



Thermoluminescent characterization of Al₂O₃-derived synthetic topaz



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ABSTRACT

Albeit the thermoluminescent properties of both Al₂O₃ and natural topaz have been documented, owing to a controlled composition, the prospective of synthetic topaz for dosimetry applications is expected to be further promising. In this contribution, the thermoluminescent (TL) properties of synthetic topaz (Al₂F_{1.44}(OH)_{0.56}SiO₄) containing materials are reported for the first time. Synthesis tests by chemical vapor deposition (CVD) were conducted using aluminum oxide (Al₂O₃) and sodium hexafluorosilicate (Na₂SiF₆) as solid precursor, varying temperature, time, Al₂O₃ compact angle position, and atmosphere during dwell stage (with and without nitrogen). Subsequently, samples were thermally treated at 500, 600, 700, 750, 800, 850 and 900 °C. Results indicate that samples treated at 800 °C show a standard deviation of 1.2% (SD %) of the area under the glow curve in the range 53–300 °C. Irradiation with ⁹⁰Sr beta-source of sample A4 (800 °C), from 0.022 Gy to 66 Gy, revealed a nonlinear response, with intensity increasing as doses increase. In addition to the fact that synthesized topaz-containing material possesses a similar TL intensity compared with that of the commercial dosimeter TLD-100, incidence of the greatest fading (<22%) during the first 20 h suggests its potential application in dosimetry.

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1. Introduction

Topaz is one of the main fluorine bearing minerals that comprises a solid solution between a fluorine end member, Al₂SiO₄F₂ (fluor-topaz) and a hypothetical hydroxyl end member, Al₂SiO₄(OH)₂. In the empirical formula (Al₂SiO₄(OH,F)₂), part of the fluorine atoms are commonly replaced by hydroxyl groups. And although topaz is usually reported with different F/OH ratios, the stoichiometry Al₂F_{1.44}(OH)_{0.56}SiO₄ is amongst the most common ones [1].

Recently, intensive investigation activities devoted to the search and development of luminescent materials for dosimetry applications, have been reported [2–9]. The variety of potential candidates may be used as doped materials, as composites or even as single phases. Owing to its structural and functional attributes, topaz can be considered an excellent candidate for dosimetry devices as well as for optical, thermoluminescent, pyroelectric and piezoelectric sensors which can even be exposed to corrosive environments

[2,3,10]. For this reason the thermoluminescent properties of topaz mined from different parts of the world have been the subject of a number of investigations [11–17].

In 1978, Moss et al. reported the characterization of topaz from Utah. The samples presented a saturation of about 653 Sv and a fading of the signal of 30% in the first 2 h followed by 9% after a month and 5% in a year [11]. One year later, Azorin published a study of thermoluminescent properties, reporting a linear behavior from 10.2 Gy up to 5 × 10² Gy. In the first 24 h the samples presented a fading of 30% of the TL signal, followed by 10% in six month and 5% in a year [12]. In 1986, C.A Ferreira Lima et al. reported four thermoluminescent glow peaks instead of 2 peaks reported by Moss et al. and Azorin [13]. In 1997, a study of 6 thermoluminescent peaks of topaz was published, revealing that peaks 1, 2 and 6 are first order kinetic peaks [14]. In 1998, Yukihara and Okuno published a study about transparent and blue topaz, presenting both samples a linear behavior at low doses and a supralinear behavior in the range between 20 and 100 Gy [15]. In 2006, Souza et al. studied the effect of the thermal treatment and found that samples heated at 400 °C show a higher intensity than those treated at 800 °C and related the intensity difference with the atomic structure defect (AlO₄[°]) [16]. Sardan et al. (2011) reported a study of topaz from Pakistan. The samples showed a linear behavior from

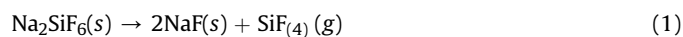
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10^{-2} – 10^2 Gy. In the first 30 h they presented a fading of 27% and 4% after 3000 h [17]. Moreover, the increasing interest of topaz in the area of dosimetry has led some authors to investigate on topaz composites and doped topaz [4–6,18–21]. Table 1 summarizes the different conditions used in the above mentioned studies, specifying for each case, irradiation source, the number of peaks detected in the glow curve and their location in the temperature range.

