

Effects of the equilibrium concentration of impurities on the reproducibility of thermoluminescence in MgO

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A study of thermoluminescent (TL) sensitivity and reproducibility is undertaken in crystals of MgO exposed to ultraviolet radiation in the as-received condition, and heat treated in air or in a mixture of CO/CO₂ at either 1000 or 1400° C. The changes in the concentrations of transition metal ions such as Fe³⁺, Cr³⁺, Mn²⁺ and V²⁺, caused by the heat treatments, are followed using electron spin resonance. It is shown that the equilibrium concentrations of Fe³⁺ and V²⁺ ions, which can be altered by heat treatments, play an important role in the reproducibility of the TL in this system.

1. Introduction

One of the problems encountered in studying thermoluminescence (TL) in MgO is the reproducibility of the TL response. In some materials, a standard heat treatment is known that will reset the sample to its original TL sensitivity [1]; in MgO no such standard treatment has been found that allows experimental reproducibility to be achieved. Ziniker *et al.* [2] mention that prolonged heating at 423° C restores the MgO crystal to its original sensitivity, while Krishnan [3] says that this can be achieved by heating at 340° C for 1 h. Luthra *et al.* [4] heated their samples at 147° C for 30 min before use. Takeuchi *et al.* [5] obtained good reproducibility when their samples experienced an ultraviolet (u.v.) pre-irradiation followed by heating at 250° C. Dhar *et al.* [6] state that such heat treatments are not necessary since reproducibility was within 6% in a test where repeated monochromatic excitation and TL measurement were carried out without intermediate sensitization or heat treatment. Dhar also reports variations of as much as 30% between different MgO single crystals, as a consequence of sample-to-sample inhomogeneities. It is the purpose of this paper to show that the non-reproducibility effect is due principally to differences in the equilibrium concentration of transition metal impurities found in

commercially available MgO and that these differences can be minimized with suitable heat treatments at high temperature.

2. Experimental procedures

MgO single crystals were supplied by the Norton Company and the W.C. Spicer Company, samples from the former having a higher total impurity concentration than the latter, as shown in Table I. The relative impurity concentrations were measured using electron spin resonance (ESR) and optical absorption (OA) techniques.

Comparing ESR and OA measurements, the relationship between the number of spins per cm³, N , and the absorption coefficient (in cm⁻¹) of the Fe³⁺ band, $\alpha(285 \text{ nm})$, yields

$$N = 0.4 \times 10^{17} \alpha(285 \text{ nm}). \quad (1)$$

This proportionality factor is 2.5 times lower than that derived by Davidge [7], probably because the u.v. absorption edge was not taken into account in the determination of $\alpha(285 \text{ nm})$. The ESR standard used was 1-diphenyl-2-picrylhydrazyl (DPPH) powder, for which the number of spins per cm³ was calculated using the Wertz and Bolton formula [8]. The relative concentrations determined from ESR agree well with the neutron activation analysis results in Table I, although the absolute

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TABLE I Semiquantitative spectrographic and neutron activation analyses of MgO

Source	Spectrographic analysis						Activation analysis	
	Total concentration (ppm)						Total concentration (ppm)	
	Fe	Cr	Mn	Al	Ti	Ni	Mn	V
Spicer	< 50	< 10	< 10	50	< 50	< 20	0.7 ± 0.3	0.6 ± 0.6
Norton	150	< 10	< 10	150	< 50	< 20	11.0 ± 5.0	0.3 ± 0.3

concentration of Mn is about 1.8 times lower using the ESR technique, which detects only Mn^{2+} , compared with the concentration determined using activation analysis. This could indicate that Mn^{3+} accounts for the remaining Mn content, although the discrepancy is within the inaccuracy of both the neutron activation analysis and the ESR DPPH standard comparisons.

