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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 Gd_2O_3 and La_2O_3 were used for the present study. The powders were mixed with NH_4HF_2 in different molar ratio and were heated up to $650^\circ C$. Pyrolysis of sample in an atmosphere of high pure argon in three sequential stages leads to the formation of nanocrystalline and anhydrous GdF_3 and LaF_3 . 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 region¹. 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 NH_4F as common fluorinating agents². Other processing routes include co-precipitation³, sol-gel⁴, and emulsion methods⁵ 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 fluorides⁶. This process requires several steps like drying, dehydration and recrystallisation to prepare purified lanthanide fluoride followed by slow heating in a horizontal tubular furnace at $800^\circ C$ for 12 hours under a gently flowing mixture of N_2 and HF. The fluoride so produced is stable only for few hours⁷. The as-synthesized fluorides are hydrated ($LnF_3 \cdot 1/2H_2O$). The water of crystallization cannot normally be removed and it tends to form

oxyfluorides prior to conversion of fluoride to metal⁸. Fluoride powders of high purity have been mainly obtained by heating the reactants under argon filled and sealed ampoules 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}.

Gd₂O₃-NH₄HF₂ 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 GdF₃ and LaF₃ powders, associated chemical reactions and technologically useful process data are reported.

2.0 Experimental

Lanthanide oxide (Ln₂O₃) 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 sample 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.

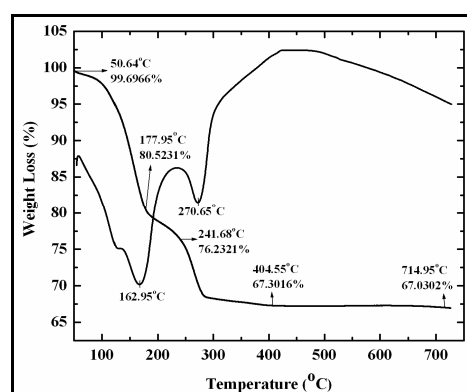


Fig.1. DTA-TGA plot of Gd-MR6 powder mixture in the temperature range of 50-700°C in argon atmosphere.

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 Gd₂O₃ and NH₄HF₂ were not observed in the products and it is clear that they have reacted to form NH₄GdF₄ phase. The product phase becomes more prominent at higher reaction temperatures (250°C). At 300°C NH₄GdF₄ phase disappears completely and only GdF₃ phase was observed. Further increasing the temperature to 650°C promotes crystallization of GdF₃ as evident from the peaks becoming sharp and intense.

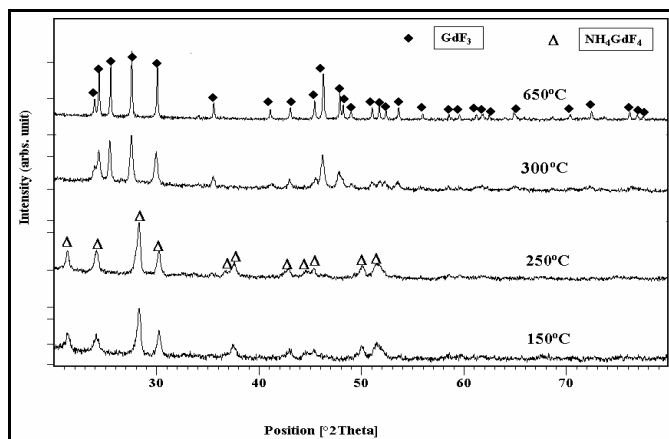


Fig.2. XRD plot of Gd-MR6 sample after reaction in the temperature range 150-650°C for 1h. The figure illustrates the formation of the intermediate product NH_4GdHF_4 (43-0832) at 250°C. Also the complete formation of phase pure GdF_3 (49-1804) at 650°C is clearly demonstrated.

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 a holding for 1h (step 3). Two hours of holding was planned at 150°C in order to have maximum utilization of NH_4HF_2 for NH_4GdF_4 conversion.

3.2 Optimization of Composition

Different molar ratios of Gd_2O_3 : NH_4HF_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_4HF_2 in the reactant was less than the stoichiometric ratio as in Gd-MR3, the X-ray diffraction peaks of unreacted Gd_2O_3 were observed along with NH_4GdF_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_2O_3 was absent and only NH_4GdF_4 phase was observed. When the sample contains a large excess of NH_4HF_2 as in Gd-MR5 & Gd-MR6, the X-ray diffraction peaks of NH_4HF_2 were also observed along those of NH_4GdF_4 .

