Materials Research. 2015; 18(1): 113-120
DOI: http://dx.doi.org/10.1590/1516-1439.284314

Recovery of α-Al_2O_3 from Ionizing Radiation Dosimetric Sensors

Edgar Aparecido Sanches[a]*, ***Ademir Geraldo Cavallari Costalonga***[b], ***Luana de Freitas Nascimento***[c,d],
Yvone Maria Mascarenhas[e], ***Yvonne Primerano Mascarenhas***[b]

[a]*Department of Physics, Federal University of Amazonas – UFAM, Manaus, AM, Brazil*
[b]*Institute of Physics of São Carlos – IFSC, University of São Paulo – USP, São Carlos, SP, Brazil*
[c]*Belgium Nuclear Research Centre, SCK-CEN, Mol, Belgium*
[d]*Brussel, Radiotherapie, Groep Medische Fysica, VUB, Faculteit Geneeskunde en Farmacie, Brussels – Belgium*
[e]*SAPRA S/A – Serviço de Assessoria e Proteção Radiológica, São Carlos, SP, Brazil*

Received: March 23, 2014; Revised: February 5, 2015

Corundum, sapphire or α-Al_2O_3 is an important technological material in many optical and electronic applications such as solid-state lasers, optical windows and, more recently, as a radiation detector. Landauer (Glenwood, IL, USA) accumulated large number of archived and stored Luxel™ dosemeters composed of Al_2O_3:C, which were subjected to a recovery process. Due to the importance of this advanced crystalline material in OSL dosimetry, a recovery process was developed based on the dosemeters calcination and Al_2O_3:C has been reused in manufacturing of new dosemeters. This paper does not aim to optimize the recovery process, but provides an opportunity to study the involved process parameters and to recover this valuable crystalline material from used dosemeters. To the best of our knowledge no other recovery process involving this dosimetric material was described in scientific literature. Fourier Transform Infrared Spectrometry (FTIR), Thermogravimetry/Differential Thermoanalysis (TG/DTA), Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Optically Stimulated Luminescence (OSL) and Rietveld Refinement were used to characterize the recovered material and to check for the stability of its structural and dosimetric properties.

Keywords: *optically stimulated luminescence, Al_2O_3:C, recovery process*

1. Introduction

The use of Al_2O_3:C in Optically Stimulated Luminescence (OSL) dosimetry is attractive for a number of technical reasons, mainly luminescence efficiency,[1-4] stability in high humidity, chemical solvents and heat[5] and high sensitivity to ionizing radiation such as electrons, photons and heavy charged particles[6]. For high-quality Al_2O_3:C dosimeters, it is necessary to grow the crystalline material in a highly reducing atmosphere in the presence of carbon[7,8]. As a result, carbon impurities are incorporated into the lattice, which act as catalysts for the formation of oxygen vacancies, both neutral and charged (F, F+ and F-centre clusters), which play an important role as luminescence centers[6,7,9]. OSL has become a commercially successful dosimetry method, as evidenced by the wide use of the Luxel™ and InLight dosimeters manufactured and distributed by Landauer, Inc., that converted ~90% of its Thermoluminescence (TL) and film dosimetry to an OSL technology that uses Al_2O_3:C phosphor[1,10]. Luxel™ detector is constructed as a thin layer of α-Al_2O_3 powder mixed with polyester binder and deposited on a clear polyester substrate film. The powder layer is protected by a thin, clear polyester tape. The light stimulation intensity is such that the bi-monthly readings deplete the OSL signal by only approximately 10% over one year[6]. Thus, after usage and archival storage, the Al_2O_3:C crystalline material in the Luxel™ dosimeters needs to be recovered and treated to be used again in new dosimeters manufacturing process. The proposed recovery process is performed in two stages of calcinations: in the first stage the Al_2O_3:C detector films are subjected to the direct flame calcination, eliminating gases and reducing the mass of its organic part through the decomposition of the polymer layers. In the second stage, the remaining material is loaded in an oven with controlled temperature to incinerate the polymer residues and recover only the Al_2O_3:C crystalline material (in a destructive process that involves a high-temperature annealing). The recovered material were characterized by Fourier Transform Infrared Spectrometry (FTIR), Thermogravimetry/Differential Thermoanalysis (TG/DTA), Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Optically Stimulated Luminescence (OSL) and Rietveld Refinement.

