

Synthesis of Phase Pure Gadolinium Gallium Garnet (GGG) Nanopowders from Ammonium Oxalate Co-precipitation

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Abstract - A mixed solution of Gd and Ga chlorides was used to make phase pure gadolinium gallium garnet (Gd₃Ga₅O₁₂, GGG) powders. The researchers looked at two alternative mole ratios of Gd⁺³ to Ga⁺³, one with a stoichiometric mole ratio of gadolinium and gallium is 3:5 (Gd/ Ga) and the other with a 9% surplus by weight of Ga₂O₃. For stoichiometric ratio impure phases were formed from 900-1200°C. For Ga⁺³ ion rich ratio phase pure GGG was formed at 1200°C for 2 hours which observed through characterization. FTIR & XRD confirms the formation of GGG nano powder. Particles size range and its morphology were observed by SEM.

Keywords: Phase pure gadolinium gallium garnet (GGG), nano powder, FTIR, XRD, SEM.

INTRODUCTION

Gallium is a metal that belongs to Group IIIA of the Periodic Table. It was invented in 1875 by French chemist Paul-Émile Lecoq de Boisbaudran [1]. In solid and liquid form, this fine silvery-blue metal has an atomic weight of 69.723, a rigidity of 1.5 mhos, and relative density of 5.904 and 6.905 g/cm³. When you hold a solid lump of gallium in your hand, it liquefies. It has an extremely wide liquid range due to its low melting temperature of 302.98 K and heating value of 2676 K. The crystal structure of solid gallium is orthorhombic, and it exhibits a conchoidal fracture like glass. Gallium may be found in six different isotopes, although only two of them, ⁶⁹Ga (60.4%) and ⁷¹Ga (39.6%), are stable and other are

unstable. Gallium may be converted into a variety of compounds, including sulphides, bromides, hydrides, chlorides, nitrides, iodides, selenides, oxides, and tellurides. Gallium has valency of +1 and +3 oxidation states. For the low temperatures, these element interacts aggressively with halogens, despite its water stability. The element dissolves readily in di water or concentrated sodium hydroxide in an aqueous solution. It also reacts with strong oxidants. The element may readily form alloys (e.g., eutectic alloys) with most metals, in addition to being a component in low-melting alloys. Gallium has aroused people's interest over the past two decades. Gallium has semiconducting properties when combined with group 15 elements [2]. In the green separation method, gallium (III) ions such as gallium arsenide (GaAs) and gallium nitride (GaN) are separated from acidic aqueous solutions using supercritical carbon dioxide extraction [3-4]. They're significant compounds in compact disc laser diodes, microwave transceivers, DVDs and other electronic equipment [5-6]. Recovery of gallium from gasification fly ash [7]. During the last decade, the supply and demand for gallium-bearing goods has steadily grown. As a result, finding an efficient gallium extraction process is critical.

Because of its intriguing optical and mechanical characteristics, gadolinium gallium garnet (GGG), a complex oxide belonging to the cubic system with a garnet structure, has gotten a lot of attention [8]. Because of the breakdown and evaporation of Ga₂O₃, good grade GGG proved difficult to generate using the Czochralski technique [9]. Because a

simple and cost-effective technique for producing high-quality GGG compounds is desired, new methods are coming in lime light for example the co-precipitation method [10-13], the sol-gel process [14-19], combustion synthesis for solutions and others [20] have been developed.

The sol-gel technique may reduce the sintering temperature, but it necessitates the use of expensive metal alkoxides as raw materials. Furthermore, during the drying process, the gel-like precursor is prone to substantial agglomeration, leading in powders with limited sinter activity. When compared to the techniques discussed above, the co-precipitation approach offers the advantages of a low treatment temperature and a rapid sintering time. On the other hand, no grinding or milling operation is required. Because such mechanical treatments might cause surface flaws and impurities, the co-precipitation technique was created to create real polycrystalline materials with excellent uniformity and purity.

