Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 1, 207–211

THERMAL DECOMPOSITION OF MIXED Ce AND Gd OXALATES AND THERMAL PROPERTIES OF MIXED Ce AND Gd OXIDES

A. Ubaldini[1], *C. Artini*[1], *G. A. Costa*[1*], *M. M. Carnasciali*[2] *and R. Masini*[3]

[1]INFM and DCCI, Via Dodecaneso 31, 16146 Genova, Italy
[2]INSTM and DCCI, Via Dodecaneso 31, 16146 Genova, Italy
[3]CNR–IMEM, Via Dodecaneso 33, 16146 Genova, Italy

The aim of the present work is to study the thermal decomposition of the mixed oxalates $(Ce_{1-x}Gd_x)_2(C_2O_4)_3\cdot nH_2O$. The mechanisms of decomposition of Ce and Gd oxalate are different, and mixed oxalates behave in an intermediate way. Their dehydration stages are more similar to those of Gd oxalate, as not all the molecules of water are equivalent like the cerium oxalate. The decomposition leads to $(Ce_{1-x}Gd_x)O_{2-x/2}$. For x close to 0 or to 1 two solid solutions exist, while for the central composition, the presence of a biphasic region can not be excluded.

Keywords: *rare earths mixed oxide, thermal decomposition*

Introduction

Solid oxides fuel cells (SOFCs) have been studied intensely because of their great technological interest; they have a high energy conversion and a very low emission of pollutants in the environment [1]. SOCFs are composed by inteconnectors, anode, cathode and of course by a solid electrolyte, generally an oxide with high ionic conductivity. One of the most known and used is the yttria stabilised zirconia (YSZ) for its excellent properties. Unfortunately it requires very high operating temperatures, about 1000°C [2, 3]. Extensive researches were performed to seek alternative materials requiring lower temperatures. Ceria doped by trivalent rare earth elements is considered as one of most promising materials as electrolyte, because of its high ionic conductivity at relatively low temperature (500 to 700°C) [2–5]. The substitution of cerium by a heterovalent cation leads to the formation of vacancies in the oxygen sublattice that keep the electroneutrality of the system; the high conductivity is due to the high mobility of the vacancies. Gd is considered one of the most effective dopants [6, 7] because of the closeness of the ionic radius of Gd^{3+} to that of Ce^{4+}, leading to large fields of existence of solid solutions [7–10]. However, there is not a perfect agreement about the wideness of these solid solutions. Grover *et al*. [10] reported that for $0.5 \leq x \leq 1$ the C-type structure exists, while for $0 \leq x < 0.5$ the fluorite structure exists. On the contrary, Tianshu *et al*. [7] and Ikuma *et al*. [8] reported that the solubility of Gd in the CeO_2 is smaller and that the solid solution exists if $x < 0.3$, then a biphasic region appears.

The mixed Ce–Gd oxides are generally produced by a coprecipitation method, a synthetic route which offers an easy way to obtain homogenous samples [8, 9]. An intermediate, normally an oxalate, is prepared adding a precipitating agent to a solution of the two cations. Then the mixed oxide is obtained from the thermal decomposition of the oxalate [7].

The aim of the present work is to present a discussion on the thermal decomposition of the mixed Ce–Gd oxalates into the correspondent oxides. In particular, compositions close to 50% were studied in order to report some results on the stability and the structure of the oxides in the critical part of the diagram.

