Thermoluminescence and defect centers in synthetic diopside

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A B S T R A C T

$MgCaSi_2O_6$ polycrystal was synthesized by the devitrification method. The dosimetric characteristics by TL of this prepared polycrystal was investigated. This material exhibits TL peaks at 115, 160, 210, 260 and 280 °C. The dosimetric peak occurs at 260 °C with a well defined glow curve structure. This peak shows a linear dose response. Electron paramagnetic resonance (EPR) studies have been carried out to identify the defect centers responsible for the TL peaks. Two defect centers in the region of $g = 2.0$ are found. One of the centers (center I) with a g factor equal to 2.0085 is identified as O^--ion and relates with the observed high temperature 250 and 300 °C TL peaks. Additional defect centers with $g = 2.0012$ (center II) and 1.982 (center III) are due to F^+-centers (electron trapped at an oxygen vacancy). Center II and III correlate with the TL peaks at 160 °C and 106 °C, respectively.

1. Introduction

Cano et al. [1,2] investigated TL properties of natural and synthetic diopside ($MgCaSi_2O_6$). Natural diopside contains, besides CaO, MgO and SiO2, as impurities Al_2O_3 (1.56% mol), Fe_2O_3 (0.53% mol), K_2O (0.44% mol), TiO_2 (0.065% mol), P_2O_5 (0.026% mol) and MnO (0.013% mol). Others impurities are found in very small amount. The diopside is one of the group of pyroxenes, whose structure is characterized by two types of cation ions, M1 and M2. M1 is smaller in size than that of M2. In diopside normally M1 is occupied by Mg and M2 by Ca, but Mn^{2+} can enter either in M1 or in M2. Mn^{2+} produces a known EPR spectra, being more intense spectrum when Mn^{2+} is found in M2. Fe^{3+} can enter at M1 site as the ion is smaller.

Cano et al. [2] produced in laboratory non-doped and doped (with Al, Mn and Fe) $MgCaSi_2O_6$. The TL glow curve of a natural sample has one strong peak around 160 °C and very weak one at 375 °C and TL as function of dose grows linearly up to about 500–600 Gy and became sublinear, saturation at around 10 kGy.

The non-doped and Mn-doped diopside have stronger TL peak at 260 °C than 160 °C peak in natural sample. Al-doped sample has as strong peak about 160 °C as the natural one, but Fe-doped diopside has one very small peak at 440 °C. It is to be noted that Fe is known as TL-killer.

Thermoluminescence is a thermally stimulated emission of light from some crystalline materials when it absorbs previously energy from electromagnetic radiation. This phenomenon is very much useful for detection or measurement of absorbed radiation in many fields as archeological and geological dating and application in the personal radiation dosimetry. The TL is a physical property of the materials that have the capability to emit light when it is irradiated and latter heated. The light emitted by the TL materials is proportional to the dose received, hence this a basic phenomenon of ionizing radiation dosimetry. Thus TL materials give the information about the quantity of energy deposited by the ionizing radiation in the TL material [3].

Nowadays, dosimetric materials are inorganic crystalline materials called nominally as phosphors.

These materials emit characteristic luminescence when suitably excited by either light or heat. Among these materials are natural and synthetic silicates. Recently, some natural and synthetic silicates have been widely investigated due to their significance for fundamental research and their high potential for application in radiation dosimetry using the TL technique [4–8]. Even though these materials present interesting luminescence properties, few studies have been carried out on the defects responsible for the TL emission of these materials [9–13].

Radiation-induced defects in phosphors and their role in their

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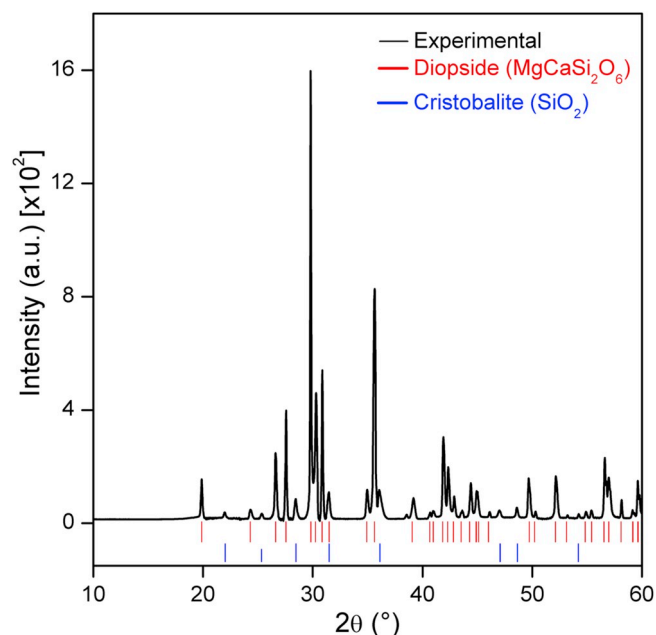
Fig. 1. X-ray diffraction of MCSO polycrystal.

