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Synthetic polycrystals of $CaSiO_3$ un-doped and Cd, B, Dy, Eu-doped for gamma and neutron detection

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ABSTRACT

The undoped and B, Cd, Dy, Eu doped synthetic $CaSiO_3$ polycrystals were produced in the laboratory. They are very sensitive γ-ray detectors with main prominent TL peak occurring at about 270 °C, this peak was obtained using 4 °C/s heating rate. The TL behavior changes very little by doping with B, Cd and Dy while Eu doping brings changes. These minerals can be used also for neutron dosimetry. Thermal neutrons react with Ca, Si and O through (n, γ) process and γ emitted in this reaction added to γ-rays of the reactor that produces thermal neutrons and are responsible for induction of thermoluminiscence. The TL response of $CaSiO_3$ is linear for dose < 10 Gy and then has a supralinear behavior up to about 7 kGy and saturating beyond.

1. Introduction

The development and study of new radiation dosimeters have been published in the past [1–16]. In fact, a large number of materials have been investigated as to their sensitivity as thermoluminescent phosphors. Of course, other physical properties have also been investigated to be used for radiation dosimetry, such as electron spin resonance, optically stimulated luminescence, etc. [17–19]. Concerning TL dosimeter, it is desirable that it detects not only electromagnetic radiation, but also charged accelerated particles as well as neutrons. Neutrons are detected through nuclear reaction with atoms in the detector. While very low energy neutrons with energy smaller than few keV interact with any element through (n, γ) reaction [20], higher energy neutrons can have reactions involving protons or even larger particles. When the (n, γ) reaction takes place, the nucleus of the element absorbs a neutron and the isotope formed drops to the ground state by the gamma emission. The detector absorbs all or part of these emitted γ-rays which induces TL on the dosimeter.

In nature, a large amount of the so called silicate minerals are found. They are very sensitive concerning the thermoluminescence is considered. Hence they are good radiation dosimeters. Beryl, tourmaline, quartz, jadeite are good examples. Natural wollastonite is $CaSiO_3$ silicate mineral that has been investigated as a possible material for radiation dosimetry [21,22].

This paper concerns synthetic $CaSiO_3$ for electromagnetic radiation and neutrons detection. There are, of course, natural wollastonites.

There are three structural modifications of wollastonite: (1) pseudowollastonite (β-$CaSiO_3$) the high temperature form, it is crystallized in triclinic symmetry; (2) wollastonite-2M and (3) wollastonite-Tc. These two last ones are referred to as low temperature form, also considered (α-$CaSiO_3$) [23]. While wollastonite-2M is monoclinic, wollastonite-Tc is triclinic. Fig. 1 show the structure of wollastonite-Tc projected in z-plane [24]. The chains of SiO_4-tetrahedra and Ca atoms are shown.

Yamanaka and Mori [25] studied the structure of a pseudowollastonite crystal showing that it is characterized by four layers, one of which is composed of ternary rings of three tetrahedra of SiO_4 and a seemingly octahedral layer. Hesse [26] found that the structure of wollastonite-2M is monoclinic with space group $P21/a$, a = 15.409. Yang and Prewitt [27] using XRD have shown that pseudowollastonite is the high temperature form of $CaSiO_3$, above 1125 °C and commonly occurs in slags, cement and ceramic materials. It has monoclinic $C2/c$ symmetry. Souza et al. [28,29] used pellets of mixed wollastonite and teflon and irradiated them with x-rays. The TL glow curve presented peaks at 85 °C and 200 °C, the second one being the prominent one. Kulkarni et al. [30] produced nanocrystalline β-$CaSiO_3$ by low

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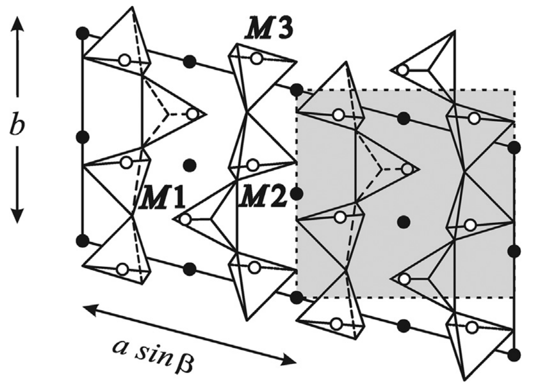

Fig. 1. Structure of wollastonite-Tc projected on (*a*, *b*)-plane showing SiO_4-tetrahedra chains. White circles (o) are Ca-ions. The dashed area is that described as having pseudomonoclinic symmetry. (After [24]).

temperature combustion method. Its TL glow curve showed a shoulder peak at 175 °C and prominent peak at 230 °C. The deconvolution has shown that high temperature peak is a superposition of 208 and 242 °C peaks.

