American Mineralogist, Volume 63, pages 732–736, 1978

Impurity-related centers in a pale green calcite crystal

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Abstract

Emission spectrographic analysis of a pale green calcite crystal from Helwan, Egypt, indicated the presence of various impurities including manganese and iron. Optical and paramagnetic resonance absorption spectra before and after X-ray irradiation were measured at room temperature. The results indicated that both the iron and manganese ions are present mainly in their divalent state. The presence of trace Mn(IV) was also indicated. Upon exposure to X-rays, the pale green calcite crystal yielded an orange-red luminescence at room temperature accompanied by a change in its color to brownish-yellow in both its optical and EPR absorption spectra. The observed changes are attributed to the formation of a number of hole and electron trap centers, associated with impurity Fe(II) and Mn(IV) ions forming Fe(III) and excited Mn(II)** centers respectively. Transitions within the Mn(II)** centers, leading to the formation of comparatively more stable Mn(II) ones, are felt responsible for the observed room-temperature phosphorescence. Heating the crystal up to 400°K for one hour caused recombination of the X-ray induced electron and hole trap centers, and produced thermoluminescence by the indirect excitation of emission at the Mn(II) impurity sites.

These data suggest that the calcite crystal precipitated in an environment that was more acidic and with a very low oxidation potential.

Introduction

Chemically-precipitated calcite occurs in limestone regions where natural waters carry considerable quantities of calcium as calcium bicarbonate. A release of CO_2 from the solution would lead to the decomposition of the bicarbonate and the formation of $CaCO_3$, which readily deposits as calcite at a pH of 7.8 or above; at lower pH, calcite tends to dissolve.

Calcite crystals are usually colorless or white; however, yellow, violet, red, and pale blue varieties are known. The yellow and violet colors of many calcites show all the criteria of radiation colors (Przibram, 1956, p. 261–267). They lose their color by moderate heating and show thermoluminescence; upon exposure to radiation they regain the color. In most cases the color and the important features of the glow curves appear to be firmly associated with impurities. Many divalent ions may partially substitute for the calcium ion in the calcite structure. A common substitution is that of magnesium, giving magnesian calcite. Manganese-bearing calcites are known. The substitution of ferrous ions for some calcium ions is fairly common. Small amounts of strontium, barium, cobalt, and zinc may also replace calcium.

The crystal structure of calcite was one of the first to be determined by X-ray methods. The rhombohedral unit cell contains two calcium ions and two sets of three carbonate ions each. These ions lie in separate layers normal to the *c* axis. A clearly illustrated description of the calcium sites is given by Kikuchi and Matarrese (1960).

A pale green calcite crystal from the limestone quarry of the National Cement Company in Helwan, 30 km south of Cairo, Egypt, was obtained and the origin of the uncommon coloration was investigated. This paper is mainly concerned with existing impurity-related as well as some X-ray-induced color centers. A discussion of the environmental conditions that prevailed during precipitation is also included.

Experimental methods

Emission spectrographic analyses were made using a VEB Carl Zeiss Jena UV Q-24 prism spectrograph. A wafer 2 mm thick was cut and optically polished

0003–004X/78/0708–0732$02.00

for the spectrophotometric studies. Optical absorption spectra were measured *vs.* air using a Beckman DK-2A ratio recording spectrophotometer. X-ray irradiation experiments were performed in a General Electric XRD-6 unit operated at 50 kV and 45 mA. The X-ray tube was a water-cooled G.E. CA type with a tungsten target. The irradiations were carried out at room temperature. The EPR spectra were measured also at room temperature before and after X-ray irradiation, using a Varian model No. V-4502 spectrometer. The post-radiation phosphorescence was detected by a photomultiplier, the output of which was amplified by an electrometer and displayed on a chart recorder. The glow curves for the thermoluminescence experiment were obtained following the procedure outlined by Calamawy (1970, p. 46–51).

Results and discussion

Emission spectrographic analysis of the pale green calcite crystal indicated trace amounts (ppm) of the impurity ions as follows: Si, 250; Al, 238; Fe, 134; Mn, 200. Manganese in calcite occupies the calcium sites. From size and charge considerations one would expect the normal valence state of manganese to be Mn(II). However, the possibility of having trace Mn(IV) ions cannot be totally excluded. The decomposition of the bicarbonate in the Mn(II)-bearing solutions or the exposure to atmospheric oxygen or dissolved oxygen during precipitation often leads to the oxidation of some divalent manganese to the tetravalent state.

