

Structural and thermal investigation of gadolinium gallium mixed oxides obtained by coprecipitation: Observation of a new metastable phase

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Abstract

Polycrystalline gadolinium gallium mixed oxides were prepared by coprecipitation and annealing at various temperatures below 1000 °C. The oxide materials appear to be X-ray amorphous after a heat treatment at 500 °C for 30 h, but after 30 h at 800 and 900 °C a major, unreported, hexagonal phase, isostructural with $TAlO_3$ compounds (where $T = Y, Eu, Gd, Tb, Dy, Ho, Er$) appears to crystallize. On the other hand, a highly energetic mechanical treatment of the amorphous powder previously annealed at 500 °C changes considerably the shape and position of exothermal events occurring in the range from 700 up to 900 °C. Subsequent annealing at 900 °C of the mechanically treated powder gives rise to the complete formation of the $Gd_3Ga_5O_{12}$ garnet structure at the expense of the hexagonal phase and of the minor $Gd_4Ga_2O_9$ oxide phase. However, a 7.0 wt% contamination is found to be due to tetragonal zirconia coming from vials and balls colliding media. The garnet phase may have strong deviations from the nominal stoichiometry of the garnet, as suggested by the refined lattice parameter obtained from the powder diffraction patterns and by the remarkable absence of intensity relative to the (220) Bragg peak position.

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1. Introduction

Materials belonging to the Gd_2O_3 – Ga_2O_3 system find important technological applications. In particular, single crystals of gadolinium gallium garnet ($Gd_3Ga_5O_{12}$, GGG), mainly grown by the Czochralski technique, have been employed as substrates for magnetic bubbles [1–3] and, when doped with trivalent lanthanide ions (Ln^{3+}), are important laser crystals [4,5]. Moreover, it has been recently shown that nanocrystalline powders of Ln^{3+} doped GGG can give rise to efficient IR-to-visible upconversion [6–9].

For these reasons, a considerable effort has been carried out, in order to obtain a detailed understanding of the Gd_2O_3 – Ga_2O_3 binary system. The equilibrium phase diagram of the Gd_2O_3 – Ga_2O_3 system was determined by Nicolas et al. [10], after substantial contributions on the subject by DiGiuseppe et al. [11], while Allibert et al. [12] and Brandle and Barns [13] pointed out the existence of non-equilibrium phases and off-stoichiometric compounds. In addition to this, Allibert et al. [12] adopted the “citric complex” method for the solid-state synthesis of oxides, which is very similar to the “modern” methods of synthesis by coprecipitation. Thermal properties of GGG were studied by Daudin et al. [14] with a view to their magnetic refrigeration applications. Following this, magnetic

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nanocomposites were also prepared by complexing the mixed nitrates with an excess of tartaric acid in aqueous solution [15]. Further, dense polycrystalline GGG were prepared by solid state reaction of the oxides by Hellstroem et al. [16], and recently several papers have appeared on the synthesis of polycrystalline and nanocrystalline GGG using combustion and coprecipitation techniques [6,7,17].

In any case, even for the chemical methods of synthesis of GGG, the crucial point appears to be the decomposition of digallium trioxide at high temperature and for this reason Zhao et al. [18] suggest to use a 2.0 wt% excess of Ga_2O_3 in order to induce the formation of a single garnet phase. Conversely, Luo et al. [19] find it useful to maintain the nominal 3:5 M ratio of the oxides but suggest to use ammonium hydrogen carbonate as coprecipitating agent, in analogy to similar observations conducted on the $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ system. In this work, we address the problem of the GGG synthesis by making use a mechanochemical approach, i.e., combining the coprecipitation method and mechanical treatment at relatively low temperature in order to make the chemical composition of the matrix homogeneous, to favour the crystallization of the equilibrium phase at low temperature.

2. Experimental

Gadolinium oxide (99.99%) and gallium oxide (99.99%) in a 3:5+ x stoichiometric molar ratio, with $x = 2$ wt% Ga_2O_3 , were separately dissolved in nitric acid and the resulting solutions were mixed and stirred at room temperature. The resulting solution was slowly added dropwise into aqueous ammonia under constant stirring, keeping the pH value around 10. The gelatinous white co-precipitate of gallium–gadolinium hydroxide was filtered, washed several times with distilled water to remove the residual nitrate ions, and finally oven dried at 60 °C to obtain the precursor powder. Selected portions were later heat-treated at 500, 800 or 900 °C for 30 h in a muffle furnace under air atmosphere.