---

*e-mail: sanches.ufam@gmail.com

2. Experimental

2.1. Dosemeters

Al_2O_3:C OSL dosemeter is a multilayer tape with dimensions of (17.0 x 28.0 x 0.30) mm^3, which is composed of two phases: a crystalline inorganic material sensitive to radiation, and an organic polymer to support the crystalline phase. The polymer substrate layer is 0.10 mm thick and the top protective layer is 0.05 mm. The Al_2O_3:C crystalline powder mixed with organic polymer binder is printed on top of the polyester substrate forming a translucent layer of about 0.15mm thick. Figure 1 shows a schematic representation of the Luxel™ multilayer sensor. The Al_2O_3:C recovery process was performed at Sapra S/A (São Carlos/SP - Brazil). It is constituted of two stages of calcinations: in the first stage the Al_2O_3:C detector films are submitted to the direct flame calcination, eliminating gases and reducing the mass of its organic part. In the second stage, the material that survived the first calcination is loaded in aluminum trays that were taken to the oven under controlled temperature for further annealing.

2.2. Electric oven

For the second stage of calcination it was used a EDGCON 1P Model oven, with 1000°C of maximum temperature, 106 cm length and two (15 x 15) cm^2 openings at each side. Symmetrical pattern of holes with 1.0 cm in diameter and 2.5 cm apart were created in the oven steel cover plates. Steel tube (0.9 cm diameter) was inserted in the front hole, crossing the oven and reaching the corresponding symmetric hole in the back plate. A K-type thermocouple was inserted in the tube and temperature measurements were acquired each 2.0 cm using a digital multimeter. While the temperature dependence was measured using one hole, the others holes were sealed. The assessment of oven temperature was performed in all holes.

2.3. FTIR analysis

FTIR data were recorded by a Perkin-Elmer 1000 IR spectrophotometer in the range of 4000-400 cm^{-1} and 24 scans. Samples were prepared by grinding and mixing powdery with KB in the ratio of 1:10 and then pressing the mixtures into pellets.

2.4. TG/DTA and DSC

TG/DTA was carried out using SDT 2960 Model, with reference and sample thermocouples made of Pt – Pt/Rh 13%, with 0.1 µg sensitivity scales. The sample mass used was 9.0436 mg. The experiment was made under O_2 atmosphere (flow of 100 mL/min) at heating rate of 10ºC/min from 30 to 1200ºC. For DSC, a Netzsch 200 Model with heating rate of 10° C/min was used. The sample was heated from the ambient temperature to 300°C.

2.5. X-ray powder diffraction (XRD) and Rietveld refinement

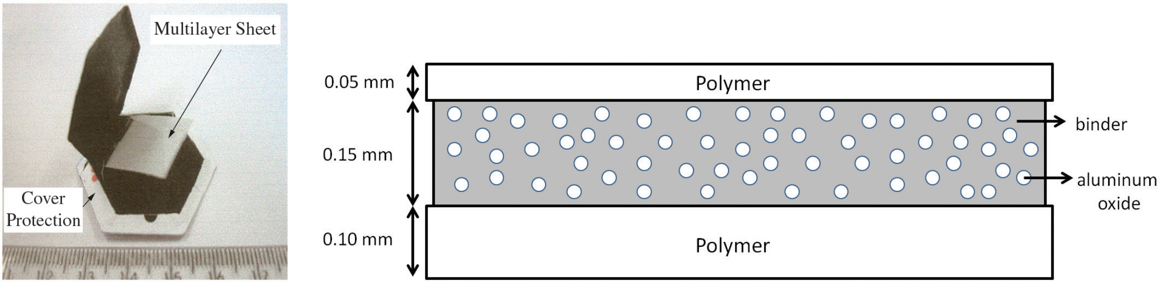
X-ray diffraction measurements were obtained on a Rigaku RotaFlex diffractometer operating at CuKα radiation (50 kV, 100 mA) and equipped with a graphite monochromator. Data collection was recorded in the range of $2\theta = 15$-110° with a step of 0.02° and 5 seconds/step. Rietveld[11] reported a profile refinement structure method, which is extensively used for structural materials characterization. Rietveld method was performed for Al_2O_3:C and SiO_2 phases, taking as initial parameters, respectively, the data obtained by Lutterotti[12] and Ogata et al.,[13] respectively. Rodríguez-Carvajal[14] proposed a program for Rietveld, profile matching and integrated intensities refinement known as Fullprof Program, which was used in this work for Rietveld structure refinement. All parameters were refined by the least-squares method, as described by Pawley[15]. Thompson et al.[16] described a pseudo-Voigt function which was used as the profile function. The parameters constituting the instrumental resolution function $(U,V,W)_{\mathrm{instr.}}$ were obtained from a LaB_6 standard. The evaluation of anisotropic size effects was made as proposed by Popa[17] so the peaks broadening was modeled using the Lorentzian part of the peak with linear combinations of spherical harmonics[18].