In spite of the increasing interest for topaz in the area of dosimetry, it is reasonable to think that differences in the thermoluminescent properties due to its geographical origin, might limit the use of mineral topaz, in addition to its foreseen depletion in the future. However, the use of synthetic topaz, where its composition can be systematically controlled, could be a possible solution to these challenges. Several routes have been proposed for the synthesis of this mineral, but they have been unattractive – from the technological and economic standpoints –, because some of them use difficult to handle reactants, long processing times and high pressures [22–27].

The chemical vapor deposition (CVD) route is an alternative for topaz synthesis due to the relatively low processing temperatures, pressures and times. Several precursors have been used in the synthesis of a variety of phases by CVD. These are associated with reduction, oxidation, nitration, hydrolysis, disproportionation and thermal decomposition reactions [28]. Sodium hexafluorosilicate (Na_2SiF_6) has been successfully used as a precursor in different investigations due to its relatively low decomposition temperature, good stability at atmospheric pressure and at room temperature. This easy-to-handle solid precursor can be dissociated thermally at relatively low temperatures under the action of the reactor thermal gradients to generate gas species (for instance, $\text{SiF}_4(\text{g})$, according to reaction 1), which can subsequently react with different substrates [29].



For instance, the same research group reported the synthesis of topaz starting from aluminum hydroxide ($\text{Al}(\text{OH})_3$), focusing the work on structural characterization and optimum processing parameters, though the thermoluminescent properties were not characterized [26]. Albeit some investigations on the thermoluminescent properties of natural topaz have been published in the related literature, specific information on synthetic topaz has not yet been reported.

The aim of this work is to study the effect of processing

Table 1
Experimental conditions used in prior studies on natural-topaz [3,11–16].

Authors	Source	Peaks	Location
Moss (1978)	X Rays ^{137}Cs ^{60}Co	2	140 °C 305 °C
Azorin (1979)	^{60}Co	2	180 °C 285 °C
Lima (1986)	^{90}Sr – ^{90}Y (7–420mGy) ^{60}Co (500–10000mGy)	4	100 °C 130 °C 200 °C 250 °C
Souza (1997)	^{60}Co UV Visible light	6	80 °C 140 °C 170 °C 230 °C 280 °C 330 °C
Yukihara (1998)	^{60}Co	2	122 °C – 126 °C 190 °C – 195 °C

parameters on the thermoluminescent (TL) properties of topaz synthesized by chemical vapor deposition (CVD), using sodium hexafluorosilicate (Na_2SiF_6) as solid precursor and aluminum oxide (Al_2O_3) as reactant compact. In addition, and based on an experimental plan, establish the processing conditions (time, temperature, atmosphere and angle position of the Al_2O_3 compact with respect to the gas flow direction) that promote thermoluminescent response.

2. Experimental procedure

The present investigation was carried out in two stages. In the first step, topaz containing samples were synthesized by CVD, and subsequently, in the second stage, the thermoluminescent (TL) behavior of specimens thermally treated was characterized. Samples were prepared using sodium hexafluorosilicate (Na_2SiF_6) compacts as solid precursor and aluminum oxide (Al_2O_3) compacts as reactant disk-shape with 60% initial porosity. Silicon tetrafluoride (SiF_4) gas produced during the thermal decomposition of Na_2SiF_6 infiltrates the Al_2O_3 interstices to react and yield topaz throughout the whole porous body, originally of alumina.

The Al_2O_3 and Na_2SiF_6 compacts were prepared weighing 10 g of each powder reagent and adding approximately 0.2 ml of distilled water, followed by a careful and thorough mixture with a mortar and pestle, separately. Using a uniaxial Carver press model 4350L, the Na_2SiF_6 and Al_2O_3 mixtures were then compacted at 40 and 20 bar, respectively. The synthesis tests were carried out in a reactor consisting of a Thermolyne tubular furnace, model 59300, provided with an alumina tube of 3.8 cm in diameter x 76.2 cm long. The Na_2SiF_6 and aluminum oxide compacts were positioned at both ends, respectively, in the reactor, placing the former on the side of gas entrance, as shown schematically in Fig. 1. Table 2 shows the sample identification and the experimental conditions used in the study.