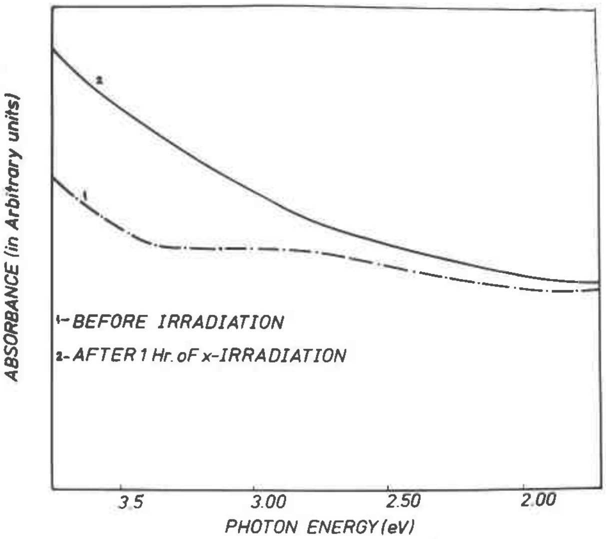

Fig. 1. Optical absorption spectra of a natural green calcite crystal before (curve 1) and after one hour of X-ray irradiation (curve 2).

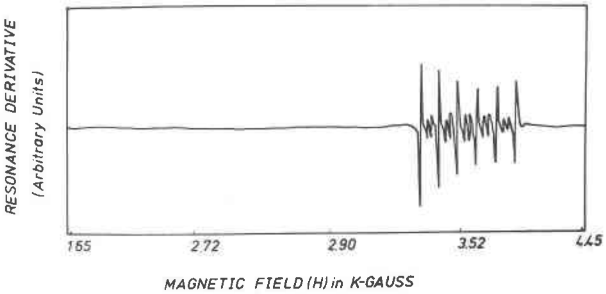

Fig. 2. EPR absorption spectrum of the crystal before X-ray irradiation.

Absorption spectra

Figure 1 shows the optical absorption spectra of a section cut from the crystal before and after one hour of X-ray irradiation at room temperature. Before irradiation a broad absorption band at about 2.8 eV (440 mμ) is observed and could be associated with transitions in the octahedrally-coordinated Mn(II) ion in calcite. The observed weakness of the absorption bands in Figure 1 is due to the fact that transitions within the Mn(II) ion are spin-forbidden; had it not been for some weak spin-orbit interactions such transitions would have been totally absent.

The presence of Mn(II) was further verified experimentally by measuring the EPR absorption spectrum of the crystal. The spectrum (Fig. 2) exhibited the well-known and previously reported six groups of five lines including five pairs of weak lines occurring midway between the principal hyperfine splitting structures (hfs) (Hurd *et al.*, 1954). This further splitting of the fine structures has been attributed by Kikuchi and Matarrese (1969) to the difference in the crystalline field at the two non-equivalent calcium sites in calcite. These resonance lines displayed a large anisotropy, which is to be expected for a trigonal field. A study of the change in the EPR spectrum of the single crystal *versus* orientation will be the subject of a future publication, and only that of a powdered specimen (presumably consisting of large numbers of randomly oriented crystals) is reported here. The color of the powdered specimen was white.

Effect of room temperature X-ray irradiation

Upon X-ray irradiation the sample exhibited an orange-red phosphorescence at room temperature. The specimen was allowed to stand at room temper-

