



Synthesis and characterization of thermoluminescent glass-ceramics $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2:\text{CeO}_2$

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ABSTRACT

Vitroceramic powders of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems (LAS), doped with 1% (LAS:1Ce) and 10% (LAS:10Ce) molar of cerianite (CeO_2) were synthesized by means of the gelification technique of metal formates of aluminum and lithium, in the presence of tetraethoxy silane and CeO_2 . The gels obtained were dried (120 °C, 2.5 h), calcined (480 °C, 5 h) and sinterized (1250 °C, 30 min). The sinterized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and microchemical analysis (EDS). There is evidence for a mixture of two phases of 64% β -spodumene ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$) and 36% β -eucryptite ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$). The LAS:1Ce system was enriched in aluminum, the LAS:10Ce system showed areas of heterogeneous composition; some regions with a shortage of CeO_2 , while others zones with cerium cumulus. From the microscopy images it was found that CeO_2 acts as a densificant agent in LAS system, favoring the sintering in the host. The chemical route and the sintering processes utilized allow the production of samples exhibiting an acceptable linear correlation between total thermoluminescent emission intensity and the irradiation dose when the CeO_2 concentration is low (less than 1%), opening the possibility of using this kind of glass-ceramic in dosimetry.

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1. Introduction

Lithium aluminosilicates, $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, are glass-ceramic systems that have attracted the attention from a technological point of view due to their low coefficient of thermal expansion, their chemical durability and their high thermomechanical resistance. In addition, they have been considered for applications in dosimetry due to their high sensibility and reproducibility in thermoluminescent responses with linear total emission intensity versus irradiation dose relationship for the typical ranges of dose exposition (up to 5 Gy) [1–8]. For dosimetry applications the traditional synthesis route based on oxides melting is inappropriate, because problems arise reaching the desired compositional homogeneity of the final product and, for this reason, to achieve reproducibility of the thermoluminescent response. Therefore, an alternate chemical route of synthesis is necessary. Sol–gel technique has been used to prepare the LiAlSiO_4 and $\text{LiAlSi}_{10}\text{O}_{22}$ compositions using Li_2CO_3 , tetraethy-

lorthosilicate (TEOS , $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to introduce Li, Si and Al, respectively [7]. A special class of sol–gel method is the aqueous sol–gel method or “route of metal formates” [9], where water-soluble metal formates are used as precursors. In this method the replacement of metal alkoxides by metal formates and the use of water as solvent instead of alcohol, which is commonly used as solvent in all alkoxide sol–gel routes, results in the reduction of temperature and cost of the process, generating homogeneous nanometer-sized multicomponent ceramic powders. On the other hand, cerianite, CeO_2 , is a nucleating agent for LAS systems [10], having little influence on thermal expansion, mechanical properties and chemical durability of similar systems [11]. To our knowledge there are no previous reports on the synthesis of CeO_2 -doped LAS systems by the route of metal formates. In the search of new materials for use in dosimetry, in this work we explore the possibility of improving technological properties of LAS doping the material with CeO_2 and carrying out the synthesis by means of the aqueous sol–gel method. The characterization and thermoluminescent behavior of the LAS glass-ceramics undoped and modified with additions of 1% and 10% molar of cerium oxide is reported.