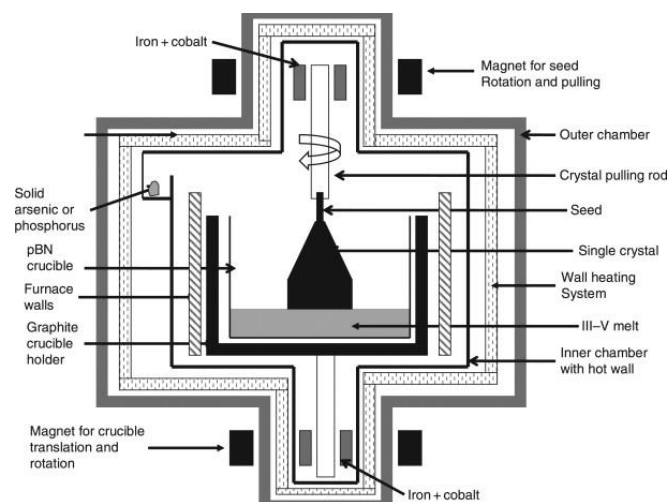


Figure 1: Sol Gel Process

Why was 9 % excess taken? GGG nanocrystalline powders with a Ga⁺³ ion rich ratio and a 9 % excess of Ga₂O₃ prepared by the co-precipitation process at three different temperatures, i.e., 900°C, 1100°C, 1200°C for 2 hours respectively, with ammonium oxalate as precipitant, and GGG nanocrystalline powders with a stoichiometric mole of gadolinium and gallium ratio 3:5 (Gd/ Ga) has been prepared by co-precipitation at three temperatures i.e. 900°C, 1000°C, 1100°C for 2 hr. with ammonium oxalate as the precipitant.

SOLVENT EXTRACTION

Gallium was originally obtained from a chloride solvent, and gallium extraction from very acidic chloride solutions has long been recognised [21-22]. The exception of germanium and iron (Fe (III)), gallium may be loaded preferentially from 6 M HCl into diethyl ether over practically any plausible concomitant element. The solvent extraction of gallium was initially used in commercial operations during the extraction of germanium and gallium from flue ash in the 1940s [23-24]. For a preliminary objection of gallium from aluminium, Bayer liquid was treated by fractional precipitation, similar to the above-reported acid technique (lime test), and chemical reduction for gallium extraction from Bayer liquor was first developed in 1967. (Bhat and Sundararajan, 1967). The precipitate was hydrolyzed using 3 M free acid aqua regia,

which contained roughly 0.6 percent Ga₂O₃. Gallium was extracted from this solvent utilizing 20% of TBP (tributyl phosphate) and afterwards restored by water stripping, resulting in a massive gallium recovery of 90%. This process still uses the chloride system for gallium solvent extraction; however, it is employed for concentration instead of direct gallium retrieval from Bayer liquor. It has the same problems as the lime technique, such as destroying the alumina liquid.

EXPERIMENT AND DISCUSSION

The Czochralski (CZ) method is a crystal development technique that begins with a tiny seed crystal inserted into a melt in a crucible and pulled upwards to form a single crystal. The technique is named after Jan Czochralski, a Polish physicist who invented it in 1916.

The Czochralski technique (Cz) is the most widely used method for producing bulk single crystals of electrical and optical materials (Figure 2). At the commencement of the procedure, the feed material is put in a cylindrically formed crucible and heated utilizing resistance or radio-frequency heaters. After the input material has completely melted, a seed crystal with a diameter of just few millimetres is dipped from the top into the free melt surface, and a little portion of the dipped seed is melted. A melt meniscus occurs when the seed and the melt come into contact. The seed is then progressively withdrawn from the melt (usually while spinning), and the melt crystallises at the interaction, resulting in the formation of a new crystal section. The form of crystal, particularly its diameter, is precisely regulated during the subsequent development phase by precisely controlling the heating capacity, the tugging rate, and the crystal's rotation rate.

SYNTHESIS

The basic materials were Gd₂O₃ (99.99 %) and Ga₂O₃ (99.99 %) powders. To begin, high-purity Gd₂O₃ and Ga₂O₃ were precisely weighed in a 3:5 stoichiometric mole ratio. Similarly, the non-stoichiometric mole ratio of 3:5. It was used to correctly weigh the high purity raw materials (9% excess of Ga₂O₃). Then 30 gramme of strong HCl was used to dissolve them. After cooling the metal ion solution, it was guaranteed that no precipitation would occur.