Fig. 2. (a) TL glow curves of MCSO polycrystal irradiated with low γ-ray doses of 0.12 Gy up to 10 Gy. (b) TL glow curves of MCSO polycrystal irradiated with γ-ray doses of 50 Gy up to 1 kGy.

thermoluminescence properties are well established. However, it is not possible to identify the defect centers responsible for the trapping of the electrons responsible for the TL emission. The EPR spectrometry is a powerful, non-destructive and nonintrusive characterization technique of crystalline materials, which yields meaningful structural and dynamical information of the gamma radiation-induced defect centers formed in a lattice responsible for the physical processes as the thermoluminescence. Therefore, EPR is a powerful tool to find the radiation induced defects in phosphors responsible for TL light emission through correlation between TL and EPR techniques.

In the present work we synthesized $MgCaSi_2O_6$ polycrystal and studied the nature of their thermoluminescence property, measuring the effects of gamma irradiation and thermal treatments through TL and EPR techniques in an attempt to find the defect centers responsible for TL emission and seeking possible applications in the area of ionizing radiation dosimetry using this synthetic material.

2. Material and experimental

A $MgCaSi_2O_6$ polycrystal labeled as MCSO, was prepared via devitrification method at 1500 °C. The starting materials used are 25.89 wt % of CaO, 18.61 of MgO and 55.49 wt% of SiO_2. The details of synthesis technique for the preparation this material is similar to the $MgCaSi_2O_6$ polycrystal described in our reported work [2].

The synthetic material of MCSO was crushed and sieved retaining grains with 0.080–0.180 mm diameters for TL and EPR measurements. Grains with diameter smaller than 0.080 mm were used for an analysis by X-ray diffraction (XRD) in order to perform the structural analysis of the synthetic sample produced.

The sample with granulometry as described above were thermally treated at 400 °C during 1 h in open atmosphere, defined for their re-utilization. Then the sample was divided into several aliquots to be irradiated to different γ-ray doses for TL emission and EPR experiments.

Irradiation of the synthetic sample was carried out with a^{60}Co gamma-ray source facility which has a dose rate of 0.739 kGy/h and a panoramic type source with a dose rate of 9.10 Gy/h at a distance of 40 cm from the source. The γ-irradiation was performed at room temperature and under conditions of electronic equilibrium.

TL measurements were carried out in a Harshaw TL Reader, model 4500, equipped with a bialkali photomultiplier (PMT) for light
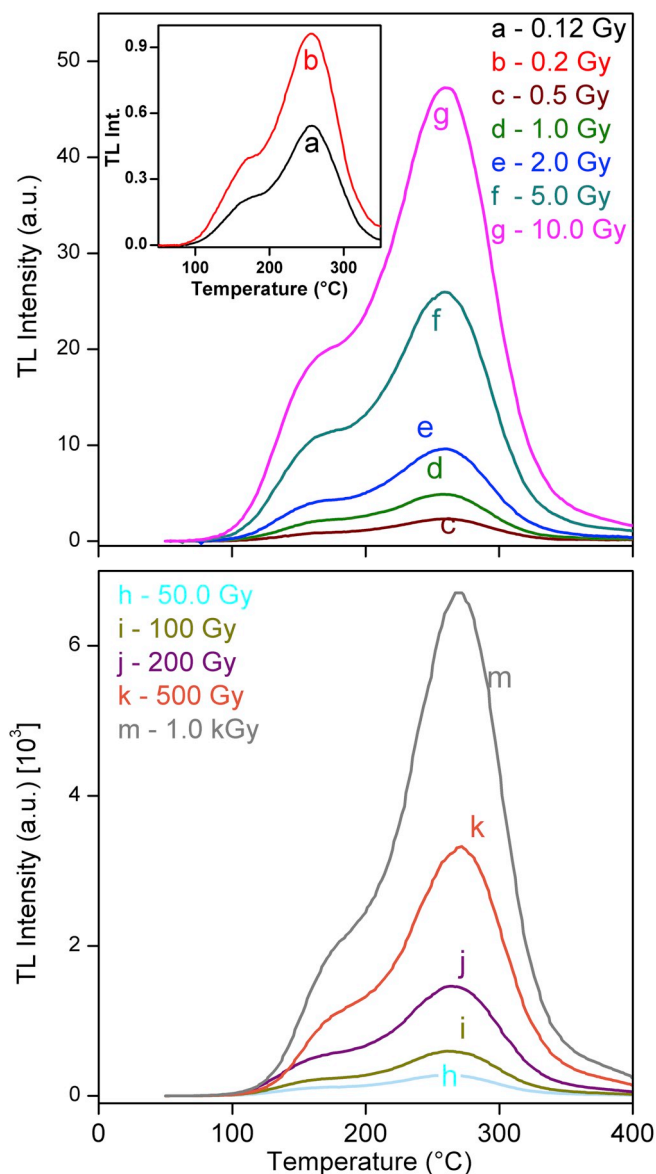
detection. The applied heating rate was 4 °C/s in nitrogen atmosphere.