2.6. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

All measurements were made using a spectrometer ICP-OES VISTA configured at 40 MHz, 1.2 kW and gas plasma flux of 15 L/min.

2.7. Optically Stimulated Luminescence (OSL)

OSL measurements were made using a two Risø automated TL/OSL readers fitted with an EMI 9635QA photomultiplier tube and three U-340 transmission filters. Readers are equipped with green and blue light sources (420–550 nm), giving an illumination intensity of about 25mW/cm^2 on the sample.



(a) (b)

Figure 1. (a) Luxel™ dosemeter and (b) schematic representation of multilayer sheet.

3. Results

3.1. Dosemeter characterization

3.1.1. TG/DTA and DSC

The curve of simultaneous TG/DTA of OSL sensor fragments is shown in Figure 2a. TG curve shows that the sample remains stable up to 260 °C and shows, in sequence, two decomposition stages: the first stage occurs between 260-480 °C followed by the second stage in the range of 480-590 °C. The solid residue present in the sample is stable up to 1200 °C, with no loss or gain of weight during the procedure. The residue obtained is 43% of the sample total mass. DTA curve shows an endothermic peak between 230-280 °C with a minimum at 250 °C, indicating the fusion of the polymer attached to the sensor. The oscillations observed from 320-410 °C are due to the evaporation of the polymer that begins to decompose itself as a viscous phase. From 410-600 °C are observed two exothermic peaks, indicating the burning of organic material. Above 610 °C there are no further peaks. Figure 2b shows the DSC curve obtained during heating of the sample. There is an endothermic peak around 260 °C. The enthalpy associated with material melting is –52.70 J/g, indicating that the material that protects the crystalline layer is made of polyester.

3.1.2. FTIR

FTIR analysis spectrum of the dosemeter polymer layer is shown in Figure 3. Ester carbonyl groups, as reported by Skoog,[19] absorb between 1750-1715 cm^{-1} (peak 1). This absorption, in addition to those obtained at 1257 (peak 2) and 1098 cm^{-1} (peak 3) is characteristic of ester groups. This result complements the information obtained by DSC and confirms that the crystalline layer is encapsulated by a type of polyester.

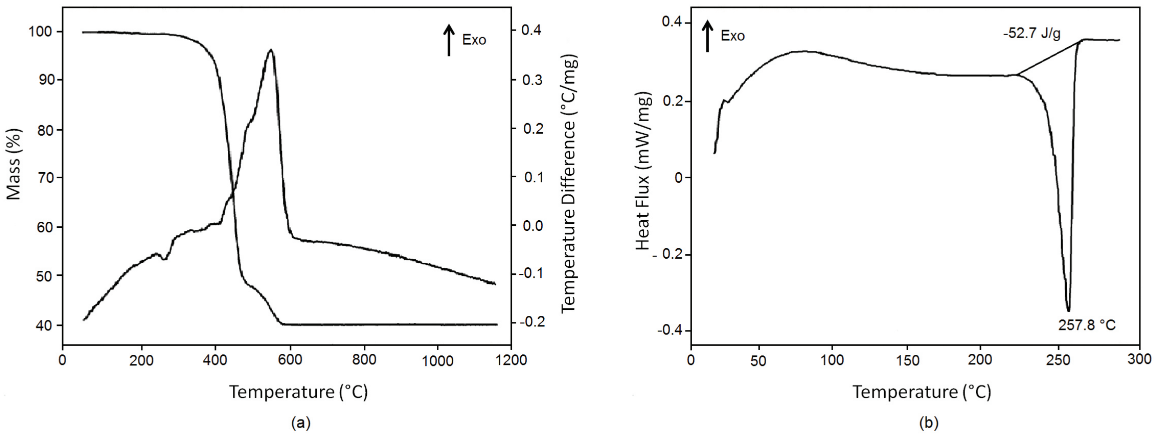


Figure 2. (a) TG/DTA curve of fragmented dosemeters and (b) DSC curve obtained during heating of the dosemeter polymer layer.