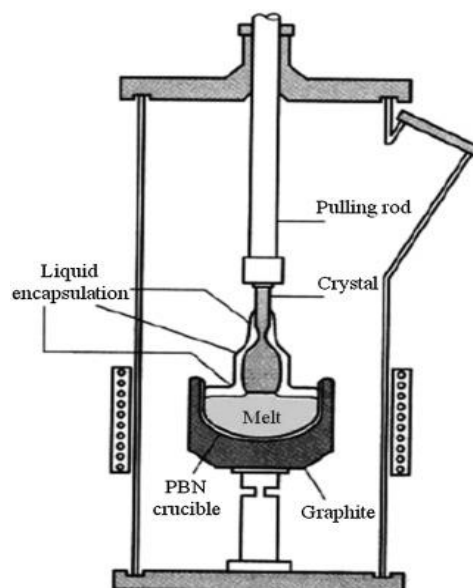


Figure 2

By dissolving 23.1 gm of Oxalic acid in 250 ml of deionized water and adding 62.5 ml of NH_4OH solution, a separate solution of Ammonium Oxalate (Precipitating Agent) was created (equal parts of NH_4OH and deionized water).

The metal ion solution was dripped into the Ammonium oxalate solution (15-20 drops/min.) while simultaneously adding NH_4OH (ACS, 28.0- 30.0 percent NH_3) and agitating the Ammonium oxalate solution on the magnetic stirrer to keep the pH between 8.33 and 8.35. When metal ion solution was added, white precipitates appeared very quickly. After the metal ion solution was added, stirring was maintained for another 10 minutes. A vacuum pump was used to filter the solution. 500 mL ethanol and acetone were used to wash the precipitates. The precipitates were then maintained for 24 hours in desiccators.

For 2 hours, the precursors were calcined at 900°C , 1100°C , and 1200°C .

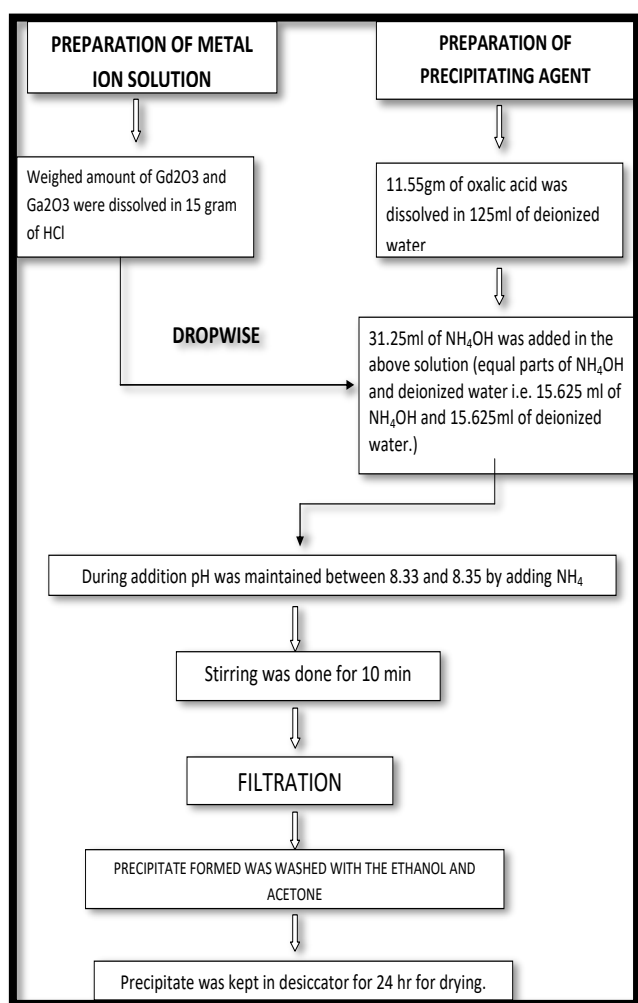


Figure 3 : shows a schematic representation of the stages involved in the Co-precipitation production of GGG nano powders utilizing ammonium oxalate as a precipitating agent.

