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Synthesis, structure and magnetic properties in the Nd$_2$O$_3$-Gd$_2$O$_3$
mixed system synthesized at 1200°C

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Abstract

Phase relation studies in the Gd₂O₃-Nd₂O₃ system have been performed on (Gd₁₋ₓNdₓ)₂O₃ samples (0 ≤ x ≤ 1) with the purpose of performing a systematic study of the composition effects on their structural and magnetic properties. All the samples were synthesized by calcination of the related oxalates at 1200°C in order to ensure the complete decomposition of the oxalates. Five phase regions, namely an A-type hexagonal, a B-type monoclinic, a C-type cubic solid solution and two biphasic mixtures of the former three phase fields were detected in this system. The magnetic susceptibility measurements showed the presence of antiferromagnetic interactions in all samples. The Curie-Weiss temperature shows a nonlinear dependence on concentration. Deduced effective magnetic moments are close to the free ion values.
1 Introduction

Rare earths sesquioxides, RE$_2$O$_3$, are of interest in the science and technology of many applications such as high temperature materials, active catalysts for a large number of organic reactions, the dehydration/dehydrogenation of alcohols, and are excellent host materials for powerful lasers or improved phosphors [1 – 4]. In addition, they can be used as precursors of high critical temperature superconductors like REBa$_2$Cu$_3$O$_7$, generally indicated as the most promising materials for power applications of superconductivity due to their high critical current density, $J_c$, which can be further enhanced if solid solutions of two or three RE elements are utilized [5].

The RE$_2$O$_3$ sesquioxides exist in different structural types depending on the ionic radii of the rare earth and can exhibit complex magnetic properties. Below about 2000 °C three distinct crystalline types have been described; these polymorphic modifications are usually labelled as A (hexagonal), B (monoclinic) and C (cubic) [6]. The larger cations form the hexagonal (A-type) modification structure with a seven-coordinated polyhedron of the metal ion and the smaller cations form a cubic lattice (C-type) with a six coordinated polyhedron of the metal ions. The intermediate groups form a monoclinic structure (B-type) with cations having both a seven and a six coordinated polyhedron in the ratio 2:1.

For every rare earth oxide, the range of existence of each phase depends on the temperature of the thermal treatment. The C form is stable from room to high temperature for lanthanides heavier than Sm. For lighter lanthanides, i.e. from La to Nd, the C – type forms below 600°C, but these oxides at room temperature are usually found in the A form. Depending on the thermal treatment, Sm$_2$O$_3$ and Gd$_2$O$_3$ can also be found at room temperature in the B structure [7], that is expected to be stable at higher temperatures, probably as the transformation rates are small at low temperature.

In order to grasp a relation between rare earth sesquioxide structures, a smooth variation of the ionic radii can be achieved by a systematic replacement of the larger cations by smaller ones, which possibly brings out a gradual structural variation.
In the RE – RE\textsuperscript{I} binary mixed oxides at a fixed temperature, the crystalline type depends on the structures of RE\textsubscript{2}O\textsubscript{3} and RE\textsubscript{I}\textsubscript{2}O\textsubscript{3} and on the difference between their cation radii \cite{8}. If the single rare earth sesquioxides possess the same structure, a solid solution forms which follows the Végard’s law. On the contrary, the oxides which do not crystallise in the same structure type, give rise to two terminal solid solutions with the structures of the two pure oxides and to one or more polyphasic regions, where A and B types or B and C types can coexist. If the difference among the ionic radii is large enough to satisfy the Goldschmidt tolerance factor, a distorted perovskitic compound forms \cite{8} for the equimolar composition.