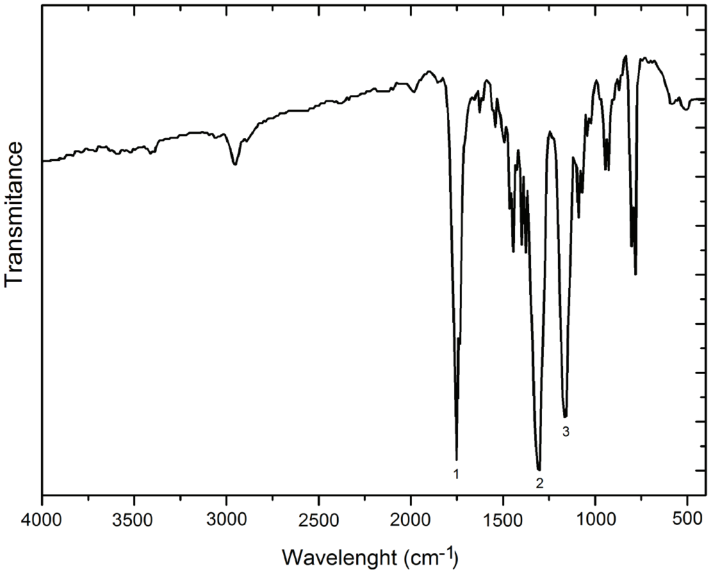


Figure 3. FTIR spectrum of polymer layer.

3.2. Temperature profile study of the electric oven

A schematic view of the temperature profile curves and spatial position for each tube is shown in Figures 4a and b. In Figure 5a is showed the oven temperature profiles for the horizontal holes (1, 2, 3 4 and 5) and in the Figure 5b the temperature profiles for the vertical holes (3, 6, 7, 8 and 9). It was observed that the desired temperature (~610 °C) is reached along the 20 cm of the oven length (between 40 and 60 cm) where the crystalline material must be positioned for proper incineration.

3.3. Crystalline material recovery from dosemeters

The description of the two stages of calcination and the study of some of their parameters are described below.

3.3.1. First stage of calcination: organic material incineration

First stage of the recovery process was carried out in a system consisting of a support positioned above gas flame burner and a steel container (15 cm in diameter and 17 cm in height). The steel container has a cover lid with locks. Cylindrical gas exhaust tube is attached at the center of the cover lid and is connected to a blow pipe, allowing the burning of the free gases during the calcination. The mass loss of the calcined dosemeters is a result of polymer decomposition. The resulting product of this calcination stage is a black material containing some uncalcined organic material mixed with Al_2O_3:C. A steel container with an internal aluminum layer was used for the calcination of the Al_2O_3:C sensors. Table 1 shows the results of ICP-OES analysis of calcined

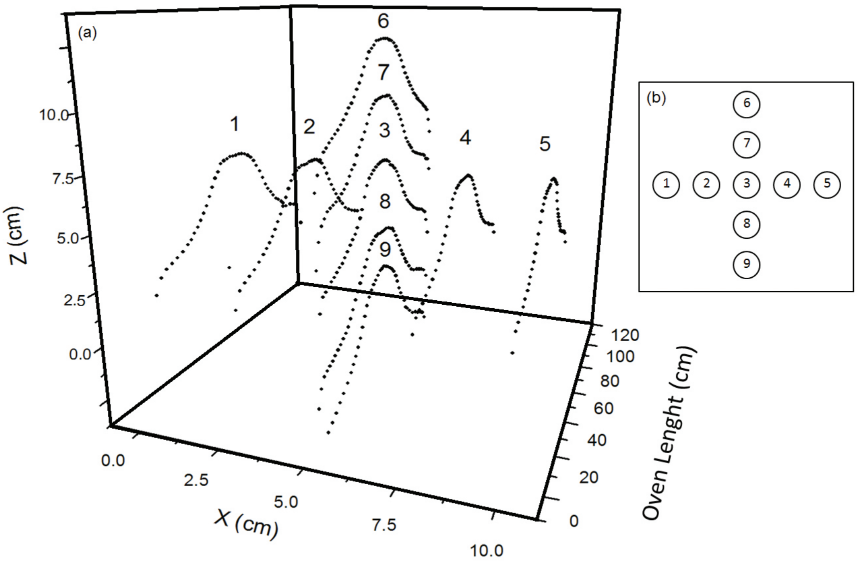


Figure 4. (a) Oven temperature behavior along each tube and (b) Related oven holes labelled by their different positions.