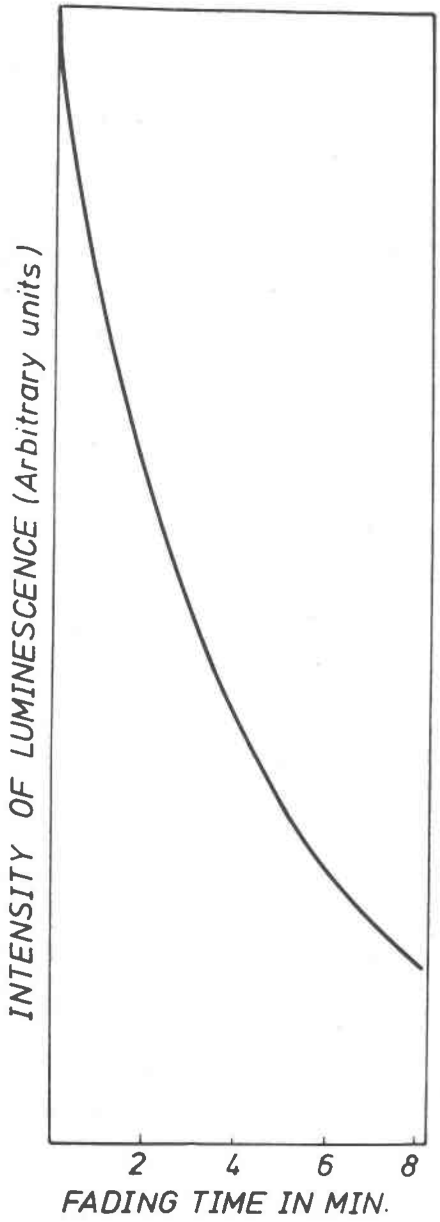

Figure. 3. Fading characteristic of the observed room-temperature luminescence of the crystal.

ature until the visual phosphorescence ceased, in about 7–8 minutes. The fading characteristic of the visually-observed light output with time (Fig. 3) could possibly be due to the draining of a shallow trap.

The optical absorption spectrum after one hour of X-ray irradiation shows evidence of a considerable growth of an absorption band(s) in the near ultraviolet (Fig. 1), beyond the range of the present measurements. The tail of this absorption band(s) extends to the visible portion of the spectrum, possibly preventing other weaker bands from showing up. The color of the calcite crystal changed from pale green to brownish-yellow, which suggests the possible photo-oxidation of some iron (II) to iron (III).

The EPR absorption spectrum was measured for the powdered specimen, which acquired a grey color after one hour of X-ray irradiation. A slight increase in the intensity of the Mn(II)-related EPR resonance lines was observed. This observation suggests that the formation of more Mn(II)-related EPR centers is favored upon X-ray irradiation (Fig. 4, curve 1). As mentioned above, the possibility of having trace Mn(IV) ions in the natural calcite crystal cannot be eliminated. Upon X-ray irradiation these trace Mn(IV) ions may trap electrons and be reduced to Mn(II). The possibility of having these centers originally formed in a highly excited state as Mn(II)**, then decayed at room temperature to the comparatively more stable Mn(II) centers, is considered reasonable.

The electrons responsible for the change in the oxidation state of Mn(IV) apparently do not come from other manganese ions but from another source, since there is a net increase in the intensity of the EPR absorption of the Mn(II)-related center. Another important change in the EPR absorption spectrum was observed. A new spectral component appeared to develop upon X-ray irradiation and continued to grow in intensity with increasing doses (Fig. 5). This

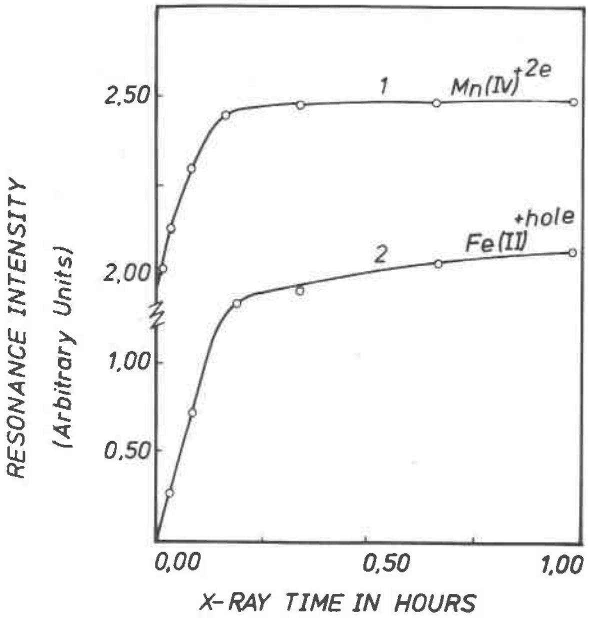

Fig. 4. Growth characteristics of the induced EPR absorption lines with X-ray dosage.

observed new resonance line could be associated with a center responsible for providing the electrons needed to reduce the Mn(IV); in other words, the center is related to a hole-trap. Possible hole-traps are the Fe(II) ions in the calcite crystal. These Fe(II) ions may easily trap holes and be oxidized to Fe(III) ions. The growth of the suggested Fe(III)-related resonance line can be correlated with the observed increase in the intensity of the Mn(II) hfs lines. The observation, as illustrated by curves 1 and 2 in Figure 4, is consistent with this proposed photo-induced oxidation-reduction reaction.

