal thermal event. Only three compounds were found in those reactions in the whole range of temperature. In the La(OH)$_3$ reaction, however, six different compounds were found between 25-700 °C. The addition of OH$^-$ radicals, with La(OH)$_3$, changed the reaction because those groups tend to easily react with the surrounding atoms. We deduce that the hydroxyl group was capable of stabilizing the arsenic oxide; while with La$_2$O$_3$ and Gd$_2$O$_3$ the arsenic oxide evaporated, in the reaction with La(OH)$_3$, As$_2$O$_3$ reacted and formed para-

Identification of phases

The reactions with La(OH)$_3$, La$_2$O$_3$ and Gd$_2$O$_3$ were further studied to find the compounds synthesized for each reaction between thermal events. A set of temperatures were selected for each of these three reactions between thermal events. The following temperatures were chosen for La$_2$O$_3$ (175, 308, 380, and 575 °C); for La(OH)$_3$ (200, 310, 440, and 600 °C), and for Gd$_2$O$_3$ (150, 345, 510, 590, 630, and 666 °C) in order to study the phases present in the reactions. The temperatures were selected using the first derivative of the DSC; the first step was identifying the pikes, temperatures at which a thermal event occurs, and the second step was selecting a temperature between two pikes, between thermal events.

About 0.2 g of each reactive reagents were heated at every temperature and then cooled by two methods, gradually cooling (C) and quenching in ice (Q). The cooled samples were studied by XRD, for La$_2$O$_3$ and Gd$_2$O$_3$ reaction, and by HRXRD, for the reaction with La(OH)$_3$, at room temperature. All the phases found by Q and C for the La$_2$O$_3$, La(OH)$_3$, and Gd$_2$O$_3$ reactions are shown in Table 2. Also, the nine HR-XRD diffractograms for La(OH)$_3$ reaction are presented in Fig. 3, the main peaks for each of the six phases found are labeled.
To conclude, the system of implementation put forward here is simple and can be used to predict what compounds can be expected with different reagents in the same family, especially in rare earth reactions, at different temperatures between thermal events. The mixture of compounds and phases can be obtained using the same reaction path, stoichiometry, and heat temperature associated to a TG and DSC analysis. The reactions $\text{REE}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3 \rightarrow 2\text{REEFeO}_3 + \text{As}_2\text{O}_3 \uparrow$ are straightforward when the rare earth reagent is in oxide form, the main event is the evaporation of arsenic oxide. When the reagent is in hydroxide form, $2\text{REE(OH)}_3 + \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3 \rightarrow 2\text{REEFeO}_3 + \text{As}_2\text{O}_3 \uparrow + 3\text{H}_2\text{O} \uparrow$, the reaction is complex. Six products were found in the La(OH)$_3$ reaction, including parasymplesite. It is important to predict what phases are going to be formed in a series of reactions, rare earth reactions in this case, to optimize time and resources.

**Experimental**

The thermal characterization of the reactions, $\text{REE}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3 \rightarrow 2\text{REEFeO}_3 + \text{As}_2\text{O}_3 \uparrow$ and $2\text{REE(OH)}_3 + \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3 \rightarrow 2\text{REEFeO}_3 + \text{As}_2\text{O}_3 \uparrow + 3\text{H}_2\text{O} \uparrow$, $\text{REE} = \text{La, Ce, Nd, Sm, Gd, Dy, Ho, Er, and Yb}$, was done by TG and DSC (Figs. 1 and 2). Reagents, except La$_2$O$_3$, La(OH)$_3$, and Gd$_2$O$_3$, were used without modification to their storage conditions. To ensure the presence of lanthanum oxide and gadolinium oxide, the compounds were dehydrated in a furnace at 1000 °C for 12 h in air and corroborated by XRD. Superficial water was eliminated heating all the reagents at 120 °C for 24 h in air. REE, Fe$_2$O$_3$, and As$_2$O$_3$ poly-crystals (purities above 99.9%) were mixed in an agate mortar and pestle until the mixture became homogeneous. The main product was identified using XRD (not presented in this paper).

The second procedure consisted on the identification of phases formed from 25 °C to 700 °C for the following reactions: a) La(OH)$_3 + \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3$, b) La$_2$O$_3 + \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3$, and c) Gd$_2$O$_3 + \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3$. To identify the changes in phases, the DSC was examined to determine temperatures between thermal events. A mixture of the reagents, about 0.2 g, was heated at these temperatures for 20 minutes in a platinum pan and then cooled down by two methods: i) by quenching (Q) in ice and ii) by gradually cooling (C) in air inside the furnace. These procedures allowed the identification of stable and metastable phases. Cooling by quenching allowed us to identify metastable phases because that phase gets trapped at

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**Fig. 3.** HR-XRD for the La(OH)$_3$ reaction at the selected temperatures using the two cooling methods, Q and C. The letters correspond to H: Fe$_2$O$_3$ (PDF 00-033-0664), L: La(OH)$_3$ (PDF 00-036-1481), A: As$_2$O$_3$ (00-036-1490), D: LaOOH (PDF 00-013-0436), P: Fe$_3$(AsO$_4$)$_2$·8(H$_2$O) (PDF 01-075-1187), and O: La$_2$O$_3$ (PDF 00-005-0602).
that temperature, gradually cooling allows the phase to rearrange and return to a stable phase. The resulting phases were characterized using XRD for the reactions with La₂O₃ and Gd₂O₃ and HR-XRD for the La(OH)₃ reaction, Fig. 3 shows the HR-XRD for the reaction with lanthanum hydroxide. Scheme 1 illustrates the process.

Characterization techniques

TG and DSC measurements were performed in a TA Instruments SDT Q600 at 10 °C min⁻¹ and 60 mL min⁻¹ flow rate of air with sample weight between 3.5 and 3.9 mg in alumina open crucible. The thermal program was 25-700-25 °C.

The samples were characterized at room temperature in air by XRD on a Bruker D-8 diffractometer coupled to a copper X-ray anode tube and a graphite diffracted beam monochromator (Cu-Kα; λ = 1.54 Å). The diffractograms were measured from 10° to 75° (2θ) with a 0.016° (2θ) step scanning.

For the reactions with La(OH)₃, HR-XRD was used. The measurement was done at Argone National Laboratory in Beamline 11-BM. The wavelength used was 0.412239 Å and the scan was measured from 0 to 30 °2θ with a step size of 0.003 °2θ. The photon source is obtained with a bending magnet (BM) with a critical energy of 19.5 keV that delivers around 5x10¹¹ phs/s @ 30 keV, and a monochromator of Si(111).

Detection was done with 12 independent analyzers with a 2 °20 separation. The analyzer consisted on Si(111) crystals and LaCl₃ scintillation detectors.

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