THE AMERICAN MINERALOGIST, VOL. 52, MARCH–APRIL, 1967

THERMOLUMINESCENCE OF SYNTHETIC FLUORITE

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ABSTRACT

Certain single lanthanide species in gamma-irradiated synthetic crystals of CaF_2 causes thermoluminescent glow curves with peak temperatures and general configurations that are characteristic of the lanthanide species. Other lanthanides fail to "activate" thermoluminescence. Relative thermoluminescence efficiency for different lanthanides and some information on optimum concentration for activation of thermoluminescence are given. A "crystallization-induced" thermoluminescence and a "gamma-radiation-induced" thermoluminescence are shown to be identical in mechanism and in end result for Dy-containing CaF_2, and it is suggested that the same relation may hold for other lanthanide-containing CaF_2 crystals. Pure CaF_2 (99.99%) is shown to be thermoluminescent only at low temperatures.

This study has proved helpful in understanding thermoluminescence of natural fluorite, and may aid in developing techniques for using thermoluminescence as an analytical and interpretive tool in geology.

INTRODUCTION

Geological interpretations of thermoluminescence in fluorite are hampered by a lack of experimental data on control material. This study of thermoluminescence of single crystals of synthetic fluorite contributes to our understanding of glow curves of natural fluorite. Twenty-two single crystal chips of synthetic fluorite were used, each crystal containing known percentages of the lanthanide elements (rare earths) or combinations Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, U (an actinide), Yb+Sm, and Ce+Sm, and one single crystal of pure synthetic fluorite. The crystals were obtained from Semi-Elements, Inc., and the selection of material was limited by the available stock of this company and was guided by knowledge of the widespread occurrence of trace amounts of lanthanides in natural fluorite.

METHODS

Material to be tested for thermoluminescence was prepared by cleaving {111} plates from the single crystal chips and grinding the cleavage plates on one side to a thickness of 0.020 inch. These plates were weighed to the nearest 0.1 mg so that intensities of emitted light could be recorded in arbitrary units per gram of sample, making it possible to compare the thermoluminescence intensities from samples of different size.

Thermoluminescence was induced in the crystals by gamma photons resulting from the radioactive decay of Co^{60}. The dose received by each sample was determined from the time of irradiation and a calibration curve based upon the original activity and the half-life of Co^{60}. Between irradiating and testing for thermoluminescence, the samples were maintained at ice-water temperature to minimize draining of low-energy electron traps.

Samples were heated in an aluminum sample holder at an approximately linear rate of 130°/min from room temperature to about 400°C. Light emission was detected with a 1P28 photomultiplier tube operated at approximately 1000 volts, and standardized for each determination with a constant light source. The output from the phototube was amplified with a d-c amplifier (Ashby and Kellagher, 1958) and the output of the amplifier was used to drive a microammeter (arbitrary light intensity units) and the X-axis of an X-Y recorder (Houston Instrument Corp. Model HR-96). The Y-axis of the recorder was driven by the signal from an iron-constantan thermocouple which recorded the temperature of the sample. Half-minute time marks were recorded by momentarily lifting the recording pen.

Results and Discussion

Crystallization-induced thermoluminescence. All of the samples, except one, were essentially non-thermoluminescent before exposure to γ-radiation. The one exception, CaF_2 containing 0.1 percent Dy, displayed an unexpected, strong, original thermoluminescence (Fig. 1). A second cleavage plate, which had not been ground, of the Dy-containing CaF_2 was tested for original thermoluminescence, and the glow curve obtained was not significantly different from the glow curve obtained from the first (ground) cleavage plate. Thus the original thermoluminescence cannot be attributed to effects of grinding. After heating, which removed all the original thermoluminescence, the crystals were subjected to sunlight and to ultraviolet light (long-wave) for periods of 10 and 6 hours; these exposures failed to produce any significant thermoluminescence. It is concluded that the original thermoluminescence of the Dy-containing CaF_2 is in fact a crystallization-induced phenomenon, which originated at the time the crystal was formed and is not a product of later effects, such as grinding or exposure to daylight.

