Process Optimization for the Synthesis of Nanocrystalline and Anhydrous Lanthanide Fluoride

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Abstract: In the present investigation an optimized process for the preparation of pure, anhydrous and nanocrystalline lanthanide fluoride is proposed. The powders of lanthanide oxides such as Gd₂O₃ and La₂O₃ were used for the present study. The powders were mixed with NH₄HF₂ in different molar ratio and were heated up to 650°C. Pyrolysis of sample in an atmosphere of high pure argon in three sequential stages leads to the formation of nanocrystalline and anhydrous GdF₃ and LaF₃. The process parameter such as composition, temperature and time were optimized. Progress of reaction at each stage was evaluated and the reaction path leading to the formation of the rare earth fluoride was identified. The principal merit of the process is that it is carried out at atmospheric pressure and is amenable to scale up.

Keywords: Gadolinium fluoride, Synthesis, Thermal analysis, X-ray diffraction.

1.0 Introduction

Lanthanide fluorides exhibit many interesting solid-state properties like low phonon frequencies, high transparencies to UV and offer possibilities of new laser applications in the IR region. It can be used as additives in optical fiber fluoride glasses and luminescent materials excited in the vacuum UV range. They are also used as a source for metal and alloy production. Considering all these it is worthwhile revisiting the synthesis routes of many of these compounds.

Generally, rare earth or lanthanide fluorides are synthesized using their oxides and salts (oxalate, chloride, and carbonate) as raw materials and hydrofluoric acid, HF and NH₄F as common fluorinating agents. Other processing routes include co-precipitation, sol-gel, and emulsion methods all of which are primarily aimed at production of nano crystalline oxides or fluorides. A typical solid state synthesis reaction is conducted at high temperatures under inert gas atmosphere, for synthesis of complex polycrystalline fluorides. This process requires several steps like drying, dehydroxylation and recrystallisation to prepare purified lanthanide fluoride followed by slow heating in a horizontal tubular furnace at 800°C for 12 hours under a gently flowing mixture of N₂ and HF. The fluoride so produced is stable only for few hours. The as-synthesized fluorides are hydrated (LnF₃·1/2H₂O). The water of crystallization cannot normally be removed and it tends to form...
oxyfluorides prior to conversion of fluoride to metal\(^8\). Fluoride powders of high purity have been mainly obtained by heating the reactants under argon filled and sealed ampules of tantalum, gold, platinum, copper or nickel or in a platinum lined inconel furnace\(^7,9\). Prolonged annealing period and use of materials like tantalum, gold, and platinum make the process expensive\(^10,11\).

Gd\(_2\)O\(_3\)-NH\(_4\)HF\(_2\) system has been investigated by several researchers\(^11,12,13\) but the exact process for the synthesis of lanthanide fluoride has not been optimized and still discrepancy subsists with respect to product phase and preparations process. In this paper a successful reaction synthesis procedure for the formation of anhydrous and nanocrystalline GdF\(_3\) and LaF\(_3\) powders, associated chemical reactions and technologically useful process data are reported.

2.0 Experimental

Lanthanide oxide (Ln\(_2\)O\(_3\)) and ammonium bifluoride were mixed in the molar ratios of 1:3, 1:4, 1:5 and 1:6 (designated as Ln-MR3, Ln-MR4, Ln-MR5 and Ln-MR6 respectively, where Ln=Gd, or Nd or La) in an agate mortar and pestle for 10 minutes. Progress of reaction on heating the samples in the range of 50-700°C in argon was evaluated by DTA-TGA. Thermogravimetry studies were carried out mainly to elucidate various stages involved in the synthesis of lanthanide fluoride powders. The mixed powders were compacted in a stainless steel die of 30 mm diameter at a uniaxial pressure of ~2MPa. The green compacts (~50g) were placed in a quartz boat. The reactions were performed in a horizontal tubular furnace in high purity argon at atmospheric pressure in three sequential steps. Argon was purified via an in line gettering system consisting of heated (T ~ 700°C) titanium turnings. Heating was carried out in several controlled steps up to 650°C. At the end of every step the weight change in the sample was measured and recorded. The objective of varying the composition and heat treatment cycles was to evolve an optimum process for the formation of anhydrous and nanocrystalline lanthanide fluoride. The raw materials and the reacted products were characterized by X-ray diffractometer (Philips X’pert), scanning electron microscopy (Vega, Tescan) and particle size analyzer (CILAS -1064L).