The crystals were exposed to non-monochromatic filtered u.v. light or monochromatic light in the region 250 to 360 nm. A Varian ESR spectrometer model V-4502 operating in the X-band was used for the ESR measurements. A Cary-14 spectrophotometer was utilized for the OA measurements. The optical system consisted of a 200 W mercury lamp with a Schoeffel lamp housing and power supply, a Jarrell-Ash 82410 0.25 Meter Ebert monochromator and an EG&G radiometer with a detector head, model 580-20A was used; the total irradiance, I_t , is reported in Wsec cm^{-2} . A Corning filter, type 7-54, transmitting about 86% at 320 nm and 5% at 240 nm and 9% at 410 nm, was used in all experiments. Heat treatments were performed either in a controlled mixture of CO and CO₂ or in air, at 1000 or 1400°C, for periods ranging from 3 to 24 h. All samples were quenched to room temperature within a period of 5 min.

3. Results and discussion

It is known that the Fe^{3+} ion absorbs at 285 nm in MgO [7]. The TL excitation spectrum in Fig. 1, curve b, relates directly to this absorption, showing an excitation band for "as-received" Norton crystals centred at about 300 nm. The peak absorption coefficient for the 285 nm band is about 45 cm^{-1} for these samples. Fig. 2 shows the TL sensitivity per unit weight as a function of crystal thickness, x_0 , for the monochromatic exposure of 289 nm and $I_t = 0.01 \text{ Wsec cm}^{-2}$. As can be seen, thickness is one of the parameters that affects the TL reproducibility: The thicker the crystal the lower the TL response. This is believed to be due mainly to the Fe^{3+} absorption. The

effective absorption coefficient, α_{eff} , may be derived from Fig. 2 and the relationship $\text{TL} = \text{TL}_0 \exp [-\alpha_{\text{eff}}(\lambda) x_0]$, where $\alpha_{\text{eff}}(\lambda)$ is an *a priori* function of wavelength and is derived to be 8 cm^{-1} .

The reason for the difference in the absorption coefficients in the measurements in Figs 1 and 2 is that α_{eff} is related to the TL emission spectrum of the sample as well as to its absorption spectrum. The emission spectrum consists of the emission lines of iron, as well as those due to transitions of other impurity ions. Krishnan [3] observed orange emissions at 645 and 659 nm, attributed them to the $\text{Fe}^{3+*} \rightarrow \text{Fe}^{3+}$ transition, in agreement with data obtained in calculations based on the Tanabe-Sugano diagrams for Fe^{3+} . It has been generally accepted that u.v. light decreases the Fe^{3+} concentration by releasing holes from these ions, which become trapped in vacancies, forming

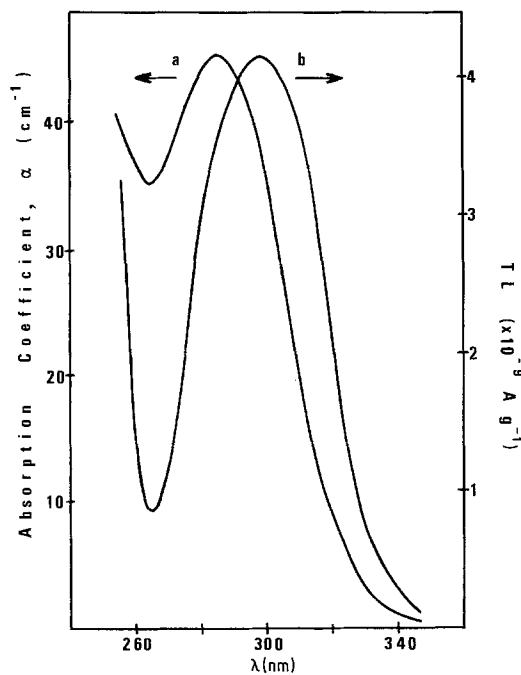


Figure 1 (a) Optical absorption in Norton samples, showing a band at 285 nm due to Fe^{3+} and (b) TL excitation spectrum in Norton samples.

