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Thermally assisted tunneling: An alternative model for the thermoluminescence process in calcite

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In this work we investigate the effect of gamma and ultraviolet radiations on the thermoluminescence of Brazilian calcite. The irradiated samples presented three thermoluminescence (TL) peaks at 150, 245, and 320°C, with a main emission band centered at 615 nm due to the $^4G \rightarrow {}^6S$ transition of the Mn^{2+}. The irradiated samples presented, besides the Mn^{2+} ESR signals, three lines related to carbonate groups. The thermal treatment and the irradiation effects on the electron-spin resonance signal lead to the conclusion that $(CO_3)^{3-}$, stabilized in two different symmetries, and the $(CO_2)^-$ ions are the electron trapping centers. It was found that the TL peaks follow a t^{-1} decay as a function of the UV illumination time. An alternative model for the TL emission of calcite is discussed, considering that the recombination of charges is processed via a thermally assisted tunneling mechanism.

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I. INTRODUCTION

Calcite is a mineral found in many geological formations. Its thermoluminescence (TL) has been studied, mainly due to its application in geological and fossil dating.[1–3] Calcite can also be used for ionizing and ultraviolet radiation dosimetry and in optical devices such as beam splitters and polarizers[4] due mainly to its expressive double refraction.

Investigations on calcite have shown different TL characteristics depending on the impurity content and on the genesis of the sample. It was also observed on artificially grown $CaCO_3$ crystals that the type and concentration of impurities modify both TL sensitivity and glow-curve shape.

Important contributions have been made to the understanding of the TL mechanism of calcite since the pioneering works of Kolbe and Smakula[5] and Medlin[6] in the 1960s. Studying the influence of manganese concentration, and by comparison of the emission spectrum of calcite with the emission of the other lattices including manganese, Medlin proposed that the emission band centered in 615 nm, corresponding to a transition from the first excited to the fundamental state of Mn^{2+} ion occupying a Ca^{2+} site. Recent works[7,8] showed that the shape of the emission spectrum changes from a broad band without structure to a well-resolved narrow band when the temperature of the TL peak increases and when the concentration of the Mn decrease. They also concluded that the orange emission is related to Mn impurity. Calderon *et al.*[9] suggested that the holes are trapped by the impurities and electrons are trapped at dislocations forming $(CO_3)^{3-}$. The irradiation with UV light was found to modify the intensity of the TL peaks suggesting that the trapped carriers can be phototransfered from deep to shallow traps.[10] Concerning the kinetics of the detrapping process, it was found that the isothermal decay follow a t^{-1} law that could not be accounted for a single trap model. Some workers explained this result assuming that the process is due to a distribution in the activation energies.[11,12] On the other hand, Visocekas *et al.*[13] suggested that, for the peaks observed on their samples below room temperature, this behavior could be due to a tunneling process.

In the present work we investigate the effect of gamma and ultraviolet radiations on the thermoluminescence of Brazilian calcite from Miranda, MS. Based on a correlation between TL and electron-spin resonance (ESR) and on the photoinduced TL decay, we suggest an explanation for the appearance of the three peaks between room temperature and 450 °C, and propose an alternative model for the thermoluminescence process.

II. EXPERIMENT

Brazilian calcite from Miranda, MS used in this work was powdered and sieved and the grains with diameters between 74 μm and 174 μm were selected. Chemical analysis by atomic absorption and x-ray fluorescent spectroscopy techniques detected the following impurities: Si($<0.1\%$), Al ($<0.1\%$), Fe($<0.05\%$), Ti($<0.05\%$), Mg($<0.23\%$), Na($<0.03\%$), and K($<0.05\%$). Electron-spin resonance measurements revealed the presence of manganese. Samples were exposed to ^{60}Co gamma rays from 50 Gy to 700 Gy. Ultraviolet irradiation was performed at a distance of 0.5 m from a high-pressure 400-W mercury lamp. A home-made TL reader was used to heat 4 mg powder samples from 30 °C to 400 °C in a nitrogen atmosphere, at a heating rate between 1 °C/s and 3 °C/s. We performed a series of monochromatic TL measurements with wavelength varying from 450 to 750 nm in steps of 10 nm. The measurements were repeated many times and the average curves were stored in a microcomputer and the three-dimensional isometric plots were constructed via software after correcting each of the monochromatic curves to the wavelength response of the system.