3.0 Results and Discussion

3.1 Optimization of Temperature

Fig.1 shows typical DTA-TGA results obtained upon heating the Gd-MR6 powder mixture in the temperature range of 50-700°C under an argon atmosphere. The DTA results indicate that the sample has three endothermic peaks in the temperature ranges 95-125°C, 130–170°C and 240-300°C. TGA of samples shows weight loss in these temperature ranges and is approximately 5wt%, 16wt% and 9wt% respectively. At temperature above 300°C, a small amount of weight change (1-2 wt %) is observed.

![Fig.1. DTA-TGA plot of Gd-MR6 powder mixture in the temperature range of 50-700°C in argon atmosphere.](image)

The Gd-MR6 samples were heated at 110, 150, 250, 300 and 650°C for 1 hour. No reaction was observed for the sample heated at 110°C. Fig.2 shows the XRD pattern of Gd-MR6 after reaction in the temperature range 150-650°C for 1 hour. On heating the mixture at 150°C the reactant phases namely Gd\(_2\)O\(_3\) and NH\(_4\)HF\(_2\) were not observed in the products and it is clear that they have reacted to form NH\(_4\)GdF\(_4\) phase. The product phase becomes more prominent at higher reaction temperatures (250°C). At 300°C NH\(_4\)GdF\(_4\) phase disappears completely and only GdF\(_3\) phase was observed. Further increasing the temperature to 650°C promotes crystallization of GdF\(_3\) as evident from the peaks becoming sharp and intense.
Fig. 2. XRD plot of Gd-MR6 sample after reaction in the temperature range 150-650°C for 1h. The figure illustrates the formation of the intermediate product NH$_4$GdHF$_4$ (43-0832) at 250°C. Also the complete formation of phase pure GdF$_3$ (49-1804) at 650°C is clearly demonstrated.

Based on the above observations (Figs. 1-2) the heating schedules were optimized in three sequential steps. The heating schedules involved heating from room temperature to 150°C, holding for 2h (step 1), followed by a second step which involved raising the temperature to 250°C and holding for 1h (step 2) and a final step of raising the temperature to 650°C and holding for 1h (step 3). Two hours of holding was planned at 150°C in order to have maximum utilization of NH$_4$HF$_2$ for NH$_4$GdF$_4$ conversion.

3.2 Optimization of Composition

Different molar ratios of Gd$_2$O$_3$: NH$_4$HF$_2$ ranging from 1:3 to 1:6 was reacted and the progress of the synthesis reaction at various steps was monitored by XRD of the reacted samples as shown in Fig. 3. When the amount of NH$_4$HF$_2$ in the reactant was less than the stoichiometric ratio as in Gd-MR3, the X-ray diffraction peaks of unreacted Gd$_2$O$_3$ were observed along with NH$_4$GdF$_4$ phase at the end of step 1 (150°C for 2h) of reaction synthesis (Fig. 3.a). At the stoichiometric ratio of the reactants as in Gd-MR4, Gd$_2$O$_3$ was absent and only NH$_4$GdF$_4$ phase was observed. When the sample contains a large excess of NH$_4$HF$_2$ as in Gd-MR5 & Gd-MR6, the X-ray diffraction peaks of NH$_4$HF$_2$ were also observed along those of NH$_4$GdF$_4$.
After step 2 (250°C for 1h) of reaction, the XRD results (Fig.3.b) for Gd-MR3 and Gd-MR4 compositions are similar to results obtained after step 1 of reaction (Fig.3.a). However, for the Gd-MR5 and Gd-MR6 compositions NH₄HF₂ phase was absent. This could be ascribed to the decomposive sublimation of NH₄HF₂ at higher temperature ¹¹. At the completion of step 3 (650°C for 1h) of reaction, X-ray diffraction peaks corresponding to gadolinium fluoride alone were observed at all proportions of mixing (Fig.3.c). The deposits on the side walls of the reaction tube of the furnace were collected and examined by XRD (See Fig.3(d)). The X-ray diffraction pattern showed predominantly the peaks of NH₄F and NH₄HF₂, confirming the formation of NH₄F during the reaction. Further it indicates that the weight loss recorded during the reaction can be attributed to the sublimation of NH₄F and NH₄HF₂. The as-synthesized GdF₃ (prepared from Gd-MR6 composition) was investigated by DTA-TGA in the temperature range of 50-700°C in argon. Neither reaction peak in DTA plot nor change in weight in TGA plot was observed which signify that GdF₃ is free of the reactants or other volatile products. After a month of storage no peak was observed in DTA plot and TG plot shows a weight loss of ~0.01% which demonstrates the stability of gadolinium fluoride synthesized (Fig. 4). This confirms that the chosen synthesis steps have resulted in synthesis of stable GdF₃.