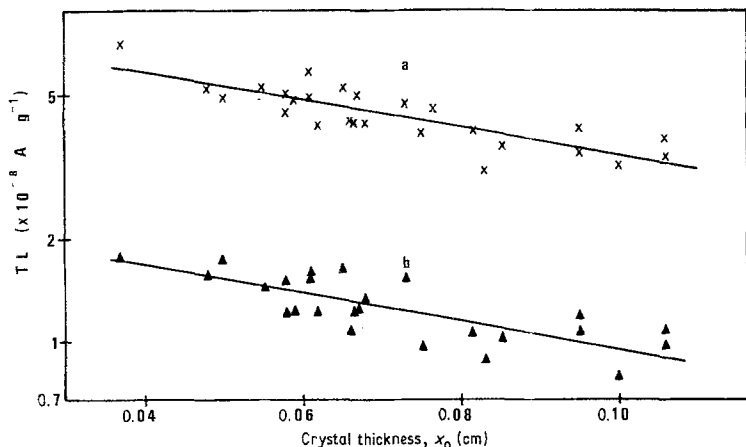


Figure 2 TL output of a set of Norton samples as a function of crystal thickness. $I_t = 0.2 \text{ Wsec cm}^{-2}$; 289 nm. (a) peak 1 and (b) peak 2.

V-type centres. This step corresponds to the OA band of Fe^{3+} ions. During the TL reading, the V centres become unstable, releasing the holes which recombine with the Fe^{2+} ions, forming excited Fe^{3+} ions, which decay to Fe^{3+} with light emission. The combined effects of absorption and emission account for the behaviour of the TL as a function of thickness. In addition to Fe^{3+} ions, V^{2+} ions were detected in our MgO samples, and play an important role in the TL mechanism, as discussed below. This is expected, since absorption bands in MgO have been reported at 240, 414 and 620 nm for V^{3+} [9], and at 310 nm [10], 502 and 714 nm [11] for V^{2+} .

The equilibrium concentration ratio between Fe^{3+} and Fe^{2+} may be changed in a given sample using heat treatments in specific atmospheres: Annealing in air causes oxidation of Fe^{2+} to Fe^{3+} while reduction of Fe^{3+} to Fe^{2+} occurs in equilib-

rium in specific CO/CO_2 atmosphere mixtures. Fig. 3 shows the TL output for Norton samples, as-received, oxidized in air and/or reduced by annealing in CO/CO_2 atmospheres; this is shown as a function of the Fe^{3+} content, as measured by ESR. These crystals were exposed to 289 nm u.v. light of $I_t = 0.2 \text{ Wsec cm}^{-2}$. The TL response of peaks 1 (74°C) and 4 (230°C , not shown) is linear as a function of $[\text{Fe}^{3+}]$, but that of peaks 2 (126°C) and 3 (162°C) shows a power function behaviour. From Fig. 3 one can say that Fe^{3+} is an activator centre for TL. However, Spicer crystals, not shown, have a lower total Fe content than Norton (see Table I) but also have a higher TL sensitivity than the Norton crystals by a factor of about 30. This suggests that a high iron content may act as a quencher of TL. In Fig. 3, the ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ changes, but the total amount of Fe is constant, so that the assignment of Fe^{3+} as an

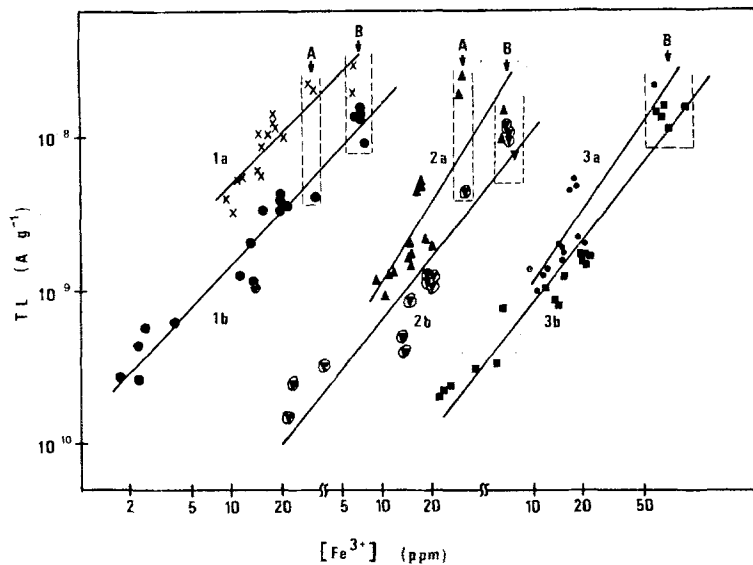


Figure 3 TL response of reduced Norton crystals as a function of Fe^{3+} concentration. Heat treated twice: (1a) peak 1, (2a) peak 2 and (3a) peak 3. Heat treated once: (1b) peak 1, (2b) peak 2 and (3b) peak 3. Also shown are the responses of the same samples "as-received" A, and air heated treated, B. Log-log scale.