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2. Experimental

Lithium and aluminum formates were obtained by reactions between lithium carbonate (Carlo Erba 98% assay) or aluminum hydroxide (Merck 98% assay), as appropriate, and formic acid (Merck 98% assay) 50%v/v in an excess of the acid (25% of excess for Li_2CO_3 and 50% of excess for $\text{Al}(\text{OH})_3$). The lithium carbonate or the aluminum hydroxide was added to the formic acid in constant stirring (400 rpm) at room temperature. The obtained lithium and aluminum formates were mixed at room temperature and subsequently the cerium oxide (Sigma 99.9% assay) and the tetraethoxy silane were added, TEOS (Merck 98% assay), according to the molar formulations: $1\text{Li}_2\text{O}-1\text{Al}_2\text{O}_3-2\text{SiO}_2-0\text{CeO}_2$ (LAS); $1\text{Li}_2\text{O}-1\text{Al}_2\text{O}_3-2\text{SiO}_2-1\text{CeO}_2$ (LAS:1Ce) and $1\text{Li}_2\text{O}-1\text{Al}_2\text{O}_3-2\text{SiO}_2-10\text{CeO}_2$ (LAS:10Ce), respectively. The 1:1:2 ratio in $1\text{Li}_2\text{O}-1\text{Al}_2\text{O}_3-2\text{SiO}_2$ was used to encourage the formation of β -eucryptite. The pH was kept between 2 and 3 to favor the hydrolysis. The mixture was conserved under constant stirring to achieve appropriate homogenization. After the synthesis, vitreous powders were obtained by means of a low temperature drying process (120 °C during 2.5 h). A particle size distribution (PSD) analysis using a Mastersizer-2000 (Malvern Instruments) was carried out on the powder. Subsequently, the samples were subjected to calcination at 480 °C during 5 h to liberate the organic matter. The samples were sifted (sieve of 20 μm). Particles sized under 20 μm were selected for the preparation of 6 mm of radius and 3 mm of thickness tablets (each of 100 g) by means of uniaxial pressing at 72 Mpa. The sintering process consisted in heating the tablets at 1250 °C for 30 min in an electric furnace stabilized by means of a heating rate of 15 °C/min. The sintered samples were characterized by means of X-ray diffraction (XRD), electronic microscope (SEM), microchemical analysis (EDS) and glow curves generation. The electronic microscopy and the microchemical analysis were carried out with the JEOL and JSM-5910LUV equipments, respectively. The diffractograms were obtained by means of a Rigaku Miniflex diffractometer using a copper source $\text{K}\alpha_1$ $\lambda = 1.54 \text{ \AA}$ to a sweeping rate of 0.5°/min. Irradiations of samples (with doses of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 Gy) were carried out in air at room temperature using a Theratron 780C Co-60 unit at a distance of 80 cm relative to the source, in a radiation field of $10 \times 10 \text{ cm}^2$. The samples were placed between two acrylic plates of 5 mm of thickness, with the purpose of reaching the conditions of electronic equilibrium. For the glow curves generation, we used a commercial Harshaw QS 4500 dosimeter manufactured by Bicorn®. From a pre-heated sample at 50 °C the data acquisition process starts and continues at a heating rate of 10 °C/s until reaching 400 °C. Samples were then annealed at 330 °C. To eliminate the infrared contribution due to the heating and to reduce the moisture effects, all the readings were carried out in an N_2 atmosphere. The emission spectrum shows that the predominant wavelength is in the range of green-yellow TL. The radiation of TL samples is detected by a Hamamatsu photomultiplier tube model R928. The spectral region is 200–650 nm. The data are stored and processed to produce a brightness curve which is plotted as a function of temperature, T .

3. Results and discussion

Table 1 shows the particle size distribution of LAS, LAS:1Ce and LAS:10Ce after heating at 120 °C, 2.5 h. LAS and LAS:10Ce presented a bimodal size distribution being characterized by maxima at 60 and 30 μm , respectively. The gel LAS:1Ce shows the biggest percentage of volume around 40 μm . The previous results indicate that the metal formates route yields fine vitreous powders.

Table 1

Particle size distribution of the dried (120 °C, 2.5 h) gels.

Composition	$d(0.1)^a$ in μm	$d(0.5)^a$ in μm	$d(0.9)$ in μm
LAS	12.677	69.681	316.926
LAS:1Ce	9.565	39.444	173.133
LAS:10Ce	8.269	43.544	276.670

^a The distribution of sizes is reported in accumulated form. For example for LAS, “ $d(0.1)$ ” indicates that 10% of the sample presents smaller or equal sizes than 12.677 μm .