Fig.4. DTA-TGA plot of synthesized and stored GdF₃ in the temperature range of 50-700°C in argon. The dashed line is the background of DTA.

4.3 Purity and Morphology

Figs.5 (a-b) shows the SEM microphotographs of as synthesized GdF₃ (prepared from Gd-MR6 composition). The GdF₃ appears as porous agglomerates of small particles and each particle is less than 0.2 micron or 200 nm in size (Fig.5.a). The EDS analysis of as synthesized gadolinium fluoride shows the presence of gadolinium and fluorine in the stoichiometric ratio (Fig.5.b). There are no peaks corresponding to oxygen. It indicates clearly that the process has resulted in the formation of anhydrous gadolinium fluoride of purity ≥99.5%. The particle size has also been obtained using a laser scattering method, which showed a bimodal distribution of particles with the two mean values at 0.2 and 2 microns respectively. The crystallite size of the samples were calculated by measuring the full width at half maximum of the prominent XRD peaks of GdF₃ samples (Fig.2, 300°C) using the well known Scherrer formula and is ~15 nm. This indicates that the particles are poly-crystalline in nature and consists of nano-sized crystallites.

Fig.5.(a-b) SEM microphotographs showing a) fine particulate and  b) EDS analysis, of GdF₃ synthesized from Gd-MR6.
3.3 Other Lanthanide Fluorides

The optimized heating schedules for the synthesis of Gadolinium fluoride were detailed in section 3.1. Other lanthanide fluoride such as NdF$_3$ and LaF$_3$ were also prepared from Ln-MR6 composition. Fig.6 shows LaF$_3$ synthesized from La$_2$O$_3$ and NH$_4$HF$_2$ (La-MR6) powder mixture by heating in three sequential steps as mentioned in section 3.1. For proper crystallization of rare earth fluoride phase and removal of excess salts, temperature as high 500 to 650°C are preferable as in case of GdF$_3$ (Fig.2).

![XRD patterns LaF$_3$ synthesized from La-MR6 powder mixture after heating in three sequential steps as detailed in section 3.1](image)

4.0 Discussion

The objective of the present investigation was to devise a procedure to prepare anhydrous and nanocrystalline lanthanide fluoride from lanthanide oxide and NH$_4$HF$_2$ powder mixture. When the Ln-MR6 powder mixture was heated progressively from room temperature to 650°C, anhydrous LnF$_3$ (Ln=Gd, Nd or La) could be successfully prepared (Figs.2-3 and 6). No reaction was observed on heating Ln-MR6 sample at 110°C for 1 hour. From this it is clear that weight change in the range of 95-125°C (1st endothermic region in Fig.1) is consistent with the loss of moisture present in the samples. The weight loss at this stage was ~5%.

The XRD results of Ln-MR6 powder mixture reacted at 150°C for 1h shows the formation of NH$_4$GdF$_4$ phase (Figs.2 & 3. (a)) and hence the following reaction scheme is proposed in step 1.

$$\text{Ln}_2\text{O}_3 + 4\text{NH}_4\text{HF}_2 \rightarrow 2\text{NH}_4\text{LnF}_4 + 2\text{NH}_3 + 3\text{H}_2\text{O} \quad \text{... (1)}$$

Reaction (1) occurs in the range of 130-170°C (2nd endothermic region in Fig.1.) The weight change of ~16% observed in the DTA-TGA experiments is attributed mainly to the loss of NH$_3$ and H$_2$O, reaction (1). A holding time of 2 hours was provided at 150°C to achieve maximum NH$_4$HF$_2$ utilization as it volatilizes rapidly beyond 170°C. The lanthanide oxide used for present study belongs mostly to group-A (Gd$_2$O$_3$, Nd$_2$O$_3$ and Eu$_2$O$_3$) of lanthanide series and so it forms NH$_4$LaF$_4$ compounds in step 2. La$_2$O$_3$ belongs to group-B and phases such as (NH$_4$)$_3$LnF$_9$ or (NH$_4$)$_3$LnF$_7$ could be observed in step 2. But in this case it is not observed because of prolonged holding of 2 hours. These compounds are unstable and further heating leads to formation of NH$_4$LaF$_4$ phase.