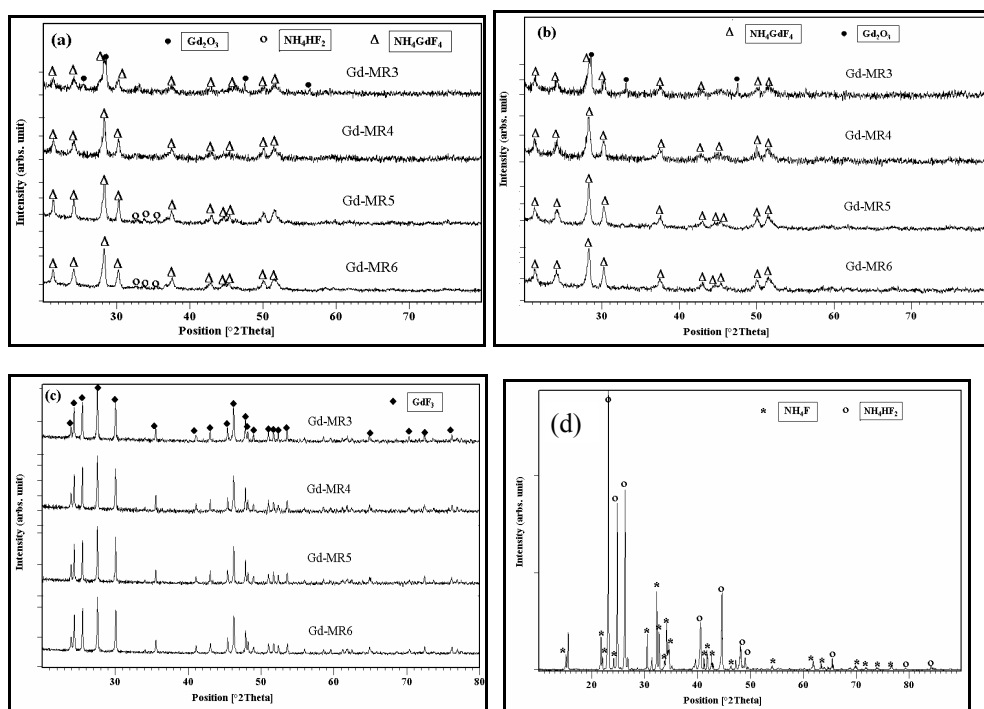


Fig.3. XRD patterns of Gd_2O_3 and NH_4HF_2 (75-0252) powder mixture in different molar ratios after reaction at (a) 150°C for 2h (step 1) (b) 250°C for 1h (step 2) (c) 650°C for 1h (step 3) and (d) XRD pattern of deposits found on the sidewalls of the reaction tube.

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 NH_4HF_2 phase was absent. This could be ascribed to the decomposive sublimation of NH_4HF_2 at higher temperature¹¹. 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 NH_4F and NH_4HF_2 , confirming the formation of NH_4F during the reaction. Further it indicates that the weight loss recorded during the reaction can be attributed to the sublimation of NH_4F and NH_4HF_2 . The as-synthesized GdF_3 (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 GdF_3 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 GdF_3 .

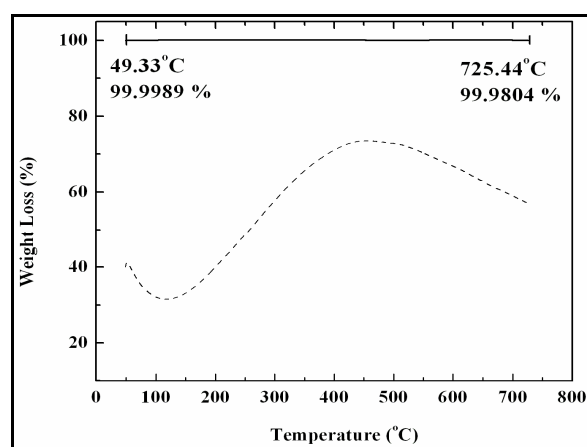


Fig.4. DTA-TGA plot of synthesized and stored GdF_3 in the temperature range of 50-700°C in argon. The dashed line is the background of DTA.

4.3 Purity and Morphology

Figs.5 (a-b) shows the SEM microphotographs of as synthesized GdF_3 (prepared from Gd-MR6 composition). The GdF_3 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 $\geq 99.5\%$. 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 GdF_3 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.

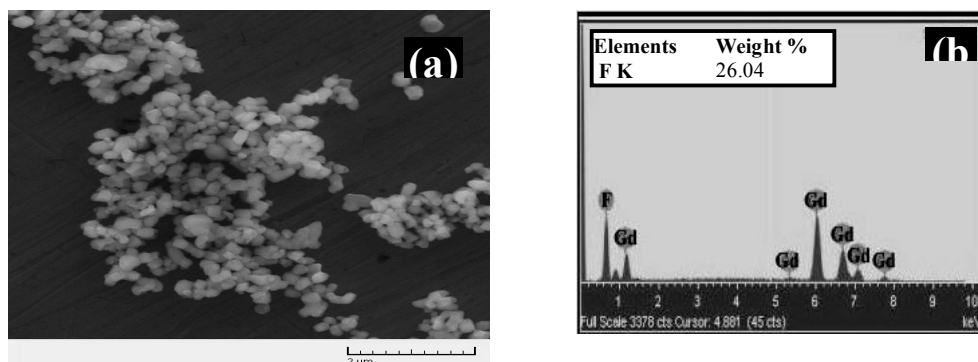


Fig.5.(a-b) SEM microphotographs showing a) fine particulate and b) EDS analysis, of GdF_3 synthesized from Gd-MR6.