ESR experiments were performed with a BRUKER ER 200D equipment, also on powdered samples at room temperature, in the *X* band and 1.0-mW microwave power (below saturation). A standard diphenyl picrylhydrazyl sample was used for calibration. The peak-to-peak height of the first derivative of the signal was considered to be proportional to the number of paramagnetic centres, since the shape of the peaks did not change under irradiation or after the thermal

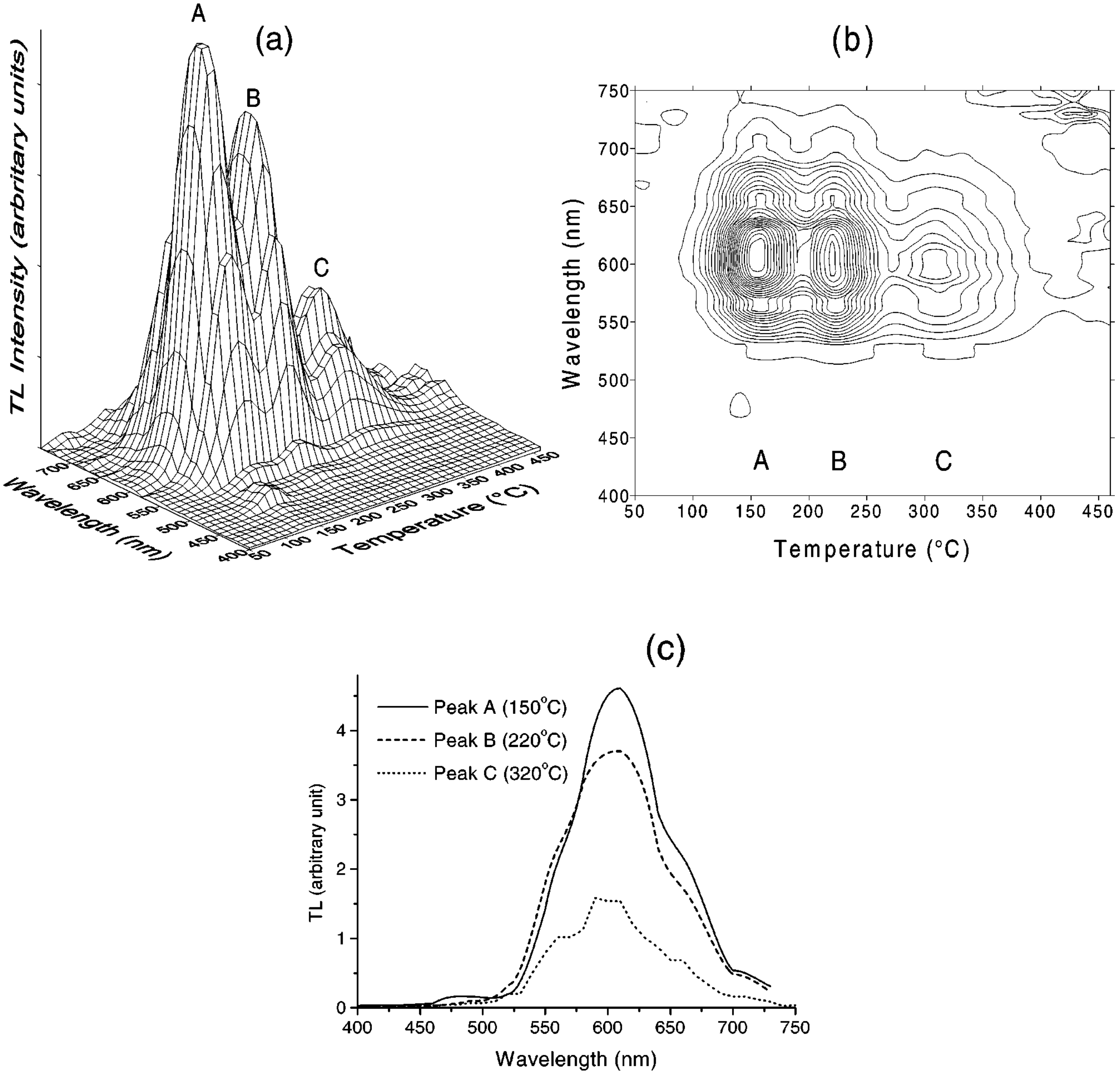

FIG. 1. Isometric plot (a), contour plots (b), and emission spectra (c) of thermoluminescent peaks of gamma-ray irradiated Brazilian calcite samples, recorded at 1.8 °C/s.

treatments. All the experiments were repeated at least five times and the average values were considered.