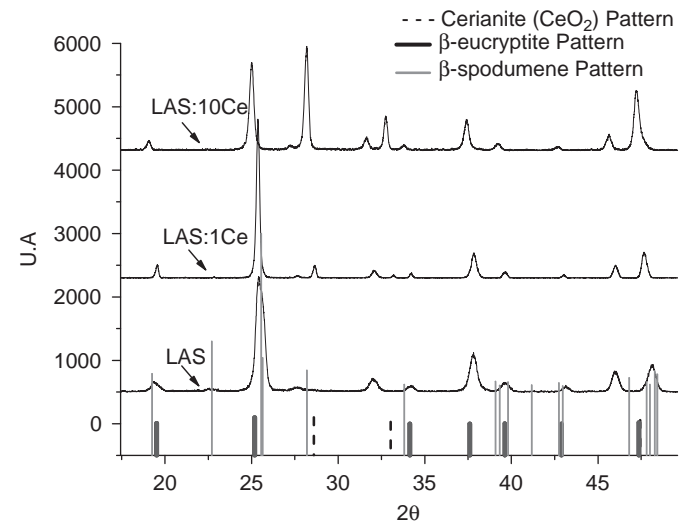


Fig. 1. XRD patterns of the phases present into CeO_2 -doped LAS compositions treated at 1250 °C during 30 min.

Crystalline phase analysis by means of XRD (Fig. 1) revealed the presence of the β -spodumene ($1\text{Li}_2\text{O}-1\text{Al}_2\text{O}_3-4\text{SiO}_2$), β -eucryptite ($1\text{Li}_2\text{O}-1\text{Al}_2\text{O}_3-2\text{SiO}_2$) and of the cerianite structure (CeO_2). It was also observed that the crystallization was not complete, amorphous residual phases remain which confer a glass-ceramic nature to the host. Additionally, the EDS analysis of LAS revealed a molar composition $1\text{Li}_2\text{O}-1\text{Al}_2\text{O}_3-n\text{SiO}_2$ with n between 1.8 and 2.3, results that are in agreement with those obtained by means of XRD. The LAS:1Ce phase showed aluminum enrichment zones (oscillating between 30% and 80%), and the LAS:10Ce phase (Fig. 2) showed heterogeneous compositional areas consisting in some regions lacking rare earth; in areas with the presence of Al, Si and Ce, but exhibiting a deficiency of the rare earth that varied between 30% and 90%, and in regions enriched with cerium, probably the result of a grade of rare-earth segregation. The microstructures of the compacts LAS, LAS:1Ce and LAS:10Ce show that the cerium acts as a densificant agent that promotes sintering.

Glow curves (Fig. 3) were analyzed in terms of the relationship of the total area under the curve (referred to, in this case, as total intensity of emission) versus the absorbed doses (Fig. 4). The LAS phase showed a linear correlation of intensity versus dose while LAS:1Ce showed a nearly linear correlation. The sample LAS:10Ce exhibited a nearly linear behavior in terms of the $\ln(\text{intensity})$ versus dose. Those results show that compositions LAS and LAS:1Ce are viable materials to develop dosimeters and that, as CeO_2 doping concentration increases, the relationship between intensity and dose becomes superlinear. The shapes of the glow curves in Fig. 3 shows the presence of a superposition between individual glow curves, which was previously studied by us by means of deconvolution analysis [12]. A study of possible linearity

