Part I. Mechanisms 1

MECHANISMS FOR THERMOLUMINESCENCE IN MgO AND CaSO$_4$

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Mechanisms for thermoluminescence (TL) in MgO irradiated with ultraviolet light, based on a charge transfer process between transition-metal ions and V-centers, are proposed. Similar mechanisms occur in rare-earth doped CaSO$_4$.

It has been reported that charge transfer mechanisms are operative in rare-earth (RE) doped CaF$_2$ [1], CaSO$_4$ [2] and LiF : Mg, Ti [3], indicating the importance of valence changes in impurity ions during TL in those materials. Current studies in MgO show that similar processes occur, involving the transition metal ions Fe, Cr, Mn and V; in CaSO$_4$ charge transfer between Dy ions and V-type centers control the TL mechanism.

MgO crystals obtained from the W.C. Spicer Company and from the Norton Company were annealed in air, respectively, at 1000°C for 3 h and 1400°C for 24 h. Figs. 1a and b show typical TL glow curves after UV irradiation for the "as received" and air heat treated Norton crystals; similar glow curves are shown in figs. 1c and d for Spicer samples. The heat treatment is seen to sensitize TL peaks 1 and 2 in the Spicer samples, along with TL peak 3 and, in a smaller extent, TL peak 2 in the Norton samples. In general, it is observed that the Norton samples which have an overall lower purity than the Spicer samples, show a lower TL sensitivity due to concentration quenching. ESR was employed to measure the concentrations of Fe^{3+}, Cr^{3+}, Mn^{2+} and V^{2+} before and after the UV exposure and after the TL reading. The concentration ratios between samples before and UV (R_1), and between samples after UV and after TL (R_2) are shown in table 1. All samples were given a UV exposure of 27.6 Ws/cm^2 from a non-monochromatic UV filtered Hg source. Ratio R_1 shows that the UV radiation decreases [Fe^{3+}] and [Mn^{2+}] in the Norton sample and decreases [Fe^{3+}], [Mn^{3+}] and [V^{3+}] in the Spicer sample. The values for ratio R_2

shows that the TL reading causes a reversible reaction which is not always complete.

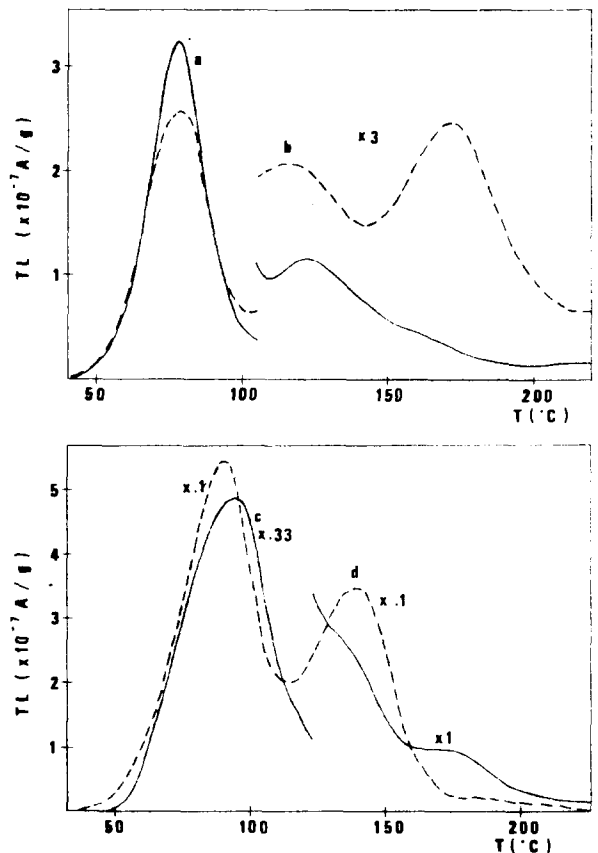Based on these results, the TL mechanisms can be

Fig. 1. TL glow curves for MgO exposed to nonmonochromatic UV radiation, 27.6 Ws/cm^2. (a) Norton sample, "as received"; (b) Norton sample, heat treated in air at 1400°C for 24 h; (c) Spicer sample, "as received"; (d) Spicer sample, heat treated in air at 1000°C for 3 h.
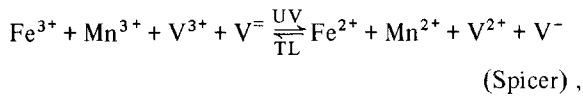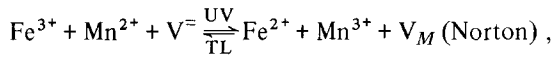
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Table 1
Ratios R_1 (before UV to after UV) and R_2 (after UV to after TL) for Fe^{3+}, Cr^{3+}, Mn^{2+} and V^{2+} concentrations in MgO measured using ESR.