III. RESULTS

The glow curve of untreated sample (without any treatment in laboratory) consists of two peaks at 220 and 320 °C when heated at a rate of 1.8 °C/s. After a laboratory dose of gamma rays, the intensity of these peaks increases and another peak, around 150 °C, appears. Hence for simplicity these peaks are labeled as peaks *A*, *B*, and *C* as their temperatures increase.

Figure 1 shows the isometric plot [Fig. 1(a)], the contour plot [Fig. 1(b)] and the emission spectra [Fig. 1(c)] of the TL peaks of the irradiated samples. The three main peaks present a broad emission band centered at 615 nm. Besides this band, the spectra also displays a very weak emission band at 480 nm [Fig. 1(a) and 1(c)], not usually reported. This emission is mainly observed in peak *A* but is also present in the peak *B*. At the peak *C* temperature the TL spectra around 615 nm displays a fine structure with at least four emission lines [Fig. 1(c)]. For peaks *A* and *B* this fine structure is not clearly visible and their spectra are mainly composed by broad emissions centered at 615 nm [Fig. 1(c)]. Treated samples (with a heat treatment at 400 °C for 1 h followed by a gamma irradiation) show a similar glow curve, without changes in the peak positions.

The growth and the saturation of the peak heights with the exposure to gamma rays are shown in Fig. 2. It can be seen that all three peaks increase until 10^4 Gy reaching the saturation.

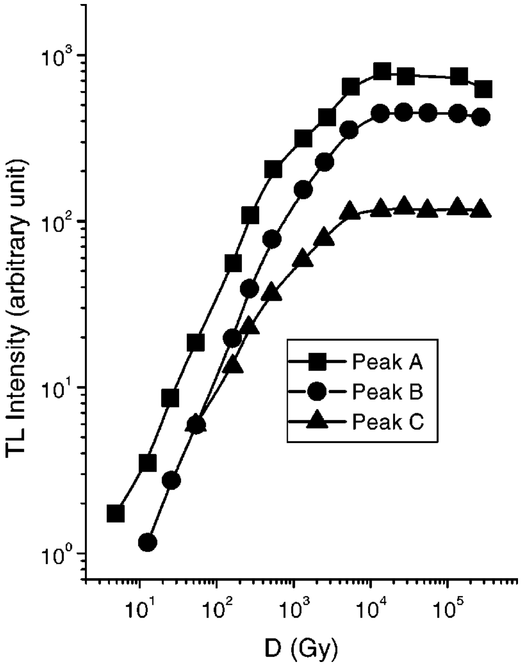

FIG. 2. TL peak heights of Brazilian calcite as a function of exposure to gamma rays.

Figures 3 show the effect of 10-min post-irradiated thermal treatment at different temperatures on the intensities [Fig. 3(a)] and positions [Fig. 3(b)] of the TL peaks. We can see that the decrease of intensity of each individual TL peak is accompanied by the dislocation of the TL peak maximum to higher temperatures indicating that the TL process can not be accounted for a first-order kinetic with one single activation energy. Peak *A* vanishes first followed by peak *B* and finally by peak *C*.

The effect of UV irradiation on the thermoluminescent properties was studied using both untreated (without any treatment in the laboratory) and treated samples (with a heat treatment at 400 °C for 1 h followed by gamma irradiation). When treated samples are irradiated with UV all the three peaks decrease and the peak maxima shift to higher temperatures (Fig. 4), similarly to the effects produced by thermal bleaching. Since we have maintained the temperature of the samples around 30 °C during the UV illumination, and considering that the time intervals used in these UV experiments are short enough to neglect the isothermal decay at this temperature, these effects are only due to the UV illumination.