Experimental

All the $(Ce_{1-x}Gd_x)_2(C_2O_4)_3\cdot nH_2O$ samples were prepared by a coprecipitation method, starting from commercial Ce and Gd_2O_3 (Aldrich, 99.99%). They were weighed in the wished amounts in order to have a ratio between Ce and Gd (x) equal to 0, 0.4, 0.5, 0.7 and 1. Two solutions were prepared using a slight excess of HCl (10% m/V) and mixed. The precipitation of a mixed oxalate was achieved rapidly adding to the solution of the two cations a solution of oxalic acid previously prepared. An excess of oxalic acid was used to ensure a complete precipitation and to avoid any possible concentration gradient. The precipitate was filtered and washed with deionized water; it was then dried in air at 80°C for 24 h. It was analysed by SEM–EDAX in order to observe the particles dimensions, shape and composition. The purity of the samples and the struc-

---

[*] Author for correspondence: Costa@chimica.unige.it

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

ture of the mixed oxides were checked by room temperature X-ray diffraction using a Philips PW 1830 diffractometer. Thermal decomposition data were collected by means of a Netzsch STA 409 thermal analyser: the samples were heated to 1000°C at 5°C min^{-1} in flowing oxygen or air. The mass of samples was about 100 mg.

Results and discussion

Oxalates characterisation

XRD analysis shows that mixed oxalates of Ce and Gd are crystalline (Fig. 1). Their XRD pattern is very similar to those of other $RE_2(C_2O_4)_3 \cdot 10H_2O$ and all peaks can be indexed assuming that they crystallise in the monoclinic system with space group $P2_{1/c}$ [11]. The reported lattice constants for Gd oxalate (a=11.04 Å, b=9.63 Å, c=10.09 Å, β=114.10°) [11] are very close to the calculated ones (a=11.02 Å, b=9.64 Å, c=10.043 Å, β=113.70°).

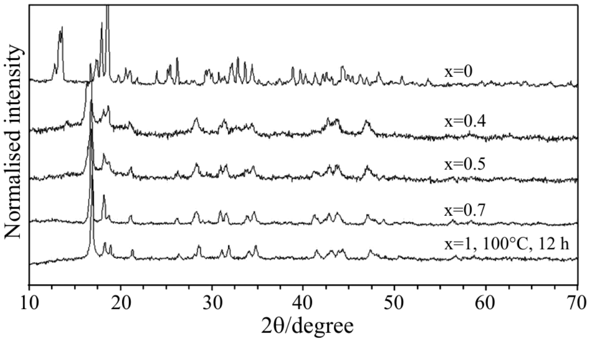

Fig. 1 XRD patterns of mixed Ce–Gd oxalate

Cerium can exist in two different oxidation states, namely Ce^{4+} and Ce^{3+}. The XRD pattern of the cerium oxalate is very similar to that one of Gd oxalate and the observed mass variation between 25 and 1000°C (52.02%) is very close to the theoretical mass variation due to the transformation of Ce oxalate decahydrate into CeO_2 (52.48%). The result of the precipitation with oxalic acid is $Ce_2(C_2O_4)_3 \cdot 10H_2O$. The cell parameters ($a$=11.26 Å, b=9.68 Å, c=10.41 Å, β=114.36°) are greater than those of Gd oxalate, in agreement with the fact that Ce^{3+} is larger than Gd^{3+}. SEM–EDAX analyses, performed on the Ce–Gd oxalates, have shown that the average composition of the precipitates is very close to the nominal one: the experimental Ce percentage, determined in many points of 5×5 μm^2 randomly selected, for the oxalates with x=0.4, 0.5, 0.7 was 63.2, 50.9 and 31.0%, respectively.

The XRD patterns of the $(Ce_{1-x}Gd_x)_2(C_2O_4)_3 \cdot nH_2O$ samples are different from those of decahydrated RE oxalate, but similar to the XRD pattern of Gd oxalate kept at 100°C 12 h. On the basis of the mass variation, it results that the latter releases two molecules of water, becoming $Gd_2(C_2O_4)_3 \cdot 8H_2O$. It is possible that during the drying stage of the preparation the mixed oxalates lose several molecules of water and that the hydration from the environment is a slow process. Therefore, the initial amount of water in these samples is lower than 10.

Thermal decomposition of oxalates

Figures 2a and b show the DTA-TG analysis of the oxalates with x=0.4, 0.5 and 0.7 performed in oxygen; heating rate equal to 5°C min^{-1}.