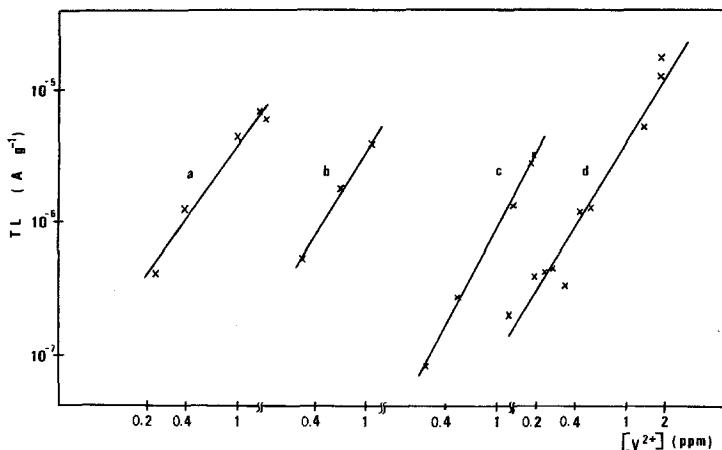
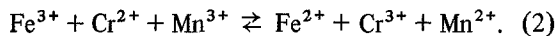


Figure 4 TL response of peak 1 in Spicer crystal, normalized for Fe^{3+} concentration (3 ppm) and thickness (1.5 mm), as a function of V^{2+} concentration. (a) $I_t = 0.2 \text{ W s cm}^{-2}$, 249 nm, $\Delta t_{\text{u.v.-TL}} = 2 \text{ h}$, (b) $I_t = 0.2 \text{ W sec cm}^{-2}$, 289 nm, $\Delta t_{\text{u.v.-TL}} = 0 \text{ h}$; (c) $I_t = 0.2 \text{ W sec cm}^{-2}$, 289 nm, $\Delta t_{\text{u.v.-TL}} = 3 \text{ h}$; (d) $I_t = 27.6 \text{ W sec cm}^{-2}$, non-monochromatic light, $\Delta t_{\text{u.v.-TL}} = 24 \text{ h}$, where $\Delta t_{\text{u.v.-TL}}$ denotes the time interval between the u.v. exposure and the TL reading. Log-log scale.

activator centre is not in conflict with the fact that an increasing total Fe content contributes to the quenching effect, as has also been seen by Lee and Crawford [12].

As a by-product of the CO/CO_2 experiments, it was observed that the heat treatments cause a slight change in the Mn^{2+} and Cr^{3+} concentrations, according to the equilibrium equation proposed by Wertz *et al.* [13]



If the TL response of peak 1 in Fig. 3 is normalized for $[\text{Fe}^{3+}]$ and plotted as a function of $[\text{Cr}^{3+}] + [\text{Mn}^{2+}]$, a small exponential decay is obtained. In other words, Cr^{3+} and Mn^{2+} also act as quenchers of TL. Other evidence pointing to Cr^{3+} as a quencher of TL is the observation that no TL emission was observed in a heavily Cr-doped MgO crystal.

In Spicer crystals V^{2+} was detected in addition to Fe^{3+} , Cr^{3+} and Mn^{2+} . This ion was observed in Norton samples only after they were strongly reduced in CO/CO_2 , leading to the conclusion that vanadium is normally present as V^{3+} in this material; the concentration of V^{2+} in the reduced Norton crystals was of the same order of magnitude as in the "as-received" Spicer samples. Assuming that the TL peak 1 (95°C) in Spicer samples is linearly proportional to $[\text{Fe}^{3+}]$ as was found for Norton samples, the TL response to u.v. light for three sets of Spicer crystals was normalized for $[\text{Fe}^{3+}]$ and for thickness and plotted as a function of $[\text{V}^{2+}]$ as shown in Fig. 4. The TL response is a power function of $[\text{V}^{2+}]$, demonstrating that the wide non-reproducibility in the TL found in that material is due to inhomogeneities in the concentration of vanadium impurities

among crystals cleaved from the same block. The functional relationship between TL and $[\text{V}^{2+}]$ indicates that the kinetics responsible for the TL mechanism are not first order, but show a slope between 1.6 and 1.8. An appropriate model to explain this behaviour must take into account the role of vacancies directly related to the vanadium ions, and the interactions between these ions and other impurities. These interactions are very important when it comes to the TL reproducibility in MgO, as discussed below.