The tests were conducted with and without a flow of nitrogen during the dwell and cooling stages, with nitrogen flow rate of $5 \text{ cm}^3/\text{min}$. The compacts were treated at 700 and 750 °C with heating and cooling rates of $15 \text{ }^\circ\text{C}/\text{min}$, for 60 and 90 min dwell time. Furthermore, the position of the aluminum compact oxide was varied with respect to the gas flow direction at 0 and 90° (angle position). Synthesis trials were conducted in three replications according to an L8 Taguchi standard experimental design. Upon cooling down to room temperature, samples were removed from the reactor, after which they were ground in an agate mortar and sieved to-100 mesh. In order to identify the phases formed, the powder specimens were characterized by X-ray diffraction (XRD) using a diffractometer Philips model 3040 under the following conditions: excitation voltage of the anode of 40 kV and current of 30 mA; monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$); 2θ range of 10 – 80° , at a scanning speed of $0.02^\circ/\text{sec}$. Phase type, morphology, distribution and composition of the specimens were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using a microscope Philips XL30 ESEM provided

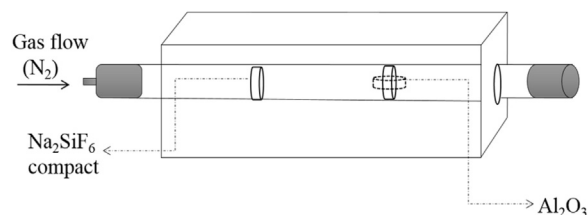


Fig. 1. Schematic diagram of the reactor for synthesis of topaz by CVD, showing position of the Na_2SiF_6 solid precursor and of the Al_2O_3 compact.

Table 2
Experimental conditions used for synthesis of topaz and semi-quantitative analysis by XRD of the phases present in the samples.

Sample identification	Temperature (°C)	Time (min)	Angle position (°)	Atmosphere	AlF ₃ (%)	Al ₂ O ₃ (%)	Al ₂ F _{1.44} (OH) _{0.56} SiO ₄ (%)
A1	700	60	90	With gas	18	62	20
A2	700	60	0	Without gas	8	60	32
A3	700	90	90	Without gas	6	54	40
A4	700	90	0	With gas	8	53	39
A5	750	60	90	Without gas	4	37	59
A6	750	60	0	With gas	3	46	51
A7	750	90	90	With gas	2	44	54
A8	750	90	0	Without gas	5	35	60

with an EDX microanalysis device. Both, secondary and back-scattered electron modes were used in the analysis, at an acceleration voltage between 20 and 30 kV.

Since the TI efficiency of several compounds improves or worsens after a thermal annealing [30–33], in order to investigate the effect on their TI response, the topaz samples were subjected to different thermal treatments after they were synthesized. Subsequently, the samples were weighed and irradiated using a ⁹⁰Sr beta-source, giving a dose rate of 0.022 Gy/min at the sample position. Furthermore, in order to establish conditions for highest TI intensity, samples were thermally treated at the temperatures of 500, 600, 700, 750, 800, 850 and 900 °C. Thermoluminescence glow curves were recorded from 50 to 450 °C with a constant heating rate of 1 °C/s by using a Harshaw-Bicron 3500 TI Reader, equipped with a Hamamatsu R6094 photomultiplier tube. In order to compare the thermoluminescent response of the sample that experimentally offered a promising behavior with the commercial dosimeter, TLD-100, both samples were irradiated with a dose of 0.22 Gy and normalized by weight. A comparison of its TI response with that of alumina was also made.

3. Results and discussion

Fig. 2 shows representative XRD patterns of samples A1, A4 and A8 after processing by CVD according to Table 2, allowing the identification of reflections pertaining to AlF₃ (symbol ●)(ICDD 01-080-1007), Al₂O₃ (symbol □)(ICDD 00-043-1484) and Al₂F_{1.44}(OH)_{0.56}SiO₄ (symbol ◇)(ICDD 01-076-0480).