CHARACTERIZATION

FTIR Analysis:

FTIR Spectra: KBR matrix was used to record FTIR Spectra using an FTIR Spectrometer (Bruker model Vector 22). For phase purity characterization, PANalyticalX'Pert Pro was

used with a 2θ value of 150 to 750. The diffuse reflectance of GGG nano powders was investigated using an ultra - violet infrared (UV-VIS-NIR) spectrophotometer (Varian Cary 5000). A Zeiss EVO18® LaB6 filament scanning electron microscopy (SEM) was used to analyses the gold-coated surface of ceramic. The excitation spectra of specimens were acquired using an Action SP2300 monochromator with an InGaAs detector and an 808 nm 3W diode laser as the excitation source. The spectral measurements (200 nm spectrum range) were made at ambient temperature with a precision of 0.1 nm in the 900 nm^{-1} range [fig 4 and 5]. In the Ftir analysis of microwave combusted precursors, the CO_3^{2-} produced during the operation triggered weak absorption peaks between 850 cm^{-1} and 900 cm^{-1} (fig 4).The vibration of the C-O and C-C bonds caused absorption peaks at 1350 cm^{-1} and 1400 cm^{-1} . Broad absorption bands observed between 400 cm^{-1} and 800 cm^{-1} , indicating that GGG formation had not occurred. The microwave precursor's FTIR spectra (fig 5) displayed GGG peaks at 671 cm^{-1} , 615 cm^{-1} , and 578 cm^{-1} after being calcined at 900°C for 2 hours.

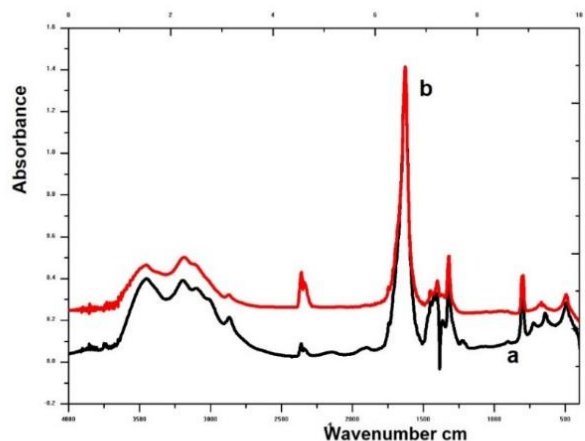


Figure 4: FTIR of Precursors.

a= GGG-CP-AO-PRE (Stoichiometric), b=GGG-CP-AO-PRE (9% Excess of Ga_2O_3)

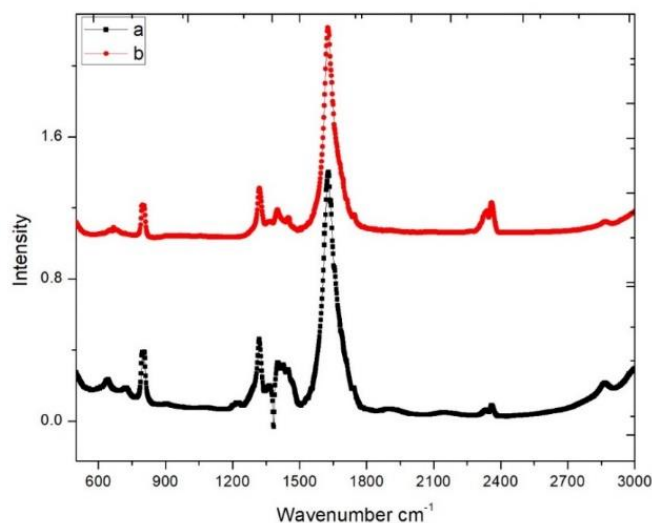


Figure 5: FTIR of calcined powders (of stoichiometric ratio)
a= GGG-CP-AO- 900°C , b=GGG-CP-AO- 1100°C , c= GGG-CP-AO- 1200°C