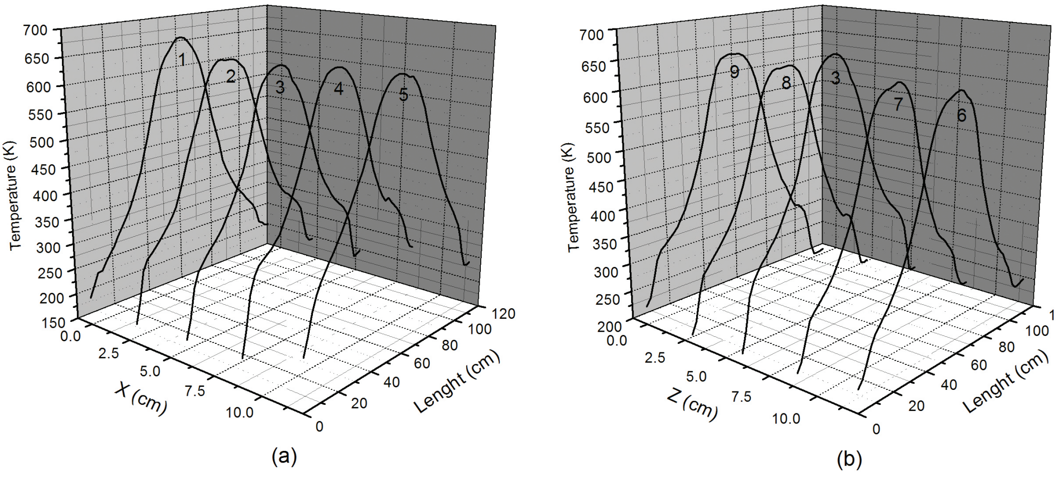


Figure 5. (a) Oven temperature behavior for horizontal and (b) vertical holes.

dosemeters after the first and second stages. No significant contamination of the recovered material was found.

3.3.1.1. Determination of the first stage calcination time

During the first calcination stage the container was loaded with 500 g of dosemeters. The optimal time of calcination was determined by analyzing the FTIR spectra after different calcination times. Calcination times of 30 min, 40 min, 50 min, 1.5 h and 2.0 h were selected. FTIR spectra of each sample are shown in Figure 6. The best results were obtained with calcination time higher than 50 min. FTIR spectra did not exhibited the carbonyl band at 1750-1715 cm^{-1} after 50 min which is an indication that at this time the polymer decomposition was completed.

3.3.2. Second stage of calcination: removal of remaining organic material and radiation-sensitive material recovery

At this stage the black material from the first stage of calcination was loaded on aluminum trays and placed in the oven with controlled temperature profile for the elimination of the remaining organic residue. The material obtained in the first calcination stage was loaded on three aluminum trays, with dimensions of (20 x 7 x 1) cm^3 and the trays were inserted in the oven at 600°C. After 2.5 h of calcination, all the remaining organic material was eliminated. Table 1 shows the ICP-OES analysis for calcinations in different trays after the second stage.

3.3.3. Grain size distribution in recovered material

A good quality of printing consists of a proper grain size distribution. As reported by Markey, Colyott and Mckeever,[20] the grain size of the Al_2O_3:C powder is in the range of 10-90μm. As it was determined from Landauer's previous experience, excessive amounts of "fine" grains (less then 38μm) and "large" grains (>75μm) can create problems during printing. The amounts of "fine" should not exceed 32% and "large" grains 10% by weight. Distributions of grain sizes from 38 to 75 μm had been never suspected to make a difference. The recovered material grain size is inside the permissible limits of grain size distribution, as showed in Figure 7. The amount of "fine" grains (<38μm) in the recovered material batches is consistent with older

Table 1. Oxides Percentages found in the recovered material in the first and second stages.

Analyzed Oxides	Dosemeters calcined in an aluminum container inserted in the steel container (%)	Recovered material obtained after calcination in aluminum tray (%)	α-Al_2O_3 hands removed from a dosemeter, without any recovery treatment (%)
SiO_2	2.39 (0.01)	2.40 (0.01)	2.33 (0.01)
Fe_2O_3	< 0.001	< 0.001	< 0.001
MnO	0.001 (0)	0.001 (0)	0.001 (0)
CuO	< 0.001	< 0.001	< 0.001
Cr_2O_3	< 0.001	< 0.001	< 0.001
TiO_2	< 0.001	< 0.001	< 0.001

