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New X-ray powder diffraction data and Rietveld refinement for Gd_2O_3 monodispersed fine spherical particles

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Abstract

Nominally pure Gd_2O_3 C-form structure from basic carbonate fine spherical particles and its differences concerning the XRD data among literature patterns using Rietveld method is reported. Gd_2O_3:Eu^{3+} from basic carbonate and Gd_2O_3 from oxalate were also investigated. All samples, except the one from oxalate precursor, are narrow sized, 100–200 nm. Only non-doped Gd_2O_3 from basic carbonate presents XRD data with smaller d_{hkl} values than the literature ones. From Rietveld refinement, non-doped Gd_2O_3 from basic carbonate has the smallest crystallite size and from oxalate shows the greatest one. Also, the unit cell parameters indicate a plan contraction of the Gd_2O_3 from basic carbonate. The presence of Eu^{3+} increases crystallite size when basic carbonate precursor is used to prepare Gd_2O_3 and avoids plan contraction. The structural differences observed among Gd_2O_3 samples obtained are related to the type of precursor and to the presence or not of doping ion.

Keywords: Gadolinium oxide; Europium(III); Gd_2O_3:Eu^{3+}; Precursor; Luminescent material; Basic carbonate

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1. Introduction

Gadolinium oxide has been extensively used in many different applications [1–3]. When activated by Eu^{3+} or Nd^{3+}, it is an effective crystal phosphor, presenting cathodoluminescence [4] and laser action [5], respectively. This oxide presents polymorphic forms, denoted as A, B and C classified as being hexagonal, monoclinic and cubic, respectively. The C-form structure cubic bixbyite type is known as the low-temperature form at ordinary pressures [6]. The sesquioxides in general are mainly prepared by the decomposition of some compounds in air or oxygen, and the most commonly used compounds are oxalates and hydroxides [6]. Nevertheless, rare-earth oxides utilizing monodispersed colloidal spheres of the basic carbonates as the starting material have received considerable attention for the formation of dense, oxide ceramic bodies. In the case of luminescent displays, the interest on doped rare-earth oxide phosphors with narrow size distribution, non-agglomeration properties, and spherical morphology for good luminescent characteristics have also been increasing. Therefore, the necessary procedures to prepare the rare-earth basic colloidal spheres have been developed [7,8] and they have been used as precursors for C-form rare-earth oxides at low temperature [9–11]. Gd_2O_3:Eu^{3+} C-form structure phosphor particles with sphericity, submicron size and non-aggregation characteristics by using continuous spray pyrolysis process were reported [12]. The aim of this work is the study on the formation of nominally pure Gd_2O_3 C-form structure obtained from basic carbonate monodispersed fine spherical particles and its differences concerning the X-ray diffractometry data among literature patterns using Rietveld method. Gd_2O_3:Eu^{3+} prepared from spherical basic carbonates and Gd_2O_3 prepared from oxalate, both C-form structures were also investigated.

2. Experimental

Gadolinium and europium oxides (99.9% and 99.99% pure, Aldrich) were used as starting materials. Other chemicals used were grade reagents. Monodispersed

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gadolinium basic carbonates, $GdOHCO_3 \cdot H_2O$, undoped and doped with 1, 2, 3, 4 or 5 at% of europium(III) were prepared and used as precursors for the corresponding oxide samples as described in Ref. [13]. Gd_2O_3 from oxalate was also obtained by heating this precursor at 800°C, during 2 h under static air atmosphere. In this case, oxalate precursor was prepared by heating cation chloride solution at 80–90°C followed by slowly adding of oxalic acid solution (3%) under mechanical stirring.

3. Results and discussion

Compounds prepared from non-doped or europium doped basic carbonates are obtained as a very fine spherical particle powder. The particle size distribution was evaluated by scanning electron microscopy (SEM) as being narrow sized in the range of 100–200 nm, just reported [13]. On the other hand, non-doped Gd_2O_3 prepared from oxalate shows larger particles without regular form.