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_2O_3 and NH_4HF_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).

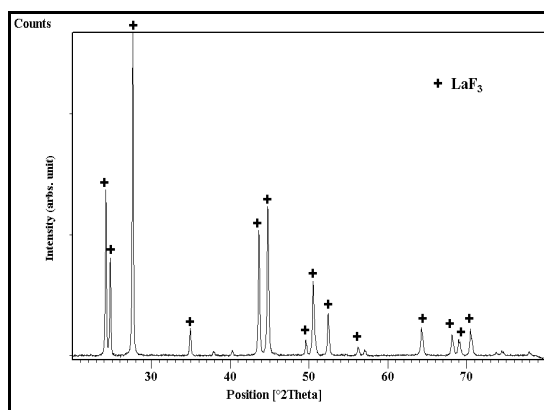
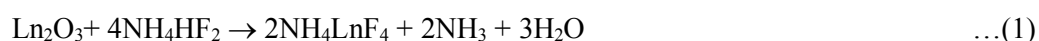


Fig.6. XRD patterns LaF_3 synthesized from La-MR6 powder mixture after heating in three sequential steps as detailed in section 3.1

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_4HF_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_4GdF_4 phase (Figs.2 & 3. (a)) and hence the following reaction scheme is proposed in step 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_2O , reaction (1). A holding time of 2 hours was provided at 150°C to achieve maximum NH_4HF_2 utilization as it volatilizes rapidly beyond 170°C¹¹. The lanthanide oxide used for present study belongs mostly to group-A (Gd_2O_3 , Nd_2O_3 and Eu_2O_3) of lanthanide series and so it forms NH_4LaF_4 compounds in step 2. La_2O_3 belongs to group-B and phases such as $(\text{NH}_4)_3\text{Ln}_2\text{F}_9$ or $(\text{NH}_4)_3\text{Ln}_2\text{F}_7$ 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_4LaF_4 phase¹².

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.

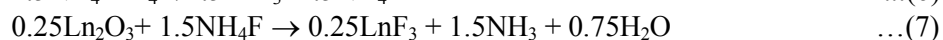
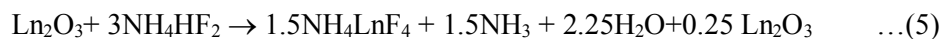


At the end of step 1, the theoretical weight loss is calculated as the loss of NH_3 and H_2O as per reaction (1). The cumulative weight change at the end of step 2 is due to the completion of reaction (1) plus the decomposive sublimation of excess NH_4HF_2 . The theoretical weight loss at the end of step 3 is the sum of the loss at the end of the step 2 and that obtained by the loss of NH_4F 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_4F in reaction (2) is confirmed by XRD of the product phases (Fig.3 (d)). It is to be noted that the NH_4HF_2 and NH_4F further decomposes¹¹ at higher temperature as follows



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_2O_3 was observed along with NH_4GdF_4 (Fig. 3(b)). The product NH_4F , reaction (2) and HF, reactions (4) will enable the fluoridisation of residual Gd_2O_3 . Thus the complete fluoridisation for Ln-MR3 composition can be reconciled by writing the following reactions.



It is proposed that in step 3, the unreacted lanthanide oxide present in reaction (5) combines with NH_4F 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 bifluoride (Fig.4. (c)). Using excess amounts of NH_4HF_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.

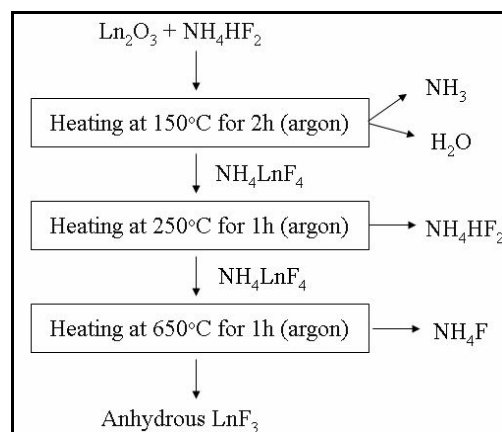


Fig.7. The process flow chart for the reaction synthesis of lanthanide fluoride from Ln-MR6 composition, based on the present work.

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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