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# PHASE STABILITY STUDY OF THE PSEUDOBINARY SYSTEM $Gd_2O_3$–$Nd_2O_3$ ($T$≤1350°C)

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The phase stability of the system $Gd_2O_3$–$Nd_2O_3$ up to 1350°C was studied. Mixed oxides were synthesized by coprecipitation of mixed oxalates. Depending on the thermal treatment, three possible structures of the oxides, namely the A (hexagonal, $P6_3/mmm$), B (monoclinic, C2/m) and C (cubic, Ia3) forms, were obtained. Below 1300°C the system $Gd_2O_3$–$Nd_2O_3$ shows three monophasic (A, B and C phase) and three biphasic regions (A+B, B+C and A+C phase). Below 550°C the C phase is stable over the whole composition range. A validation procedure for the existence of the C phase in pure $Nd_2O_3$ was also set up.

***Keywords:*** *phase stability, rare earth sesquioxides, X-ray diffraction*

## Introduction

Due to their physical and chemical properties, rare earth (RE) sesquioxides are applied in many technological fields, such as catalysts for a large number of organic reactions [1, 2], host materials for powerful lasers [3] or improved phosphors [4]. They are also used as precursors of high critical temperature superconductors [5] like $REBa_2Cu_3O_7$, generally indicated as the most promising materials for power applications of superconductivity. Particularly, some superconducting cuprates containing solid solutions of two or three RE, exhibit high critical temperature and current density [6].

It is well known that rare earth sesquioxides ($RE_2O_3$) exist in five distinct crystalline types depending on their RE ionic radius and on temperature. These polymorphic modifications are usually labelled with the letters A and H (hexagonal), B (monoclinic), C and X (cubic). The X and H forms are stable above 2000°C, while below this temperature A, B and C are commonly observed [7, 8].

The C form (space group Ia3) is the most stable for lanthanides from Tb to Lu, while the A form (space group $P6_3/mmm$) is typical for lanthanides from La to Nd; the intermediate rare earth oxides exist both in the B- and C-type polymorphs, the B form (space group C2/m) being stable above 875, 1000 and 1250°C for $Sm_2O_3$, $Eu_2O_3$ and $Gd_2O_3$, respectively; [9] however, these oxides can also be found in the B structure at room temperature because their transformation rates are low. The sesquioxides of the largest ions from $La_2O_3$ to $Nd_2O_3$ are usually reported to crystallise in the A-type structure [8]. The question whether they can exist in the C form, if the synthesis conditions are appropriate [10], is still open in literature [8, 11–14].

Dealing with mixed rare earth oxides $(RE_{1-x}RE'_x)_2O_3$, if the two parent oxides have the same structure, a complete solid solution which follows the Vegard's law forms. Otherwise, two terminal solid solutions develop with the structure of the parent oxides and a polyphasic system exists for intermediate values of $x$. If the difference between the RE ionic radii is large enough to satisfy the Goldschmidt tolerance factor [15], a perovskitic compound forms for the equimolar composition.

An extensive literature exists on the rare earth mixed oxides synthesis, generally consisting of a direct solid state reaction between the pure oxides [16, 17], a combustion synthesis [18] or a coprecipitation of mixed hydroxides [16]. Considering the high thermal stability of these materials and the low diffusion coefficients, high temperatures, usually greater than 1400°C, are required in order to attain equilibrium. For this reason the low temperature region ($T$<1300°C) of the phase diagrams is generally not considered.

This work focuses on the $(Gd_{1-x}Nd_x)_2O_3$ system ($0 \le x \le 1$). Since these mixed oxides are often used as

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precursors for new materials [5, 19], the existence of a complete solid solution at room temperature is very important and it is necessary to define the existence fields of the monophasic regions as a function of temperature and composition.

As $Nd_2O_3$ can exist in the C and the A form, while $Gd_2O_3$ exhibits the C- and B-type structures at room temperature and above 1250°C, respectively, the phase diagram of the mixed oxides system is rather complex below 1350°C. This leads to large monophasic and polyphasic regions, depending on the Gd/Nd ratio. This work reports on the results of the $Gd_2O_3$–$Nd_2O_3$ phase diagram up to 1350°C. The mixed oxides were prepared by thermal decomposition of the corresponding mixed oxalates.