In this respect, the system Nd\textsubscript{2}O\textsubscript{3} – Gd\textsubscript{2}O\textsubscript{3} is particularly interesting because the two single oxides usually crystallise in different structures: the former belongs to the A – type, the latter to the C – type, allowing the formation of three solid solutions and two biphasic regions. Moreover, the mixed binary rare earths oxides are very attractive magnetic materials, as they display a large number of different behaviours. In general they are paramagnetic at high temperature and have an antiferromagnetic ordering at low temperature, but in Gd\textsubscript{2}O\textsubscript{3}, for example, the persistence of spin correlations up to 100 times the ordering temperature was observed \cite{9}. Otherwise, like in Er\textsubscript{2}O\textsubscript{3} or Yb\textsubscript{2}O\textsubscript{3}, \cite{10} complex magnetic orderings have been found. In the mixed rare earth systems, in addition, it should be considered that the magnetic properties depend also on the composition. For (Gd\textsubscript{x}Y\textsubscript{1-x})\textsubscript{2}O\textsubscript{3}, the Curie – Weiss law is followed \cite{11}, while other systems like (Eu\textsubscript{x}Gd\textsubscript{1-x})\textsubscript{2}O\textsubscript{3} \cite{12} or (Tm\textsubscript{x}Y\textsubscript{1-x})\textsubscript{2}O\textsubscript{3} \cite{13} show a complex dependence of the magnetic susceptibility on the temperature and composition. In the present work, a series of solid compositions with varying concentration of two different rare earth oxides, namely Gd\textsubscript{2}O\textsubscript{3} and Nd\textsubscript{2}O\textsubscript{3}, and the subsequent change in lattice structure and magnetic properties are studied.

2 Experimental

In order to have a very high homogenization degree, mixed oxides samples were synthesized by a coprecipitation method. A solution was prepared dissolving stoichiometric amounts of Nd\textsubscript{2}O\textsubscript{3} and
Gd$_2$O$_3$ (Aldrich – both 99.99% pure) in a slight excess of HCl (13% m/V). The precipitation of the mixed oxalate was achieved by carefully adding an excess of an oxalic acid solution. The precipitate was filtered and washed with deionized water till the neutrality was achieved and no residual trace of Cl$^-$ was detected. The precipitate was dried in air for 48 h and then calcined in air at 1200 °C for 16h. The structure of all the samples was investigated by X-ray powder diffraction using a Philips PW1830 diffractometer (Cu-K$_\alpha$ radiation) and by Raman spectroscopy at room temperature using a Renishaw System 2000 Raman imaging microscope with a 633 nm He–Ne laser. The spectra were the result of 16 accumulations repeated on several points, each one lasting 10 seconds, in the range 80 - 1000 cm$^{-1}$, with a magnification of 50x.

Magnetic measurements were performed by a Lake Shore Mod. 7121 ac susceptometer operated at a frequency of 333 Hz and a rms field value of 25 Oe in the 77 – 285 K temperature range.

For comparison with the mixed oxides another set of samples was prepared by mixing stoichiometric amounts of cubic Gd$_2$O$_3$ and hexagonal Nd$_2$O$_3$ powders in the desired ratio, hereafter referred as “mechanical mixture”.

3 Results and discussion

3.1 Structural properties

Typical XRD patterns normalised to the most intense peak of some compositions depicting the different phase fields observed are shown in Fig.1; normalised Raman spectra of the same samples are reported in Fig. 2. For very low concentrations of Nd, only the peaks of the cubic phase are recognisable, but the solubility of Nd in the C – type structure is quite low at 1200°C, as already for $x = 0.06$ some new weak peaks appear that can be referred to the B – type structure. Increasing the Nd concentration, the peaks of the cubic structure decrease in intensity and completely disappear at 12%. Hence in the $0.06 < x < 0.12$ composition range the B and C type phases coexist.

As Nd$^{3+}$ is greater than Gd$^{3+}$, it can be expected that the substitution of Gd by Nd leads to the increase of the cell parameters, but as the range of existence of the solid solution with the C - form is narrow, it
is difficult to observe whether the Végard’s law is followed. The calculated $a$ axis increases very slightly for the oxide with the smallest Nd content, being $10.812(2)$ Å for Gd$_2$O$_3$ and $10.822(2)$ Å for (Gd$_{0.97}$Nd$_{0.03}$)$_2$O$_3$. C-type RE sesquioxides are body centred cubic, $T_h$, $Z = 16$ [14]. From the irreducible representations 22 Raman lines are predicted. Raman spectra data concerning Gd$_2$O$_3$ sample are in good agreement with literature [15, 16]. However, it should be noticed that the number of bands is lower than the theoretically expected ones: the reason of these absences have to be searched in the nature of the samples. Since they are powders, the defects concentration could be high with low crystallinity, leading to a reduction of the symmetry [17]. For the lowest concentration of Nd, the Raman spectra are very similar to pure Gd$_2$O$_3$, in agreement to the fact that a solid solution has formed. Increasing $x$, the main peaks of C and B-type structures are present (Fig 2b).