Reaction (1) was found to be complete at 250°C (Fig. 3.(b)) at the end of step2. The XRD results of Gd-MR6 powder mixture reacted at 300°C for 1 hour shows the formation of GdF$_3$ (Fig.2). This indicates that the third endothermic region present in the range 250-300°C corresponds to reaction (2) (Figs. 2 & 3) in step 3.

$$\text{NH}_4\text{LnF}_4 \rightarrow \text{LnF}_3 + \text{NH}_4\text{F} \quad \text{... (2)}$$

At the end of step 1, the theoretical weight loss is calculated as the loss of NH$_3$ and H$_2$O as per reaction (1). The cumulative weight change at the end of step 2 is due to the completion of reaction (1) plus the decomposive sublimation of excess NH$_4$HF$_2$. The theoretical weight loss at the end of step 3 is the sum of the loss at the end of the step 2 and that obtained by the loss of NH$_4$F shown in reaction (3). It is gratifying to note the close agreement between the theoretical weight loss and experimental weight loss at every step of reaction.
The formation of NH$_4$F in reaction (2) is confirmed by XRD of the product phases (Fig. 3 (d)). It is to be noted that the NH$_4$HF$_2$ and NH$_4$F further decomposes at higher temperature as follows

$$\text{NH}_4\text{HF}_2 \rightarrow \text{NH}_3 + 2\text{HF}$$  \hspace{1cm} (3)
$$[\text{NH}_4\text{F}] \rightarrow \text{NH}_3 + \text{HF}$$  \hspace{1cm} (4)

In our experiments we note that the GdF$_3$ formation is complete even for sub-stoichiometric composition, Gd-MR3. For this composition, at the end of step 2, Gd$_2$O$_3$ was observed along with NH$_4$GdF$_4$ (Fig. 3(b)). The product NH$_4$F, reaction (2) and HF, reactions (4) will enable the fluoridisation of residual Gd$_2$O$_3$. Thus the complete fluoridisation for Ln-MR3 composition can be reconciled by writing the following reactions.

$$\text{Gd}_2\text{O}_3 + 3\text{NH}_4\text{HF}_2 \rightarrow 1.5\text{NH}_4\text{LnF}_4 + 1.5\text{NH}_3 + 2.25\text{H}_2\text{O} + 0.25 \text{Ln}_2\text{O}_3$$  \hspace{1cm} (5)
$$1.5\text{NH}_4\text{LnF}_4 \rightarrow 1.5\text{LnF}_3 + 1.5\text{NH}_3$$  \hspace{1cm} (6)
$$0.25\text{Ln}_2\text{O}_3 + 1.5\text{NH}_4\text{F} \rightarrow 0.25\text{LnF}_3 + 1.5\text{NH}_3 + 0.75\text{H}_2\text{O}$$  \hspace{1cm} (7)

It is proposed that in step 3, the unreacted lanthanide oxide present in reaction (5) combines with NH$_4$F produced by the dissociation reaction 6, leading to the formation of LnF$_3$, reaction (7). That is why GdF$_3$ formation was complete even in Gd-MR3 sample which was deficient in ammonium biflouride (Fig. 4. (c)). Using excess amounts of NH$_4$HF$_2$ (Ln-MR5 and Ln-MR6) in the reactants help in the formation of phase pure lanthanum fluoride without residual oxygen. Higher temperature (650°C) chosen for step 3 facilitates GdF$_3$, NdF$_3$, and LaF$_3$ conversion and removal of excess salts. Based on these observations a process flow chart is proposed for LnF$_3$ synthesis (Fig. 7). LnF$_3$ prepared by the method is stable in normal storage conditions, as can be seen by the fact that the X-ray diffraction of the product remains unchanged even after a month of preparation.

![Fig.7. The process flow chart for the reaction synthesis of lanthanide fluoride from Ln-MR6 composition, based on the present work.](image)

### 5.0 Conclusions

A direct, low temperature, solid state reaction process is described for the preparation of high purity lanthanide fluoride. The chemical reactions in various stages of the reactions are reconciled with the thermal analyses of the reactants and X-ray diffraction characterisation of the products. The temperatures and the proportion of the reactants needed for complete conversion to lanthanide fluoride have been optimized. A process flow chart has been proposed for the preparation of lanthanide fluoride. The process is rapid, energy efficient and has the potential for scale up. Pure, anhydrous lanthanide fluoride of average particle size in the range 0.2-2 micron, and which is stable during storage is produced by the process.

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