The inverse of the intensity of the three TL peaks were ploted as a function of the UV illumination time ''t'' in Fig. 5. The straight lines are least-square fits to the experimental points considering that the TL intensities of the peaks are proportional to t^{-1}. The fits are reasonably good indicating that a t^{-1} law can account for the TL decay due to UV light in calcite.

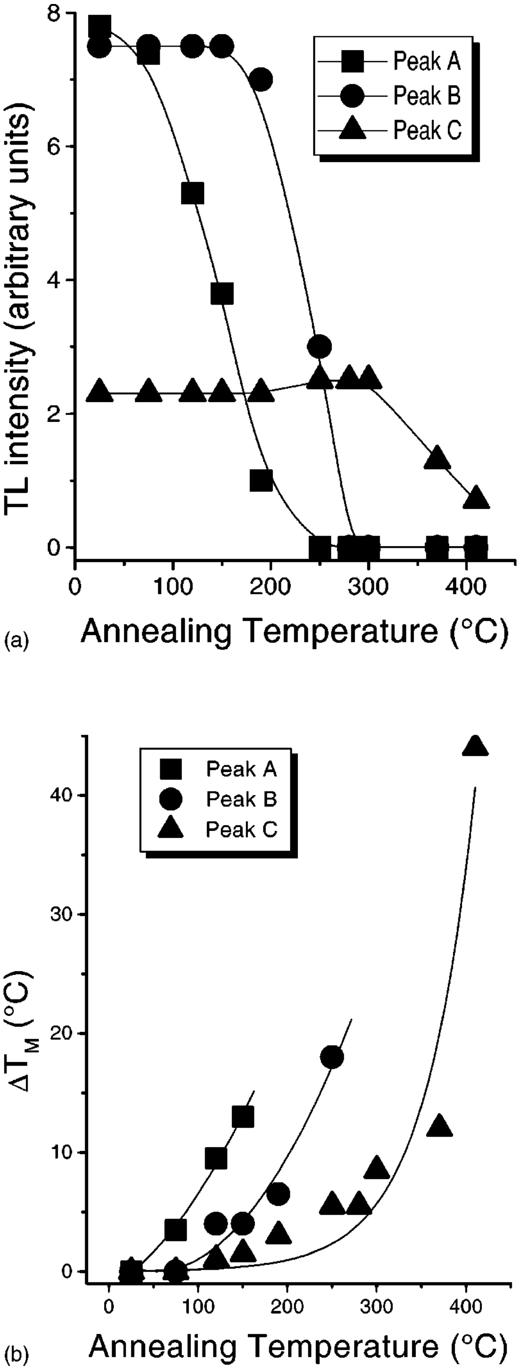

FIG. 3. Decay of TL intensity (a) and change in the TL peaks positions (b) as a function of the annealing temperature during 10 min of calcite samples previously irradiated with a laboratory dose of gamma rays.

In Fig. 6 the ESR response of the natural and irradiated samples is shown. The ESR measurements were performed at room temperature in powdered samples. We can see the well-known signal of the Mn^{2+} [Fig. 6(a)]. In Fig. 6(b), the region marked on Fig. 6(a), curve ii, is magnified to show in detail the signals labled 2, 3, and 5. In Fig. 7 the variation of the intensities of the ESR signals were plotted as a function of the radiation dose. It is possible to see that increasing the gamma-ray doses, the well-known signals of the Mn^{2+} ion present in the samples decrease to about 77% of their original intensities. At the same dose range the three signals labeled 2, 3, and 5 markedly increase. These signals present g values of $g_2 = 2.0036$, $g_3 = 2.0032$, and $g_5 = 2.0006$ that are typical values of free radicals. The effect of the post-irradiation thermal treatment at different temperatures during