The process used in the synthesis of the sample containing Dy resulted in the Dy being present in the divalent state, rather than in the more stable trivalent state (Joseph V. Fisher, Semi-Elements, Inc., written communication), accounting, at least in part, for the intense original thermoluminescence. This may be of importance in geological applications of thermoluminescence. Most attempts to apply thermoluminescence to age determination of minerals have assumed that the mineral was essentially nonthermoluminescent immediately after crystallization, and that the potential thermoluminescence has built up gradually as a result of absorption of terrestrial radiations (Blanchard, 1966). Although

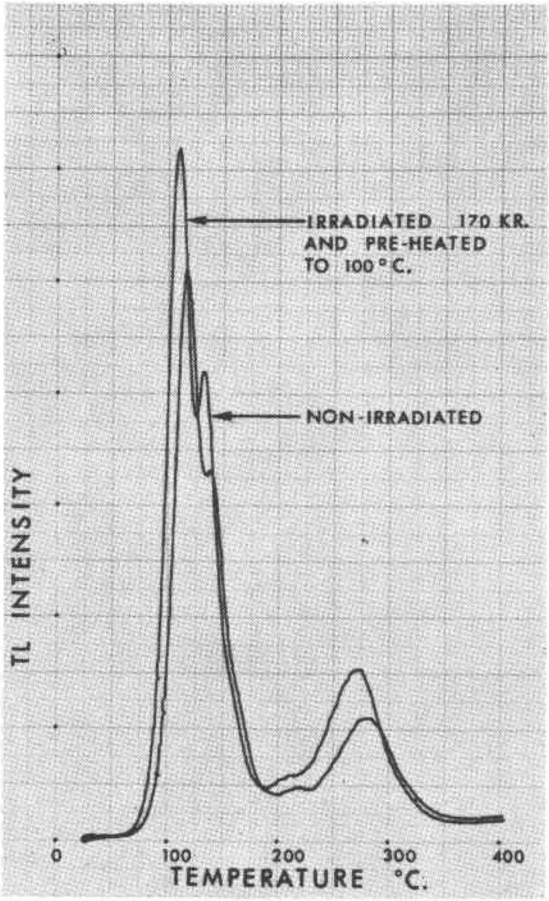

FIG. 1. "Crystallization-induced" and "radiation-induced" thermoluminescence of CaF_2 containing 0.1% Dy.

this may be essentially true for most fluorite, apparently the presence of divalent Dy can cause intense original thermoluminescence. The presence of other characteristically trivalent lanthanides in the divalent state also might cause an original or crystallization-induced thermoluminescence. Whether or not fluorite can form in nature with lanthanide impurities in the reduced state is not known. If it can, this would negate the assumption that fluorite is always nonthermoluminescent immediately after crystallization. According to Moeller (1963), all divalent lanthanides (except Eu^{++}) in solution must revert to the trivalent state. Thus it would seem that unusual conditions would be required for fluorite to precipitate with divalent lanthanide impurities.

Thermoluminescence of irradiated "pure" CaF_2. It is well known that trace elements influence luminescence of minerals, and it is commonly implied and sometimes stated that trace elements are necessary for luminescence. Results presented here show that even the pure CaF_2 emits very intense low temperature thermoluminescence (at about 75°C) after exposure to suitable radiation (Fig. 2). This sample is 99.99 percent CaF_2, with the major impurities being Ba and Sr, and with the transition elements in the part-per-million range (Joseph V. Fisher, written communication). In some of the doped synthetic fluorites, glow-curve peaks appear at approximately the same temperature (about 75°C), but the intensities of the peaks are either greater or (more commonly) less than the 75°-peak of pure CaF_2. The doped samples probably contain approximately the same kinds and quantities of accidental impurities as the pure CaF_2. It is not clear whether the low-temperature thermoluminescence in pure CaF_2 is related to minute traces of accidental lanthanide impurities, or whether it is related to either the perfect or defect CaF_2 structure. From earlier studies of natural fluorite, no correlation could be found between thermoluminescence and Sr content. Possibly trace elements are not necessary for low-temperature thermoluminescence in CaF_2, and certain trace elements may even reduce the potential for low-temperature thermoluminescence.

Influence of trace elements in irradiated CaF_2. Figure 2 shows representative glow curves of doped and pure CaF_2. All of the doped crystals contain 0.1 percent of the indicated impurity, except for Nd (3%), Tm (0.5%), and Ce+Sm (1.0%). All of the glow curves illustrated in this figure are from samples which received γ-radiation doses of 585,000 R. The amplifier sensitivity (scale factor) for each glow curve is given, ranging from ×0.01 to ×100. The jagged character of the glow curves obtained at high amplifier sensitivity is from photomultiplier noise.