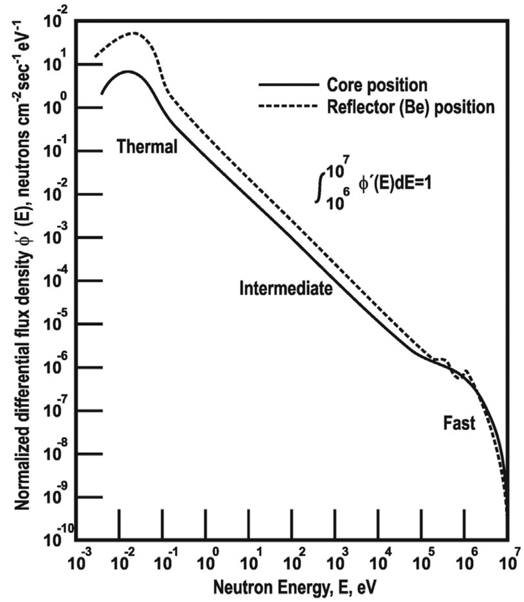

Fig. 2. Neutrons flux in a research reactor.

2. Materials and methods

The synthesis process to produce an artificial pure $CaSiO_3$ polycrystals starts with weighing stoichiometric quantities of reagent grade CaO and SiO_2. In the present, we used 12.0 g (48.3 wt%) CaO and 12.8 g (51.7 wt%) of SiO_2. It then placed in an oven heated to 1500 °C to melt the above mixture, for two hours. The melt is then cooled slowly using a temperature controller so that the room temperature is reached after about 24 h. This process produces a polycrystalline material. To produce doped $CaSiO_3$, before melting 392 ppm Cd, 135 ppm B, 500 ppm Dy, and 1000 ppm Eu was added in each batch.

These polycrystalline samples of $CaSiO_3$ doped and undoped were crushed and sieved to retain grains 0.080–0.180 mm in size for TL measurements, while grains smaller than 0.080 mm in diameter were used in the X-rays diffraction analysis.

TL measurements were carried out using Harshaw TL reader model 4500 in a nitrogen atmosphere; the heating rate was kept at 4 °C/s. Each point in the glow curve is an average of five readings.

The irradiations for low dose of the order of mGy and high doses in the region of hundreds of Gy were done at the Radiations Technology Center (CTR) of the Institute for Energy and Nuclear Researches (IPEN) using a ^{60}Co source type gamma-cell with a dose rate of 0.739 kGy/h, and a panoramic type source with a dose rate of 9.10 Gy/h at 40 cm from the source. For very low dose irradiation (mGy), was used a ^{137}Cs source of 662 keV gamma rays and with a dose rate of 9.54 mGy/s at 30 cm from the source. The γ-irradiation was performed at room temperature and under conditions of electronic equilibrium.

The research reactor IEA-R1 belonging to the Institute for Energy and Nuclear Researches is a swimming pool type reactor operating at 5 MW power. Fig. 2 shows approximate Normalized differential Flux Density ϕ´(E) of neutrons in $cm^{-2}s^{-1}eV^{-1}$ of a research reactor, adapted from [31]. Thermal neutrons are considered those with energy < 0.5 eV.

Synthetic, pure, polycrystals of $CaSiO_3$ with grains size selected between 0.080 and 0.180 mm sizes were sealed in silica tubes each of about 4 mm diameter and 20 mm long. Each such tube has been placed inside a somewhat larger aluminum tube to be irradiated in a position called 13B inside IEA-R1. For technical reason the irradiation was carried out in two different periods: in the first the detectors were irradiated with (6.0, 15, 30, 60) $x10^{13}$ n/cm^2; in the second with (2.1 and 30)$x10^5$ n/cm^2 fluences in two different positions.