The material obtained after calcination at 500 °C for 30 h was mechanically treated for 30 min using a Spex mixer/mill model 8000 with vial and ball colliding bodies [20] made of hardened ZrO_2 .

Thermo-gravimetry (TG) and differential thermal analyses (DTA) were conducted using a Setaram instrument from room temperature up to 900 °C at an heating rate of 20 °C/min under inert atmosphere.

Powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8 diffractometer in the Bragg–Brentano geometry using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray generator worked at a power of 40 kV and 40 mA and the goniometer was equipped with a graphite monochromator in the diffracted beam.

The resolution of the instrument (divergent and antiscatter slits of 0.5°) was determined using $\alpha\text{-SiO}_2$ and $\alpha\text{-Al}_2\text{O}_3$ standards free from the effect of reduced crystallite size and lattice defects. The powder patterns were analyzed according to the Rietveld method [21] using the programme MAUD [22] running on a personal computer.

Morphological features and particle sizes of materials were determined with a JEOL 200 CX transmission electron microscope (TEM) operating at 200 KV and diffraction patterns were collected in selected area diffraction with a camera length of 82 cm.

3. Results and discussion

Fig. 1 shows the XRD diffraction patterns of sample with nominal composition $3\text{Gd}_2\text{O}_3 \cdot 5\text{Ga}_2\text{O}_3$ treated at various temperatures. It can be seen that the powders annealed at 500 °C display a diffuse pattern (dots are experimental intensity data points) with the first halo located at about 31° in 2θ and a second minor oscillation around 54° in 2θ indicating the persistence of an amorphous structure up to this temperature. The full line represents the best-fit curve according to the

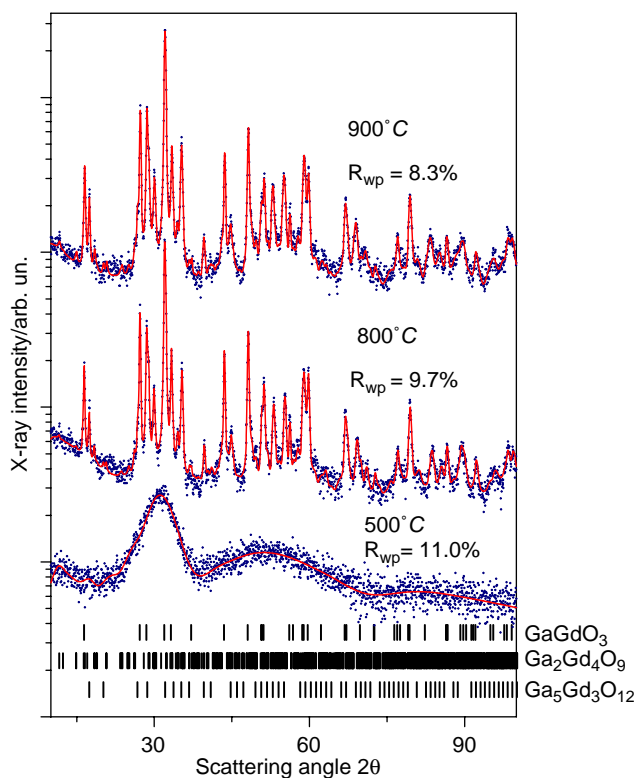


Fig. 1. The XRD patterns of powders annealed for 30 h at the quoted temperatures. Data points are experimental intensities, full lines are the result of the Rietveld refinement. The agreement factors R_{wp} are also reported. The bar sequences at the bottom mark the peak positions expected for the phases on the basis of refined crystallographic data.

Rietveld for disordered materials approach [23], using a monoclinic structure as “pseudo crystalline” factor for the amorphous condition.