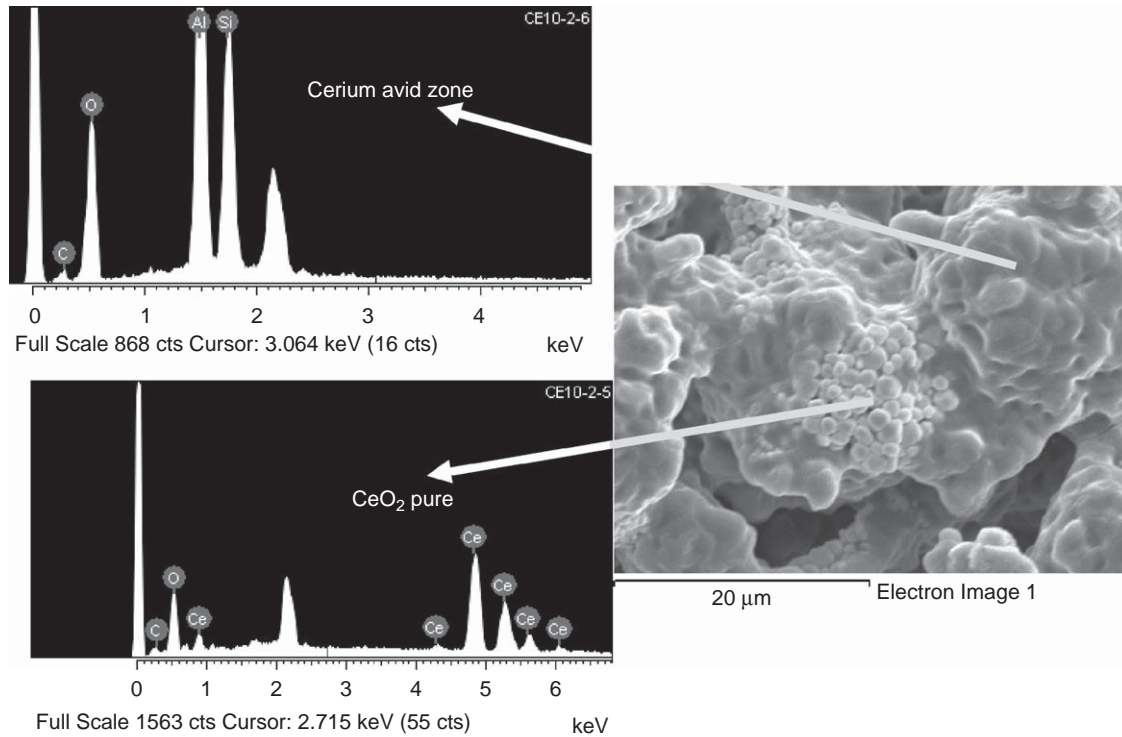


Fig. 2. EDS Analysis on phase LAS:10Ce.