Thermal bleaching

Thermal bleaching of the induced centers was done by heating the specimen following a program that was pursued in all experiments. The fading characteristic of the Fe(III) center as shown by the dashed curve in Figure 6 indicates that heating up to about 400°K is sufficient to reverse the previously suggested photo-oxidation reaction. Meanwhile, the specimen was found to produce an orange-red thermoluminescence similar to what has been previously reported by several investigators for irradiated calcite crystals (Schulman *et al*., 1947).

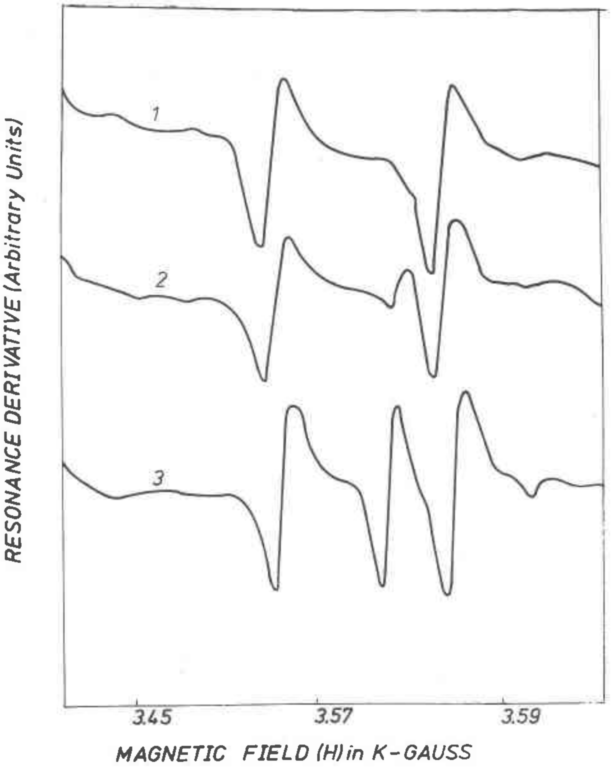

Fig. 5. EPR absorption spectra of the crystal before (curve 1), after two minutes (curve 2), and after one hour of X-ray irradiation (curve 3).

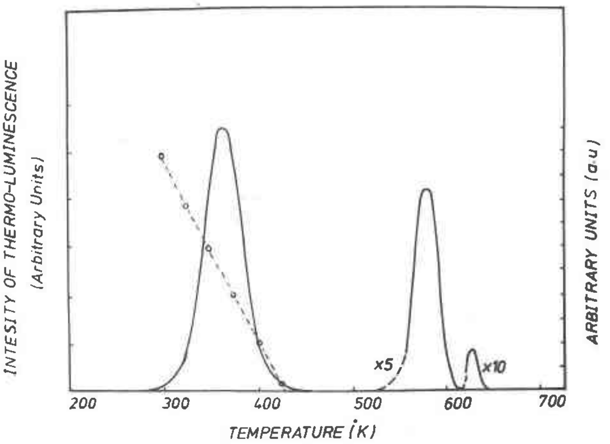

Figure 6. Thermal bleaching characteristic of the X-ray induced Fe(III) center (— — —) and the measured glow curve (———) of the X-ray irradiated crystal.

Thermoluminescence experiments

Thermoluminescence experiments were performed on both irradiated and unirradiated specimens. The X-ray irradiated specimen exhibited the glow curve shown in Figure 6, indicating a prominent peak centered at about 365°K and two other weak ones at 575°K and 625°K. No glow curve could be obtained from the unirradiated specimen. A similar glow curve was obtained by Medlin (1964), but the positions of the peaks were at somewhat different temperatures (350°K, 500°K, and 600°K). The decay of the luminescence associated with the 365°K peak correlates with the decrease in the resonance intensity of the Fe(III) line (dashed curve in Fig. 6), which clearly indicates that both are related. Medlin (1959 and 1963) associated the orange emission of the prominent glow peaks with the $^4G(T_{1g})\rightarrow{}^6S$ transition in the divalent manganese ion which occupies substitutional sites in the calcite structure. This transition is forbidden, so it cannot be directly excited by optical absorption. However, indirect excitation is possible, and luminescence can be produced. As was also pointed out by Medlin (1964), trapping centers in calcite are somewhat analogous to sensitizing ions; both provide processes for exciting the forbidden Mn(II) transitions. It is clear that in the present crystal thermal bleaching of the X-ray-induced Fe(III) center furnished conditions favorable to indirectly excite emission at the Mn(II) sites. However, it seems that this might not be the only process in operation, since upon further heating the irradiated specimen exhibited other weaker glow peaks as shown in Figure 6. The results indicate that other indirect excitation processes were also provided, probably through the host-structure absorption of X-rays.

