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A NEW MODEL OF TL IN CARBONATES

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ABSTRACT

Thermoluminescence (Tl), Radioluminescence (Rl), Photoluminescence (Phl) as well as optical absorption(Ab) and E.P.R. spectra of X-irradiated natural carbonates have been obtained. Our results give evidence of a strong correlation between; i) decrease of U.V. absorptions bands and Tl peaks, and ii) irradiation process and E.P.R. spectrum. An emission band in the 400 nm region is always detected in all samples.

These experimental results support a new model for the radiation damage and thermoluminescence process in carbonates. The main point in this model is that holes become trapped at impurities and the electrons are self-trapped or localized in CO_3^{-3} anionic centres.

INTRODUCTION

Previous work on Tl and Rl in calcite (Calderon et al, 1983, 1984) is meaningful in order to understand the luminescence behaviour of carbonate minerals. In fact, the recombination process proposed served us to explain the greatest part of Tl and Rl seen in this mineral.

In the present paper, our contention is that similar processes can also occur in the case of Tl and Rl of Trigonal and orthorhombic carbonates and then a general model can account for the luminescence processes in all carbonates. In order to check the model we made a comparison of Tl, Rl, Pht, Ab and E.P.R. features of natural carbonates (calcite, aragonite, dolomite and smithsonite) from several localities. As a result of this study, a new mechanism to explain

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the origin of Tl of carbonates at temperatures above RT is proposed.

EXPERIMENTAL

Natural carbonate samples of calcite (Marocco), dolomite (Navarra (Spain) , aragonite (Herrenground. C.S.S.R.) and smithsonite (Spain) have been used in this study. Identification of samples has been made by means of A.A. (atomic absorption spectrophotometry) and x-ray diffraction.

Samples were x-irradiated with a Siemens x-ray machine Kristalloflex 2H at 50 Kv, 30mA through a 2 mm aluminium filter. For Tl (above RT) measurement, an EMI-9558 QB photomultiplier tube was used. The photomultiplier output was detected with a Keithley 610 C electrometer. For measurements below RT, a cryostat Cryogenic CTi with closed helium circuit was used, and the luminescence was detected with an EMI 6256 S photomultiplier. The photomultiplier output was measured with a Cary 401 vibrating-reed electrometer. A Bauch& Lomb high -intensity monochromator was used to analyse the emission spectra. Absorption spectra were obtained with a Cary 17 spectrophotometer with a device to heat the sample. Luminescence (excitation and emission) spectra were measured with a Jobin Yvon, JY-3CS spectrofluorimeter coupled with a computer and a closed-cycle helium cryostat. E.P.R. spectra were obtained by means of a Varian E-12 X-band spectrometer using a 100 KHz field modulation.

RESULTS AND DISCUSSION

In Fig. 1 the absorption spectra of some representative studied carbonates are shown before and after x-irradiation. A great difference in the absorption level, as well as absorption bands produced in the U.V. range (which increase with dose up to saturation) can be comparatively observed.

Tl between 300-600 K as well as evolution of U.V. bands with increase of temperature have been studied. All carbonate samples show complex Tl peaks above RT, (Fig. 2a) which can be related with decrease of U.V. bands (Fig. 2b). In the spectral composition of Tl peaks of x-irradiated calcites, aragonites and dolomites, Mn^{2+} emission can be easily identified. It extends from 580 to 700 nm according to Aguilar et al.(1983). The variation of Mn^{2+} emission (Fig.2c) in the studied carbonates, is observed in a typical plot lg I versus 1/T, showing its evolution for high temperatures. The same Fig. 2c shows the evolution of 400 nm emission band, detected in all carbonates, which will be quenched for higher temperatures. This emission that cannot be related with impurities has been proposed as an intrinsic emission (Ugumori, 1980; Calderón, 1983).

Electron Paramagnetic Resonance (E.P.R.) of calcium carbonate enabled the detection of cation impurities like Mn^{2+}, before and after x-ray irradiation (Fig. 3 a-b). A decrease of Mn^{2+} E.P.R. signal after irradiation is observed. It is well known that E.P.R. studies have allowed the identification of some paramagnetic centres formed by self-trapped holes or electrons, such us CO_2^- (McMillan et al. 1968), CO_3^- and CO_3^{-3} (Serway et al. 1967 a,b). CO_3^- has been identified having axial (Serway et al, 1967) and orthorhombic symmetry (Serway et al. 1967 b). The former (axial CO_3^-) is unstable above 90 K and the latter (orthorhombic CO_3^-) is unstable above 146 K (Serway et al. 1967 b). The CO_3^{-3} center is not stable at 300 K (it has a lifetime of 10 h), although it can be stabilised up to 500 K if the centre is associated with impurities present in the crystals (Marshall et al. 1968). In accordance with these facts, the CO_3^- centres cannot be accountable for the Tl peaks observed above room temperature. At this point it is suggested that electrons trapped in CO_3^{-3} become mobile when the temperature is raised, until it is near an impurity which has a trapped hole. Then, the electron should be transferred to the impurity (M^{3+}), possibly by a tunnelling mechanism, leaving behind the CO_3^{-2} in the excited state: then the mechanism proposed is:

$$CO_3^{-3} + M^{3+} \longrightarrow (CO_3^{-2})^* + (M^{3+} + e) \longrightarrow CO_3^{-2} + h\nu_{INT} + \\ + M^{2+} + h\nu_{IMP.}$$

from this model, it is expected that the divalent impurity concentration should decrease after x-irradiation. (Fig. 3 b), and intrinsic/impurity emission should be observed in Tl.

