

UDC 535.377:661.883.1

E. Rubio (Puebla, México)

D. Mendoza (Estado de México, México)

V. Rodríguez (Pachuca, Hidalgo, México)

V. M. Castaño* (Santiago de Querétaro, México)

**meneses@unam.mx*

Sulfur-enhanced thermoluminescence of γ -radiated zirconia

Sulfur-modified zirconia with various S contents have been characterized and analyzed for potential applications in dosimetry. The thermoluminescent signal induced by gamma radiation in pure zirconia and sulfated zirconia in the tetragonal phase has been considered. Experimental results show that the thermoluminescent glow peak depends on both the crystalline structure and sulfate concentration and that the response is linear for an ample range of irradiation.

Keywords: *thermoluminescence, gamma radiation, pure zirconia, sulfated zirconia, crystalline structure.*

INTRODUCTION

Zirconia is, perhaps, one of the more versatile ceramic materials in today's industry. Indeed, this important material, one of the hardest known, has already found important commercial applications [1–6], ranking from abrasives and jewelry (as a Diamond-like stone) to lasers, automobile, aerospace, and even music technology (i.e., Panasonic's low distortion headsets), through its various crystallographic phases [2–7]. Among the reasons for this, one can mention the interesting chemical and physical properties of zirconia, which can be somehow tailored by adding impurities or by using different phases since, for example, the electronic band gap is dependent on whether cubic, tetragonal, monoclinic, or amorphous structures are present. The other attractive characteristic of zirconia is that it is readily available in nature and/or can be synthesized by using various techniques, including low temperature routes [7–10], which make this mineral suitable for many industrial uses.

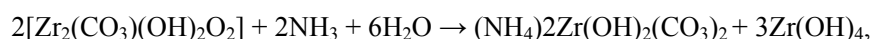
Given the very high thermal, electrical, and mechanical stability of zirconia, its use for dosimetry of ionizing radiation seems extremely attractive, as most commercially available dosimeters are made out of rather weak materials, mainly alkali halides [12–15], which can also become an environmental hazard, when disposed, whereas zirconia is currently employed for bioengineered devices *in situ*.

One important requirement for an ionizing radiation thermoluminescent (TL) dosimeter, however, is the need of reproducibility, linear behavior within the radiation range required for, as an example, biomedical uses, and, very relevant, the capability of controlling the TL response depending on the operation conditions of the dosimeter [15–20].

Accordingly, in previous works we have reported the suitability of zirconia for TL applications [13–18, 20] for as-prepared specimens, including different synthesis routes. In the present manuscript we describe how a very simple sulphurization of zirconia can control, to a great extent, the TL response of zirconia.

EXPERIMENTAL

Commercial ammonia zirconium carbonate white paste (Magnesium Electron Inc.), formed by 40 % zirconium compounds and 7 % CO₂ was utilized, as purchased. A zirconium sol was prepared according to the following reaction [14–16]:



using ammonia (Baker) with 7.6 % of NH₃.

Then, 616.9 g of zirconium carbonate were mixed with 1261.3 ml of NH₄OH 1.58 M. To ensure full dispersion of the paste, alumina balls were added and refluxed for 24 h, obtaining an aqueous solution of ammonia zirconium carbonate (NH₄)₂Zr(OH)₂(CO₃)₂.

Aging at room temperature leads to evaporation of humidity and ammonia, thus increasing viscosity. After a week, a transparent monolith is obtained, which was characterized in a TGA-DTA instrument SDT 2960 TA in the range of 50 to 1100 °C. X-ray diffraction of samples calcined at 300, 450, 600 and 800 °C for 1 h was carried out in a Siemens D-5000 equipment.

The sulfated zirconia was obtained by preparing three 50 ml aqueous solutions with 0.5, 1, and 2 ml sulfuric acid, respectively, which led to CO₂ liberation and a white powder precipitates, which were filtered and dried at 60 °C for 24 h. These samples were calcined at 600 °C for 1 hour. Sulfur concentration was determined by EDS in a JEOL 5900 LV SEM.