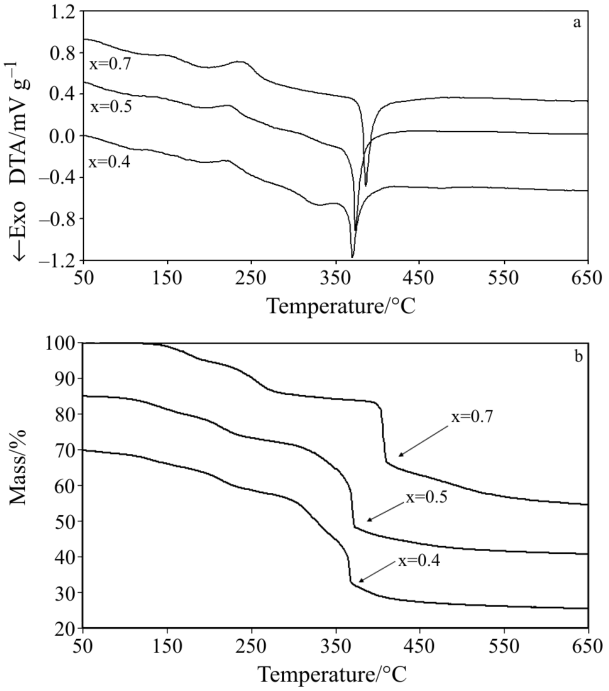

Fig. 2 a – DTA and b – TG analysis performed on mixed Ce–Gd oxalates in O_2 (DTA and TG curves are shifted for clarity)

For x=0, two DTA peaks are present, to which two steps in the TG curve are associated. The former is endothermic, presents the onset at about 100 and the maximum at 134°C. In correspondence of this peak there is a mass diminution equal to the calculated one for the complete release of water. In other words, the anhydrous Ce(III) oxalate forms in this range of temperature [12]. The second peak is a very high exothermic peak whose onset is at 275°C and the maximum at 295°C. In this stage there is the complete conversion of the initial oxalate into CeO_2, as the total experimental mass loss is 52.12%, close to the theoretical one (52.48%).

The case of the Gd oxalate is more complex, as in this case the molecules of water are not equivalent as the dehydration leading to the anhydrous Gd oxalate occurs in many passages, partially overlapped. From room temperature to around 100°C there is a continuous mass decreasing of about the 4.3%, i.e. close to the calculated mass variation (4.73%) for the loss of two molecules of water. After this, there are three endothermic DTA signals. The first has the onset at around 100 and the maximum at 115°C. The second DTA peak has the onset at 155 and the maximum at 169°C and the mass release between 25 and 200°C is 18.5%, i.e. similar to that one associated to the transformation $Gd_2(C_2O_4)_3{\cdot}10H_2O{\rightarrow}Gd_2(C_2O_4)_3{\cdot}2H_2O$ (18.73%). Finally, the last peak presents T_{onset} 200°C and T_{max} at 222°C. During this step the total loss of water occurs, as the experimental mass variation between 25 and 300°C is 23.5%, while the theoretical one is the 23.7%. The $Gd_2(C_2O_4)_3$ is stable in a narrow range of temperatures, between about 300 and 390°C. Moreover, the sample mass slight decreases even in this temperature range, meaning that the decomposition is a continuous process. From about 390 to 550°C there is a great mass loss, very similar to the expected one for the transformation of the sample into the oxocarbonate $Gd_2O_2(CO)_3$. In this interval there are two exothermic DTA signals, the former at about 415°C, the latter, the most intense, at 520°C, and it should be noticed that the slope of the TG curve is not constant. According to a previous work [13], it results that the decomposition of $Gd_2(C_2O_4)_3$ passes initially through the formation of $Gd_2O_2(CO)_3$ and $Gd_2(CO_3)_3$. Finally there is a small endothermic process at about 575°C, where the formation of Gd_2O_3 occurs.