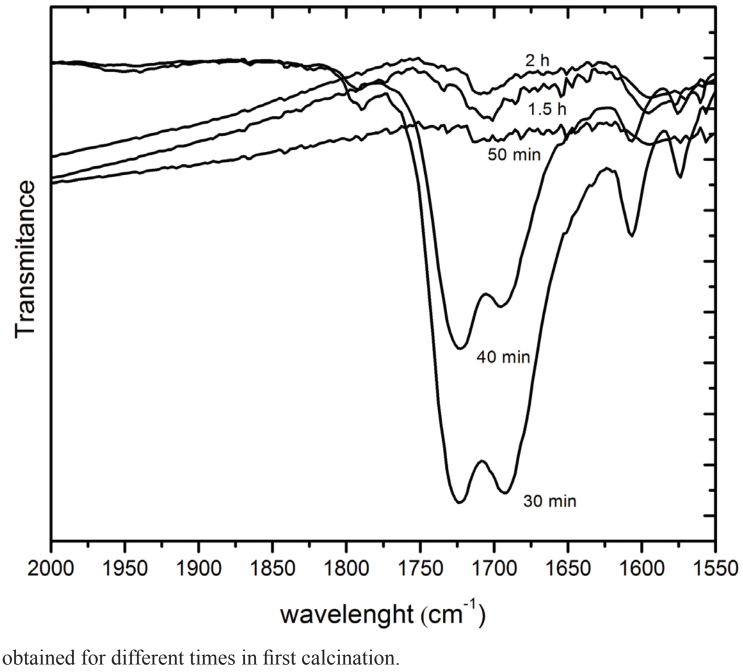


Figure 6. FTIR spectra obtained for different times in first calcination.

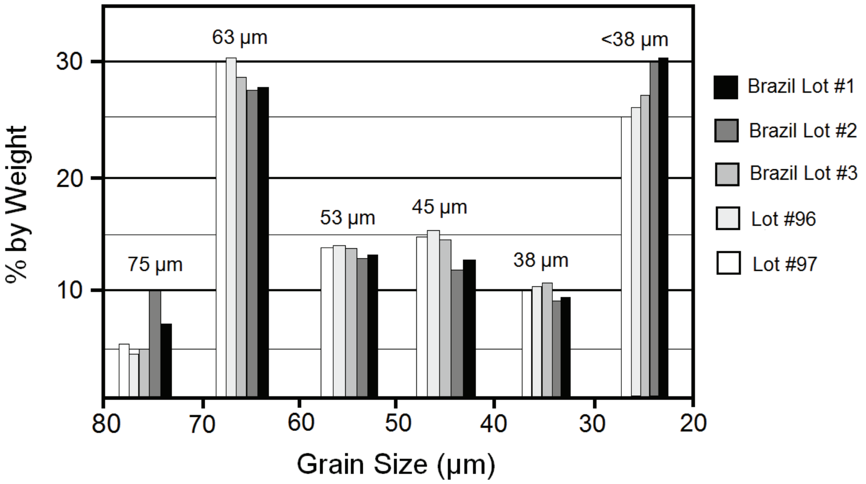


Figure 7. Grain size distribution.

Table 2. OSL sensitivity for the standard and recovered material.

Samples	Sample weight (mg)	Powder OSL sensitivity, irradiation 1R			Powder OSL norm. to the weight 18mg
		OSL, counts	DOSL1, %	DOSL2, %	
Recovery α-Al_2O_3	17.7	52700	3.2	2.6	53593
	14.8	46096	3.3	2.4	56063
	17.3	54141	2.9	3.1	56332
	17.8	47325	3.7	2.1	47857
	17.8	54572	3.1	2.5	55185
Average for Standard Sample α-Al_2O_3			3.2	2.5	53806
Std Dev%					6
Standard α-Al_2O_3	15.7	44457	2.8	2.8	50970
	15.6	40411	2.9	2.9	46628
	14.9	37002	2.7	2.7	44700
	14.3	45311	2.4	2.4	57035
	14.0	46434	2.5	2.5	59701
Average for Recovery Sample α-Al_2O_3			2.7	2.7	51807
Std Dev%					12

powder lots (Lotes #96 and 97) and is within the expected percentage range, as well as it is within the expected percentage corresponding to 75 µm grains.

3.3.4. Characterization of the recovered material by OSL

The OSL sensitivity and OSL background signal of the recovered powder in comparison with the standard Al_2O_3:C from Landauer Crystal Growth Division is shown in Table 2. It was observed that the change in sensitivity of the standard and recovery Al_2O_3:C does not exceed the standard deviation of measurements.