Formation of aluminum fluoride (AlF₃) is ascribed to the reaction between aluminum oxide and silicon tetrafluoride (reaction 2), being the latter, a gaseous reaction product from the thermal decomposition of Na₂SiF₆ (reaction 1). The presence of the topaz in the samples is attributed to two possible reactions (3 and 4); reaction (3) occurs between aluminum oxide, water vapor and silicon tetrafluoride, whilst reaction 4 takes place between the products of reaction 2 with water vapor. The thermodynamic feasibility of the reactions was determined using the FactSage[®] program and databases and from the literature [34].

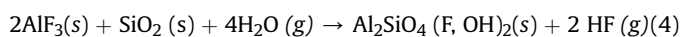
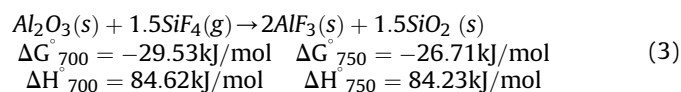
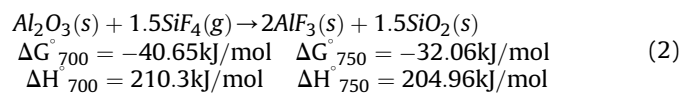


Fig. 3a and b are representative SEM micrographs of samples A4 and A8 after synthesis by CVD, respectively. As shown in Fig. 3a – in accord with the results of characterization by XRD (Fig. 2) –,

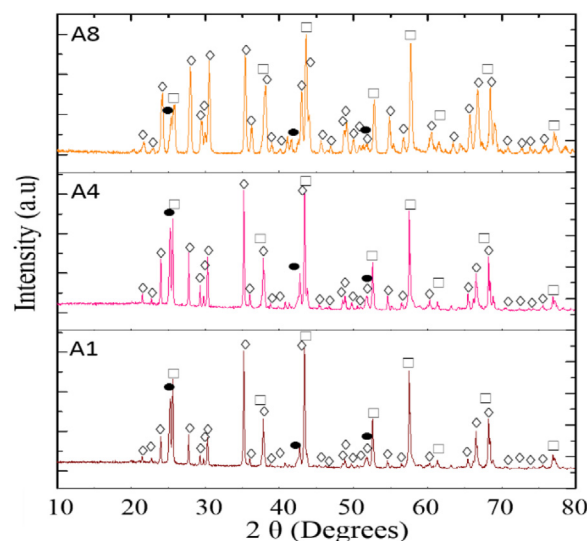


Fig. 2. Representative XRD patterns showing the presence of topaz (ICDD 01-076-0480) Al₂F_{1.44}(OH)_{0.56}SiO₄: ◇, alumina (ICDD 00-043-1484) Al₂O₃: □ and aluminum fluoride (ICDD 01-080-1007) AlF₃: ●, after processing by CVD.

analyses by EDS of samples A4 reveal the presence of aluminum oxide and topaz, exhibiting the latter a morphology of rectangular bars. Fig. 3b shows the presence of rectangular bars with homogeneous distribution of solely topaz (in lengths of 10 and 15 μm).

Using the X Powder[®] program – which is based in the nonlinear least squares method –, a semi-quantitative phase analysis of the amount of topaz formed (Table 2) was conducted. It is observed that the samples processed at 750 °C (A5–A8) have a larger amount of topaz formed than those processed at 700 °C. Results from the analysis of variance (Anova), presented in Table 3, show that temperature is the parameter with the highest impact on the variability in the quantity of topaz formed, with a contribution of 78%. Temperature is a significant parameter because the higher the temperature, the larger is the decomposition degree of the solid precursor (Na₂SiF₆), thus yielding a greater amount of SiF₄ gas, which may react with the reactant compact (Al₂O₃) to form topaz. Although the contributions of the other parameters are not as significant, their influence on the amount of topaz, can clearly be justified. Firstly, 90 min is the processing time that enhances and maximizes topaz formation (A3, A4, A7 and A8) because with this time level, there is a better interaction between SiF₄ gas and Al₂O₃. Secondly, the presence of N₂ during the holding time is associated to its drag effect on the produced SiF₄ towards the aluminum oxide compact. And thirdly, the reason why the best compact position is 0° – with respect to the gas flow direction – is related with the effective area exposed (upper and lower faces) for interaction with SiF₄ gas.