In the case of the mixed oxalates the decomposition is completed below 600°C. The observed total mass losses between 25 and 700°C for the samples with x=0.4, 0.5, 0.7 are, respectively, 45.32, 44.48 and 45.43%. In the presence of oxygen the Ce–Gd oxalates convert into $(Ce_{1-x}Gd_x)O_{2-x/2}$ following this general mechanism:

$$(Ce_{1-x}Gd_x)_2(C_2O_4)_3{\cdot}nH_2O + (2-x/2)O_2\rightarrow 2(Ce_{1-x}Gd_x)O_{2-x/2} + 6CO_2 + nH_2O \tag{1}$$

The observed mass variations are close to the calculated ones assuming n=4, being for x=0.4, 0.5, 0.7, respectively, 44.20, 44.79 and 45.38%. Probably the equilibrium value of n is 10 [10] like in the pure oxalates of Ce and Gd, but it seems that these sample form with a lower amount of water. The substitution of Ce by Gd makes the molecules of water not equivalent. Instead of a single stage during which all the water is released as for the Ce oxalate, more steps are observed. In the case of the sample with x=0.4, there is a small endothermic peak at 128°C and the sample mass changes between 25 and 170°C of about 5.25%, i.e. a quantity close to the theoretical variation due to the loss of two molecules of water (5.71%). Then there is a second endothermic peak with onset at 200 and the maximum at 218°C. The mass variation (11.49%) is almost equal to theoretical one due the complete release of water (11.43 %). These two steps are present also in the other case, but their temperature increases as the Gd content increases. The first peak has for x=0.5 and 0.7 the maximum at 137 and 144°C, respectively, while for the second one the maximum shifts to 222 and 231°C. Moreover, the area of the second peak increases. The behaviour of the anhydrous mixed oxalates is complex, and different solid intermediate phases can form. For x=0.4 and 0.5 two exothermic signals can be noticed, while for x=0.7 the former is almost absent. For the first signal T_{onset} (310°C for x=0.4 and 330°C for x=0.5) and its T_{max} (330°C for x=0.4 and 340°C for x=0.5) increase as a function of x, as a possible consequence of the fact that Gd is heavier than Ce. Moreover, its area decreases for Gd rich samples. The second peak is the most intense and analogously to the former, it is observed at higher temperatures as the Gd content increases. The sample mass decreases reaching the final mass in a complex way. For x=0.4 the sample mass is almost constant between 235 and 300°C, then between 300 and 360°C, there is a continuous mass decrease equal to 15%. Then, in a very narrow interval, between 360 (the onset of the most intense exothermic DTA peak) and 373°C, there is a mass release equal to 8%. At the end of the DTA signal the sample decomposition is almost complete. For x=0.7, on the contrary the sample mass is almost constant until the T_{onset} of the DTA peak, about 370°C. Between 370 and 390°C the sample loses 18% of its mass. Then the slope of TG curve decreases and the sample reaches slowly its final mass. The oxalate with x=0.5 behaves in an intermediate way. These results can indicate that the decomposition follows a different route changing the value of x. In any case, it seems very probable that during the decomposition several solid intermediates can form. Further analyses are required in order to determine their nature and to present a rigorous decomposition path.

The partial pressures of the gaseous substances involved in the decomposition are an important parameter in the decomposition of RE oxalates, in agreement with the Eq. (1). Figure 3 shows DTA analysis performed on the oxalate with x=0.4 in oxygen and in air.

The total mass loss is almost the same in all the cases. Moreover, the XRD analyses have shown that the final product of the decomposition is the same. The same number of DTA peaks and steps in TG curve can be observed meaning that the same solid intermediate phases form during the decomposition. It is possible to notice that the different atmospheres have not any important effect on the dehydration steps, as it could be expected. Actually, the only gaseous species produced