The TL response for several Spicer crystals, heat treated in air, is shown in Tables II and III, for non-monochromatic and 289 nm u.v. light, respectively. The TL output has been normalized for weight, Fe^{3+} content (3 ppm) and thickness (1.5 mm). Annealing in air oxidizes all the V^{2+} ions to V^{3+} ; the ions reduce to V^{2+} upon u.v.

TABLE II TL response of Spicer crystals heat treated in air, with corresponding V^{2+} concentrations. Exposure to non-monochromatic light, $I_t = 27.6 \text{ W sec cm}^{-2}$, The TL response is normalized for $[\text{Fe}^{3+}]$ (3 ppm) and for thickness (1.5 mm)

Crystal	TL peak 1 ($\times 10^{-6} \text{ A g}^{-1}$)	$[\text{V}^{2+}]$ (ppm)	Heat treatment
1	0.34	0.05	1000° C 3 h
2	0.85	0.1	
3	1.43	0.7	
4	2.27	0.3	1400° C 3 h
5	2.43	0.5	
6	3.03	0.4	
7	1.68	0.6	1400° C 24 h
8	2.78	0.5	
9	2.44	0.5	
Average for crystals 4 to 9	2.30 ± 0.56 ($\pm 24\%$)	0.47 ± 0.10 ($\pm 21\%$)	

TABLE III TL response of Spicer crystals heat treated in air at 1400° C for 3 h, with corresponding V^{2+} concentrations. Exposure to 289 nm u.v. light of $I_t = 0.2 \text{ W s cm}^{-2}$. The TL response is normalized for $[\text{Fe}^{3+}]$ (3 ppm), for thickness (1.5 mm) and for fading occurring between exposure and readout, as noted

Crystal	TL peak 1 ($\times 10^{-7} \text{ A g}^{-1}$)	$[\text{V}^{2+}]$ (ppm)
4	4.51	0.3
	4.51*	0.3
	4.51*	0.2
5	5.24	0.5
	6.64*	0.3
	5.75*	0.3
6	5.65	0.4
	5.96*	0.3
	6.62*	0.3
Average	5.49 ± 0.85 ($\pm 15\%$)	0.32 ± 0.08 ($\pm 25\%$)

*Normalized for fading.

exposure, suggesting that the same TL mechanism is operative as noted above for Fe^{3+} . However, the expected re-conversion to V^{3+} after a subsequent TL reading was not observed. The data indicate that the V^{2+} equilibrium concentration tends to a value of about 0.4 ppm after annealing in air at 1400° C; the standard deviation for $[\text{V}^{2+}]$ is of the order of 20% after the 1400° C heat treatment, compared with a variation in $[\text{V}^{2+}]$ for non-heat treated crystals (Fig. 4) of a factor > 10 . The fact that the V^{2+} equilibrium concentration becomes more homogeneous after annealing is believed to be responsible for the improved TL reproducibility observed in these samples. Average TL responses and standard deviations are also shown in Tables II and III. After the heat treatment the variation in TL response is 15 to 24%, as compared to a factor of 100 before heat treatment (Fig. 4).

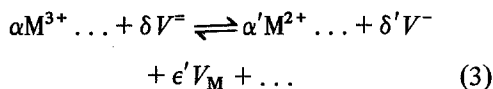
If the TL response of the Norton samples in Fig. 2 is normalized for thickness, but not for $[\text{Fe}^{3+}]$, the standard deviation is only 10%. This value could be reduced even more after normalizing for $[\text{Fe}^{3+}]$, since crystals from the same block, showing inhomogeneities in Fe^{3+} content, had a tendency to differ in the TL response in proportion to the Fe^{3+} concentration. The conversion $\text{V}^{3+} \rightarrow \text{V}^{2+}$, expected to occur with u.v. exposure in these samples (since they seem to contain V^{3+} ions) was not observed. This could be the reason for a better TL reproducibility seen in these Norton crystals compared with the Spicer

crystals, since V^{3+} ions would be stabilized in the former but not in the latter, as far as the u.v. exposure is concerned.