3.3.5. Characterization of the recovered material by XRD and Rietveld refinement

Rietveld refinement was performed taking as initial parameters the structures obtained by Lutterotti[12] and Ogata et al.[13] for, respectively, Al_2O_3:C and SiO_2 phases. In the dosemeter manufacturing process, Cabosil™ (fumed silica of submicron size) is added to aluminum oxide powder for better rheological properties during printing. Cabosil is added to the mixture of aluminum oxide powder and the binder. The composition of crystalline phases of the recovered material obtained by Rietveld refinement was found as (94 ± 3)% f corundum and (6 ± 3)% of silica. The refined structural parameter for corundum phase with trigonal crystal system and R -3 C space group were: $a = 4.76102$ (2) Å; $b = 4.76102$ (2) Å; $c = 12.9992$ (2) Å; $\alpha = 90°$, $\beta = 90°$ and $\gamma = 120°$ and V = 555.1 (0.5) Å^3. For silica phase with trigonal crystal system and P 32 2 1 space group the refined structural parameter were: $a = 4.9120$ (2) Å; $b = 4.9120$ (2) Å; $c = 5.4020$ (2) Å; $\alpha = 90°$; $\beta = 90°$; $c = 120°$ and V = 112.8 (0.5) Å^3. The obtained agreement factors (Conventional Rietveld R-factor for pattern) were: $R_P = 0.0876$ and $R_{WP} = 0.1171$. XRD pattern of the recovered material is shown in Figure 8. It was verified that the recovered material has kept its crystal structure.

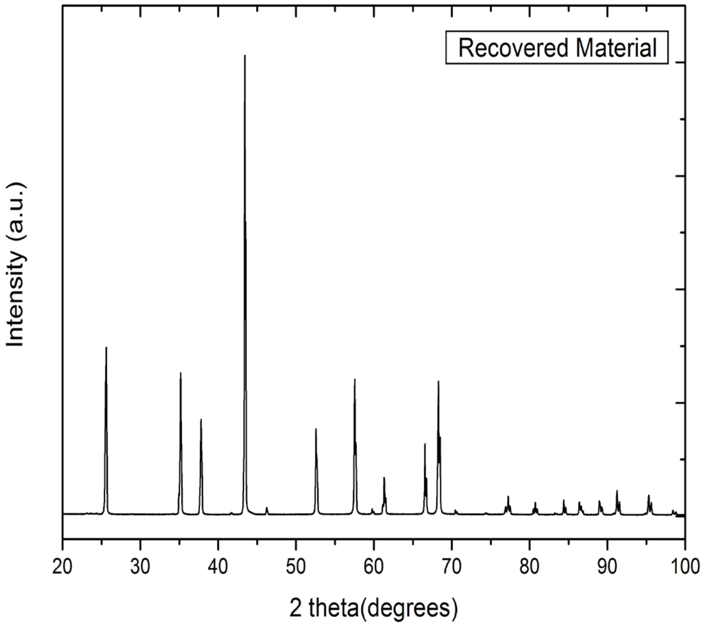


Figure 8. XRD pattern of the recovered material.

4. Conclusion

This work proposes a recovery process for Al_2O_3:C from used Luxel™ dosimeters. Thermal analysis suggested that the Luxel™ polymer should be a type of polyester. X-ray diffraction showed that the crystalline material is predominantly α-alumina. It was estimated by FTIR spectra the best time for the first stage of calcination around 50 min. Regarding the studies of the second stage of calcinations, the shortest time was obtained when 240g of the survived material from the first stage was placed and calcined on three aluminum trays. ICP-OES technique showed contaminants percentage less than 0.001% in the recovered material. Diffractogram of the crystalline material obtained after the recovery process showed that the material kept its structural properties. Through Rietveld refinement data processing it was possible to identify and quantify the phases present in the crystalline material, showing that it is constituted by (94 ± 3) % of α-Al_2O_3 and (6 ± 3) % of silica. The proposed recovery process is destructive as it involves a high-temperature annealing, however, it seems interesting (from an economical point-of-view) to recycle Luxel™ dosimeters rather than growing new crystals and preparing them by grinding and sorting. Further study on the optimization of the process is foreseen.

Acknowledgements

Authors would like to thank Landauer Inc. for providing the dosemeters used in this study; Sapra S/A; Institute of Physics of São Carlos and CNPq for the financial support.