The pure and doped polycrystlas of $CaSiO_3$ were irradiated in thermal (largest portion), epithermal (smaller portion) and fast neutrons (very small fraction). Since thermal and epithermal neutrons interact with Ca, Si and O trough (n, γ) reaction and out coming γ that induces TL in the dosimeters what we are measuring is essentially thermal and epithermal effects

3. Results and discussion

The diffractograms of the undoped, and Cd, B and Dy doped polycrystals are shown in Fig. 3. Comparing the powder XRD pattern to the 96-901-1914 and 96-900-2180 files of the Match Program, all the peaks of the polycrystals were identified as belonging to wallastonite-2M ($CaSiO_3$ undoped) and pseudowollastonite (for Cd, B, Dy and Eu doped), respectively. This result shows that the polycrystals obtained by the devitrification method is adequate to obtain polycrystals with crystalline structure of the wollastonite.

The dose response of synthetic materials for dosimetry applications is a very important property. An ideal dosimeter should have linear behavior for all dose range. In order to determine the dose response of the un-doped, and Cd, B, Dy and Eu doped samples from low dose of the order of mGy up to high dose (kGy), the samples in powder form were irradiated with different gamma-doses.

Just for practical purpose let us assume in this paper that wollastonite refers to natural minerals and $CaSiO_3$ to synthetic polycrystals.

The undoped samples irradiated with doses higher than about 10 mGy presented TL peaks at 270 °C. TL glow curves of undoped $CaSiO_3$ samples irradiated with low dose between 10 mGy and 1 Gy are shown in Fig. 4(a). Fig. 4(b) shows the glow curves of $CaSiO_3$ undoped and irradiated with gamma rays with doses larger than 5 Gy up to 50 kGy. This results show that the synthetic pure $CaSiO_3$ is a very sensitive ionic crystal as far as its thermoluminescence is concerned and to wide range of gamma-rays dose, from mGy to 30–50 kGy.

Fig. 5 shows the TL response of the main TL peak for doses ranging from mGy to kGy range. Analyzing the dose response curves with log axes in the same scale, as shown in Fig. 5, it can be observed that the TL response of peak at 270 °C has a linear behavior as the curve slope equals to 45° in the dose range from few cGy up to about few Gy and after that TL response is supralinear up to about 7 kGy and then it saturates. This means that we have here a detector that responds from few cGy to 7 kGy.

As to the models that explain supralinearity there are, in fact, many.

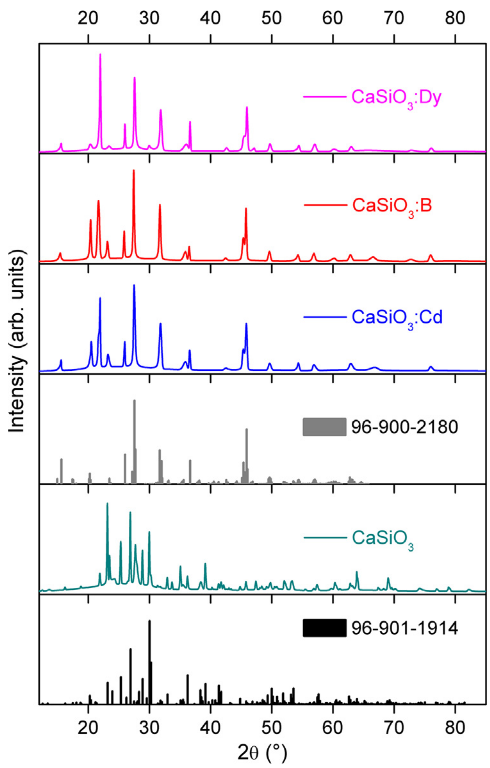

Fig. 3. XRD pattern of $CaSiO_3$ and $CaSiO_3$ doped with Ca, B and Dy produced in this work, to be compared with XRD patterns from Archive 96-901-1914 (wallastonite-2M) and 96-900-2180 (pseudowollastonite) - program Match!.