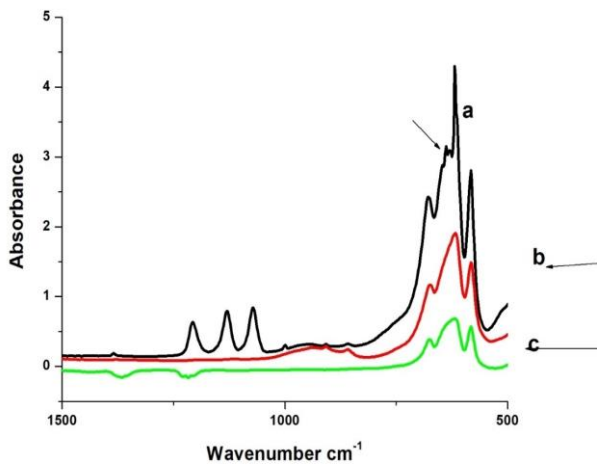


Figure 6: FTIR of calcined powders (with 9% excess of Ga_2O_3)

a= GGG-CP-AO-900^oC, b= GGG-CP-AO-1100^oC, c= GGG-CP-AO-1200^oC

XRD Analysis :

Impure phases are generated during 900-1200 °C calcination, as shown by XRD of GGG employing a 9 % excess of GaO. Figure 8 shows the XRD spectra of the as-precipitated precursor and powders calcination temperature at different conditions. The diffraction patterns confirm the following phase evolution. In the diffraction pattern for the as-precipitated precursor, only $[(NH_4)_2C_2O_4]$ (PDF No. 33-0060) appears. When heated to 900°C, the powders are amorphous and contain a small amount of cubic Gd_2O_3 . After calcination at 1100°C, the particles almost completely crystallize into cubic Gd_2O_3 . There was no apparent peak associated with the Ga species.

When, we increase the temperature to 1200 °C, a new diffraction peaks appears, this might be explained by the cubic $Gd_3Ga_5O_{12}$ (GGG, PDF No. 13-0493). Another intermediate phase is present, most probably hexagonal Gd_2O_3 (PDF No. 24-0430). The cubic GGG produced from our diffraction data has a lattice parameter that is around 0.5 % bigger than the normal position. We believe it has something to do with probable composition shifts during crystallite formation, although the specific explanation is unknown. This pattern also shows strong diffraction peak widening due to size effect and lattice distortion. The intensity of the cubic GGG diffraction peaks rises as the calcination temperature rises, whereas the Gd_2O_3 peaks decrease considerably. When the temperature approaches 1200 °C, GGG becomes the only phases in the XRD pattern, and the diffraction patterns become compact and strong. The results reveal that pure-phase GGG powders may be made from a stoichiometric composition of Gd_2O_3/Ga_2O_3 with a mole ratio of gadolinium and gallium ratio 3:5 using AHC as the precipitant at a temperature of 1200 °C, which is much lower than the solid-state approach [25]. There is no visible reduction of Ga species during this time.

As contrast to ammonia water, using AHC as the precipitating factor allows for the production of GGG from stoichiometric raw components [26].