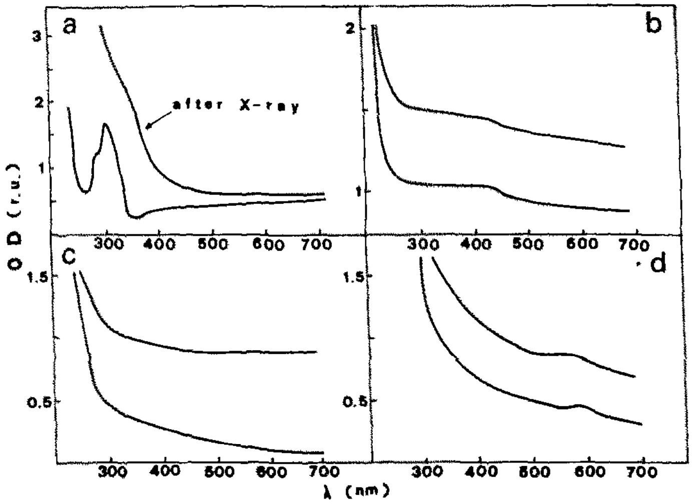

Fig. 1.- Optical absorption spectra from calcite aragonite, dolomite and smithsonite before and after x-irradiation: (a) calcite; (b) aragonite; (c) dolomite, (d) smithsonite.

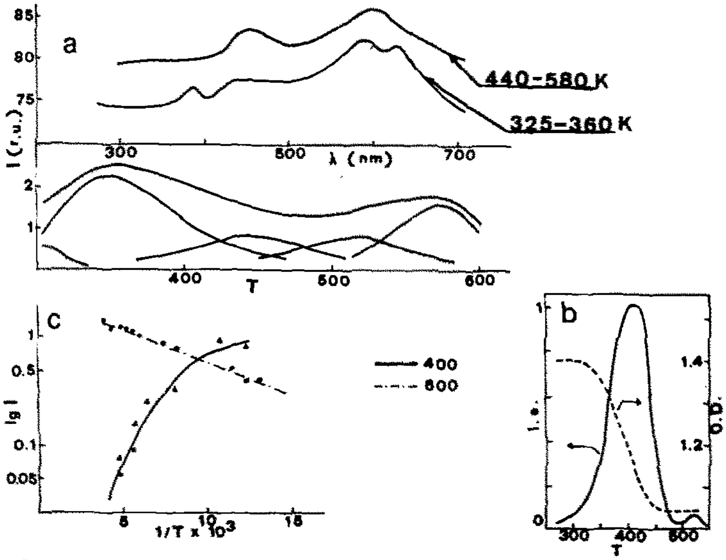

Fig. 2.- Full curve: Thermoluminescence spectra; (a) dolomite; (c) broken curve thermal bleaching of U.V absorption for calcite; (b) semilogarithmic plot of the emission intensity versus 1/T(K): (●) Mn^{2+} emission and (▲) 400 nm emission.

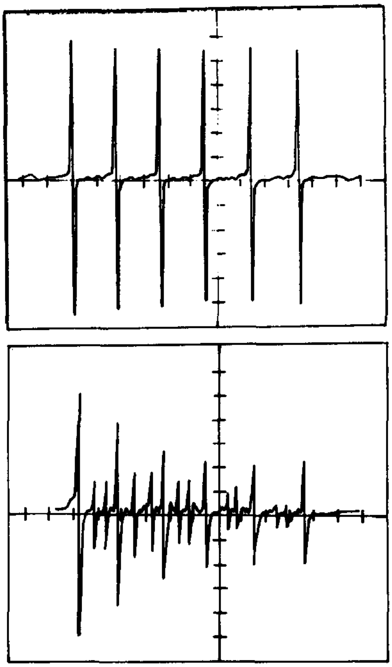

Fig. 3.- E.P.R. spectrum of calcite (9.169 to Hz; horizontal axis, 1 unit ≃ 100 G, and H (0) = 3.3 KG; RT). (a) Mn^{2+} E.P.R. spectrum before x-irradiation, (b) after 1 h of x-irradiation.

CONCLUSIONS

1.- An emission band in the 380-400 nm region has been detected in all studied carbonates which can't be related with cation impurities. It is suggested that this emission is an intrinsic one due to electron-hole recombination in the anionic sub-lattice.

2.- The origin of the Tl peaks is the thermal liberation of quasi-self-trapped electrons (localized electrons as CO$_3^{-3}$ centres) from different traps (dislocations, defects, etc) that migrate to a luminescent impurity which has a trapped hole. The electrostatic attraction forced the CO$_3^{-3}$ + M^{3+} recombination that can produce the intrinsic and impurity luminescence.

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