For Nd concentrations from 12% up to 90%, the XRD patterns show only the peaks of the B – type phase (Fig. 1c). In this composition range, the cell parameters change as a function of the concentration of Nd. As expected from the Vegard’s law, the volume cubic roots for all samples in the range $0.12 < x < 0.90$ increases linearly as a function of $x$, indicating that a solid solution has formed as shown in Fig. 3a. The extrapolated value to $x = 0$ is in close agreement with the calculated cubic root from the monoclinic Gd$_2$O$_3$ cell constants, space group $C2/m$ [6, 8]: $a = 14.061$ Å, $b = 3.566$ Å, $c = 8.760$ Å and $\beta = 100.10^\circ$ ($V^{1/3} = 7.562$ Å).

As in the case of the C – type oxides, the real number of lines is lower than those expected from the irreducible representations of the B –type oxide [16]. Observed Raman spectra are very similar to those of pure B – type Gd$_2$O$_3$ and, in general, to those of monoclinic RE$_2$O$_3$. The position of the bands depends on the Nd content, confirming that a solid solution forms. Due to the lanthanidic contraction, decreasing the reduced mass a decrease of Raman shift is observed, while the variation of the cell parameters acts in the opposite direction, as smaller average distances among the oxygens and the cations lead to stronger force constants. The Gd replacement by Nd should have accordingly two opposite effects: the average cation mass reduction and the cell volume increase, as Nd$^{3+}$ is lighter and larger than Gd$^{3+}$. For the C–type oxides the force constant variation is the dominant parameter for the
high wavenumber bands [15]: the partial substitution of a cation by a bigger one in cubic RE$_2$O$_3$, results in a monotonic band positions decrease [17]. This happens also in the B – type sesquioxides, in fact we can observe the positions of the bands with wavenumber higher than about 245 cm$^{-1}$, mainly due to stretching modes, shift towards lower positions as x increases, meaning the force constants weaken. This last trend is shown in figure 3b, where the Raman shift of the most intense line as a function of the Nd content is reported. The low wavenumber bands are mainly due to bending vibrations [14] and for this reason they are less sensitive to the force constant variation. In this range, the mass variation would be the dominant factor, but the difference between Gd atomic mass and Nd one is too small to expect a large shift.

For x greater than 0.90, A and B phases coexist, as confirmed by the XRD patterns and the Raman spectra (Fig. 1d, 2d). Finally, for x greater than 0.94, only the A phase is present in the system (Fig. 1e, 2e). A – type Nd$_2$O$_3$, whose space group is $D_{3d}^3$, has one formula unit per unit cell [18, 19]. Four Raman active phonons (2A$_{2u}$ + 2E$_{u}$) should be expected, but again, only three Raman active modes are found. The same behaviour was observed by Burns et al [19], who studied sintered Nd$_2$O$_3$ ceramics, while Raman spectra collected on single crystals exhibit the expected number of bands [18]. Even in single crystals, however, the separation between the highest wavenumber bands is small, so that it is possible that in ceramic materials and powders they overlap.

The boundary lines of biphasic fields (B + C and A + B) can be determined from the trend of the parameters of the B phase or the relative percentage of the two phases from the XRD patterns. Assuming that the area of the most intense peak depends linearly on the concentration of that phase, it is possible to interpolate the x value for which the area of that peak shrinks to 0, i.e. the value for which that phase is no more present in the system. It is possible to estimate that at 1200$^\circ$ C the pure C form exists for x lower than 0.06, C and B type phases coexist for 0.06 < x < 0.12, then pure B – type solid solution is detected in the range 0.12 <x < 0.90, both A and B type forms for 0.90 < x < 0.94 and finally only A – type solid solution is present for x > 0.94.
3.2 Magnetic properties