Increasing the temperature at 800 °C and annealing for 30 h gives rise to almost complete crystallization of the powder (middle curve). This powder pattern was resolved as a contribution of a weak amorphous component and three crystalline phases, namely: cubic $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (garnet phase, S. G. $Ia-3d$, $a_0 = 12.453(\pm 1)\text{Å}$), monoclinic $\text{Gd}_4\text{Ga}_2\text{O}_9$ (S. G. $P2_1/c$, $a = 7.569(\pm 2)\text{Å}$; $b = 10.707(\pm 2)\text{Å}$; $c = 11.396(\pm 2)\text{Å}$, $\beta = 108.7(\pm 1)^\circ$) and a hexagonal GdGaO_3 (S. G. $P6_3/mmc$, $a = 3.781(\pm 1)\text{Å}$, $c = 10.768(\pm 1)\text{Å}$) not reported in the literature.

The earliest complete phase diagram of the Gd_2O_3 – Ga_2O_3 system was determined by Nicolas et al. [10] above 1200 °C. The following Gd–Ga–O crystalline phases were reported: orthorhombic Gd_3GaO_6 isostructural with Nd_3GaO_6 ; monoclinic $\text{Gd}_4\text{Ga}_2\text{O}_9$ isostructural with $\text{Eu}_4\text{Al}_2\text{O}_9$; perovskite-like GdGaO_3 isostructural with GdFeO_3 and, of course, cubic $\text{Gd}_3\text{Ga}_5\text{O}_{12}$. The present new hexagonal phase observed after annealing at 800 °C appears to be isostructural with the TAIO_3 oxide series (for $T = \text{Y, Eu, Gd, Tb, Dy, Ho, Er}$) reported by Bertaut and Mareschal [24].

The full line reported in correspondence of the experimental intensities represents the result of the quantitative Rietveld fit which gave the following wt% phase composition: 56(±2)% GdGaO_3 ; 31(±2)% $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ and the remaining 13(±2)% $\text{Gd}_4\text{Ga}_2\text{O}_9$. The amorphous phase contribution was excluded from this evaluation. From the line broadening analysis it was found that the average (volume weighted) crystallite size of the hexagonal phase, after correction for instrument broadening is around 600 Å, with an average micro-strain of 0.001. Confirmation of this microstructure is supplied by the TEM micrograph reported in Fig. 2,



Fig. 2. Transmission electron microscope image of the gadolinium gallium oxide powder heat treated at 800 °C for 30 h. The viewgraph shows a microstructure with features in the 500–700 Å range size.

where average domain size in the 500–700 Å range are visualized directly.

Heat treatments of the powder up to 900 °C does not seem to change the situation significantly, as confirmed by the pattern at the top of Fig. 1. In fact, the quantitative Rietveld analysis gave: 49(±2)% GdGaO_3 ; 37(±2)% $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ and the remaining 14(±2)% $\text{Gd}_4\text{Ga}_2\text{O}_9$. For the minor $\text{Gd}_4\text{Ga}_2\text{O}_9$ phase the lattice parameters appeared to be unchanged within experimental error. As for the lattice parameters of the hexagonal phase, while the a value in sample annealed at 900 °C was confirmed to be $a = 3.750(\pm 1)\text{Å}$, the c value turned out to be $c = 10.750(\pm 1)\text{Å}$, slightly lower than the corresponding figure observed at 800 °C. Moreover, for the garnet phase it was found $a = 12.490(\pm 1)\text{Å}$, which is also significantly different with respect to the value observed at 800 °C. To our knowledge, Brandle et al. [1] were the first to observe lattice parameter variations for the garnet phase and they related this behaviour to the Gd/Ga atomic ratio. Allibert et al. [11], based on the approach of Brandle et al. [1], determined a concentration range for the existence of the garnet phase and reported that the garnet, melting congruently above 1700 °C, has a composition significantly different from the nominal stoichiometry. Thus, from the lattice parameter variations as a function of the heat treatment, it seems possible that also the new hexagonal phase may be subjected to variations with respect to the nominal Gd/Ga ratio 1:1.