Tests on the existence of C-type $Nd_2O_3$ not stabilized by $H_2O$ or $CO_2$ were also performed by thermal decomposition of $Nd(OH)_3$.

## Experimental

All $(Gd_{1-x}Nd_x)_2[C_2O_4]_3 \cdot nH_2O$ samples ($0 \leq x \leq 1$) were prepared by a coprecipitation method, starting from commercial $Gd_2O_3$ and $Nd_2O_3$ powders (Aldrich; 4N). Due to the $Nd_2O_3$ hygroscopicity, the starting powders were calcined at 600°C overnight. A solution was prepared using a slight excess of HCl (10% *m*/*V*), afterwards the precipitation of mixed oxalates was achieved by adding an excess of a solution of oxalic acid. The precipitate was filtered and washed with deionized water till neutrality and successively dried in air at 80°C for 24 h. The chemical composition of the so prepared powders was checked by SEM-EDAX.

The precursor powders were quickly heated up to a defined temperature in a Carbolite STF 15/450 tube furnace (uniform length: ±1°C in 4 cm) in the range $500°C \leq T \leq 1350°C$ and quickly cooled. In order to attain the final equilibrium, different calcination times were scheduled depending on the temperature: 24 and 72 h for $T > 1000°C$ and for $800 \leq T \leq 1000°C$ range, respectively. Below 800°C a one week calcination was performed.

C-type $Nd_2O_3$ samples were also synthesized starting from $Nd(OH)_3$ powders heated in static air at 550°C and then in flowing $O_2$ (99.999%) at the same temperature to remove the residual water. Effusion technique was used in order to attain a complete decomposition.

The boundaries between the phase fields were determined studying the structures of all the samples by X-ray powder diffraction, using a Philips PW1830 diffractometer ($CuK_\alpha$ radiation) in the range $15° < 2\theta < 78°$.

## Results and discussion

### $Gd_2O_3$–$Nd_2O_3$ phase stability

At 600°C the decomposition of oxalates is complete for every *x* value [20]. XRD analyses performed on samples treated at this temperature show that the C form is stable over the whole range. As shown in Fig. 1, the cell parameters follow the Vegard's law increasing with *x* and a complete solid solution forms.

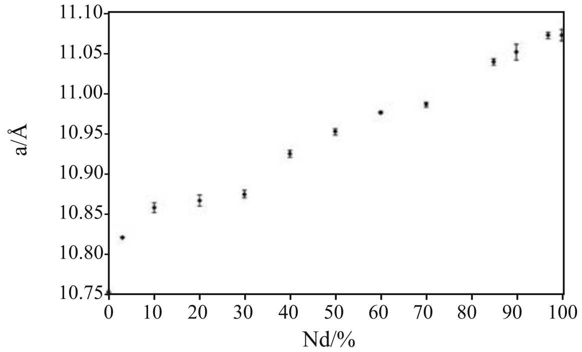

**Fig. 1** Vegard's law for the C-type $(Gd_{1-x}Nd_x)_2O_3$ over the whole composition range

Increasing temperature above 650°C, the C phase field narrows, so that at 1200°C the C phase extent is limited to the range $0 \leq x \leq 0.05$. Correspondingly, the A phase field, typical of samples with high Nd content, widens towards the $Gd_2O_3$ side, reaching $x=0.97$ at 1200°C. The B field is positioned between the A and the C field and it becomes larger towards the $Gd_2O_3$ side as the temperature increases, so that over 1250°C it extends from $x=0$ to 0.9. Therefore, in the range 650–1250°C three monophasic, as well as two biphasic regions (C+B and B+A) between them are present; above 1250 up to 1350°C, two monophasic (B and A) and one biphasic regions are observed.