Sample	Fe^{3+}		Cr^{3+}		Mn^{2+}		V^{2+}	
	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
Norton, 1400°C	1.45	0.90	0.93	1.02	2.02	1.02	–	–
Spicer, 1000°C	3.78	0.28	1.01	0.92	0.48	2.05	0	1.03

summarized with the equilibrium reactions

$$Fe^{3+} + Mn^{2+} + V^= \underset{TL}{\overset{UV}{\rightleftharpoons}} Fe^{2+} + Mn^{3+} + V_M \text{ (Norton) ,}$$

$$Fe^{3+} + Mn^{3+} + V^{3+} + V^= \underset{TL}{\overset{UV}{\rightleftharpoons}} Fe^{2+} + Mn^{2+} + V^{2+} + V^-$$

$$\text{(Spicer) ,}$$

where $V^=$ are cation vacancies, V^- centers are vacancies which have captured a hole, and V_M are V^- centers associated with trivalent metal ions M. These reactions indicate the formation of V-type centers when cation vacancies capture holes released from the impurity ions by the UV radiation; these centers are annealed out during the TL reading, the released holes recombining with the impurity ions, giving off light. The TL peak temperatures are related to the stability of these V-centers which act as trapping centers for TL. Thus, in Norton samples, the 77°C peak is probably associated with V_{Al} centers, which have a half-live of a few hours [4], while in Spicer samples, the trapping centers are primarily V^- centers which are known to be very stable. The sensitization of the 120°C peak 2 was found to be related to the amount of Fe^{3+} produced by the oxidizing treatment in air; we propose that V_{FE} centers, which are assumed to be more stable than V_{Al} but less stable than V^- centers, act as trapping centers for that TL peak.

The activator centers are identified as Fe^{3+} for Norton samples and as Fe^{3+}, Mn^{3+} and V^{3+} for Spicer samples. The sensitization effect of the 166°C peak 3 in the Norton sample is possibly associated with the conversion of Mn^{2+} to Mn^{3+}, where Mn^{2+} ions act as hole traps for that peak. The reverse reaction does not occur, as shown by the ratio R_2, indicating that Mn^{3+} is not a recombination center for TL emission. In Spicer crystals, the TL mechanism for Mn is reversed, and Mn^{2+} is identified as a recombination center rather than a trapping center. In all samples, the behavior for Mn is fundamentally different from pre-

vious reports [5] that this ion is very stable under UV irradiation and other treatments. The ratio R_1 is zero for V^{2+} in Spicer samples because all the vanadium is present as V^{3+} after the oxidizing treatment, being reduced to V^{2+} by UV exposure. This reaction is not reversed by the TL readout showing that, while V^{3+} is an activator center, V^{2+} is not a recombination center for TL. V^{2+} is not detected in Norton samples. The recombination center common to both samples and to all TL peaks, as revealed by ESR and partial TL readings not reported here, is the Fe^{2+} ion which captures holes during the TL readout.

$CaSO_4$: Dy mixed with LiF and sintered into chips obtained from Harshaw Chemical Company were subjected to various gamma exposures and annealing treatments prior to TL readout. Initial test exposures of 150R with ^{137}Cs gamma rays indicated the as-received $CaSO_4$: Dy chips were in a sensitized state, although the TL peak at 400°C, reportedly due to the deep traps influencing the sensitizing in this material, was absent [6]. Anneals at 400°C for one hour between exposures did not reduce sensitivity; one anneal at 600°C for one hour with rapid cooling did. Subsequent to the 600°C anneal, sensitizing exposures followed by 300°C anneals for one hour did cause sensitization with additional glow curve structure, including a broad TL peak centered at 400°C. The absence of this structure in the sensitized material before the 600°C anneal indicates the traps are influenced by the annealing process.

Computer simulations were obtained for the kinetic equations governing the TL process in $CaSO_4$: Dy based on the equilibrium equation

$$4\,Dy^{3+} + 3\,V^= \underset{TL}{\overset{gamma}{\rightleftharpoons}} 4\,Dy^{2+} + 2\,V^- + V^0 ,$$
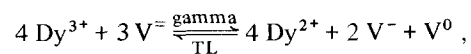
where $V^=$ and V^- centers are cation vacancies, as described for MgO, and the V^0 center is a vacancy that has captured two holes. In the model proposed the deep traps (V^- centers) and the dosimetric traps

(V^0 centers) are uniquely coupled; for example, the location of the V^0 peak depends on the parameters of the high temperature peak, and the location of the V^0 peak shifts to lower temperatures with increasing sensitization.

We conclude that the same type of TL mechanisms operate in MgO and CaSO$_4$: Re dosimeter materials. In MgO, the "direct TL" is the result of charge transfer mechanisms between transition metal ions and V-type centers. In CaSO$_4$: RE, charge transfer occurs between rare earth impurities and V-type centers which accounts for the TL behavior in this material.

References

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