Luo et al. [19] reported the XRD of $3\text{Gd}_2\text{O}_3 \cdot 5\text{Ga}_2\text{O}_3$ powders heat treated for 10 h at temperatures from 600 °C to up 1100 °C. At 800 °C they observed mainly the cubic $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ garnet and the monoclinic $\text{Gd}_4\text{Ga}_2\text{O}_9$ phase with a further intermediate phase, not completely resolved and tentatively attributed to hexagonal Gd_2O_3 . Also Zhao et al. [18], using coprecipitation via ammonia, encountered unidentified structures at temperatures between 800 and 1000 °C with powder pattern different from the desired garnet. In order to obtain a more homogeneous chemical composition at microscopic level and at low temperature, we have subjected the amorphous powders to a mechanical treatment for 30 min. The mechanical treatment in an agate mortar for prolonged times was employed by Hollstrom et al. [16] to obtain gadolinium gallium garnet by solid state reaction but no study was reported on the metastability of the milled products.

Fig. 3 shows the heat flow curves of our coprecipitated powders in the temperature range from 730 to 900 °C. For the unmilled sample we observe a relatively sharp exothermic effect at about 850 °C, which is very likely to represent the effect of the amorphous-to-crystalline transformation observed after annealing the specimen at 800 °C for 30 h. This transformation peak appears to be broadened and shifted to lower

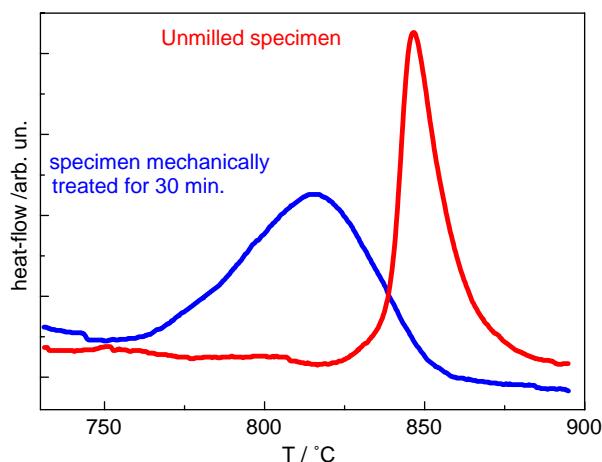


Fig. 3. DTA traces of gadolinium gallium oxide powders, unmilled and milled for 30 min, respectively, as a function of temperature (heating rate 20 °C/min). From the different shape of the two exothermic events different kinetic processes can be surmised.

temperature (maximum now at about 815 °C) due the mechanical treatment.

Also, the skewness of the peak appears reversed, suggesting that another mechanism of crystallization may be established after the mechanical treatment.

A confirmation of such different crystallization mechanism is supplied by the XRD pattern reported in Fig. 4, which refers to the specimen ball milled and annealed at 900 °C. Here we observe only the garnet phase, except for one peak at around 30.60° in 2θ scale due to the 7.3 wt% contamination of tetragonal ZrO_2 from the milling tools. The average crystallite size is 400 (± 50) Å and the microstrain amounts to 0.0010 (± 1). The lattice parameter of this phase from XRD turns out to be 12.581 (± 1) Å which is indeed one of the largest reported in the literature for gadolinium gallium garnet; this behaviour may be related to important deviations of the true chemical composition from the nominal $3\text{Gd}_2\text{O}_3 \cdot 5\text{Ga}_2\text{O}_3$ stoichiometry. These stoichiometric deviations are also confirmed by the weak if not absent diffracted intensity in correspondence of the (220) peak of the garnet phase at $2\theta = 20.45^\circ$ in Fig. 4. In fact, the R_{wp} agreement factor was calculated from best-fit of the simple garnet lattice, composed of an oxygen framework and three distinct cation coordinations—a dodecahedral site (Gd ions in positions 24c), an octahedral site (Ga ions in positions 16a) and a tetrahedral site (Ga ions in positions 24d). After defining a model R_{wp}° involving a partial substitution by Gd^{3+} ions ($X_{\text{Gd}^{3+}}$) for Ga^{3+} sites in six-fold coordination [16], a Hamilton significance test [25] was performed and reported in Fig. 5 in terms of the normalised agreement factor $R = R_{\text{wp}}/R_{\text{wp}}^\circ$ vs. the substitution degree X_{oct} . The relative minimum found for $X_{\text{oct}} = 0.3$ ($R_{\text{wp}} = 6.53\%$, $R_b = 5.23\%$, number of refined parameters: 30, number of reflections: 118) suggests that a better chemical composition of the