In the monophasic areas the Vegard's law is followed, while in the biphasic regions, as expected, the cell parameters do not change. The positions of the phase boundaries have been determined by X-ray diffraction, calculating the percentage amount of each phase from the ratio between the areas of the most intense peaks, according to the following equation:

$$\alpha_{\%} = \frac{A_\alpha^{\max}}{A_\alpha^{\max} + A_\beta^{\max}} \cdot 100$$

where $\alpha_{\%}$ is the α phase percentage amount, $A_\alpha^{\max}$ and $A_\beta^{\max}$ are the most intense peak areas of the α and β phase, respectively. In Table 1 the data concerning the percentage amounts of B and C phase for some *T* and *x* values are reported.

On the basis of the XRD patterns of all the considered samples, it is possible to draw a representation

**Table 1** Percentage amounts of B and C phase for some $T$ and $x$ values

| $T$/°C | $x$ | B phase/% | C phase/% |
|---|---|---|---|
| 950 | 0.30 | 42 | 58 |
| 950 | 0.40 | 75 | 25 |
| 900 | 0.40 | 13 | 87 |
| 850 | 0.60 | 4 | 96 |
| 800 | 0.70 | 18 | 82 |
| 750 | 0.78 | 60 | 40 |
| 750 | 0.80 | 70 | 30 |

of the $Gd_2O_3$–$Nd_2O_3$ phase diagram in the range 550–1350°C, as shown in Fig. 2. The dashed line in the Nd rich part at low temperature is referred to a not yet well defined region where many phase boundaries may be present.

As can be observed from the phase diagram, increasing temperature the $Nd^{3+}$ solubility in C-type $Gd_2O_3$ decreases, while the $Gd^{3+}$ solubility in A-type $Nd_2O_3$ slightly increases; moreover, at any temperature above 600°C, the transition C→B→A occurs increasing the Nd content. This evidence can not be explained considering the crystallographic properties of the involved structures. Phase transitions associated to a coordination number and density increase, as well as to a contemporary symmetry decrease, as observed moving from C to B to A, are in fact expected to be favoured by a temperature decrease or a mean cationic radius reduction. However, the same phenomenon is observed over the whole series of the rare earth sesquioxides, as the transition C→B→A is well established at any temperature below 2000°C moving from the biggest to the smallest rare earth ions [7].

From the analysis of the phase diagram it can also be noticed that the boundary separating the A from the A+B field is characterized by a very steep slope, in contrast to what is observed between the C and the B+C field, meaning that the solubility of $Gd^{3+}$ in the A structure is very low in comparison with the solubility of $Nd^{3+}$ in the C structure. This evidence can be explained by the different features of the three crystal structures. Since density and coordination number increase moving from C to B to A, the C form could easily accept a partial substitution of $Gd^{3+}$ by a bigger cation, while this is more difficult for the A form. Similarly, the boundary between the B and the B+A field has a steeper slope than the one detected between the B and the B+C field.

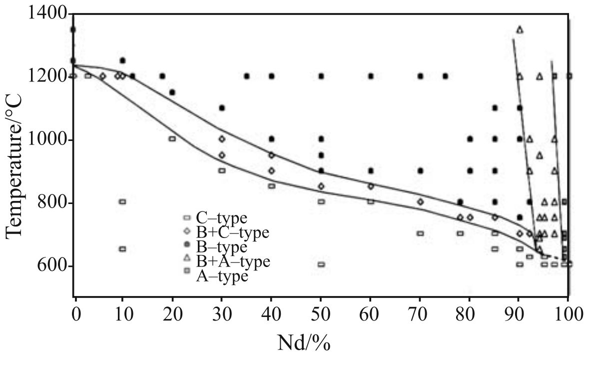

**Fig. 2** Pseudobinary phase diagram of the system $Gd_2O_3$–$Nd_2O_3$. Lines are a guide for the eyes

The phase stability in rare earth sesquioxide systems is driven by three main factors: temperature, pressure and cationic size, since a pressure decrease causes the stabilization of the B form [9, 21], the substitution of $Nd^{3+}$ by a smaller cation as $Gd^{3+}$, acting like a decrease of an external applied pressure, promotes the B type arrangement of the atoms. On the other side of the diagram, the substitution of $Gd^{3+}$ by $Nd^{3+}$ behaves in the opposite way widening the C field.