Samples were irradiated with a ⁶⁰Co source, which emits 1.31 MeV gamma radiation, with a half life time of 5.3 years and a dose rate of 0.59 Gy/min. The range of radiation utilized was 4.16 to 100 Gy.

TL was characterized in a Harshaw 4000 as follows: preheating at 30 °C, then heated in the range 50 to 300 °C at a rate of 10 °C/s and acquisition time of 30 s, under N₂ atmosphere.

RESULTS AND DISCUSSION

Full physicochemical characterization of the sulfur-modified zirconia has been described previously [17–19]. The table summarizes the EDS characterization of the S content of the samples prepared. The TL behavior is illustrated in Figs. 1, 2 and 3, in terms of exposure to gamma irradiation, from 7.5 up to 240 min, for sulfated zirconia samples corresponding to 1.3, 2.4, and 4 wt % sulfur content, respectively.

S content of sulfated samples (by EDS)

Sample	S content, wt %
1	0
2	1.3
3	2.4
4	4.0

Exposure to gamma irradiation produced very interesting TL spectra, since the maxima, at 118, 135, and 110 °C, depend on the sulphur content (1.2, 2.4, and 4 wt %, respectively). It is known that the degree of crystallinity is a factor that largely determines the presence and intensity of the TL signal in many cases and one could think this is the present case. However, Fig. 4 shows typical X-ray diffraction patterns of the pure and S-containing zirconia, revealing the presence of the tetragonal zirconia phase. The same pattern is observed for the samples with different concentrations of S.

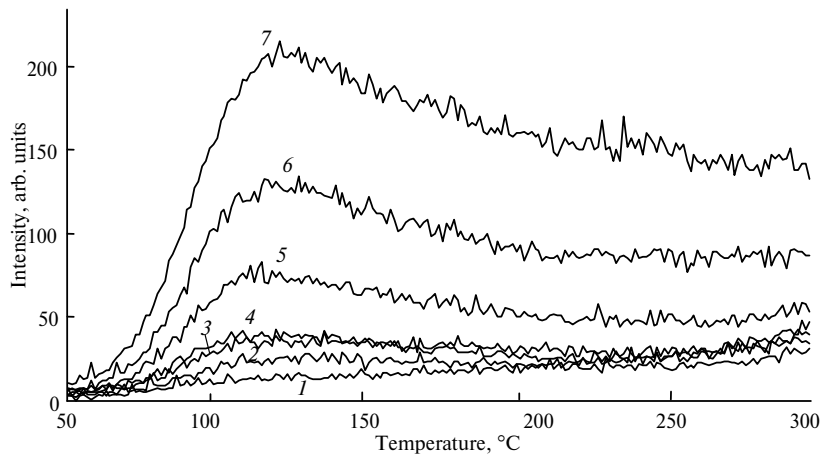


Fig. 1. TL behavior of 1.3 wt % content S of zirconia for gamma irradiation for 7.5 (1), 15 (2), 22 (3), 30 (4), 60 (5), 120 (6), 240 (7) min.

