

Study of the formation temperature of mixed LaREO₃ (RE ≡ Dy, Ho, Er, Tm, Yb, Lu) and NdGdO₃ oxides

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Abstract Mixed LaREO₃ (RE ≡ Dy, Ho, Er, Tm, Yb, Lu) and NdGdO₃ oxides were prepared by thermal decomposition of the corresponding co-precipitated mixed oxalates. The decomposition of La/RE and Nd/Gd oxalates was studied by means of differential thermal analysis and thermogravimetric (DTA-TG) measurements; in particular the last step, consisting of the loss of a CO₂ molecule from the corresponding oxycarbonate, has been thoroughly investigated, as it is particularly interesting for the study of the formation temperature of mixed rare earth oxides. After the release of CO₂, the oxides crystallize in a distorted perovskitic cell or one of the structures typical of rare earth sesquioxides, depending on the cationic size difference and on the average cationic radius. The mixed rare earth oxycarbonate decomposition has been studied in comparison to the decomposition of single rare earth oxycarbonates. A trend of the mixed oxides formation temperature as a function both of the average cationic size and of the cationic sizes difference has been observed and compared to the behaviour of single rare earth oxides.

Keywords Thermal analysis · Phase stability · Rare earths oxides · Perovskites · Rare earths oxycarbonates

Introduction

Rare earth (RE) mixed oxides constitute a wide and very important class of materials, as their technological significance is huge in several fields, for optical [1–5] and superconductive applications [6], as well as for solid oxide fuel cells [7, 8]. A particular family of materials belonging to the group of RE mixed oxides is formed by intra RE perovskites with formula LaREO₃; they could potentially act as hosts for luminescent ions or undergo an insulating-conductor transition by introduction of another rare earth or a transition metal at the RE site; nevertheless, only few studies [9, 10] report on their synthesis, characterization and stability.

Rare earth (RE) mixed oxides can be obtained by various synthetic methods, such as solid state reaction of individual oxides [11], splat cooling [12], melting and subsequent annealing of the oxides [13], citrates [14], mixed hydroxides [13] or oxalate [6] precipitation. The choice of co-precipitation followed by thermal decomposition proves to be particularly advantageous, as it permits avoiding high temperature thermal treatments in order to obtain a high homogenization degree and to study the stability field of the system also at low temperatures.

The study of the mixed oxalate decomposition shows that the last step of the process involves the loss of one CO₂ molecule from the corresponding oxycarbonate RE^IRE^{II}O₂CO₃. Oxycarbonates can crystallize in three different structural types [15, 16], namely in the tetragonal (I), monoclinic (Ia) and hexagonal (II) types, depending on the rare earth size and on temperature [17]; the hexagonal structure forms at higher temperature than the others and is the most stable of the three. The formation temperature of the hexagonal form depends on the rare earth, as it increases with the atomic number [15].

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Below 2000 °C, rare earth sesquioxides crystallize in one of the three following possible polymorphic forms: A (hexagonal), B (monoclinic) and C (cubic) [18], depending on the rare earth ionic radius and on temperature; with increasing temperature and ionic size the structural forms appear in the order: C → B → A. At sufficiently low temperature, all the rare earths sesquioxides have been reported to crystallize in the C form, although some of them (from La₂O₃ to Nd₂O₃) could be metastable. The structural type of mixed oxides depends on the structure of the individual sesquioxides, on the size difference between the two rare earths and on temperature: monophasic (A, B or C) as well as biphasic (A + B or B + C) regions can appear in the phase diagram of each RE₂O₃/RE'₂O₃ pseudobinary system, depending on the structural form of the parent compounds [19]. If the size difference between the two rare earths is large enough to satisfy the Goldschmidt tolerance factor t [20], the perovskitic structural form appears around the equimolar composition. For a generic perovskite ABO₃, the t factor is defined as $(R_A + R_O)/\sqrt{2}(R_B + R_O)$; its value can vary between 1 and 0.75, where 1 represents the ideal cubic case and 0.75 the lower boundary of phase stability. The closer to 0.75 is the t value, the more pronounced is the orthorhombic distortion of the perovskitic structure and the wider is the perovskitic stability field as a function of temperature [21].