EPR measurements were carried out using a Miniscope EPR spectrometer, model 5500 of Freiberg Instruments operating at X-band frequency with 100 kHz modulation frequency, microwave power of 1 mW, field modulation amplitude of 0.1 T at room temperature and using an average sample mass of 100 mg.

The structural analysis of the MCSO polycrystal was investigated by XRD using the MiniFlex 300 from Rigaku, with Cu Kα radiation (λ = 1.5418 Å) and the data collected over the 2θ range 10–60° at room temperature. The data then analyzed by utilizing software X'pert HighScore.

3. Results and discussions

The diffractogram of the MCSO synthetic material is shown in Fig. 1, together with the pattern of diopside crystal (PDF-2, No. 01-072-1497) and of the cristobalite crystal (PDF-2, No. 01-082-1232). All the diffraction peaks in the spectrum are coincident of the diopside crystal pattern. At the same time, a little amount of cristobalite (polymorphic
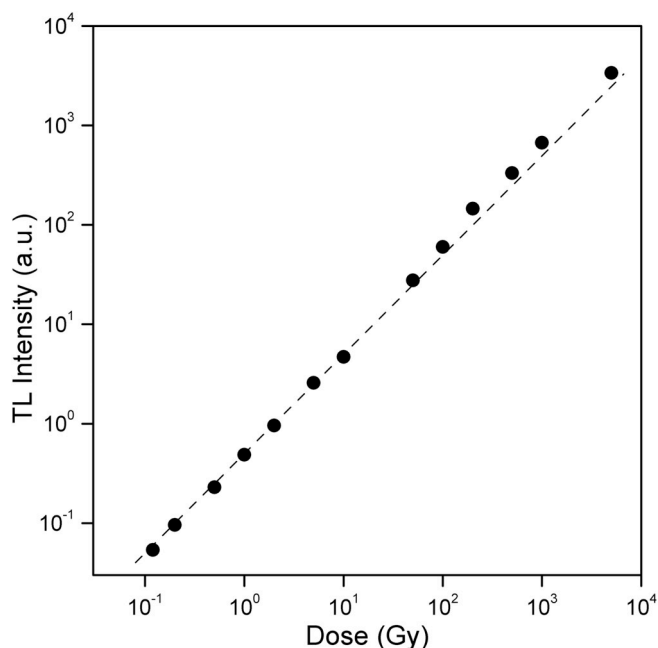
Fig. 3. TL intensity behavior of the 260 °C peak as a function of gamma radiation doses, the dashed line indicates linearity.
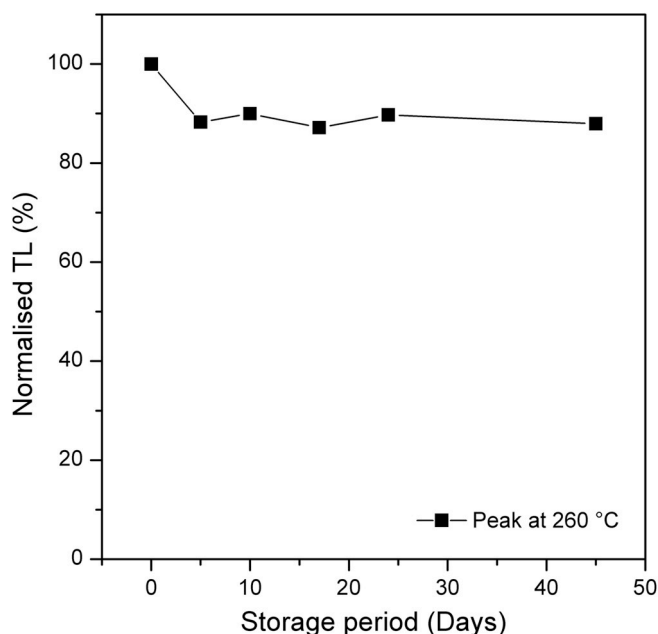