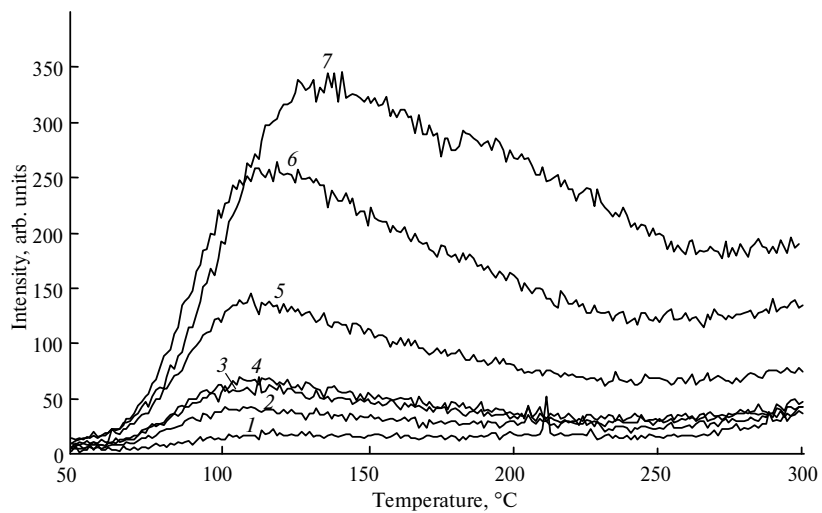


Fig. 2. TL behavior of 2.4 wt % content S of zirconia for gamma irradiation for 7.5 (1), 15 (2), 22.5 (3), 30 (4), 60 (5), 120 (6), 240 (7) min.

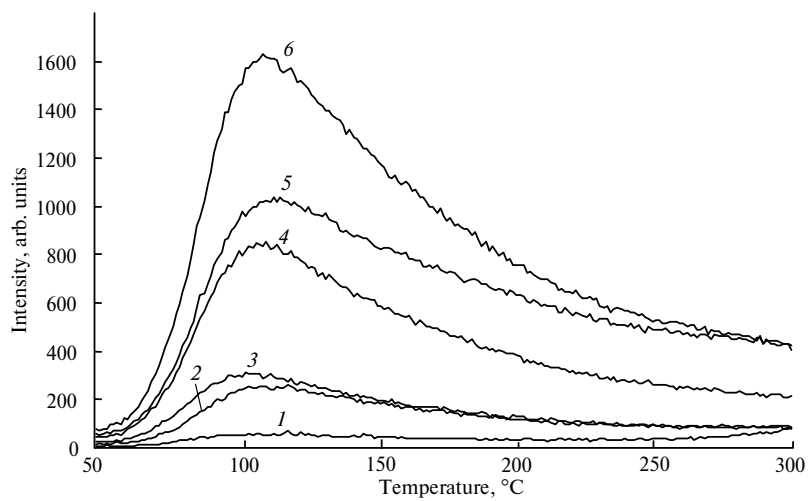


Fig. 3. TL behavior of 4 wt % content S of zirconia for gamma irradiation for 7.5 (1), 15 (2), 30 (3), 60 (4), 120 (5), 240 (6) min.