Before irradiation with a dose of 2.2 Gy, the synthesized samples

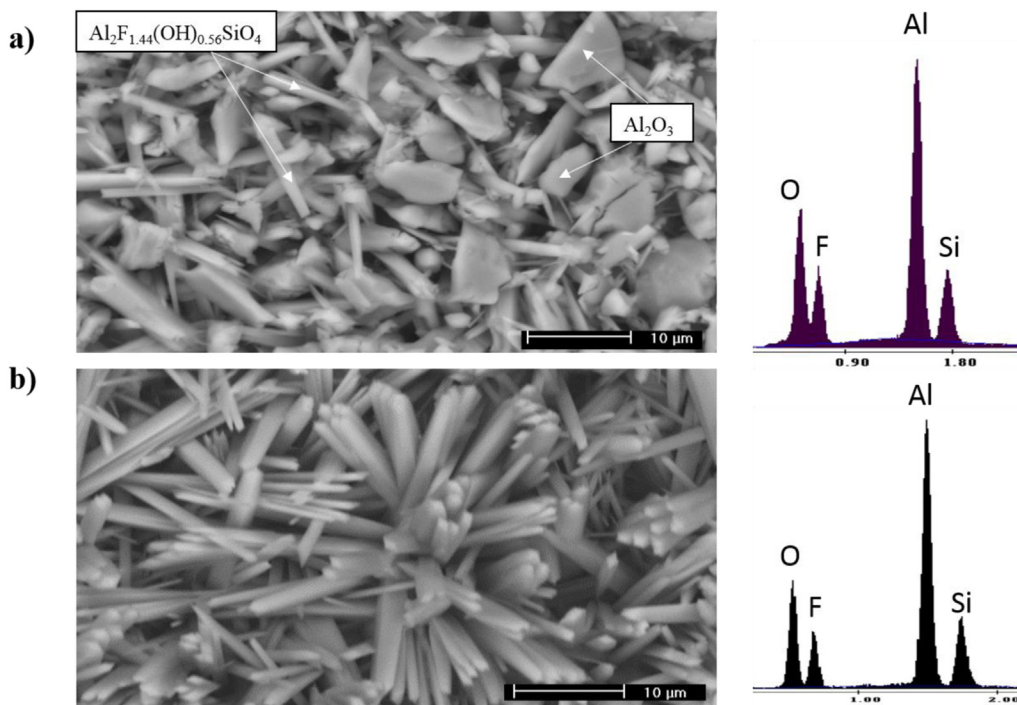


Fig. 3. Representative SEM micrographs of specimens A4 (a) and A8 (b) after synthesis trials.

Table 3

Pooled ANOVA table for percentage of topaz formed.

Parameter	SS	V	P (%)
Temperature	1081	1081	78
Time	120	120	9
Angle position (°)	10	10	1
Atmosphere	91	91	7
Error	88	88	5
Total	1390	1390	100

SS is sum of squares, V is variance, and P is percentage contribution.

were thermally treated at 500 °C. From all the processing conditions tested, sample A4 (processed at 700 °C, 90 min, 0° of aluminum oxide angle position with respect to the gas flow direction, and with gas) exhibited the most intense glow curve. Fig. 4 shows the glow curve of sample A4 irradiated with a beta dose of 2.2 Gy. A main TL peak centered at 271 °C and a low temperature glow peak at 135 °C can be observed. This second glow peak presents two shoulders, the first one between 50 and 100 °C and the second one between 150 and 200 °C. The behavior exhibited by sample A4 might be associated to presence of defects whose formation was promoted during processing, namely, 700 °C, 90 min, 0° and nitrogen flow during the holding time. According to the literature, the center of topaz is related to a center similar to the well-known one in quartz or silica $[\text{AlO}_4]^\circ$. The $[\text{AlO}_4]^\circ$ centers are formed when an Al impurity substitutes for the Si with an extra hole [16,19, and 35].