Fig. 4. Fading characteristic of MCSO polycrystal of the TL peak at 260 °C at room temperature.

of quartz - SiO_2) phase was also detected. PANalytical X'Pert HighScore Plus software was used for the refinement and to determine the percentage of each crystalline phase in the sample. The results showed that 98.4% of the sample was diopside and 1.6% was cristobalite. This result shows that the devitrification method is adequate to obtain polycrystals with crystalline structure of the diopside.

Fig. 2 shows the glow curve of MCSO sample in powders exposed to gamma radiation of ^{60}Co. This glow curve exhibited two peaks centered at 160 °C and 260 °C. All TL experimental results were obtained for MCSO sample previously thermally treated at 400 °C before of the gamma-irradiation.

Fig. 3 shows TL response of the 260 °C peak of MCSO sample as a function of gamma absorbed dose. As can be seen in this figure, MCSO

sample showed a behavior linear in the range from 0.12 Gy to 5 kGy. Other TL characteristic is fading; this is the TL response remaining in the material at different post irradiation time [3]. In order to determine the fading characteristics, MCSO sample was annealed and irradiated to a dose of 50 Gy. The sample was stored in dark conditions at room temperature. In order to minimize the effect of a possible reader drift, the sample was exposed at different periods of time prior to readout. Readout was performed for all the irradiated samples at the same time.

This fading experiment for MCSO sample demonstrated a very small decrease of the TL response of the 260 °C peak during the elapsed period of time. After 5 days, MCSO sample showed a fading value of 12% compared with that value obtained just after irradiation. This behavior is showed in Fig. 4.

The TL glow curve of the MCSO sample was analyzed by the *E*-Tstop [3,14] and CGCD [15] methods and the characteristic parameters (i.e. *E*, *s*, and the lifetime) for each peak were calculated.

Fig. 5 shows the obtained activation energies (*E*) using the *E*-Tstop method. With these results and applying the CGCD equations proposed by Kitis et al. [15] we obtain the deconvolution of the TL glow curve of MCSO sample irradiated with a dose of gamma-ray 10 Gy. The inset of Fig. 5 shows the five TL peaks separated using second order kinetics in the region between 50 and 400 °C. The deconvolution analysis has shown that the TL glow curve of the polycrystalline sample is composed of five peaks in the region between 50 and 400 °C. The positions, frequency factors (*s*), activation energies (*E*) and life times (*τ*) of the TL peaks are presented in Table 1. The obtained high lifetime value of the 256 °C TL peak indicate its stability at room temperature and the linear behavior with gamma dose irradiation, allowing us to use the MCSO sample for dosimetric purposes.

$MgCaSi_2O_6$ system contains divalent (Mg^{2+} and Ca^{2+}) and tetravalent (Si^{4+}) ions. Due to antisite disorder, it is possible that some of the Si^{4+} ions may get replaced by divalent Ca^{2+} and Mg^{2+} ions. These disorders are point defect in crystal lattices. Theoretical calculations [16] predict the presence of such disorders in crystal systems. Confirmation of their presence has been made possible by experimental investigations [17,18]. Advanced microscopic techniques have enabled a direct observation of these defects [19]. Cation disorder along with non-stoichiometry in MCSO may result in the formation of oxygen vacancies. It may be mentioned that theoretical calculations suggest the ease of formation of oxygen vacancies in a lattice with cation exchange disorder [20].