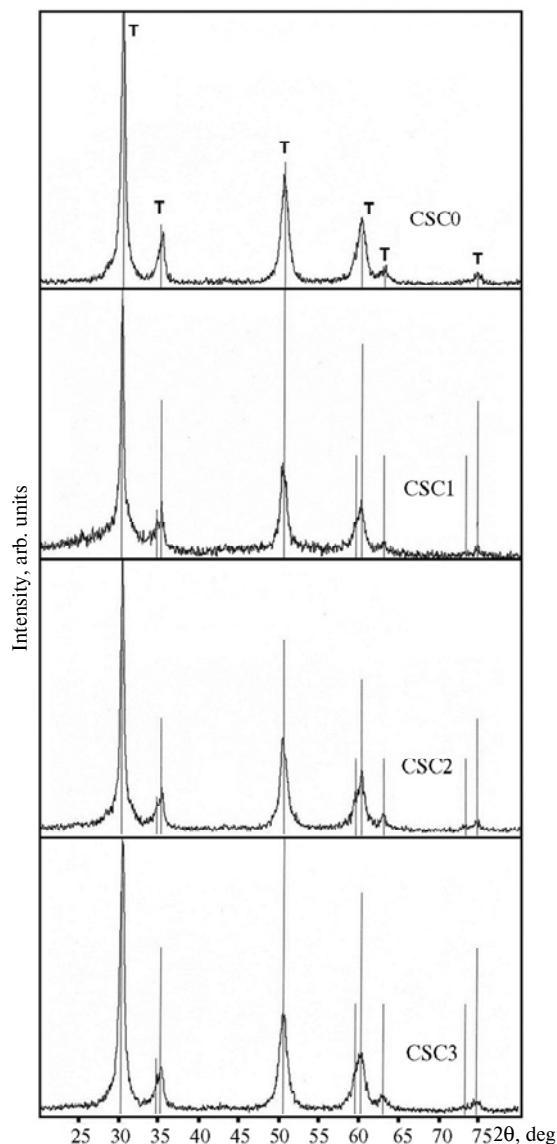


Fig. 4. X-ray powder diffraction of zirconia with different contents of S: 0 (1), 1.3 (2), 2.4 (3), 4 (4) wt %; T – tetragonal zirconia.

Figure 5 shows the TL response of the 2.4 wt % content of S to various doses of gamma irradiation, where two main peaks, located at 274 and 147 °C are clearly observed for the S-containing samples, whereas the pure zirconia specimen shows no evidence of the higher temperature peak, indicating that deeper electron traps are formed by the incorporation of S, thus demonstrating that the electronic structure of zirconia can be controlled by adding S, as indicated.

Figure 6 summarizes the results of the present investigation, for it shows the plots of the TL intensity vs. the gamma irradiation period, for selected S-containing samples, as compared to the pure zirconia case. Two features are to be noticed in this figure, first, the clear dependence on the S content, as mentioned above and, second, the highly linear behavior found.

The TL response generally comprises four regions, namely supralinear, linear, sub-linear, and saturation. The linear region is the most important, both from the

dosimetry and electronic devices points of view. Generally speaking, in this region, the TL sensitivity increases with dose, but this has also been observed at low doses. The origin of this phenomenon is still not well understood and it has been suggested that seems associated to surface states, which would correspond to the S-modified zirconia. Indeed, since the TL response depends on imperfections of the crystal lattice and of the impurities in the zirconia, greater sensitivity would be expected for higher concentrations of S.

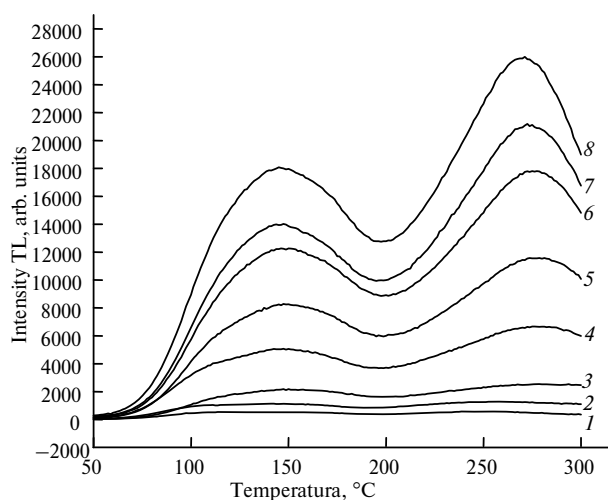


Fig. 5. TL response to various gamma irradiation doses of the 2 wt % content S of zirconia: 4.16 (1), 8.25 (2), 16.5 (3), 33.0 (4), 50.0 (5), 66.0 (6), 82.5 (7), 100.0 (8).