The thermoluminescent response of samples A1–A8 could be associated to both, topaz and the remaining aluminum oxide, and though Al_2O_3 by itself exhibits thermoluminescent properties, the response of these samples is not attributed solely to this oxide. If it were attributed only to the amount of Al_2O_3 present, the sample identified as A1 would have presented the best thermoluminescent response, but this is not the case. The same reasoning applies to the quantity of topaz formed, where the sample identified as A8 – with

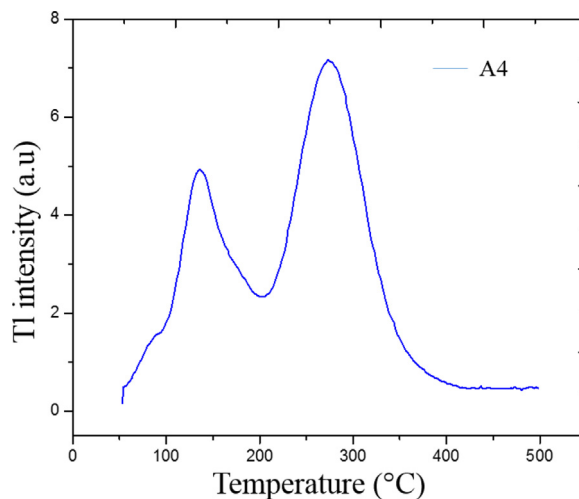


Fig. 4. Representative TL glow curve of the sample A4 irradiated with a beta dose of 2.2 Gy (500 °C).

the highest percentage topaz – does not exhibit the best thermoluminescent response (Table 3). The glow curves of the sample identified as A4 and of aluminum oxide, both treated thermally at 500 °C and irradiated with a beta dose of 0.22 Gy, are shown in Fig. 5. It can be seen that although alumina shows a perceivable TL response, the intensity of the highest peak for synthesized topaz is about one order of magnitude higher than that of the highest peak of alumina.

In order to select the best thermal treatment, of which the sample presents high repeatable response, the standard deviation for each of the specimens in the treatments, based on the glow curves was determined. The values of the area under the glow curve of the different thermal treatments of the sample A4 are observed graphically in Fig. 6. In Fig. 6, each point on the graph corresponds

to the average of three measurements, being analyzed in two temperature ranges, namely, from 53 to 174 °C and from 53 to 300 °C. This was done to determine in which temperature range, the sample measurements are more reproducible. The standard deviations corresponding to each of the thermal-treatment temperatures were calculated.

Results indicate that the sample treated at 800 °C showed the lowest standard deviations (SD %), namely 1.2% and 1.6% in the ranges between 53 to 300 °C and 53–174 °C, respectively. Besides, the glow curve of the sample treated at this temperature shows the highest Tl intensity under the same beta dose. Similar results have been observed by Botter-Jensen et al. in PTTL and OSL study of sedimentary and synthetic quartz samples [31].

Fig. 7a shows the Tl glow curves of samples irradiated at different beta doses. The glow curves show two intense Tl glow peaks at about 135 °C and 275 °C. The Tl signals as a function of dose are shown in Fig. 7b. Fig. 7b was constructed by calculating the area under the glow curve in the temperature range 53–174 °C. It can be observed that the Tl response increases as the dose increases up to 66 Gy, with an approximately linear behavior with an adjustment of 97.7%. The calculation of the adjustment was carried out in two ranges of the glow curve of 53–174 °C and 53–300 °C, but the first range presents the best linear fitting.

Fig. 8 shows graphically the fading undergone by sample identified as A4 (800 °C), revealing that the greatest loss of information – which is lower than 22% –, occurs during the first 20 h. The monotonic decay curve in Fig. 8 is composed of 7 points corresponding to the integrated Tl signals for each of the elapsed times (0, 1, 6, 14, 24, 45 and 70 h) after that the specimens were irradiated, and which correspond to numbers of the curves in the inset. It is observed from the inset and the decay curve that the shoulder between 50 and 100 °C decreases as the storage time increases and completely disappears in the first 20 h. It should be noted that the fading – attributed to the existence of shallow traps in the material – observed in sample A4, is similar to that reported by other authors [12,17].