Lattice defects arising from the reasons mentioned above act as trapping centers. Electrons may get trapped at oxygen vacancies during irradiation resulting in the formation of F^+ - centers. On the other hand, holes may get trapped at Mg and Ca vacancies to form O^- ions. In O^- ion, the unpaired electron resides in an oxygen *p*-orbital. Electrostatic attraction between a cation vacancy present in the proximity of O^{2-} ion provides stability to the hole on the oxygen. This model of an O^- ion gives rise to positive *g*-shifts.

The room temperature EPR spectrum of gamma irradiated MCSO sample is shown in Fig. 6. Based on thermal annealing experiments, it was inferred that several defect centers contribute to the observed spectrum. These labeled centers are shown in Fig. 6. Center I is characterized by an axially symmetric *g*-tensor with principal values $g_{||} = 2.0033$ and $g_{\perp} = 2.0090$. It is seen that the center exhibits positive *g*-shifts. The EPR line is broad (linewidth ~ 10 G) indicative of an interaction with the neighboring cations or impurity nuclei. Hence, center I is tentatively assigned to an O^- ion. Stability to the ion is provided by nearby cation vacancy viz., $Ca^{2+}/Mg^{2+}/Si^{4+}$ vacancy. Center I features are very similar to O^- ion observed in $MgAl_2O_4$ by Ibarra et al. [21]. O^- ion in $MgAl_2O_4$ has a *g*-value of 2.011. It was possible to identify the center as O^- ion based on EPR results along with optical absorption data.

The EPR spectra obtained for the samples irradiated with different γ doses are shown in Fig. 7. The three EPR signals growth with the γ irradiation.
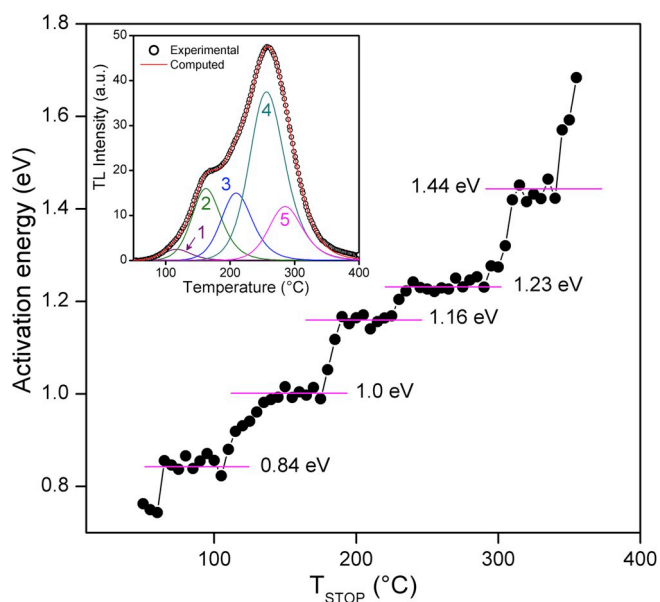
Fig. 5. Activation energy vs. T_{STOP} obtained by the E-T_{STOP} method. In inset, TL glow curve from MCSO polycrystal irradiated with γ-ray dose of 10 kGy. A good fit between the experimental glow curve (circles) and the simulated glow curve (red line) can be achieved by assuming the presence of five peaks. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
TL parameters of the MCSO polycrystal sample taken by GCD and E-T_{STOP} method.

Peak	Kinetic order	Tm (°C)	Activation energy (eV)	Frequency factor (s^{-1})	τ (years at 25 °C)
1	2nd	116	0.84	1.95×10^{10}	2.54×10^{-4}
2	2nd	162	1.00	9.37×10^{10}	2.7×10^{-2}
3	2nd	209	1.16	3.09×10^{11}	4.17
4	2nd	256	1.23	1.06×10^{11}	185.6
5	2nd	283	1.44	2.42×10^{12}	2.88×10^{4}

Thermal annealing behavior of center I was examined using the step-annealing method. The observed behavior is shown in Fig. 8. It is seen that the center becomes unstable at about 185 °C and decays in the temperature range 185 °C–400 °C. The TL peak at 260 °C relates with this decay and center I could be associated with this TL peak.