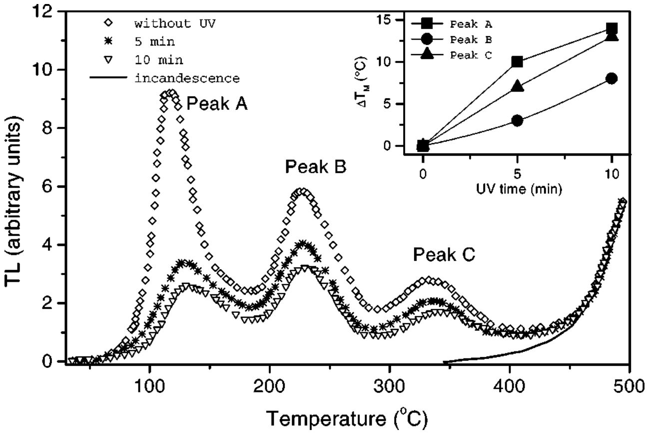

FIG. 4. Glow curve of calcite previously exposed to gamma rays and illuminated with UV during 5 and 10 min. A glow curve without UV illumination is also shown. Inset: Change in the TL Peak position as a function of the exposure time to UV light.

10 min on the labeled ESR signals are shown in Fig. 8. The increase of temperature of post-irradiation heat treatments causes the increase of the Mn^{2+} signal of about 20%, almost recovering the original signal intensities observed before the irradiation. At the same time it is possible to see the decrease firstly of the signal 3, at the 75–150 °C range, followed by the signal 2, at 200–350 °C, and finally the signal 5, starting at 280 °C (Fig. 8). Thermal treatment at 400 °C during 1 h eliminate all the 2, 3, and 5 signals produced by the irradiation.

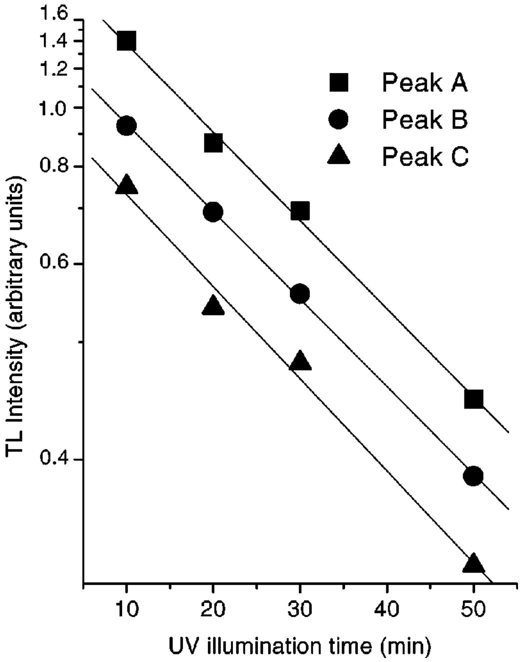

FIG. 5. Reciprocal of the TL peak heights of thermally treated calcite as a function of UV exposure time.