Although there are several Tl materials available for ionizing radiation dosimetry, only four of them are characterized as tissue equivalent materials ($Z_{\text{eff}} \approx 7.4$) as they have a response similar to that of human tissue. These are lithium fluoride (LiF), lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), beryllium oxide (BeO) and magnesium tetraborate (MgB_4O_7) and they are used for medical application and personnel monitoring. The most widely used material is the LiF doped with magnesium and titanium (TLD-100) which consists of 92.5% of ^7Li and 7.5% of ^6Li [36]. The glow curve of TLD-100 has 6

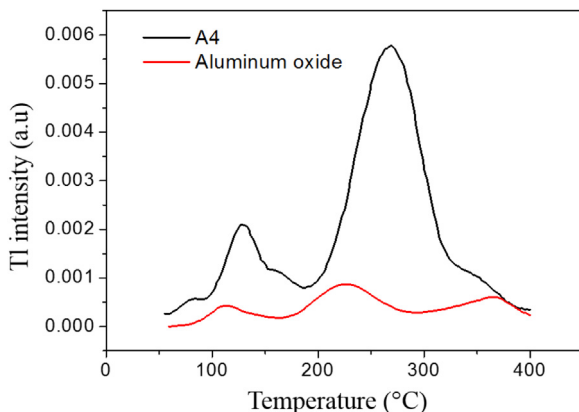


Fig. 5. Comparison of Tl glow curves for Al_2O_3 and synthesized topaz both annealed at 500 °C and then irradiated with a beta dose of 0.22 Gy.

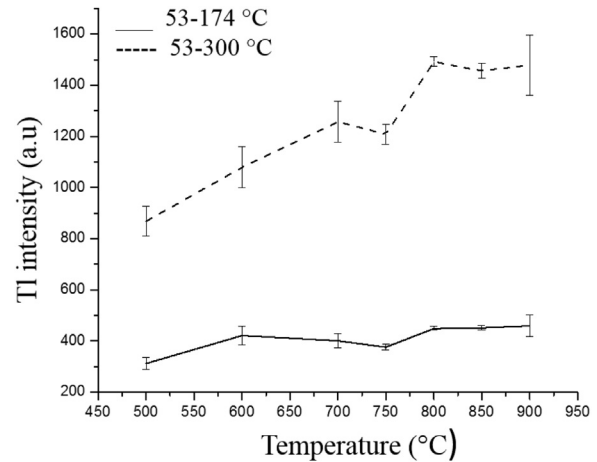


Fig. 6. Graphical representation of the areas under the glow curves corresponding to each of the thermal treatment temperatures, for the temperature ranges of 53–174 °C and 53–300 °C.

characteristic peaks at different temperatures in the interval between 25 and 300 °C, as shown in Fig. 9.

In general, the sum of the areas of peaks #4 and #5 or the area of peak #5 separated from peak #4 by CGCD (Computerized Glow Curve Deconvolution) are the used ones for environmental, clinical or personnel dosimetry. Furthermore, the TLD-100 material has a TL fading of 10% monthly [36] and after the TLDs are readout, they are annealed in order to ensure the signal has been completely removed and the TLD is again ready for use. For the TLD-100 the annealing is not as simple, as it is first heated at 400 °C for an hour and then at 80 °C for 24 h [36].

In the case of topaz synthesized in this work, the area of the broad peak centered at 270 °C is approximately the same as the sum of the dosimetric peaks #4 and #5 of TLD-100 dosimeter (see Fig. 9). Besides, this peak did not show fading and it was not necessary an annealing procedure after each measurement. These facts suggest a potential applicability of the synthesized material in the assessment of the radiation dose received by the human body.

4. Conclusions

An investigation on the thermoluminescent response of synthetic topaz prepared by chemical vapor deposition (CVD) has been conducted. Synthesis trials were conducted subjecting the Al_2O_3 reactant compact and sodium hexafluorosilicate (solid precursor) under the following conditions: temperature (700 °C and 750 °C), time (60 and 90 min), Al_2O_3 compact position with respect to the gas flow direction (0 and 90°) and, with and without a flow of nitrogen during the dwell stage. Experimental results by XRD, SEM and EDS show the feasibility to synthesize topaz by CVD within the framework of the experimental conditions. Sample A4 – processed at 700 °C for 90 min, with gas, and placed at 0° with respect to the flow direction of gas (N_2) – showed the best thermoluminescent response. Annealing sample A4 at 800 °C allowed obtaining the highest intensity in the glow curve and the lowest standard deviation. Its Tl response exhibits a nonlinear behavior with an adjustment of 97.7%. Although topaz synthesized in this work was not detected as a unique phase, its fading is similar to that reported for natural topaz in the first 20 h, with a fading of the 22%. A similar Tl intensity compared with that of the commercial dosimeter TLD-100 suggests its potential application in dosimetry. Comparison of the Tl glow curves of Al_2O_3 and synthesized topaz, treated under the same conditions, showed the dominance of topaz as a