Broadly, they are divided into that is assumed to happen in the irradiation stage and the other during heating for reading TL.

One of the first models was introduced by Cameron and Zimmerman [32]; it assumes that besides existing TL traps the irradiation creates new traps that are responsible for supralenearity. Cameron and Zimmerman [33] proposed a model in which the radiation create new centers of recombination. Suntharalingam and Cameron [34] proposed competing trap model. The track interaction was introduce by Claffy et al. [35], but Mische and McKeever [36] introduced track interaction model different from that of Claffy et al. [35].

The reproducibility of the dosimeters can be affected after repeated usage [37]; therefore, this is one of the most important factors for dosimeter materials. For analysis the reproducibly of undoped synthetic $CaSiO_3$ polycrystals sample, 1.8 mg of sample in powder form was irradiated with 1.0 Gy of test dose, read and annealed, and irradiated again; this procedure was repeated four times to the same sample. The Fig. 6 shows the reproducibility and the sensitivity by intensity of peak at 270 °C, decreasing by 18% after of first sequence of radiation-reading-annealed during the procedure of TL readout.

Another important property of any TL material is the fading [38]. We irradiated $CaSiO_3$ with 1 Gy γ-rays and kept it in the dark. Its TL was read out after, one, two, etc. hours up to 32 days. The result is shown in Fig. 7. It shows that there is decay is about 20% in the first 2–3 h, but after that there is no decay. Therefore, we say $CaSiO_3$ has small fading.

To compare with the glow curves from undoped samples, in Fig. 8, the glow curves of doped synthetic samples with Cd, B and Dy and irradiated between 0.5 and 50 kGy are presented. The pure sample has shown peak around 270 °C. This result indicates that this TL peak in $CaSiO_3$ is due to intrinsic defects.

In a silicate crystal, it is known that oxygen vacancies are produced at room temperature [39,40]. Under irradiation, for example, with ^{60}Co γ-rays two facts occur. First, it creates a large number of electron-hole pairs and two electrons are captured by oxygen vacancy. Second, the radiation produces new oxygen vacancies that capture electrons. The

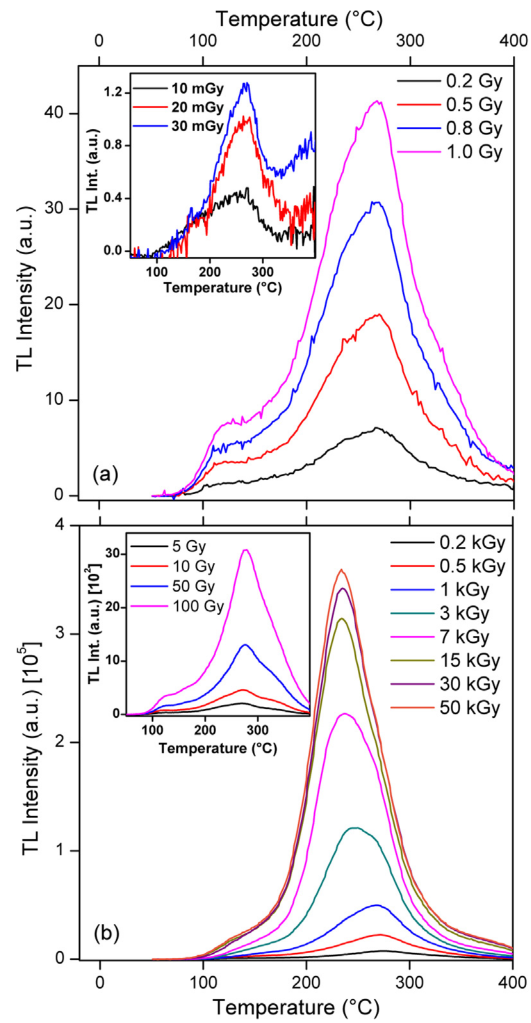

Fig. 4. (a) TL glow curves of $CaSiO_3$ irradiated with low γ-ray doses of 10 mGy up to 1.0 Gy using a mass about 5.6 mg. (b) TL glow curves of $CaSiO_3$ irradiated with γ-ray doses (^{60}Co source) of 5 Gy up to 50 kGy using a mass about 1.8 mg.