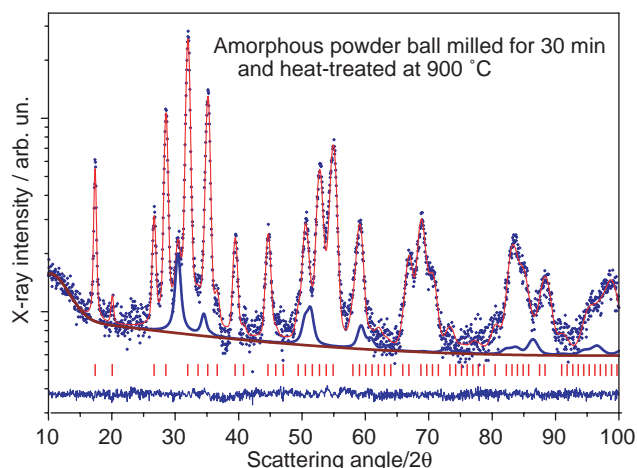


Fig. 4. The XRD pattern and the Rietveld fit (log intensity scale) of amorphous gel ball milled for 30 min and annealed at 900 °C. The main phase is the garnet structure, which is slightly contaminated with the tetragonal zirconia (above the background line) owing to the high energy of the mill employed.

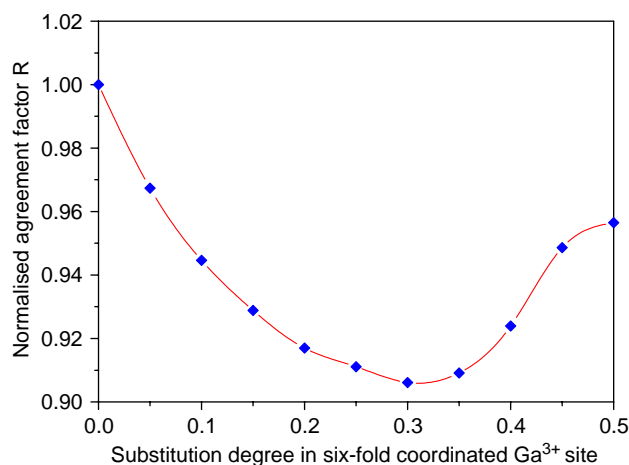


Fig. 5. The agreement factor ratio $R = R_{\text{wp}}/R_{\text{wp}}^\circ$ vs. the substitution degree X_{oct} of Ga^{3+} octahedral sites by Gd^{3+} cations (Hamilton significance test). The relative minimum found for $X_{\text{oct}} = 0.3$ is due mainly to the ability of the model to account for the disappearance of the (220) garnet peak at $2\theta = 20.45^\circ$. The minimum corresponds to an R_{wp}° value of 6.53%.

system could be $\text{Gd}_{3.65}\text{Ga}_{4.35}\text{O}_{12}$, although we cannot disregard the hypothesis of cationic exchange also for the tetrahedral and dodecahedral sites.

4. Conclusions

Preparation of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ may be attained with relative success via the coprecipitation method for heat treatments at temperatures below 1000 °C. However, the crystallization process, which is induced by the thermal treatment is not polymorphous and involves the formation of various metastable phases. In fact, a new

hexagonal phase of GdGaO₃ stoichiometry appears to be the major product of crystallization after treating the sample above 800 °C. This new phase is isostructural with the TAlO₃ oxide series (where T = Y, Eu, Gd, Tb, Dy, Ho, Er) studied earlier by Bertaut and Mareschal [24].

A mechanical treatment of the amorphous powder previously annealed at 500 °C is able to select new kinetic paths and to drive the system toward complete formation of the Gd₃Ga₅O₁₂ garnet at the price of some contamination from the milling tools. The garnet has a nanocrystalline structure but shows also a lattice parameter of 12.581(±1) Å, which is considered quite high and seems to reflect the difficulties of properly controlling the chemical composition of the sample during the various stages of the processing.

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