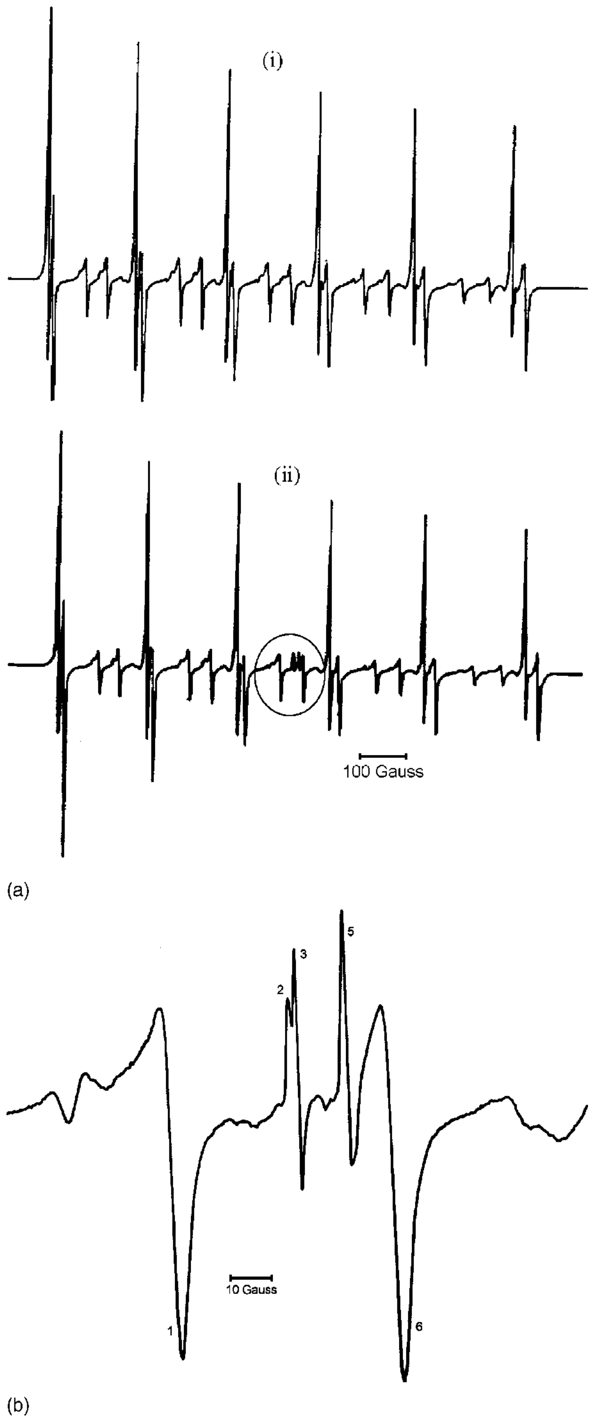

FIG. 6. (a): ESR response of the natural (curve i) and irradiated (curve ii) samples of the Brazilian calcite. (b): Magnification of the region marked on curve ii showing the the signals 1, 2, 3, 5, and 6.

IV. DISCUSSION

A. Electron and hole traps

At present, the plain understanding of thermoluminescent emission requires the identification of the luminescence and the trapping centers and the indication of the charge-carrier transfer and recombination processes. The results presented in this work allow us to fulfill the above requirements and to point out an alternative model to the charge-carrier transfer.

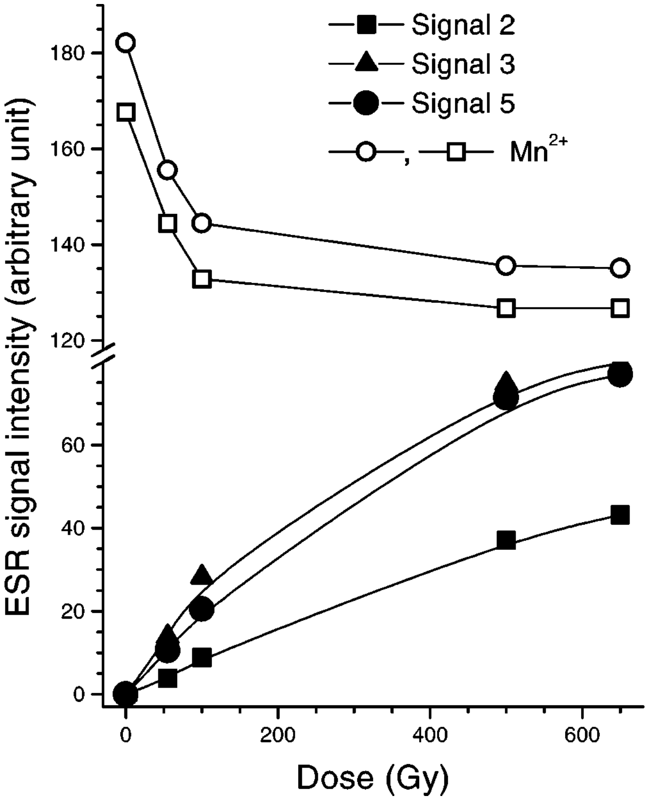

FIG. 7. Intensity of ESR signals of a Brazilian calcite sample as a function of exposure to gamma rays.