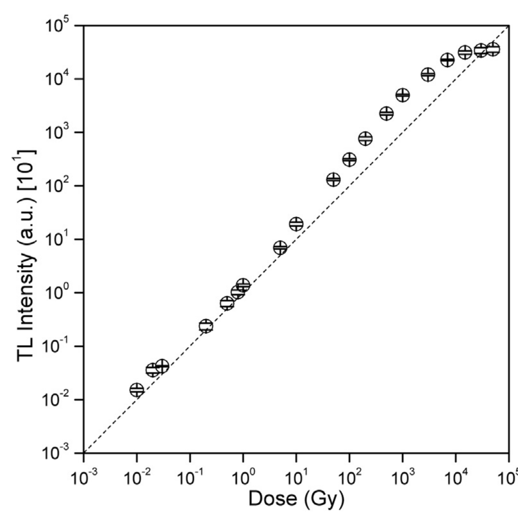

Fig. 5. TL intensity behavior of the 250–270 °C peak as a function of gamma radiation doses, the dashed line indicates linearity. In the inset of the figure, the TL intensity versus doses of the TL peaks at 270 °C for low dose irradiation is shown.

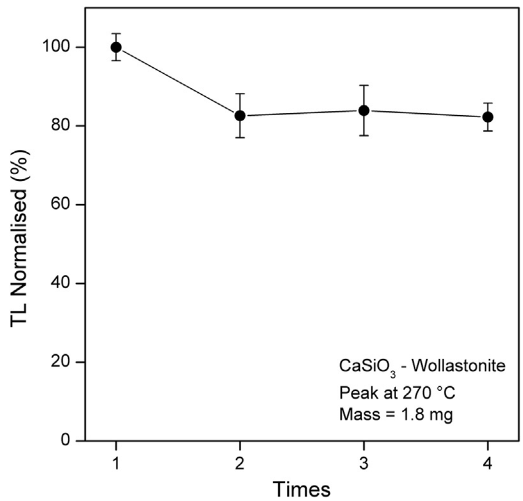

Fig. 6. Reproducibility of TL response of undoped $CaSiO_3$ synthetic irradiated with 1 Gy of ^{60}Co.

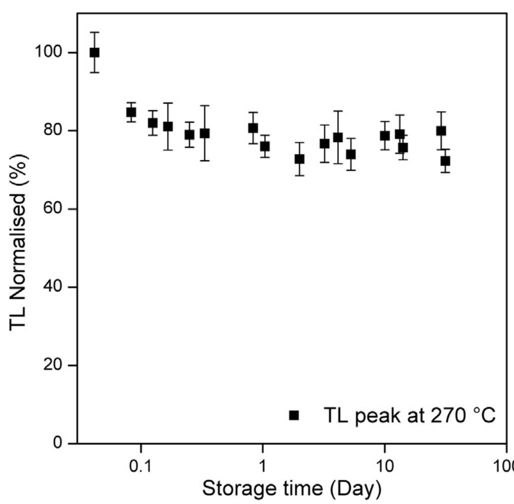

Fig. 7. TL intensity of the samples irradiated with 1 Gy against the storage time at room temperature for the undoped wollastanite.