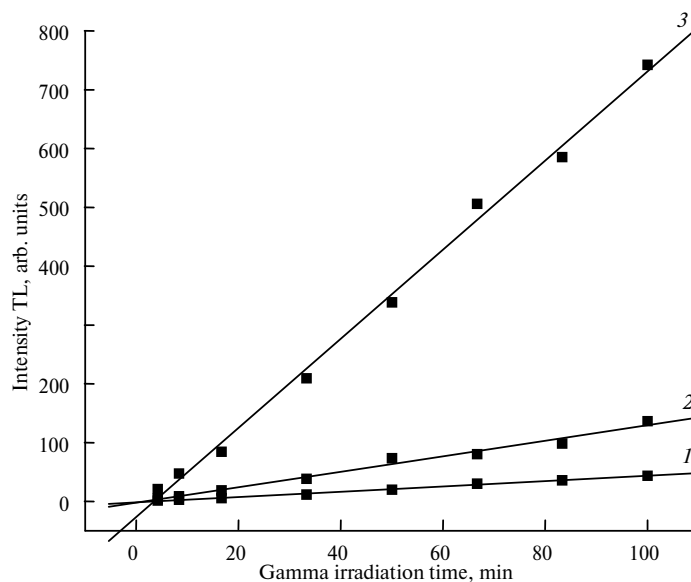


Fig. 6. TL intensity vs. gamma irradiation time for zirconia with 0 (1), 0.9 (2) and 2.4 (3) wt % content of S.

It is also seen that the intensity of TL response follows a linear behavior with respect to the dose for the UV radiation in the range of 10 to 180 s of exposure and with gamma radiation in the range of 14.6 to 100 Gy, this indicates that the equipment for detection of gamma radiation within these ranges may be used.

TL obtained signal determines the kinetics, which can be expected in this case is the unique characteristic of the material that TL response linearity and dependence presents dose rate during irradiation. The structure of the peaks indicates a continuous distribution of traps.

For use in dosimetry, the existence of TL bands, above room temperature relatively high temperatures indicate the existence of very stable while one can observe a strong signal fading over time with traps.

CONCLUSIONS

The addition of S to native zirconia has been found to clearly affect the TL response of the material. In general, an excellent TL sensitivity is presented for irradiation doses ranging from 4.16 to 100 Gy of radiation, a very broad range that would allow readings within the range of radiation used in therapy for humans and animals.

Зразки модифікованої сірою двоокису цирконію з різним вмістом сірки охарактеризовано і проаналізовано з точки зору потенційного застосування в дозиметрії. Розглянуто термолюмінісцентний сигнал, викликаний гамма-випромінюванням в чистому і сульфатованому двоокису цирконію в тетрагональній фазі. Експериментальні результати показують, що пік термолюмінісцентного світіння залежить як від кристалічної структури, так і від концентрації сульфату. Ця характеристика лінійна для великого діапазону опромінення.

Ключові слова: термолюмінісцентний сигнал, гамма-випромінювання, двоокис цирконію, сульфатований двоокис цирконію, кристалічна структура.

Образцы модифицированной серой двуокиси циркония с различным содержанием серы охарактеризованы и проанализированы с точки зрения потенциального применения в дозиметрии. Рассмотрен термолюминисцентный сигнал, вызванный гамма-излучением в чистой и сульфатированной двуокиси циркония в тетрагональной фазе. Экспериментальные результаты показывают, что пик термолюминисцентного свечения зависит как от кристаллической структуры, так и от концентрации сульфата. Эта характеристика линейна для большого диапазона облучения.

Ключевые слова: термолюминисцентный сигнал, гамма-излучение, двуокись циркония, сульфатированная двуокись циркония, кристаллическая структура.