Summary and conclusion

The results suggest that the pale green coloration can be regarded as an impurity-related color and not a radiation one. The natural crystal did not show the known criteria of radiation color. Careful chemical analysis indicated the presence of a number of impurity ions. A study of the optical and resonance absorption spectra of the calcite crystal before and after X-ray irradiation has provided useful information about the impurity ion oxidation states and hence the conditions under which the calcite formed.

X-ray irradiation effect and luminescence

The results clearly indicate that while the post-radiation room-temperature phosphorescence is attributed to some transitions in the X-ray induced Mn(IV)-related electron-trap center, the thermoluminescence exhibited at about 400°K is an indirect emission produced mainly by the annihilation of the Fe(II)-related hole-trap center. The following summarizes the sequence of events and the proposed oxidation-reduction and excitation reactions which may have occurred in the present calcite crystal during X-ray irradiation and subsequent thermal treatment:

(1) Exposure of the calcite crystal to ionizing radiation at room temperature results in the formation of free electron and positive holes. These free electrons and holes are trapped by trace Mn(IV) and Fe(II) ions present to form Mn(II)** and Fe(III) radiation centers respectively.

(2) The Mn(II)** centers appear to be in a highly excited state. Certain transitions within these Mn(II)** excited centers taking place at room temperature are thought to be responsible for the observed post-radiation phosphorescence and to the formation of comparatively more stable Mn(II) centers.

(3) Upon warming the crystal to about 400°K, the X-ray induced Mn(II) and Fe(III) centers become thermally unstable, the result being the recombination of the electrons and holes. The energy released during the recombination processes excites emission centers and produces thermoluminescence by allowing certain transitions in some of the Mn(II) impurity ions which were forbidden otherwise. Other Mn(II) excited centers formed by the direct absorption of X-rays may be partially responsible for the observed glow peaks.

Color and precipitation conditions

The pale green color of the calcite crystal is attributed to the presence of trace Fe(II) ions masking the very pale pink shade expected to occur due to the presence of Mn(II) ions substituting for Ca(II). Calcite is known to deposit at a pH of 7.8 or higher, and as the pH decreases, it readily dissolves. On the other hand, the presence of Fe(II) and Mn(II) ions demands a very acidic environment or one with a very low oxidation potential; otherwise, the Fe(II) ions would have been readily oxidized to Fe(III). Therefore, it is suggested that the present calcite crystal was probably formed in a special environment which could have been more acidic, slightly warmer, and with a very low oxidation potential.

Acknowledgments

The author thanks her colleague Mr. Sobhi Agaibi of the Egyptian National Cement Company for providing the pale green calcite crystal, and the American University in Cairo for awarding her a summer research grant which made this work possible. Thanks are also due to Mr. F. Fattal for conducting the thermoluminescence experiment.

References

Calamawy, S. (1970) *Traps and trap distribution in commercial zinc sulphides phosphor.* M.Sc. Thesis, American University in Cairo.

Hurd, F. K., M. Sachs, and W. D. Hersbberger (1954) Paramagnetic resonance absorption of Mn^{++} in single crystals of $CaCO_3$. *Phys. Rev., 93,* 373–380.

Kikuchi, C. and L. M. Matarrese (1960) Paramagnetic resonance absorption of ions with spin 5/2:Mn^{++} in calcite. *J. Chem. Phys., 33,* 601–606.

Medlin, W. L. (1959) Thermoluminescent properties of calcite. *J. Chem. Phys., 30,* 451–458.

—— (1963) Emission centers in thermoluminescent calcite, dolomite, magnesite, aragonite, and anhydrite. *J. Opt. Soc. Am., 53,* 1276–1285.

—— (1964) Trapping centers in thermoluminescent calcite. *Phys. Rev., 135,* A1770–A1779.

Przibram, K. (1956) *Irradiation Colors and Luminescence.* Pergamon Press, London.

Schulman, J. H., L. W. Evans, R. J. Ginter and K. J. Murata (1947) The sensitized luminescence of manganese-activated calcite. *J. Appl. Phys., 8,* 732–739.

Manuscript received, August 11, 1976; accepted for publication, January 23, 1978.