It is noteworthy that for $x$=0.5, where the Gd/Nd average cationic radius is as large as that corresponding to $Sm^{3+}$ ion (1.100 and 1.098 Å, respectively), the transition temperature between the C and C+B fields, around 850°C, is very close to that reported for the transition C/B for $Sm_2O_3$ (875°C) [9], indicating that the average ionic radius plays an essential role in the phase stability of these systems.

### *C-type $Nd_2O_3$*

The thermodynamic stability of C-type $Nd_2O_3$ is a controversial point in literature: even though the transition C→B or C→A occurs at gradually lower temperatures moving from heavier to lighter rare earths [22], the C field is reported to extend from Nd to Lu oxide [11], and in fact several authors report on the successful synthesis of C-$Nd_2O_3$ [23–26]. For example, recently Tong and Eyring [13] reported a TEM study of the in situ thermal decomposition of $Nd(OH)_3$ into C-type $Nd_2O_3$ at about 450°C. Nevertheless, some works question $Nd_2O_3$ thermodynamic stability, stating that it could be metastable [8, 27] or stabilized by impurities, such as $CO_2$ or $H_2O$ [28]. In order to determine its thermodynamic stability in the range 550–600°C and whether it is stabilized by the presence of $H_2O$ or $CO_2$, the following test has been performed.

$Nd(OH)_3$ powders have been heated in air in a quartz tube at 550°C for three days. The obtained sample consists of $Nd_2O_3{\cdot}0.3H_2O$, as calculated by the observed mass loss, and the X-ray analysis shows that it belongs to the C form. To investigate whether the C phase is stabilized by the presence of water, the sample has been reheated at 550°C in flowing $O_2$ to ensure the removal of water. A sample of anhydrous $Nd_2O_3$ has been obtained and its diffraction pattern, reported

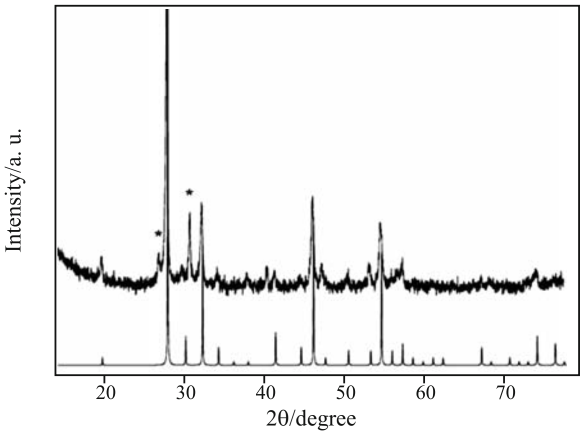

**Fig. 3** $Nd_2O_3$ experimental and theoretical C-type XRD patterns. * – two A-phase main peaks

in Fig. 3 shows the C-type peaks, as well as the two A phase main peaks as a minor impurity.

The same thermal treatment performed on $Nd_2[C_2O_4]_3 \cdot 10H_2O$ resulted in a C-type $Nd_2O_3$, confirming that $Nd_2O_3$ is stable at 550°C in the C form without retaining $H_2O$ or $CO_2$.

## Conclusions

The pseudobinary phase diagram of the system $Gd_2O_3$–$Nd_2O_3$ has been studied in the range 550–1350°C by X-ray diffraction. The samples have been prepared by thermal decomposition of mixed oxalates at different temperatures and for different times, in order to ensure the reaction completion.

In the range 600–1250°C three monophasic and two biphasic regions can be observed, while above 1250°C only the A, B and A+B fields are present.

The existence of $Nd_2O_3$ in the C form has been proved: by the analysis of the experimental results it is possible to conclude that the $Nd_2O_3$ C form is not stabilized by the presence of $H_2O$ or $CO_2$.

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