In this work, we undertook a study of the decomposition of mixed oxalates in order to investigate the formation temperature of some mixed oxides with RE'/RE'' equimolar proportions compared to the one of single RE oxides. A relation between the formation temperature of the resulting oxide, its crystal structure and the ionic size difference between the two RE has been observed. This result may be useful in predicting the stability of perovskitic phases where one of the two rare earths is partially substituted by another ion and to obtain new insight into the knowledge of existence fields of the starting oxycarbonates structures.

Experimental

LaRE(C₂O₄)₃· n H₂O (RE = Dy, Ho, Er, Tm, Yb, Lu) and NdGd(C₂O₄)₃· n H₂O samples were prepared by co-precipitation, as described in [6], starting from the commercial sesquioxides powders. The oxalate decomposition was studied by DTA-TG by means of a NETZSCH 408 thermal analyser. The measurements consisted of a heating step from room temperature up to 1100 °C at 5 °C min⁻¹ in flowing oxygen (100 cm³ min⁻¹), followed by an isothermal plateau lasting 1 h and then by cooling down to room temperature.

To study the occurrence of the different crystal structures of the oxides, the co-precipitated mixed oxalates were

dried at 80 °C for 24 h and successively decomposed in air at the different decomposition temperatures. The structure of the so obtained oxides was investigated by X-ray powder diffraction, using a Philips PW1830 diffractometer (Cu-K_α radiation) in the range 10° ≤ 2θ ≤ 80°.

Results and discussion

In Fig. 1, the thermogram performed on La/Dy oxalate is reported; it can be explained analogously to the thermal analyses performed on Nd/Gd oxalates and described in [22]. Like in all the DTA-TG measurements carried out on La/RE oxalates, at this heating rate the decomposition starts just above 200 °C with an endothermic peak due to the loss of some hydration molecules. Around 400 and 600 °C two exothermic peaks appear and from the TG curve it can be inferred that three CO and two CO₂ molecules are released; these signals are related to the transformation of the anhydrous oxalate into the oxycarbonate. The last peak is endothermic and located at temperatures ranging from 810 to 1020 °C, depending on RE: it refers to the loss of the last CO₂ molecule from the oxycarbonate and to the formation of the mixed oxide.

As described, the last step in the oxalates decomposition refers to the formation of the oxide from the oxycarbonate through the loss of one CO₂ molecule. Figure 2 shows the trend of the decomposition temperature of single RE oxycarbonates, adapted from [15]. It can be seen that the smallest RE crystallize in the tetragonal (I) and the biggest ones in the hexagonal (II) form of the oxycarbonates, while RE characterized by an intermediate value of the ionic size can present both structures. Besides, the decomposition temperature increases linearly with the ionic size, notwithstanding the structural form of the starting oxycarbonate. All the oxycarbonates are reported to decompose into the oxide C structure, except La₂O₃, Pr₂O₃ and Nd₂O₃, that crystallize in the A form.