Assuming that for charge compensation reasons, Fe^{3+} ions are associated in some way with vacancies, perhaps forming $\text{Fe}^{3+}[100]$ centres, it is reasonable to say that the number of vacancies increases with the number of Fe^{3+} ions. This reasoning applies to the results of Fig. 3, where the number of V -type centres or vacancies increases with the Fe^{3+} content. The TL sensitivity is lower for curves 1b, 2b and 3b in Fig. 3 than for the corresponding curves 1a, 2a and 3a. The former results are from samples that had been heat treated twice, causing a decrease in Fe^{3+} and thus a further reduction in the number of vacancies. It was observed that the reduction of Fe^{3+} as a function of the CO/CO_2 partial pressure ratio involves two different mechanisms, indicating possibly the annealing of at least two different types of vacancies; these could be the V_{Al} and $\text{Fe}^{3+}[100]$ centres, for example, since V_{Al} centres are thought to be associated with TL peak 1. The power function relationship for TL peaks 2 and 3 is likely to be related to the $\text{Fe}^{3+}[100]$ centres, which could correspond to the trapping centres for these peaks; annealing in air sensitizes both peaks, while the Fe^{3+} concentration and the number of vacancies increase.

Since the number of vacancies plays an important role in determining the equilibrium concentration of impurities in their divalent or trivalent states, and therefore in the TL mechanism, the temperature of heat treatments and the quenching procedure are seen as critical steps in achieving good TL reproducibility. Quenching from high temperatures has been reported as determining the concentration of vacancies [14, 15]; since faster quenching produces a larger number of vacancies, small differences in cooling rate could be the cause of the fluctuations in the TL response in Fig. 3. The very process of crystal growth, where high temperatures and different cooling rates are involved, is itself critical in the equilibrium concentration of impurities and, therefore, in the TL behaviour.

In studying the TL mechanisms involving charge transfer between impurities and V -type centres that occur during u.v. exposure and TL reading [16], the following general reversible reaction was observed to be operative in our MgO samples:



where M is a transition metal ion, V^{\ominus} represents vacancies, V^- is the intrinsic V centre, and V_M is a V^- centre associated with a transition metal ion including the $Fe^{3+}[100]$ centre. More than one M ion can take part in the reaction, which is characterized by an equilibrium constant proportional to $[V^{2+}]^{\beta}/[Fe^{3+}]^{\alpha}$, where $\beta = 1.6$ (from Fig. 4) and $\alpha = 1.0$ (from Fig. 3). Similar charge transfer mechanisms have been seen in systems such as rare-earth doped CaF_2 [17] and rare-earth doped $CaSO_4$ [18]. That β is larger than α seems to suggest that the forward reaction is more probable than the reverse, as actually observed in some cases. The reaction not being completely reversible could explain the poor reproducibility observed in the TL response of some crystals successively exposed to u.v. light.

4. Conclusions

It is evident from these results that heat treatments during crystal growth and subsequent to it are very important in establishing the equilibrium of impurities in MgO. Impurity equilibrium affects the TL reproducibility of this material when subjected to u.v. exposures and TL readings, known to disturb this equilibrium in one direction or the other. The fact that several low temperature standardization treatments have been reported could signify that they are not critical, provided that the starting material is homogeneous with respect to the impurity concentration. One method of improving the homogeneity of impurity concentration seems to be the heat treatment in air at $1400^{\circ}C$, which has a tendency to equilibrate the V^{2+} concentration, resulting in a better TL reproducibility. The quenching rate is a critical parameter and probably responsible for the large standard deviation in TL response, even after the heat treatment. In any case, due to the non-homogeneous and non-equilibrium nature of MgO, it is unlikely that any low temperature (i.e. $400^{\circ}C$) annealing will improve reproducibility in the TL response.

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