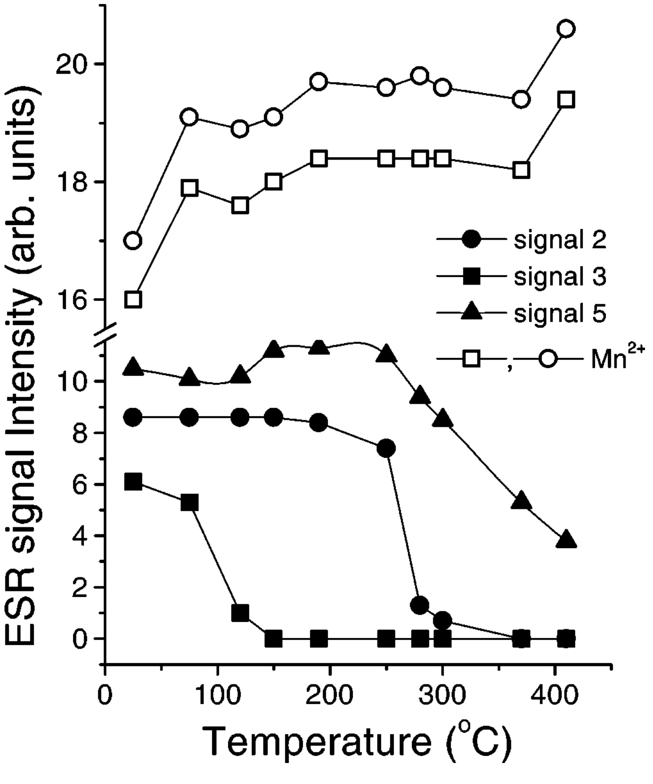

FIG. 8. Effect of the annealing temperature for 10 min in the ESR signals of calcite irradiated with gamma rays.

From Fig. 1 we can see that the three TL peaks have the same emission band centered at 615 nm. According to Medlin[6] this emission is due to a nonradiative resonant transfer of energy from the $Ca^{+}-(CO_3)^{-}$ recombination process to the Mn^{2+} ion that undergoes to the $^4G \rightarrow {}^6S$ transition. In the Medlin's model of the TL process in $CaCO_3$ the Ca^{2+} and the $(CO_3)^{2-}$ ions are the electron and the hole traps, respectively, the recombination center being at the Ca^{+}. The Mn^{2+} was only the luminescence center.

In Figs. 7 and 8, we showed that the ESR signal related to Mn^{2+} decreases with the irradiation dose and is almost completely recovered if the sample is heated. This result can not be explained within the framework of the Medlin's model. The results clearly establish that the Mn is the trap formed upon irradiating the crystal and that during the heating it is both the recombination and the luminescence center.

Marshall *et al.*[14] and Serway and Marshall[15,16] have performed ESR measurements in irradiated samples of single crystals of calcite and they observed that the $(CO_3)^{3-}$ center is anisotropic having $g_{\parallel}=2.0013$ and $g_{\perp}=2.0031$. They also observed that the $(CO_3)^{-}$ center, with $g_{\parallel}=2.0051$ and $g_{\perp}=2.0161$, is unstable above 146 K. Rossi and Poupeau,[17] on the other hand found, for the $(CO_3)^{3-}$ center in natural calcite speleothems, the values of $g_{\parallel}=2.0021$ and $g_{\perp}=2.0036$. Marshall *et al.*[18] measured the $(CO_2)^{-}$ in calcite and they found that below 250 K this center exhibits an orthorhombic symmetry with $g_x=2.003\,20$, $g_y=1.997\,27$ and $g_z=2.001\,61$. Above 250 K the center changes to an axial symmetry having $g_{\parallel}=2.0032$ and $g_{\perp}=1.9995$. A recent work by Bartoll *et al.*[19] confirmed these results.

In powdered samples, De Canniere *et al.*[20] and Rossi *et al.*[21] observed two ESR lines with $g=2.0032$ and 2.0036, the same as our lines g_3 and g_2. The authors attributed these lines to the $(CO_3)^{3-}$ center since they behave like the $(CO_3)^{3-}$ lines observed in the single crystals.

A number of signals with g ranging from 2.007 to 2.000 were found by Bartoll *et al.*[19] in calcite crystals, calcite powders, aragonitic shell and coral samples. The authors found that the signal with $g=2.007$ is quite stable and is related to isotropic related to $(CO_2)^{-}$ center, in quite good agreement to our g_5 signal.