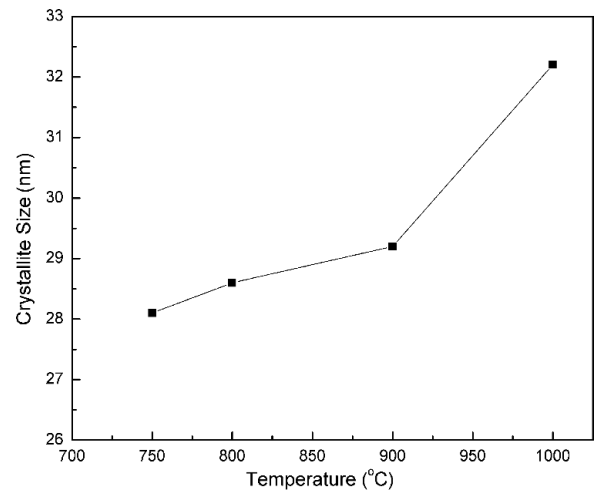


Figure 7: Temperature dependency on crystalline size

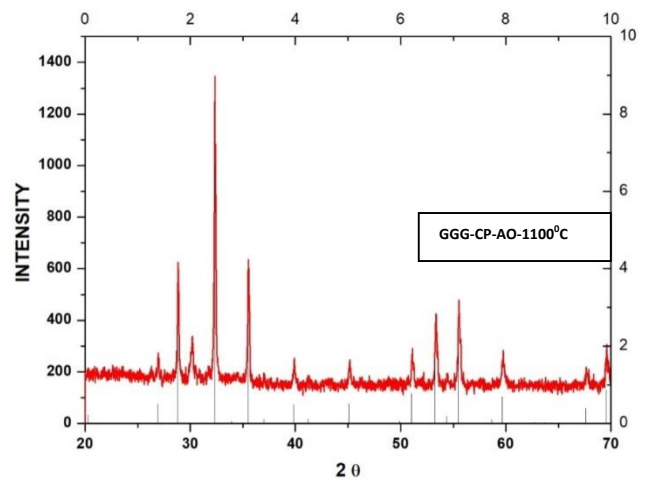


Figure 8: FTIR of GGG-CP-AO with 9% excess of Ga_2O_3

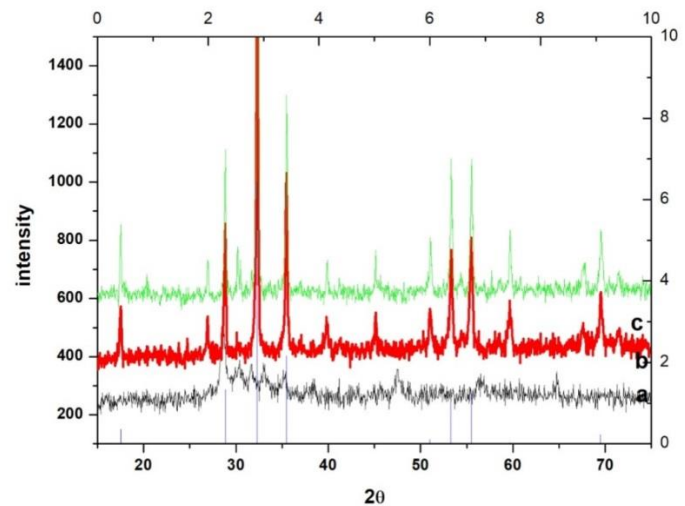


Figure 9: a= GGG-CP-AO-900^oC, b= GGG-CP-AO-1100^oC, c= GGG-CP-AO-1200^oC (Stoichiometric ratios)

SEM Analysis :

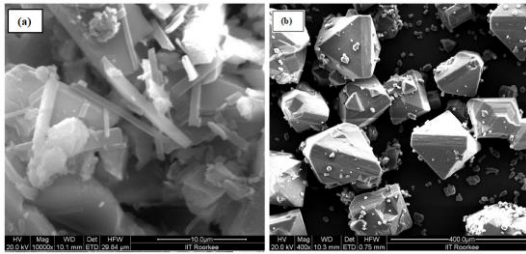


Figure 10 : a= GGG-CP-AO-1100°C, b= GGG-CP-AO-1200°C (with 9% excess of Ga₂O₃)

In general, the morphology of pure and doped GGG samples was found to be fairly comparable, indicating that the presence of the dopant had no discernible effect on the morphology of the samples. Two example SEM pictures at different magnifications are presented in Fig9. The material displays a characteristic porous, sponge-like shape at this sub-micron scale, as seen in comparable oxides produced via propellant synthesis.

CONCLUSION

Pure-phase GGG powders were successfully generated from a mixture solution of stoichiometric mole ratio (3:5) gadolinium and gallium (Gd/Ga) chloride using ammonium oxalate as a co-precipitant. The Gd₃Ga₅O₁₂ and Gd₂O₃ intermediate phases may be converted to pure GGG at temperatures ranging from 900 to 1200°C. The resulting GGG powders were loosely agglomerated exhibiting good dispersity and sinterability[27].

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