Conditions for powder data collection are specified in Table 1. In Fig. 1 X-ray diffractograms for non-doped Gd_2O_3 samples obtained from basic carbonate and oxalate precursors are presented as well as for one doped representative sample. Commercial Gd_2O_3 diffractogram is also included in Fig. 1 in order to compare all results. All oxides prepared, as well as the commercial one, give interplanar distances in agreement with Gd_2O_3 C-form structure from Powder Diffraction File PDF 43-1014 [14]. However, non-doped oxide obtained from monodispersed basic carbonate shows smaller d_{hkl} values than the others. In Fig. 1(a) it is possible to observe that the reflection planes of Gd_2O_3 from basic carbonate are all shifted to larger 2θ values than the other oxides. Non-doped oxides from basic carbonate were also prepared varying experimental conditions, like temperature (800°C, 900°C and 950°C), time (4, 15 and 24 h), and atmosphere (argon or static air) of decomposition reaction. Independently on the experimental conditions used, every non-doped Gd_2O_3 from basic carbonate presented similar X-ray powder data with smaller d_{hkl} values than the indexed literature data. Therefore, it is possible to suggest that the structural differences observed on these non-doped samples obtained from basic carbonate may be related to the type of precursor and to the presence or non-presence of doping ion.

Rietveld method was applied mainly in the purpose of evaluating unit cell parameters of all samples. For the refinement the DBWS-9807 program was used [15], which is an upgraded version of DBWS-9411 described by Young et al. [16]. The refinement of all Gd_2O_3 samples were started using the crystal structure model of the C-form of Gd_2O_3 gotten from Powder Diffraction File PDF 43-1014: space group $Ia\bar{3}$, $a = 10.813$, atomic positions for Gd1 in 8*b*, Gd2 in 24*d* with $x = -0.03243$, and O in 48*e* with $x = 0.391$, $y = 0.1518$, and $z = 0.37545$ and isotropic atom displacement $B = 0.25$ (Gd1), $B = 0.21$ (Gd2), and $B = 0.5$ (O). The refinement was performed for unit cell, FWHM parameters and atom position. The atom displacements were fixed in the values of the literature. Final Rietveld refinement parameters are summarized in Table 2 and Fig. 2 shows the Rietveld plots for the cubic C-form of Gd_2O_3 prepared from basic carbonate and from oxalate. In spite of the low quality data ($R_e > 20\%$), it was possible to get reasonable unit cell parameters to observe a significant difference between non-doped sample prepared from basic carbonate and the other ones. The difference concerning FWHM values between doped and non-doped samples were considered only to evaluate differences in the crystallite size. Analyzing

Table 1
Conditions for powder data collection

Radiation type, source	X-ray, Cu
Instrument power	45 kV, 35 mA
Goniometer	SIEMENS D5000 with secondary graphite monochromator
Detector	Scintillator
Divergence slit	2 mm
Receiving slit	0.6 mm
Scattering slit	2 mm
Temperature	25°C
Specimen form	Horizontally packed powder in a diffractometer holder
Range of 2θ	4–70°
Step width	0.02° (2θ)
Measurement time	3 s

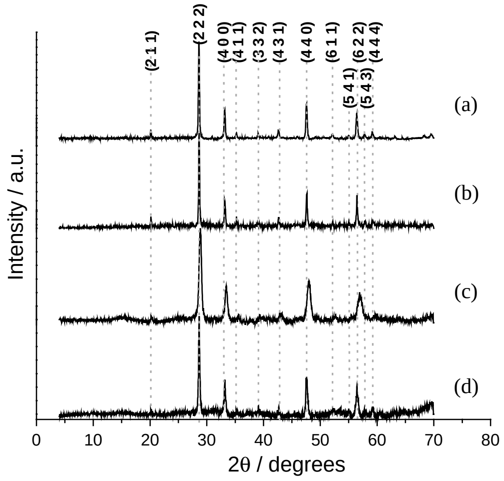

Fig. 1. X-ray diffractograms recorded for (a) commercial Gd_2O_3 (Aldrich 99.99%), non-doped Gd_2O_3 prepared using (b) oxalate and (c) basic carbonate as precursors and (d) $Gd_2O_3:Eu^{3+}$ (5 at%) prepared from basic carbonate.