Before dealing with the magnetic susceptibility data, a calibration of the instrument was performed. Proper calibration implies that the sample utilized has the same volume and shape as the samples for which calibration is sought. Gd$_2$O$_3$ was chosen for low-field susceptibility calibration since it combines the advantages of all paramagnetic salts (independence of $\chi$ on field value and frequency) with a high specific susceptibility, a high chemical stability (no oxidation and little hydration in air) and a well-defined temperature correction. Gd$_2$O$_3$ has a tabulated specific magnetic susceptibility and its temperature dependence above 50K is described by the Curie-Weiss law [20]. Our measurements give a value of the ac susceptibility which is, on average, 3% smaller than the handbook value in the temperature range of interest [20,21]. Equivalently, dealing with a Nd$_2$O$_3$ sample, which has on the contrary a smaller specific susceptibility and lower chemical stability especially to hydration in air [22], yielded an ac susceptibility value 6% on average smaller than the tabulated ones [20,21,23]. It must be pointed out anyway that the system reproducibility and accuracy is within $\pm 1.0\%$.

The temperature dependencies of the measured molar susceptibilities of all (Gd,Nd)$_2$O$_3$ samples are shown in Fig. 4. The paramagnetic behaviour in the 77 – 285 K temperature range was analyzed and fitted to the modified Curie-Weiss law $\chi = \chi_0 + [C_M/( T - \theta)]$, which includes a temperature independent parameter, $\chi_0$ [23–25].

Fig. 5a shows the fitted $\chi_0$ as a function of $x$. It can be noticed that basically $\chi_0$ values retain an average almost constant value of $- (1.1 \pm 0.5) \times 10^{-3}$ emu/mole for both the mixed oxide and the mechanical mixture samples, which is one order of magnitude higher than the calculated one obtained by adding the gram ion susceptibility values given by Selwood [25].

The Curie molar constants $C_M(x)$, shown in Fig.5b, are given by $C_M = N_A g^2 J(J+1) \mu_B^2 / 3k$ where $N_A$ is the Avogadro's number, $g$ is the Lande's factor, $J$ is the quantum number for the total ion angular momentum, and $k$ is the Boltzmann constant. A linear dependence of $C_M$ for all the $x$ values is observed. It seems, moreover, reasonable that in this case there is no clear difference in the behaviour
between a system consisting of a mechanical mixture of rare earth oxides, a homogeneous mixed oxides system (which retains their valence) or biphasic system since the structure variation does not change the valence and, accordingly, the magnetic moment of the rare earth. Since, moreover, the oxygen atoms do not bear a substantial magnetic moment with respect to that of the rare earths, the different oxygen environment in these systems do not modify significantly their magnetic behaviour.

Therefore, by using the $C_M$ values, the effective magnetic moments $\mu_{\text{eff}}$ of the rare earth ions in the mixed $(\text{Gd}_{1-x}\text{Nd}_x)\text{O}_3$ oxides as well as the mechanical mixture samples were calculated and reported in Fig. 5c. It must be pointed out that the values obtained for the end member samples ($x = 0, 1$), corresponding to pure Gd$_2$O$_3$ and Nd$_2$O$_3$ respectively, are $(8.02 \pm 0.01) \mu_B$ and $(3.75 \pm 0.10) \mu_B$, which are equal or close, within the error, to the corresponding calculated free ion values of $7.9 \mu_B$ and $3.65 \mu_B$ respectively [20]. The effective magnetic moment $\mu_{\text{eff}}$, not influenced by the crystalline structure, is the sum of the magnetic moments carried by the rare earths. Since these latter are very different, a linear dependence as a function of the concentration is clearly visible.

Different is the case when dealing with the Curie-Weiss temperatures shown in Fig. 5d. Since it accounts for the exchange interaction between the magnetic moment carried by the rare earth and nearest neighbourhood ions, we can suppose that it depends only on the crystallographic state and hence on the reciprocal atomic positions of the various ions. Since these latter are different in different structures, the biphasic regions should linearly depend on the concentration. On the contrary, solid solution single phase regions should essentially retain a constant value. Moreover, the negative $\theta$ values obtained indicate a predominance of antiferromagnetic interactions with end members values of $-(17.14 \pm 0.1) \text{ K}$ and $-(31.45 \pm 4.68) \text{ K}$ for the Gd and Nd sesquioxides respectively, again in agreement with literature data [20]. As expected, the mechanical mixture data display a completely linear dependence.
Hence the crystalline environment in which the rare earth nearest neighbour ions interact must be taken into account since different crystalline structures have substantial differences in their interatomic rare earth - oxygen distances.