The identity of lanthanide impurities in CaF_2 is related to the thermoluminescent efficiency, the number of glow-curve peaks, and the temperatures at which they appear (Fig. 2). The most strongly thermoluminescent sample emitted light about 50,000 times as intense as the most weakly thermoluminescent (both subjected to the same radiation dose). With the radiation doses used (at six levels ranging from 44,000 to 1,400,000 R), and for the trace-element concentrations used (mostly 0.1%), the thermoluminescent efficiency for glow-curve peaks between 200° and 300°C (intensity of thermoluminescence divided by radiation dose) is profoundly different for samples containing different trace elements, and the efficiency may be represented as $Pr > Nd > Gd > Dy > Tm > Tb > Eu > U$ and $Yb+Sm > Sm$, **Ho**, Er, Yb, and Ce+Sm, in

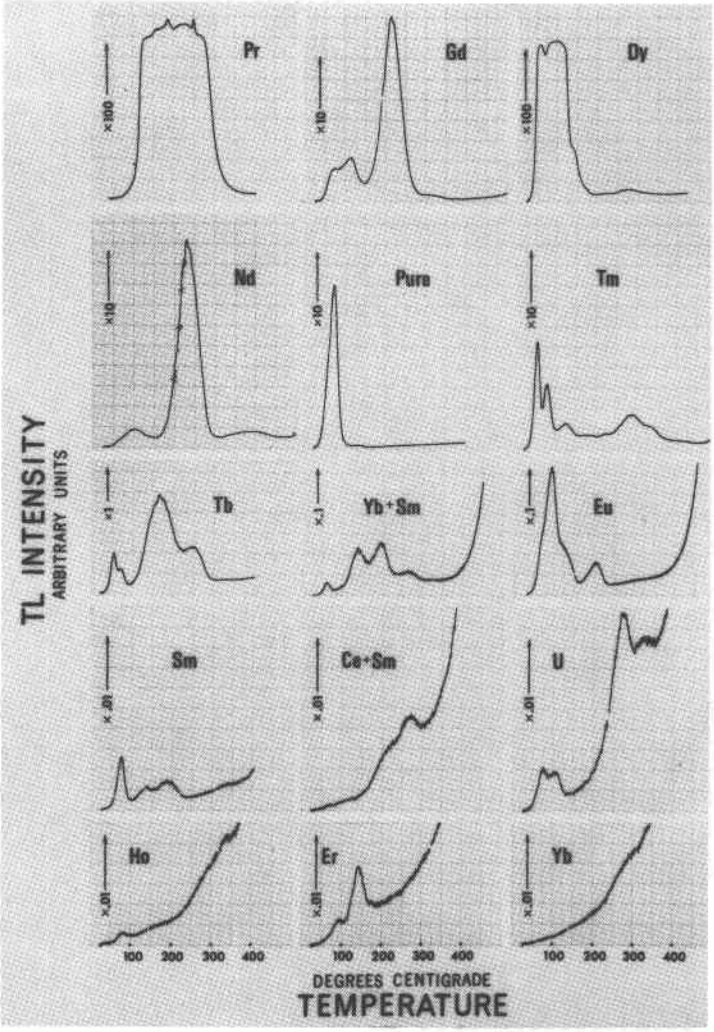

FIG. 2. Representative glow curves of doped and pure CaF_2.

CaF_2. The first six or seven elements produce strong enough thermoluminescence so that they may well be responsible for natural thermoluminescence in fluorite, but the others could not be responsible for the usual levels of intensity of natural thermoluminescence unless the efficiency of thermoluminescence increases greatly with decreasing concentration of the element. This latter possibility does not hold for crystals containing Gd, as explained below.

Thermoluminescence efficiency for different concentrations of Gd in CaF_2 was determined by comparison of glow curves from samples containing 0.02, 0.1, 0.25, and 0.5 percent Gd, all subjected to the same γ-radiation dose (50,000 R). Figure 3 shows data obtained from these glow curves, plotted as intensity of the 215° peak against percentage of Gd, and this graph indicates that the optimum concentration of Gd is approximately 0.1 percent. The same experiment was repeated using a radiation dose of 707,000 R, and the optimum concentration of approximately 0.1 percent was confirmed. This concentration is one to three orders of magnitude greater than is usual in natural fluorite. Material was not available for determination of optimum concentrations for the other impurity elements.