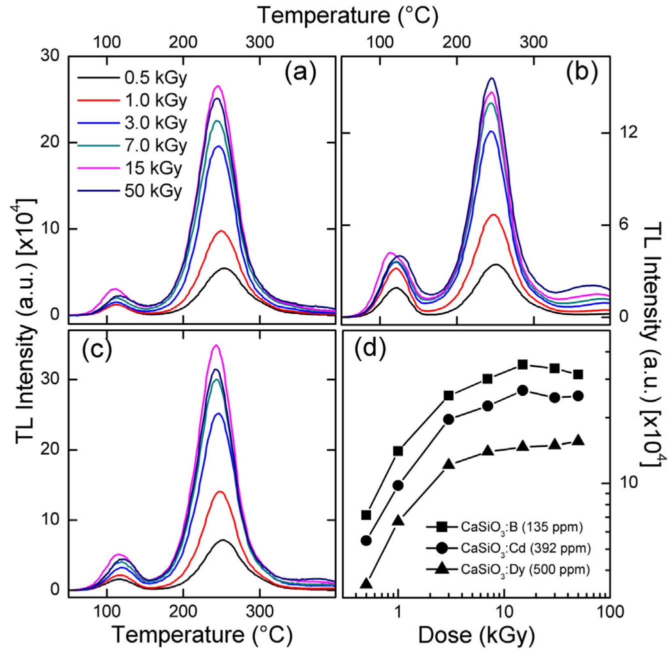

Fig. 8. TL glow curves of $CaSiO_3$:x (a) x = Cd, (b) x = Dy and (c) x = B irradiated with gamma dose of 0.5–50 kGy. (d) TL intensity versus doses of the TL peaks at 270 °C for three doped samples.

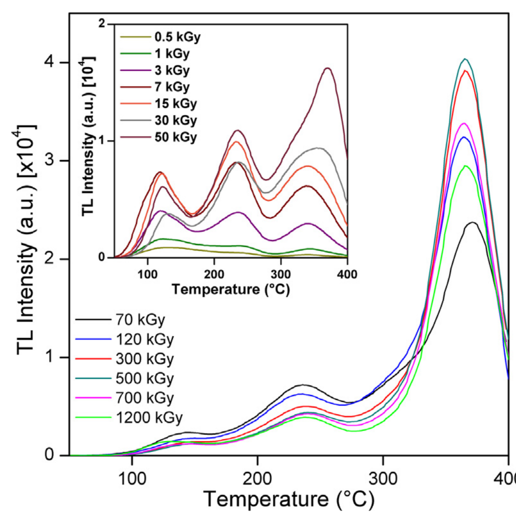

Fig. 9. TL glow curves of $CaSiO_3$:Eu (1000 ppm) irradiated with gamma dose of 0.5–1200 kGy.

radiation also creates aluminum centers, $[AlO_4/h]$ [18]. With heating crystal up to 300 °C, one electron from oxygen vacancy with two electrons is liberated creating E'_1-center which is one oxygen-vacancy with one electron. Above 300 °C the remaining electron is liberated. These liberated electrons recombine with holes in the aluminum center and emit TL light (TL peaks) [41].

In Fig. 9 glow curves of $CaSiO_3$:Eu are shown for radiation doses from 0.5 up to 1200 kGy. Although the glow curves shown in Fig. 9 exhibit three peaks as in B, Cd, Dy doped $CaSiO_3$, Fig. 8. We note that there is the following difference, in Eu doped $CaSiO_3$ the peak 3 is prominent while in other cases the peak 2 is very intense compared to peak 3. Nothing was found in the literature about this effect of adding 1000 ppm Eu as impurity. This will be subject of future work.

Fig. 10(a) shows glow curves of undoped $CaSiO_3$ irradiated with thermal neutrons with fluence indicated in the figure. Fig. 10(b) shows glow curves of $CaSiO_3$:Dy irradiated with neutrons with fluence as indicated in the figure. Similar glow curves are exhibited by $CaSiO_3$ doped with B and Cd. Compared to the glow curve of undoped $CaSiO_3$, it is to be noted that the doping induces smaller peaks around 120–125 °C and other one around 375 °C. Now Fig. 10(c) shows glow curves of $CaSiO_3$:Eu, which is essentially the same as that of Eu-doped $CaSiO_3$ irradiated with gamma-rays. Fig. 10(d) presents TL intensity as function of neutron fluence in linear-log scale.

At this stage, we can only surmise following mechanism of TL emission:

a) Ca substitutes for Si in SiO_4 tetrahedra. To compensate the charge disequilibrium, $[CaO_4]^{2-}$ attract either 2 monovalent cations or one divalent cation:

$$(SiO_4)\xrightarrow{Ca}(CaO_4) + Si$$
$$(CaO_4)^{2-} + 2M^{+} \rightarrow (CaO_4/2M^{+})$$

under irradiation $2\,M^{+}$ will be liberated leaving a $(CaO_4/2\,h)$- two holes center. During heating electrons liberated by oxygen vacancy that captured two electrons recombine with holes in $(CaO_4/2\,h)$ and emit TL light.