Figure 7 shows that the signals related to the $(CO_3)^{3-}$ center (g_3 and g_2) and related to the $(CO_2)^{-}$ center (g_5) increase with the irradiation dose and decrease with the thermal treatment at different temperatures (Fig. 8). Signal 3 bleaches at the same temperature of the TL peak *A* while signal 2 bleaches at the temperature of the TL peak *B*, suggesting that two different types of $(CO_3)^{3-}$ are created upon irradiation on the crystal lattice. Signal 5, related to the $(CO_2)^{-}$ center, bleaches at the same temperature range of the TL peak *C*. These results point out to an unambiguous correlation between the *A*, *B*, and *C* TL peaks and 3, 2, and 5 ESR signals.

Considering that the ESR signals 2, 3, and 5 increase with the dose and combining this result with the correlation of these signals with the TL peaks described in the preceding paragraph, we can conclude that the $(CO_3)^{3-}$ and the $(CO_2)^{-}$ are the electron-trapping centers and the holes are trapped at the Mn^{2+} centers.

B. Recombination process

The results presented by Medlin[11,22] showed that the isothermal decay of the phosphorescence of calcite crystals follows a t^{-1} law. This type of decay can be explained by a distribution in the activation energies of the traps, as chosen by Medlin[11] and Pagonis *et al.*[12] in calcite, or by a tunneling process, as used by Visocekas *et al.*[13] in calcite, Delbecq *et al.*[23] in KCl:AgCl and KCl:TlCl and Avouris and Morgan[24] in Zn_2SiO_4:Mn.

In a previous work, Lima *et al.*[25] employed the $T_m xT_{stop}$ method in natural calcite. This method was initially proposed by McKeever[3] as a tool for distinguishing different kinetics and mechanisms. The results found by Lima clearly indicated that the distribution in activation energies can not account for the TL peaks in Brazilian calcite.

In the present work UV light was used to release the trapped electrons and generates the electron-hole recombination process (Figs. 4 and 5). The results obtained from these measurements showed that the decay of the gamma-ray induced TL peaks due to exposure to UV light is inversely proportional to the illumination time, as we can see in Fig. 5, in agreement with previous results .

Although the decay of the TL peaks with the UV illumination time follows the same t^{-1} law as it was observed in the isothermal decay in calcite, the effect of the UV light can not be explained by a distribution in activation energies of the traps but can be accounted for a tunneling mechanism.

In addition, it was showed by Medlin[26] that the TL peaks in calcite are not accompanied by any thermally stimulated conductivity peaks, and that the emission of light during the recombination process is generated in a ‘‘localized-type’’ mechanism.[27]

Taking into account all these results we are proposing that the charge-transfer mechanism is processed via a thermally assisted tunneling from the carbonate groups to the Mn ions.

V. CONCLUSION

In conclusion, the results observed in the present work clearly establish the role of the $(CO_3)^{3-}$ and $(CO_2)^{-}$ ions as the main trapping centres and the role of the Mn^{2+} as the recombination and the luminescence center in the TL processes in calcite. The recombination of charges between the electron and the hole traps are via a tunneling process. If that happens, both centers should be close enough to enable the tunneling process to take place. Hence, we suggest that during the irradiation of the samples the $(CO_3)^{3-}$ and $(CO_2)^{-}$ centers are formed in the vicinity of a Mn^{3+} substituting for a Ca^{2+} of the calcite matrix. The two different $(CO_3)^{3-}$ observed in the ESR measurements can be attributed to carbonate groups at nearest-neighbor and at next-nearest-neighbor positions of the Mn dopant.

The observed TL peaks can be explained as follows: during irradiation Mn^{2+} ions change to Mn^{3+}, losing one electron that is captured in a $(CO_3)^{2-}$, forming $(CO_3)^{3-}$ ion or $(CO_2)^{-}$ ion. The $(CO_3)^{3-}$ can be formed either in a nearest-neighbor or in a next-nearest-neighour position to the Mn^{3+} dopant generating two different $(CO_3)^{3-}$ ions. Upon heating, the electron recombines with the hole left in the Mn^{3+}, after a thermally assisted tunneling from a trap close to the manganese. The resulting Mn^{2+} is formed in an excited state, whose decay is responsible for the 615-nm emitted light during the TL process.

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