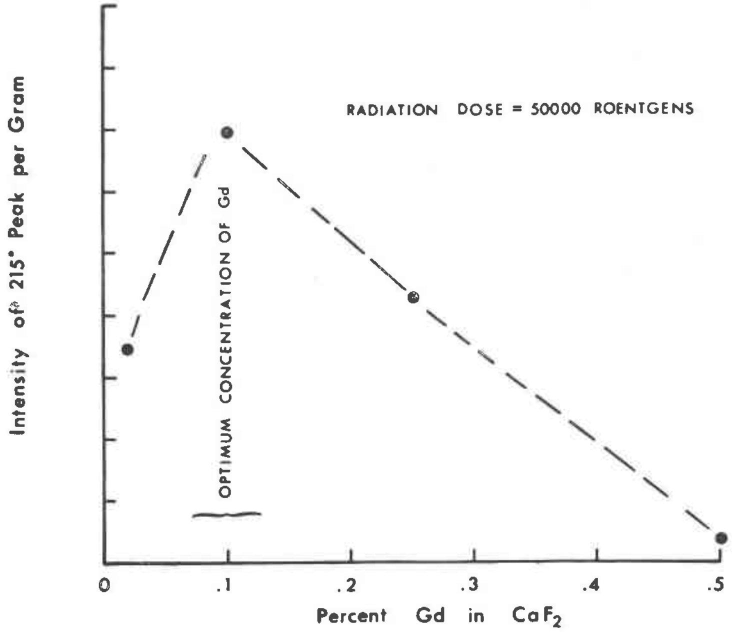

FIG. 3. Efficiency of thermoluminescence for different concentration of Gd in CaF_2.

The different trace elements are also responsible for differences in the temperature of glow-curve peaks (Fig. 2), and probably the variability in configuration of glow curves from natural fluorite is largely related to differences in lanthanide impurities in the fluorite. Possibly, glow curves could be used in detecting and identifying minute quantities of trace elements; however, application to natural fluorite would almost certainly be complicated by the multiplicity of trace elements present. Unfortunately, material was not available for systematic study of the effects of several different trace elements present simultaneously.

Effects of γ-radiation. Five samples, each containing 0.1 percent Gd, were subjected to γ-radiation doses of 24,500, 49,000, 98,000, 196,000 and 392,000 R and were tested for thermoluminescence. The intensity per gram of the glow-curve peak at 215° for each of the five samples was plotted against the respective radiation dose, and the resulting graph (Fig. 4) is convex upward. Similarly shaped graphs can be produced for natural fluorite. From this graph it is apparent that even at the largest radiation dose, thermoluminescence saturation is not reached. The same five samples were reirradiated with a dose of 49,000 R, tested for thermoluminescence, and the glow curves so produced were only slightly different from each other (attributed to measuring errors), indicating that the various levels of prior radiation had no noticeable effect on the

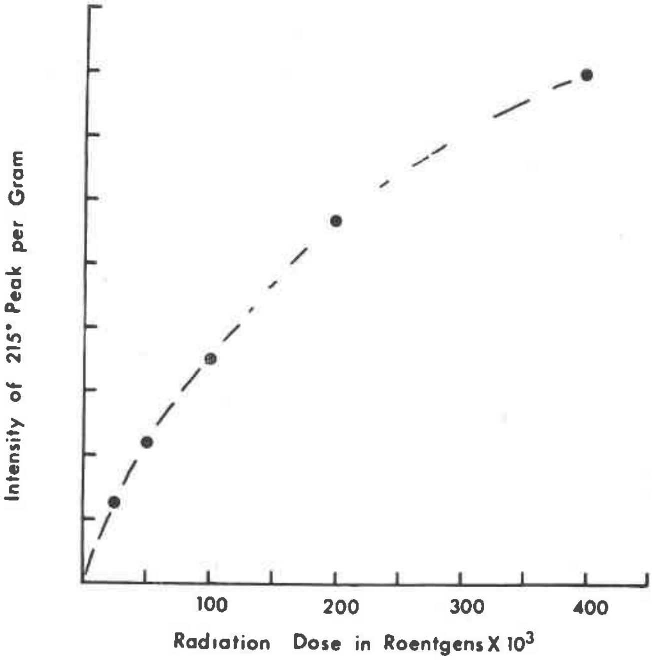

FIG. 4. Dependence of intensity of thermoluminescence on γ-radiation dose, for CaF_2 with 0.1% Gd.

thermoluminescence produced by reirradiation. It is concluded that γ-radiation causes filling on electron traps, and perhaps produced temporary new traps, but does not cereate permanent new traps.