1. Ward D. A., Ko E. I. One-step synthesis and characterization of zirconia-sulfate aerogels as solid superacids // J. Catal. – 1994. – **150**, N 1. – P. 18–33.
2. Yamaguchi T. Recent progress in solid superacid // Appl. Catal. – 1990. – **61**, N 1. – P. 1–25.
3. Yamaguchi T., Tanabe K., Kung Y. C. Preparation and characterization of ZrO₂ and SO₄²⁻-promoted ZrO₂ // Mater. Chem. Phys. – 1987. – **16**, N 1. – P. 67–77.
4. Arata K., Hino M. Preparation of superacids by metal oxides and their catalytic action // Mater. Chem. Phys. – 1990. – **26**, N 3–4. – P. 213–237.
5. Brinker C. J., Sherer G. W. Sol-gel science. The physics and chemistry of sol-gel processign. – New York, Academic Press, USA, 1990. – 912 p.
6. Chen F. R., Coudurier G., Joly, J.-F., Vedrine J. C. Superacid and catalytic properties of sulfated zirconia // J. Catal. – 1993. – **143**, N 2. – P. 616–626.
7. Limaye A. U., Helble J. J. Morphological control of zirconia nanoparticles through combustion aerosol synthesis // J. Am. Ceram. Soc. – 2002. – **85**, N 5. – P. 1127–1132.
8. Livaje J., Henry M., Sanchez C. Sol-gel chemistry of transition metal oxides // Prog. Solid State Chem. – 1998. – **18**. – P. 259–341.
9. Matijevic E. Monodispersed colloidal metal oxides, sulfides and phosphates // Ultrastructure processing of ceramic, glasses and composites / Eds L. L. Hench, P. R. Ulrich. – New York: Wiley and Sons, 1984. – P. 334–352.
10. Mendoza-Anaya D., González Martínez P., Rodríguez-Lugo V., Castaño V. M. γ -radiation induced termoluminescence of Fe-doped silica gels // J. Mater. Sci.: Mater. in Electron. – 1999. – **10**, N 1–3. – P. 623–625.

11. *Mendoza-Anaya D., Angeles-Chávez C., Salas P., Castaño V. M.* TEM and TL análisis of silica samples with metallic impurities synthesized by sol-gel method // *Acta Microscopica*. – 2001. – **10**, B. – P. 213–216.
12. *Harani R., Hogarth C. A., Lott K. A. K.* Electron spin resonance in phosphate glasses mixed transition metal ions // *J. Mater. Sci.* – 1984. – **19**, N 5. – P. 1420–1427.
13. *Salas P., De la Rosa-Cruz E., Mendoza-Anaya D. et al.* Thermo-luminescence induced by gamma irradiation in sol-gel prepared zirconia–silica materials // *Mater. Res. Innov.* – 2001. – **4**, N 1. – P. 32–35.
14. *Rubio E.* Síntesis, propiedades y aplicaciones de nuevos materiales de óxido de circonio: Ph. D. thesis (Engineering). – Universidad Autónoma de Querétaro, 2005.
15. *Pat. Mexico.* Method for preparing dosimeters from sulfated zirconia and applications therein / E. Rubio, V. Rodríguez, V. M. Castaño. – Pat. application (under revision), 2013.
16. *Rubio E., Rodríguez-Lugo V., Rodríguez R., Castaño V. M.* Nano zirconia sulfated zirconia from ammonia zirconium carbonate // *Rev. Adv. Mater. Sci.* – 2009. – **22**. – P. 67–73.
17. *Salas P., De la Rosa E., Mendoza D. et al.* High temperature thermoluminescence induced on UV-irradiated tetragonal zirconia prepared by sol-gel // *Mater. Lett.* – 2000. – **45**, N 5. – P. 241–245.
18. *Salas P., De la Rosa E., Mendoza D. et al.* Thermoluminescence induced by gamma irradiation in sol-gel prepared zirconia-silica materials // *Mater. Res. Innov.* – 2000. – **4**, N 1. – P. 32–35.
19. *Bazhanov D., Knizhnik A., Safonov A. et al.* Structure and electronic properties of zirconium and hafnium nitrides and oxynitrides // *J. Appl. Phys.* – 2005. – **97**, art. 044108.
20. *Hernandez M., Bernal R., Cruz C. et al.* High dosage thermoluminescence diamond dosimeters // *J. Superhard Mater.* – 2012. – **34**, N 4. – P. 234–238.

Centro Universitario de Vinculación,
 Benemérita Universidad Autónoma de Puebla, México
 Instituto Nacional de Ciencias Nucleares,
 Centro Nuclear de Salazar, Estado de México, México
 Universidad Autónoma de Hidalgo, Pachuca, Hidalgo, México
 Centro de Física Aplicada y Tecnología Avanzada,
 Universidad Nacional Autónoma de México,
 Santiago de Querétaro, México

Received 14.01.15