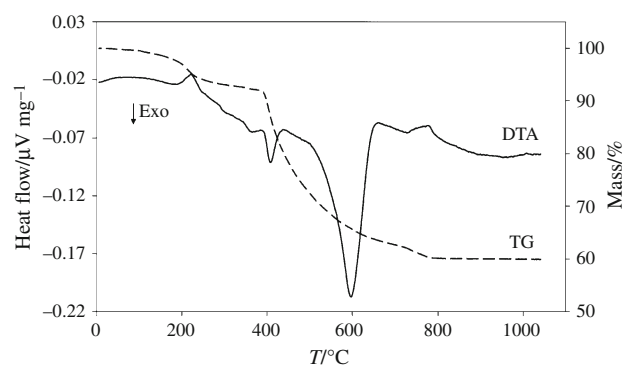


Fig. 1 DTA (continuous line) and TG (dotted line) curves for La/Dy oxalate

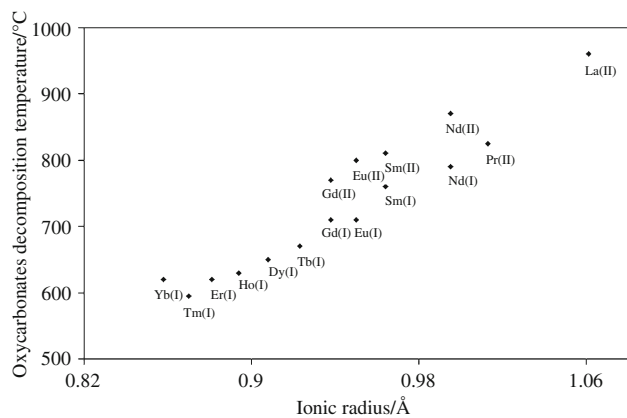


Fig. 2 Decomposition temperatures of single rare earths oxycarbonates as a function of cationic radius (adapted from Turcotte et al. [15])

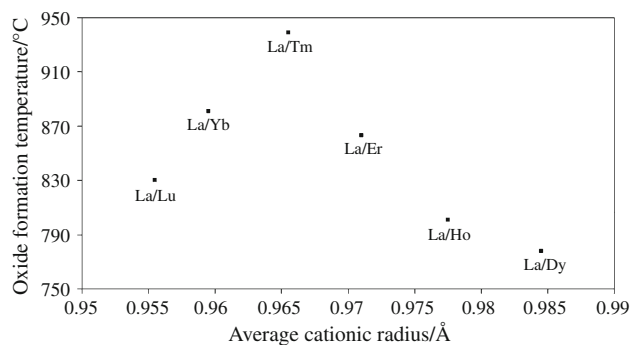


Fig. 3 Formation temperatures of La/RE oxides as a function of average cationic radius

The trend of the mixed oxides formation temperature as a function of the average ionic radius is reported in Fig. 3. Two behaviours can be recognized in the diagram, as the formation temperature increases from RE \equiv Lu to RE \equiv Tm through RE \equiv Yb and decreases when the RE ionic radius further increases, meaning that the formation temperature does not depend only on the average ionic radius. From RE \equiv Lu to RE \equiv Tm the oxycarbonate changes directly into the perovskitic form as soon as the CO₂ molecule is released, so it is possible to infer that the transformation temperature is driven by the perovskite formation for LaLuO₂CO₃, LaYbO₂CO₃ and LaTmO₂CO₃; as can be seen in Table 1, where the Goldschmidt factor is reported for LaLuO₃, LaYbO₃ and LaTmO₃, the t values, and as a consequence the perovskitic stability, decrease when the RE ionic size increases; correspondingly, as shown in Fig. 4, the perovskitic formation temperature increases, meaning that the less stable is the phase, the more energy it requires to be formed. By this argument it is possible to predict that for larger RE ionic sizes the formation of the perovskitic phase should take place at higher temperatures; this evidence could be observed thermally

Table 1 t values for LaLuO₃, LaYbO₃ and LaTmO₃

Sample	t
LaTmO ₃	0.8560
LaYbO ₃	0.8605
LaLuO ₃	0.8632

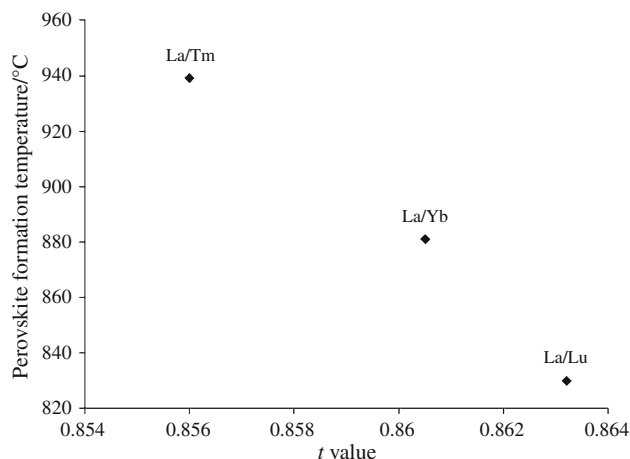


Fig. 4 Formation temperatures of La/RE perovskitic oxides as a function of t

treating La/Er and La/Ho oxalates: in the first case the perovskitic structure appears as a single phase at 1000 °C, while LaHoO₃ crystallizes in the perovskitic structure (accompanied by a small amount of the B form) at 1100 °C [21]. This result also suggests that LaDyO₃ could show the perovskitic structure if treated at sufficiently high temperature, although it can not be excluded that the compound does not crystallize in this structure at all, notwithstanding the treatment temperature.