Thermoluminescence in synthetic fluorite containing lanthanides seems to accompany and be related to changes in oxidation state of the lanthanide elements. McClure and Kiss (1963) have shown that in CaF_2, trivalent lanthanides occupying cubic sites are reduced in place to the divalent state by gamma-radiation. Gamma-radiation also renders crystals containing certain lanthanides thermoluminescent. In the Dy-containing sample used in this study, divalent Dy in CaF_2 was prepared by chemical reduction in the melt; this crystal showed intense thermoluminescence prior to irradiation (Fig. 1); after heating, γ-radiation reactivated the thermoluminescence with glow-curve peaks identical with those in the original material. In Figure 1 the crystallization-induced and radiation-induced glow curves (labeled "nonirradiated and irradiated") are considered to have "identical" peak temperatures; the small discrepancy is attributed to error in measurement of the actual sample temperature. The irradiated sample was first heated to remove the original, crystallization-induced thermoluminescence, then irradiated (about 50,000 R), and finally warmed to 100°C to partly remove low-temperature radiation-induced thermoluminescence. By trial and error, with radiation doses and warming, it would be possible to duplicate exactly the crystallization-induced thermoluminescence of the nonirradiated sample. It appears that a crystallization-induced thermoluminescence is identical in mechanism and end result with a radiation-induced thermoluminescence, and that activation and removal of thermoluminescence in fluorite accompanies, and is related to, reduction and oxidation of certain lanthanide impurities, caused by absorption of high-energy radiation and heating.

CONCLUSIONS

The following conclusions, bearing on thermoluminescence of synthetic fluorite, can probably be extrapolated to natural fluorite.

1. In γ-irradiated CaF_2 crystals which have been synthesized in the same way, but which contain different lanthanide impurities, the temperature of glow-curve peaks is a function of the identify of the impurities.
2. Among the impurity elements studied, Pr, Nd, Gd, Dy, Tm, Tb, and possibly Eu are likely to be activators of thermoluminescence in natural fluorite; Sm, U, Ho, Er, and Yb are probably not important as activators and may even reduce the potential for thermoluminescence.
3. The optimum concentration of Gd for activation of thermolumines-

cence is approximately 0.1 percent; considerably greater or lesser concentrations result in reduced potential for thermoluminescence.

4. Dy, and probably other lanthanides which activate CaF_2, if originally present in a divalent state, cause "crystallization-induced" thermoluminescence. It is thus conceivable that some natural fluorite might be intensely thermoluminescent immediately after crystallization.

5. Irradiated pure CaF_2 (with transition elements in the part per million range) exhibits thermoluminescence at a temperature too low for the energy to be stored under normal geologic temperatures; moderate and high temperature thermoluminescence is absent. The low temperature peak may be unrelated to trace elements but characteristic of the perfect or defect structure of the fluorite crystal. This peak is modified or eliminated by the presence of appreciable quantities of lanthanide impurities.

6. Storage of energy and its liberation as thermoluminescence apparently accompanies, and is related to, reduction of trivalent lanthanide ions (substituting for Ca^{++}) by γ-radiation or by chemical reduction in the formation of the crystal. Heating restores the more characteristic trivalent state and light is emitted. No permanent electron traps are created during the process of irradiation.

ACKNOWLEDGMENTS

I thank Mr. Joseph V. Fisher, president of Semi-Elements, Inc., for supplying all of the synthetic crystals to the Department of Geology at a cost greatly below list. Irradiation of the crystals was accomplished with facilities made available by the Department of Nuclear Engineering, University of Florida, and students in the Department of Geology assisted in the irradiation of samples.

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Manuscript received, May 16, 1966; accepted for publication, July 25, 1966.