References

1. Akselrod MS and McKeever SWS. A radiation dosimetry method using pulsed optically stimulated luminescence. *Radiation Protection Dosimetry*. 1999; 81(3):167-175. http://dx.doi.org/10.1093/oxfordjournals.rpd.a032583.
2. West WG, Kearfott KJ and Bernal SM. The sunlight OSL response of a commercially available alpha-Al2O3:C personnel dosimetry material. *Radiation Protection Dosimetry*. 2006; 119(1-4):344-349. http://dx.doi.org/10.1093/rpd/nci691. PMid:16644934
3. Akselrod MS, Kortov VS, Kravetsky DJ and Gotlib VI. Highly sensitive thermoluminescent Anion-Defect Alpha-Al2O3:C single crystal detectors. *Radiation Protection Dosimetry*. 1990; 33:119-122.
4. McKeever SWS and Moscovitch M. On the advantages and disadvantages of optically stimulated luminescence dosimetry and thermoluminescence dosimetry. *Radiation Protection Dosimetry*. 2003; 104(3):263-270. http://dx.doi.org/10.1093/oxfordjournals.rpd.a006191. PMid:14565734
5. McKeever SWS, Moscovitch M and Townsend PD. *Thermoluminescence dosimetry materials: properties and uses*. Ashford: Nuclear Technology Publishing; 1995.
6. Nascimento L, Vanhavere F, Boogers E, Vandecasteele J and De Deene Y. Medical dosimetry using a RL/OSL prototype. *Radiation Measurements*. 2014; 71:359-363. http://dx.doi.org/10.1016/j.radmeas.2014.05.028.
7. Botter-Jensen L, McKeever SWS and Wintle AG. *Optically stimulated luminescence dosimetry*. Amsterdam: Elsevier; 2003.
8. Akselrod MS, Kortov VS and Gorelova EA. Preparation and properties of Alpha-Al2O3:C. *Radiation Protection Dosimetry*. 1993; 47:159-164.

9. Summers GP. Thermoluminescence in single crystal Alpha-Al2O3. *Radiation Protection Dosimetry*. 1984; 8:69-80.
10. Miller SD and Murphy MK. Technical performance of the Luxel Al(2)O(3):C optically stimulated luminescence dosemeter element at radiation oncology and nuclear accident dose levels. *Radiation Protection Dosimetry*. 2007; 123(4):435-442. http://dx.doi.org/10.1093/rpd/ncl500. PMid:17164274
11. Rietveld HM. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*. 1969; 2:65-71. http://dx.doi.org/10.1107/S0021889869006558.
12. Lutterotti L and Scardi P. Simultaneous structure and size-strain refinement by the Rietveld method. *Journal of Applied Crystallography*. 1990; 23(4):246-252. http://dx.doi.org/10.1107/S0021889890002382.
13. Ogata K, Takeuchi Y and Kudoh Y. *Z.* Structure of α-quartz as a function of temperature and pressure. *Krist.* 1987; 179(1-4):403-413. http://dx.doi.org/10.1524/zkri.1987.179.1-4.403.
14. Rodríguez-Carvajal J. Recent developments in the program FullProf. *Newsletter.* 2001; 26:12-19.
15. Pawley GS. Unit-cell refinement from powder diffraction scans. *Journal of Applied Crystallography*. 1981; 14(6):357-361. http://dx.doi.org/10.1107/S0021889881009618.
16. Thompson P, Cox D and Hastings J. Rietveld refinement of Debye-Scherrer synchrotron X-ray data from Al2O3. *Journal of Applied Crystallography*. 1987; 20(2):79-83. http://dx.doi.org/10.1107/S0021889887087090.
17. Popa, NC. The (*hkl*) dependence of diffraction-line broadening caused by strain and size for all laue groups in rietveld refinement. *Journal of Applied Crystallography.* 1998; 31:176-180. http://dx.doi.org/10.1107/S0021889897009795.
18. Popa N. The *(hkl)* Dependence of diffraction-line broadening caused by strain and size for all laue groups in rietveld refinement. *Journal of Applied Crystallography*. 1998; 31(2):176-180. http://dx.doi.org/10.1107/S0021889897009795.
19. Skoog DA, Holler FJ and Nieman TA. *Princípios de análise instrumental*. 5a ed. São Paulo: Bookman; 2002.
20. Markey BG, Colyott LE and McKeever SWS. Time-resolved, optically stimulated luminescence from α-Al2O3:C. *Radiation Measurements*. 1995; 24(4):457-463. http://dx.doi.org/10.1016/1350-4487(94)00119-L.