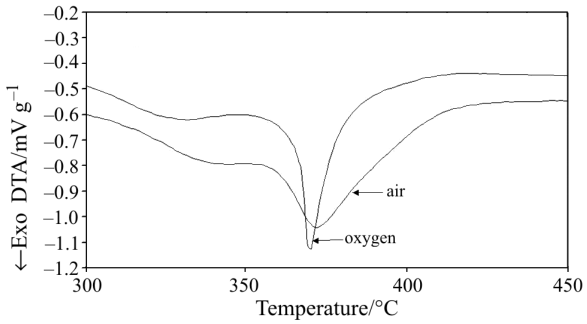

Fig. 3 DTA analysis performed on Ce–Gd oxalate with x=0.4 in O_2 and in air

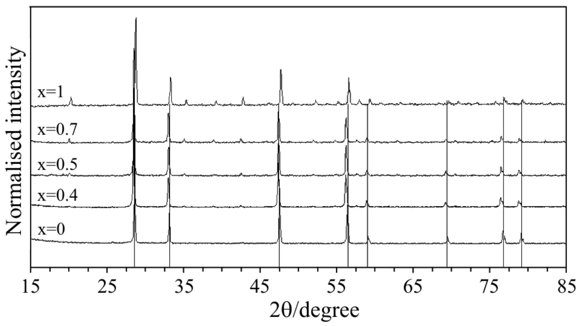

Fig. 4 XRD patterns of the $(Ce_{1-x}Gd_x)O_{2-x/2}$ with x=0, 0.4, 0.5, 0.7 and 1; lines mark the peaks of the F-type structure

during these processes is water and thus the chemical equilibria do not depend on the oxygen partial pressure. On the contrary the peaks due to the decomposition of anhydrous oxalates depend on the oxygen partial pressure. Increasing oxygen partial pressure leads to a decrease of their temperatures. It results that the former one shifts towards slightly higher temperatures in air in comparison to the analysis performed in O_2: the maximum temperatures are at about 340 and 334°C, respectively. For the second process, the difference of temperature in air and in oxygen is smaller, being about 3°C.

Structure of Ce–Gd oxides

CeO_2 is a fluorite-like cubic oxide (F-type), belonging to the spatial group Fm-3m and the metal atoms are eight coordinated. Gd_2O_3 crystallises in a body center cubic structure, called C-type, belonging to the spatial group Ia3. For this structure Z=16 and so there are 32 cations and 48 oxygen atoms in the unit cell. The structure of the C-type RE oxides is formally derived from that of REO_2 oxides (F-type) removing one fourth of the oxygen atoms from this network along nonintersecting strings in the four <111> directions [9, 14]. Every cation is six coordinated [9]. As the structures and the reduced cell volumes of Gd_2O_3 and CeO_2 are very similar, it can be expected that their XRD patterns are also similar. Actually, the main peaks of the diffractogram of Gd_2O_3 are at almost the same angles as those of CeO_2, but in the former many weak reflections are present that do not appear in the latter, as it is possible to observe in Fig. 4.

The results of this work show that for all the intermediate compositions many small peaks exist, which can be referred to the C-structure. It results that the ratio between the areas of these secondary peaks and the main peak increases as function of x.

The main reflection is at about 28° and one of the most intense peaks not present in the pure CeO_2 is at about 43°: the ratio between these peaks for x=0.7, 0.5 and 0.4 decreases, being 0.033, 0.021 and 0.015, respectively. This behaviour is due to the fact that the small peak is due only to C-type $(Ce_{1-x}Gd_x)O_{2-x/2}$ solid solution, while the main peak is due both to the contribution of this phase and of fluorite-type solid solution. However, in no cases the main peaks are divided in two peaks, as it could be expected if the system was formed by two separate phases, namely a Ce saturated C-type solid solution and a Gd saturated F-type one.