Table 2
Rietveld refinement parameters and reliability factors [16] of non-doped and europium doped Gd_2O_3 samples prepared

	Gd_2O_3[a]	Gd_2O_3[b]	Gd_2O_3:Eu^{3+} (1 at%)	Gd_2O_3:Eu^{3+} (2 at%)	Gd_2O_3:Eu^{3+} (3 at%)	Gd_2O_3:Eu^{3+} (4 at%)	Gd_2O_3:Eu^{3+} (5 at%)
a (Å)	10.722(4)	10.817(2)	10.820(2)	10.819(4)	10.825(2)	10.820(2)	10.820(3)
V $(Å)^3$	1232.7(8)	1265.6(5)	1266.5(4)	1266.3(9)	1268.3(5)	1266.8(5)	1266.7(5)
d_x (g/cm^3)	7.814	7.610	7.605	7.474	7.594	7.603	7.604
R_P (%)	18.31	29.82	20.60	19.79	17.37	18.77	22.17
R_{WP} (%)	24.97	39.84	27.84	26.20	23.13	25.67	29.32
R_e (%)	21.93	34.49	25.85	22.72	19.63	22.48	26.82
$S = R_{WP}/R_e$	1.14	1.15	1.08	1.15	1.18	1.14	1.09
[c]D–W, d	1.72	1.57	1.76	1.54	1.43	1.79	1.62
Number of obs.	3301	1321	3301	3301	3301	3301	3301
Number of parameters	16	16	16	16	16	16	16

[a] Gd_2O_3 from basic carbonate.
[b] Gd_2O_3 from oxalate.
[c] Durbin–Watson statistic, d [17].

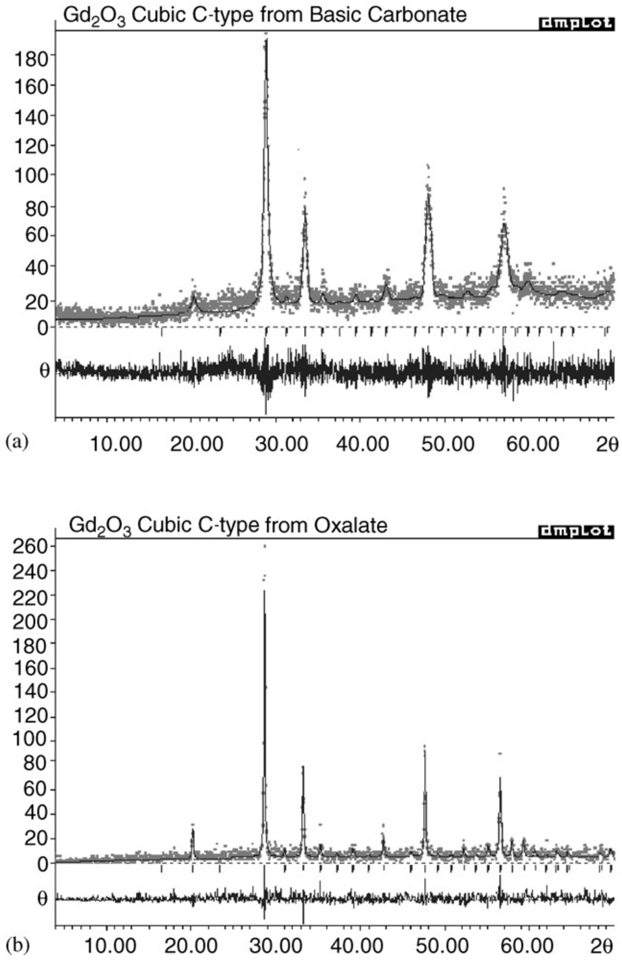

Fig. 2. The final Rietveld plot of non-doped Gd_2O_3 prepared using (a) basic carbonate and (b) oxalate as precursors. Doped oxide samples plots present similar feature as (a). The upper traces illustrates the observed data as dots, and the calculated pattern as solid line; the lower solid trace is a plot of the difference, observed intensity minus calculated one. The vertical markers show positions calculated for Bragg reflections.