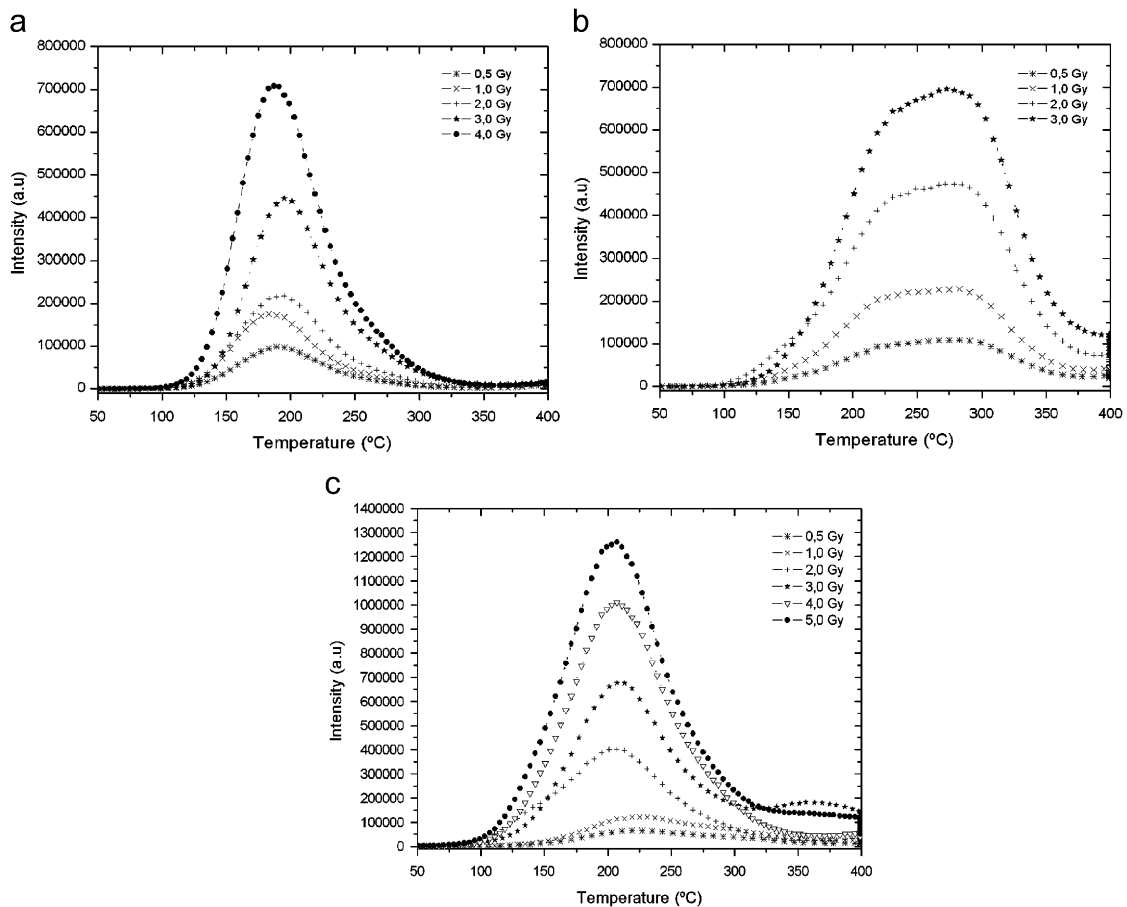


Fig. 3. TL Glow curves between 50 and 400 °C for (a) Li₂O–Al₂O₃–SiO₂, irradiated at 0.5, 1.0, 2.0, 3.0 and 4.0 Gy. (b) Li₂O–Al₂O₃–SiO₂:1%CeO₂, irradiated at 0.5, 1.0, 2.0 and 3.0 Gy. (c) Li₂O–Al₂O₃–SiO₂:10%CeO₂, irradiated at 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 Gy.