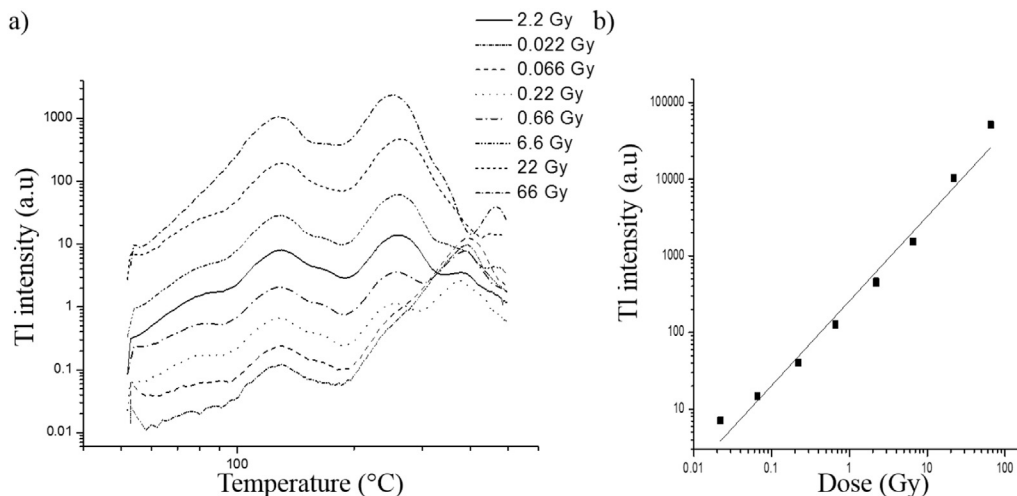


Fig. 7. a) TL glow curves of the samples exposed to different doses b) TL response as a function of the beta doses (Gy).

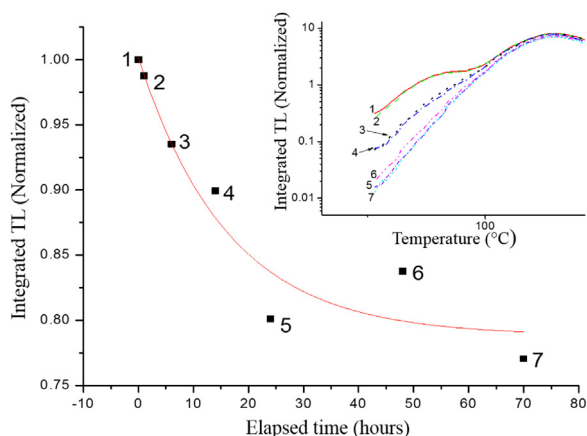


Fig. 8. Study of fading of sample A4 irradiated with a dose of 2.2 Gy. In the inset: magnification of TL glow curves, observing that the shoulder between 50 and 100 °C decreases as the storage time increases.

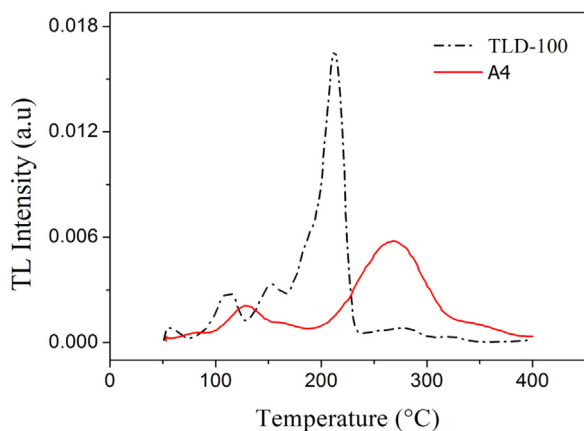


Fig. 9. TL glow curve of sample A4 compared to that of TLD-100 commercial dosimeter (dose of 0.22 Gy).

thermoluminescent material.

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