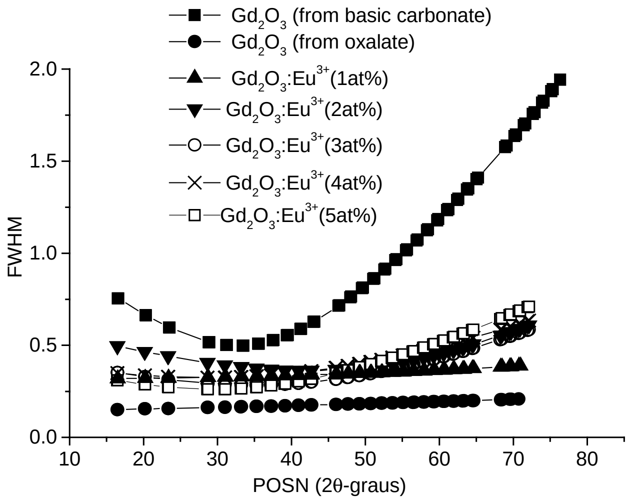

Fig 3. Graphs of HW (half-width) versus POSN (*hkl* positions) obtained from Rietveld refinement for non-doped Gd_2O_3 prepared using basic carbonate and oxalate as precursors and Gd_2O_3:Eu^{3+}(1–5 at%) from basic carbonate.

the graphs represented in Fig. 3, non-doped sample from basic carbonate presents the smallest crystallite size and the non-doped sample from oxalate shows the greatest one. The europium doping ion presence seems to increase the degree of crystallinity when Eu-doped monodispersed basic carbonate precursor is used to prepare Gd_2O_3:Eu^{3+}. It's important to remark that Eu_2O_3 phase is not detected in any Gd_2O_3:Eu^{3+} X-ray patterns. Moreover, from spectroscopic studies, the doping ion distribution in the oxide samples can be considered homogeneous because it is not observed concentration quenching, as well as a significant difference among the calculated lifetime for each sample [13]. Table 2, the unit cell parameters, $\boldsymbol{a}$, $\boldsymbol{V}$ and $\boldsymbol{d_x}$ indicates a unit cell contraction of the non-doped oxide compound obtained from monodispersed basic carbonate precursor. This plan contraction may be related to the degree of crystallinity discussed before. Then, the Gd_2O_3 source, i.e., the preparation method related to the precursor type, must be considered. In Gd_2O_3 prepared from oxalate the X-ray powder data do not present displacement in the interplanar distances and its cell parameters are identical to the literature values indexed. As viewed in Fig. 3, this oxide from oxalate precursor shows the highest degree of crystallinity. The contraction of the atomic plans of the Gd_2O_3 should be dependent on the precursor's precipitation method in terms of the formation mechanism of an oxide with different structural characteristics. Oxides prepared from monodispersed basic carbonates present small particles with high superficial area, and then the surface can contain hydroxide groups that would justify the presence of gadolinium vacancies for the maintenance of the electroneutrality. As hydroxide groups were not detected by IR spectroscopy in the oxide after thermal treatment, the appearance of current nonstoichiometric or lattice point defects must also be considered. Nonstoichiometry is not probable, since the Gd^{3+} ion has a semi-filled configuration and it is not reduced, nor oxidized. The point or lattice defects, on the other hand, can be generated by vacancies or by the presence of impurities in the system. It would be a homogeneous type defect because all the plans suffered displacement. Jollet et al. [18] considered vacancies of oxygen in Y_2O_3, which were only produced after a strong treatment, i.e., by heating the oxide at 1770°C during 2–10 h, which is an experimental condition stronger than the one used in this work. Nevertheless, basic carbonate can present Schott defect, so Gd_2O_3 prepared from this precursor could have a decrease of the interplanar distances due to the presence of cation vacancies, compensated by oxygen vacancies, both probably created during precursor heating. The inclusion of Eu^{3+} doping ion in precursor's precipitation, as being slightly larger than Gd^{3+} ion, can cause an increasing of cell parameters avoiding the plan contraction after precursors heating. Besides that, reduction processes related to Eu^{3+} ion could induce the formation of oxygen vacancies, resulting in a plan contraction. However, this mechanism is less probable because no Eu^{2+} emission can be detected, which is corroborated by the fact that according to X-ray data Eu-doped Gd_2O_3 samples do not present this kind of plan contraction. On the other hand, in the preparation of oxides starting from oxalate decomposition, in spite of the precipitation of this, precursor also can be used for material purification, the process involves a fast nucleation by saturation of the bulk with oxalic acid, generating large particles and possibly dragging another ions in solution. Therefore, during oxalate precursor heating, dragged ions could occupy gadolinium vacancies not allowing plan contraction. Then, based on all results, it is possible to conclude that the structural differences observed on non-doped Gd_2O_3 samples obtained from basic carbonate may be related to the type of precursor and to the presence or non-presence of doping ion.