In oxide systems, a likely center which can form is the F^+ - center (an electron trapped at an oxygen vacancy). The center was first observed in alkali halides where it exhibited a large linewidth of about 100 G [22]. The main feature of the center is the g-value which was close to 2.0023 (free-electron value). The inherent linewidth of the center is very small and is about 1 G as observed in MgO system [23]. The amount of delocalization of the electron and interaction with immediate neighbors (the relative abundance of their isotopes and the respective magnetic moments) decides the linewidth. In systems like alkali halides, the electron interacts not only with the immediate neighbors but also with alkali and halide ions from successive neighboring shells. This leads to large linewidths. For example, in KCl and LiCl large linewidths of 20 G and 58 G are observed [24]. F^+- centers are observed in alkali halides and also in oxide systems. An anion vacancy traps an electron during irradiation and this forms the basis for the formation of F^+ - center. The main feature of F-centers (F^+ -centers in oxides) is the g-value which is observed to be close the free-electron value. The g-shift could be positive or negative. Center II in the present system, $MgCaSi_2O_6$, has a g-value of 2.0012 (small g-shift) and the linewidth is about 2.5 G. On the basis of known features of F^+ -center,
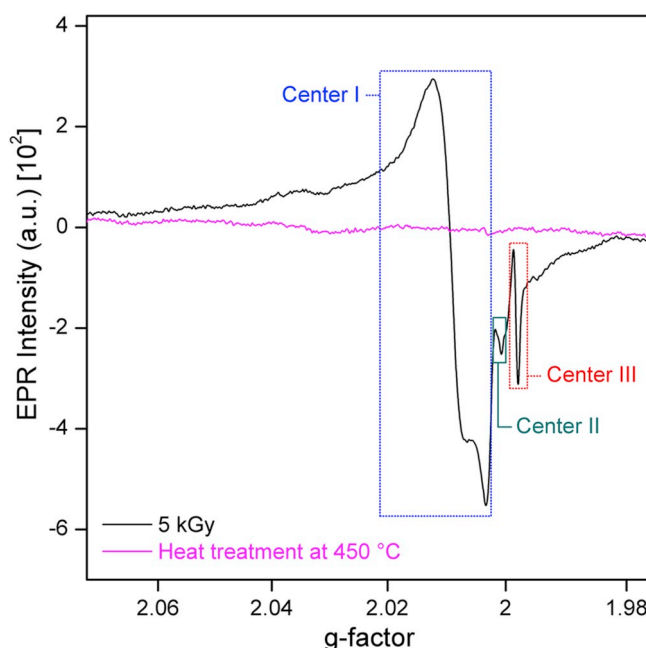

Fig. 6. Room temperature EPR spectrum of irradiated MCSO sample (gamma dose: 5 kGy). Line labeled as I is due to an O^- ion. Center II line is assigned to a F^+ center and center III is also attributed to a F^+ center.
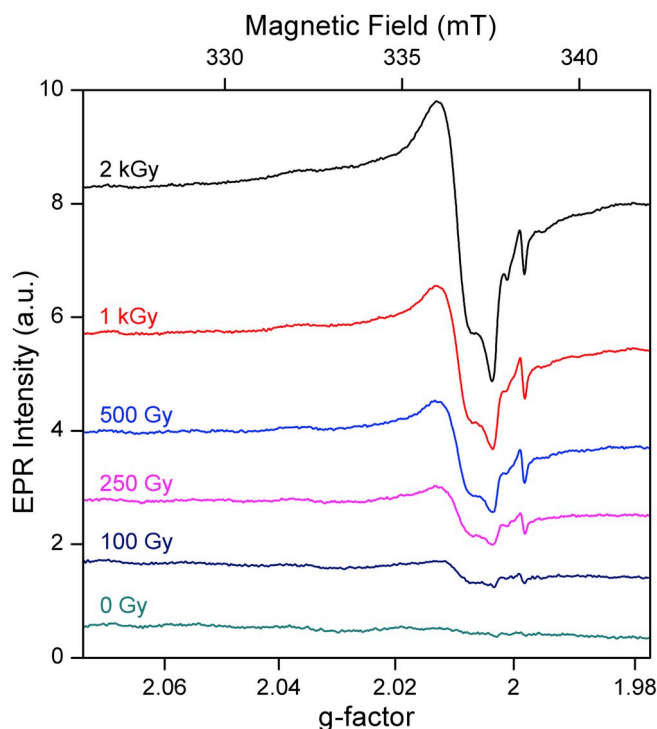

Fig. 7. EPR spectra of MCSO sample irradiated with different gamma doses between 100 Gy and 2000 Gy.