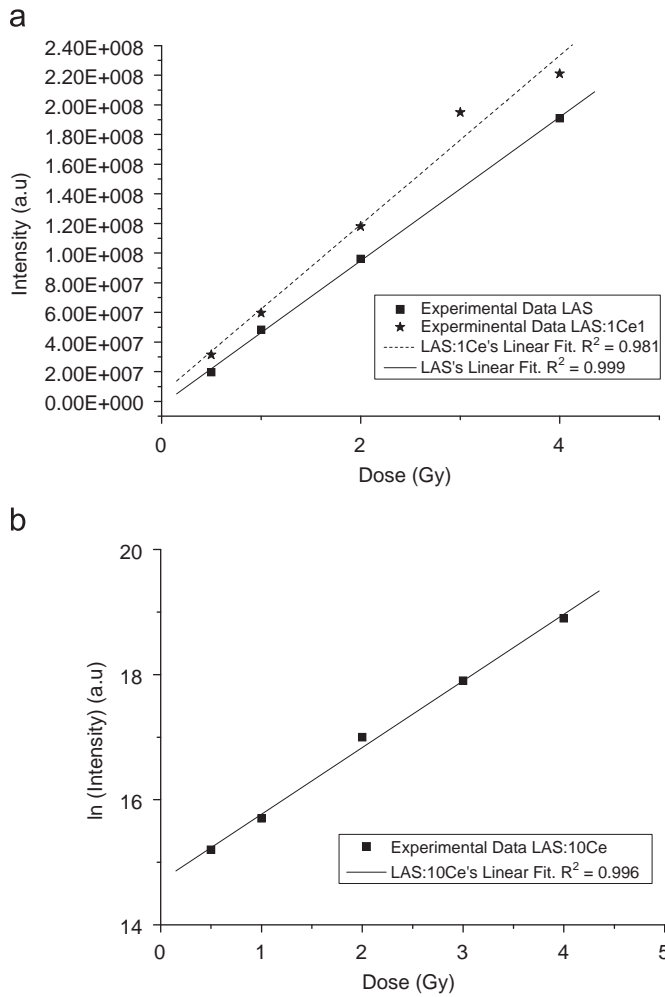


Fig. 4. (a) Relationship intensity versus dose for LAS and LAS:1Ce. (b) Relationship $\ln(\text{intensity})$ versus dose for LAS:10Ce.

of thermoluminescent response versus irradiation dose for the separate signals components is in progress. The results will be published elsewhere.

4. Conclusions

The synthetic route implemented allowed us to obtain amorphous and homogeneous powders useful to produce compacts that, with the sintering processes, stimulate the crystal-

lization of β -spodumene and β -eucryptite in all the samples studied. The electronic microscopy images confirmed that cerium acts as a densificant agent, favoring the sintering processes of the host matrix and improving its technological aptitudes. In the case of high concentration of CeO_2 (samples with 10%), the resulting phases are heterogeneous. Therefore, high CeO_2 concentrations are not recommended for use in dosimetry.

The plots of total thermoluminescent emission versus the absorbed doses show that compositions LAS and LAS:1Ce are viable materials to develop dosimeters and that as CeO_2 doping concentration increases this possibility is less viable. However, it is necessary to carry out additional studies of linear relationships for the individual components of deconvoluted thermoluminescent glow curves. This study is being carried out and will appear elsewhere.

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References

- [1] M.C. Goncalves, L.M. Santos, R.M. Almeida, C.R. Chim. 5 (12) (2002) 845.
- [2] S. Mandal, S. Chakrabarti, S.K. Das, S. Ghatak, Ceram. Int. 33 (2) (2007) 123.
- [3] D.U. Tulyaganov, S. Agathopoulos, H.R. Fernandes, J.M.F. Ferreira, Ceram. Int. 30 (6) (2004) 1023.
- [4] V. Correcher, J. Garcia-Guinea, L. Sánchez-Muñoz, A. Delgado, J. Mater. Process. Technol. 143–144 (2003) 871.
- [5] B.N. Lakshminarasappa, H. Nagabhushana, F. Singh, Nucl. Instrum. Methods B. 244 (1) (2006) 153.
- [6] D.G. Hong, M.J. Kim, J.H. Choi, N.A. El-Faramawy, H.Y. Göksu, Nucl. Instrum. Methods B. 243 (1) (2006) 174.
- [7] V. Correcher, L. Sanchez-Muñoz, J. Garcia-Guinea, J.M. Gomez-Ros, A. Delgado, Nucl. Instrum. Methods A. 562 (1) (2006) 456.
- [8] S.O. Souza, G.M. Ferraz, S. Watanabe, Nucl. Instrum. Methods B. 218 (2004) 259.
- [9] N.N. Ghosh, P. Pramanik, Mater. Sci. Eng. C 16 (2001) 113.
- [10] A.M. Hu, K.M. Liang, F. Zhou, G.L. Wang, F. Peng, Ceram. Int. 31 (1) (2005) 11.
- [11] S.B. Sohn, S.Y. Choi, Y.K. Lee, J. Mater. Sci. 35 (2000) 4815.
- [12] Edison Osorio, et al., J. Lumin. 2009, in press, doi:10.1016/j.jlumin.2008.12.020.