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References

[1] U. Kolitsch, H.J. Seifert, F. Aldinger, J. Alloys Compd. 257 (1997) 104–114.

[2] I. Koiwa, T. Kanehara, J. Mita, Electron. Commun. Japan Part 2. 79 (8) (1996) 31–40.

[3] G.A.M. Hussein, J. Phys. Chem. 98 (1994) 9657–9664.

[4] A.O. Dmitrienko, I.A. Akmaeva, N.V. Rudneva, A.F. Bol'shakov, Saratov State University, Translated from Izvest. Akad. Nauk SSSR Neorganich. Mater. 27 (5) (1991) 988–991.

[5] A. Brenier, G. Boulon, J. Lumin. 82 (1999) 285–289.

[6] R.G. Haire, L. Eyring, in: K.A. Gschneidner Jr., L. Eyring, G.R. Choppin, G.R. Lander (Eds.) Handbook on the Physics and Chemistry of Rare Earths, Vol. 18, Lanthanides/Actinides: Chemistry, Comparisons of the binary oxides Elsevier Science B.V., North-Holland, 1994, pp. 413–505 (Chapter 125).

[7] E. Matijevic, W.P. Hsu, J. Colloid Interface Sci. 118 (1987) 506–523.

[8] M. Akinc, D. Sordelet, Adv. Ceram. Mater. 2 (3A) (1987) 232–236.

[9] Z.C. Kang, M.J. McKelvy, L. Eyring, Z. Anorg. Allg. Chem. 616 (1992) 125–132.

[10] Z.C. Kang, L. Eyring, J. Alloys Compd. 225 (1995) 190–192.

[11] H.T. Qian, S.K. Ruan, Z.C. Kang, M.Z. Su, Chem. J. Chin. Univ. 16 (5) (1995) 661–665.

[12] Y.C. Kang, S.B. Park, I.W. Lenggoro, K. Okuyama, J. Phys. Chem. Solids 60 (1999) 379–384.

[13] A.M. Pires, M.F. Santos, M.R. Davolos, E.B. Stucchi, The effect of Eu^{3+} ion doping concentration in Gd_2O_3 fine spherical particles, J. Alloys Compd. 344 (2002) 276–279.

[14] Powder Diffraction File PDF-2 database sets 1-44, Pennsylvania Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, copyright 1988, PDG number 43-1014 (CD-ROM).

[15] R.A. Young, Rietveld Analyses Program DBWS-970, copyright 1998, upgrade of the DBWS-9411, upgrade of the DBWS programs for The Rietveld Refinement, J. Appl. Crystallogr. 28 (1995) 366–367.

[16] R.A. Young, D.B. Wiles, J. Appl. Crystallogr. 15 (1982) 430–438.

[17] R.J. Hill, H.D. Flack, J. Appl. Cryst. 20 (1987) 356–361.

[18] F. Jollet, C. Noguera, M. Gautier, N. Thromat, J.-P. Duraud, J. Am. Ceram. Soc. 74 (2) (1991) 358–364.