b) Rudra and Fowler [39] statement that in quartz, oxygen vacancies are formed in large concentration at room temperature and assumed that the same oxygen vacancies $(VO)^{2+}$ are found also in silicate

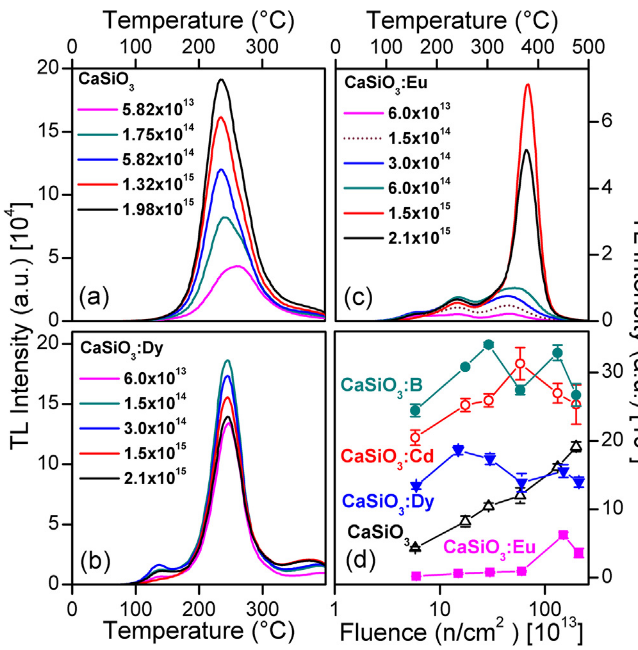

Fig. 10. Glow curve of (a) undoped $CaSiO_3$, (b) $CaSiO_3$:Dy and (c) $CaSiO_3$:Eu irradiated with neutrons from research IEA-R1 with different fluencies. (d) TL intensity vs. neutron fluence for all samples.

minerals. When the crystal is irradiated with ionizing radiation large numbers of electron-hole are produced and oxygen vacancies capture each two-electrons: (VO, 2e). Toyoda and Ikeya [40] have shown that when the crystal is heated up to about 300 °C one electron from (VO, 2e) is liberated leaving E'_1 center. From 300 °C to about 450 °C the remaining electron is liberated.

Here, we assume that the irradiation produces non-bonding oxygen hole center (NBOHC) or (wet OHC) proposed by Ikeya [18]. During heating liberated electrons will recombine with hole in NBOHC and emit TL light.

At this moment, we cannot decide which one among (a) and (b) is the possible mechanism for TL emission. A work plan will be carried out in near future, for example, there is such Ca-hole-center, by EPR. Also by EPR we will find the concentration of NBOHC centers.

4. Conclusions

In this work $CaSiO_3$ polycrystals both pure and doped with B, Cd, Dy and Eu have been produced for electromagnetic radiation and thermal neutron detection. In the near future heavy ions dosimetry will be carry out. $CaSiO_3$ detectors are suited for that proposal.

$CaSiO_3$ (doped or not) is sensitive to low doses of the order of mGy, therefore it can be used in radiotherapy or nuclear medicine. Actually, we already have done application in nuclear medicine with good results. $CaSiO_3$ is also sensitive to high doses in the region of kGy, therefore it is a detector with wide range dosimetric capability.

One advantage of $CaSiO_3$ detectors is that although it has three TL peaks in the glow curve, the peak at about 250 °C is dominating, such that the two other peaks can be ignored.

Doped with B, Cd and Dy $CaSiO_3$presented a similar behavior as the pure one, however, doping with Eu, the crystal presented a prominent third peak and weak first and second peak. One possibility, to be confirmed, is to Eu^{3+} substitute for silicon ion in $[SiO_4]$ and transforms into $[Eu^3O_4/h]$ center, such that the main electron-hole recombination occur around 320–370 °C.

We are carrying out several EPR measurements under several radiation dose irradiation and under different annealing temperatures. Under heavy irradiation we expect to identify the defects centers and the annealing procedures can establish connexion of these defects to TL peak temperatures.

The irradiation of $CaSiO_3$ with thermal neutrons the main effect is the (n, γ) reactions that takes place with Ca, Si and O. Therefore, the effect is that of irradiation of CaSiO3 with γ-rays.

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