For RE³⁺ larger than Tm³⁺, the LaREO₃ compounds crystallize in the C or in the B form when the oxycarbonates decompose, and in the perovskitic form only at higher temperatures. By the calculation of the average cationic size, it has been verified that these compounds crystallize in the same crystal structure as the single RE oxides with similar ionic size. For this reason, if the formation temperature of mixed oxides was driven only by the ionic size, it should be expected to follow the trend shown in Fig. 2 as a function of the average ionic radius, analogously to what happens for single RE oxides. The trend displayed in Fig. 3 shows that from RE \equiv Er to RE \equiv Dy the mixed oxide formation temperature decreases, contrary to the behaviour of single RE sesquioxides reported in Fig. 2. This phenomenon can be explained by taking into account the ionic size difference between La and RE. It is well known that RE sesquioxides can host at the RE site another lanthanide ion preserving their structural form, up

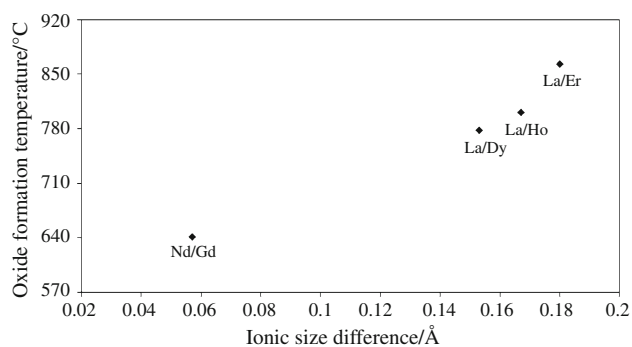


Fig. 5 Formation temperatures of La/RE oxides with B or C structure as a function of the cationic size difference

to a concentration that is inversely proportional to the size difference between the two cations: the bigger is the size difference, the stronger is the structural strain due to the mismatch between the lanthanides and the most limited is the stability extent of the solid solution. Considering this evidence, it appears reasonable to suppose that a stronger mismatch between the lanthanides leads to a higher energy request for the structure formation. In order to verify this hypothesis, the formation temperature of NdGdO_3 was studied, this compound being characterized by a smaller ionic difference than the oxides belonging to the La/RE series. From the decomposition of $\text{NdGd}(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ it was observed that the mixed oxide forms at a significantly lower temperature than the La/RE mixed oxides previously described. The diagram of the formation temperature versus the ionic size difference for La/RE oxides (from RE \equiv Er to Dy) and NdGdO_3 is shown in Fig. 5, where a direct relationship between structural strain and formation temperature can be observed. This evidence confirms that in mixed oxides with B and C structure the average ionic radius determines the crystal structure, but the formation temperature is driven by the cationic size difference.

Conclusions

The behaviour of the formation temperature of mixed La/RE (RE \equiv Dy, Ho, Er, Tm, Yb, Lu) and Nd/Gd oxides with cationic equimolar composition was studied by decomposition of the corresponding mixed oxalates. Two different trends of the formation temperature versus the average ionic radius have been detected for the oxides that crystallize in the perovskitic structure and in the B or C structure, respectively. Taking into account that the Goldschmidt t value (for perovskitic oxides) and the cationic size difference (for oxides with B or C structure) are indicators of the structural strain, and as a consequence of the structural stability, a close relation between oxide formation temperature and structural stability of the phases

can explain in both cases the evidences observed: the oxide formation temperature decreases in fact when the perovskitic t factor increases and when the cationic size difference diminishes, i.e. when the structure becomes more stable.

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