4. Conclusions

The mixed oxalates coprecipitation method is a suitable technique to synthesize very homogeneous mixed oxides rare earth samples. The effect of a gradual change in composition is picked out both from X-ray diffraction and from Raman spectroscopy wherein the peaks, ascribed to the different phases, are clearly distinguishable.

At 1200 °C, in the (Gd$_{1-x}$Nd$_x$)$_2$O$_3$ system the solubility of Nd in Gd is limited to 6% while, in the opposite case, it is very low, of the order of 1%. B-type phase covers a very broad composition region between 12% and 90% Nd content.

In summary, five phase regions, namely an A-type hexagonal, a B-type monoclinic, a C-type cubic solid solution and two biphasic mixtures of the former three phase fields were observed in this system.

The molar Curie constant calculated in the 77 – 285K temperature interval was found to depend linearly on the concentration x. The effective magnetic moment $\mu_{\text{eff}}$, obtained from the same temperature range, varied from ($8.02 \pm 0.01$) $\mu_B$ for $x = 0$ to ($3.75 \pm 0.10$) $\mu_B$ for $x = 1$, which are close to the calculated free ion values. The Curie-Weiss temperature shows the presence of antiferromagnetic interactions in all the samples and a nonlinear dependence on the concentration, which can be explained in terms of coordination of magnetic ions in cubic (C) and monoclinic (B) samples. Assuming that superexchange is the dominant mechanism, the number of superexchange paths (cation-anion-cation) as well as their geometry (bond lengths and angles) differ in the two phases.
References


Figure captions

Fig. 1 – Normalized XRD patterns in the (Gd_{1-x}Nd_x)_{2}O_3 system: (a) Gd_{2}O_3, (b) (Gd_{0.94}Nd_{0.06})_{2}O_3, (c) (Gd_{0.5}Nd_{0.5})_{2}O_3, (d) (Gd_{0.1}Nd_{0.9})_{2}O_3 and (e) Nd_{2}O_3. C = cubic ( ), B = monoclinic ( ), A = hexagonal (ξ).

Fig. 2 – Normalized Raman spectra in the (Gd_{1-x}Nd_x)_{2}O_3 system: (a) Gd_{2}O_3, (b) (Gd_{0.9}Nd_{0.1})_{2}O_3, (c) (Gd_{0.5}Nd_{0.5})_{2}O_3, (d) (Gd_{0.1}Nd_{0.9})_{2}O_3, (e) Nd_{2}O_3. C = cubic, B = monoclinic, A = hexagonal.

Fig. 3 – (Gd_{1-x}Nd_x)_{2}O_3 samples: volume cubic roots (a) and Raman shift of the most intense line (b) in the 0.12 < x < 0.90 B - type composition range.

Fig. 4 – Molar magnetic susceptibility of (Gd_{1-x}Nd_x)_{2}O_3 as a function of temperature.

Fig. 5 – Curie – Weiss paramagnetic parameters of (Gd_{1-x}Nd_x)_{2}O_3 versus Nd concentration: (a) χ_0, (b) molar Curie constant C_M, (c) effective magnetic moment μ_eff, (d) Curie-Weiss temperature θ. Dashed line joins end members. (Open symbols: mechanical mixture powders – Filled symbols: coprecipitated mixed oxide samples)
Figure 1

The figure shows the X-ray diffractogram for different samples labeled C (a), B + C (b), B (c), B + A (d), and A (e). The intensity is plotted on the y-axis in arbitrary units (a.u.), and the 2θ angle is on the x-axis. The peaks in the diffractograms correspond to specific crystallographic planes in each sample.
Figure 2

![Graph showing Raman spectra for different samples: (a) C, (b) B + C, (c) B, (d) B + A, (e) A. The x-axis represents the Raman shift in cm$^{-1}$, and the y-axis represents the intensity in arbitrary units (a.u.).]
Figure 3

(a) 

(b) 

Nd concentration (x) 

Raman shift (cm$^{-1}$) 

$V^{1/3}$ (Å)
Figure 4
Figure 5

(a) 

(b) 

(c) 

(d) 

Figure 5