center II is tentatively identified as F^+ - center. As oxygen vacancies are present in MCSO due to reasons mentioned earlier, electron can get trapped at the vacancies resulting in the formation of F^+ - center. The thermal annealing behavior of the center is shown in Fig. 9. Center II is observed to become unstable around 120 °C and decays in the temperature range 120 °C–220 °C. This decay relates with the observed TL peak at 170 °C.
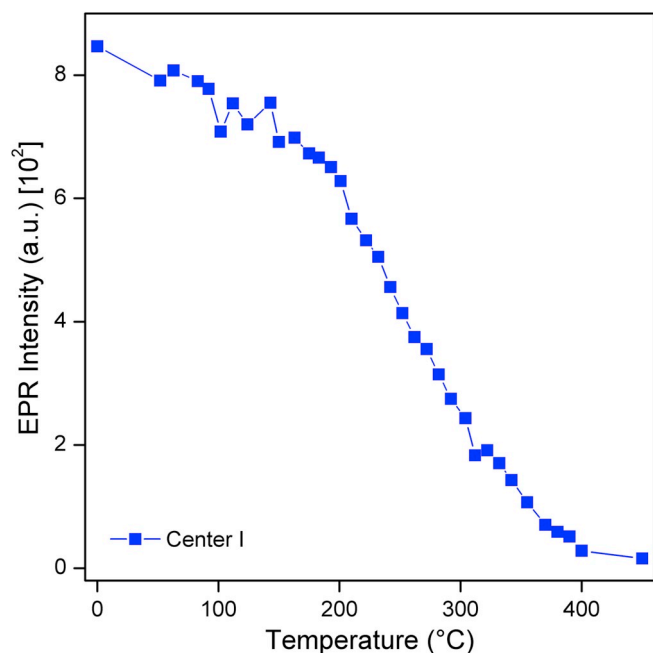
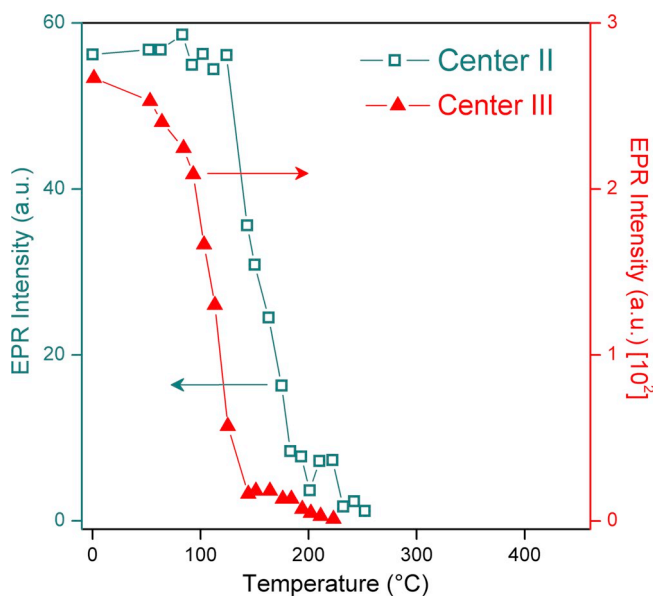**Fig. 8.** Thermal annealing behavior of center I.

Fig. 9. Thermal annealing behavior of centers II and III.

Center III seen in the EPR spectrum shown in Fig. 6 has an isotropic *g*-value equal to 1.9982 and a linewidth of 1.3 G. This center is also tentatively attributed to F^+-center based on the reasons mentioned earlier. The thermal annealing behavior of the center is shown in Fig. 9. It is seen that the center becomes unstable at about 50 °C and decays in the temperature region 50 °C - 150 °C. This decay relates with the TL peak 106 °C and the center is associated with this TL peak.

4. Conclusions

MCSO polycrystal exhibits TL glow peaks at about 115, 160, 210, 260 and 280 °C. The TL intensity as function of dose in log-log representation of 260 °C peak has shown that its TL intensity grows

linearly up to 5 kGy. Three defect centers are identified in the irradiated MCSO polycrystal. These centers are tentatively assigned to O^- ion (center I) and F^+-centers (center II and II). Center I appears to correlate with the 260 °C TL peak as well as with the 280 °C TL peak. The center II has the possibility to be associated with the 160 °C TL peak and the center III relates with TL peak at 115 °C.

Acknowledgments

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