This could be due to the fact that this separation can not be instrumentally solved, in our experimental conditions, or to the fact that it does not exist. As a consequence, we can not exclude the presence of a biphasic region or the existence of a superstructure. Several reports exist on the structures of these mixed oxides [7–10]. The authors are in agreement on the fact that for values of x close to 0 a solid solution characterized by the fluorite structure exists, while for x close to 1 a solid solution with C-type structure forms, but some disagreements exist about the range of existence of these solid solutions. It is important to notice that the cell constants reach the greatest value for x close to 0.5, starting from both sides of the diagram, so deviating from the Vegard's law. For x>0.5 this phenomenon can be explained considering that the Ce ionic radius is slightly larger than that of Gd, while for x<0.5 considering that the oxygen content decreases to keep the electroneutrality of the system and so the repulsion force among the cations increases. Considering the presence of the F-phase as well as of the C-phase, the calculated lattice parameters are reported in Table 1. They are in agreement with the values presented in literature independently from the synthesis method [10, 15].

Table 1 Calculated lattice parameters of $(Ce_{1-x}Gd_x)O_{2-x/2}$

x	F-phase	C-phase
0.4	5.430(1) Å	10.860(2) Å
0.5	5.425(3) Å	10.850(5) Å
0.7	5.428(2) Å	10.846(3) Å

Conclusions

Several mixed Ce–Gd oxalates were prepared by a coprecipitation method. The thermal decomposition of these mixed oxalates was studied. All samples are hydrated, but the initial water content can be lower than the equilibrium content. Ce oxalate decahydrated decomposes into CeO_2 following a two steps mechanism, passing through the anhydrous oxalate. The Gd oxalate decomposes according to a more complex mechanism, with many dehydration steps, as not all the molecules of water are equivalent, and through the formation of several intermediates. The substitution of Ce by Gd makes not equivalent the molecules of water. Oxygen partial pressure is an important parameter for the thermal decomposition. In all these cases the decomposition product is $(Ce_{1-x}Gd_x)O_{2-x/2}$. For x close to 0 or to 1 two solid solutions exist and for the central compositions the presence of a biphasic region or the existence of a superstructure can be inferred.

References

1 Y. Okawa and Y. Hirata, J. Eur. Ceram. Soc., 25 (2005) 473.
2 J. Ma, T. Zhang, L. Kong, P. Hing, Y. Leng and S. Chan, J. Eur. Ceram. Soc., 24 (2004) 2641.
3 V. V. Kharton, F. M. B. Marques and A. Atkinson, Solid State Ionics, 174 (2004) 135.
4 J. F. Q. Ray and E. N. S. Muccillo, J. Eur. Ceram. Soc., 24 (2004) 1287.
5 S. Zha, C. Xia and G. Meng, J. Power Sources, 115 (2003) 44.
6 J. Ma, T. S. Zhang, L. B. Kong, P. Hing and S. H. Chan, J. Power Sources, 132 (2004) 71.
7 Z. Tianshu, P. Hing, H. Huang and J. Kilner, Solid State Ionics, 148 (2002) 567.
8 Y. Ikuma, K. Takao, M. Kamiya and E. Shimada, Mater. Sci. Eng. B, 99 (2003) 48.
9 R. G. Haire and L. Eyring, Handbook on the Physics and Chemistry of Rare Earths, Eds K. A. Gschneidner Jr. and L. Eyring, North-Holland Publishing Company, 1994, Vol. 18, p. 413.
10 V. Grover and A. K. Tyagi, Mater. Res. Bull., 39 (2004) 859.
11 A. Elizabeth, C. Joseph, I. Paul, M. A. Ittychen, K. T. Mattew, A. Lonappan and J. Jacob, Mater. Sci. Eng. A, 391 (2005) 43.
12 Y. Altas and H. Tel, J. Nucl. Mater., 298 (2001) 316.
13 G. A. M. Hussein, M. H. Khedr and A. A. Farghali, Colloids Surf. A, 203 (2002) 137.
14 E. Antic-Fidancev, J. Hölsa and M. Lastusaari, J. Alloys Compd., 341 (2002) 82.
15 D. J. M. Bevan and E. Summerville, Handbook on the Physics and Chemistry of Rare Earths, Eds K. A. Gschneidner Jr. and L. Eyring, North-Holland Publishing Company, 1979, Vol. 3, p. 401.

DOI: 10.1007/s10973-005-7209-3