ELECTRIC FIELD EFFECT ON THE LUMINESCENCE OF KI : Ti

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Thermoluminescence of KI : Ti, X- or β-irradiated at T ≈ 77°K shows two main peaks at 105°K and 170°K. They are respectively attributed to the recombination of mobile V_K centres with Ti^0 centres and to the recombination of thermally released electrons from Ti^0 centres with Ti^{2+} centres. Similar experiments performed under static electric fields (E < 40 kV cm⁻¹) show that the intensity of the second glow peak is strongly reduced. The relative intensity variation is anticorrelated with the intensity of glow peaks occurring at T > 230°K. We suggest that in the temperature range in which Ti^0 centres are thermally ionised, the effect of the electric field is to favour the retrapping of these electrons on other traps (still unknown). Irradiation doses also play an important role and their effects are studied at T ≈ 77°K and T = 200°K.

1. Introduction

Irradiation of alkali halide crystals by ionising particles produces defects either by the displacement of ions out of their normal lattice sites or by the capture of electrons and holes created in the crystal. The latter process is particularly important in crystals doped with impurities. The case of thallium, for instance, is specially interesting since this impurity is known to trap both entities. In this way a high concentration of defects can in principle be frozen in the crystal if the irradiation is performed at sufficiently low temperature.

By heating a previously irradiated crystal at a controlled rate, several thermoluminescence glow peaks are usually observed at well defined temperatures. These photon emissions are associated with the radiative recombination of charges or defects migrating in the crystal following their thermal detrapping. This very sensitive thermoluminescence technique brings important information concerning the nature and the energy depth of the different traps as well as their migration and eventually their recombination kinetics [1].

In KI : Ti crystals [2] X- or β-irradiated at T = 77°K the hole-type defects frozen in the crystal are essentially the V_K centres. Some Ti^{2+} were also found. The elec-

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Fig. 1. (A) The two processes associated with the thermal migration of $V_K$ centres (\sim 105 °K) in KI: Ti, X- or $\beta$-irradiated at $T \geq LNT$; (1) radiative recombination at Ti\textsuperscript{0} site ($h\nu = 2.9$ eV); (2) retrapping at Ti\textsuperscript{+} site with formation of Ti\textsuperscript{2+} centres. (B) Process associated with the thermal ionisation of Ti\textsuperscript{0} centres (\sim 170 °K) in KI: Ti, X- or $\beta$-irradiated at $T \geq LNT$; (3) electron radiative recombination at Ti\textsuperscript{2+} centres ($h\nu = 2.9$ eV).

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Tl^0 + (kT) → Tl^+ + e^−, \quad e^- + Tl^{2+} → Tl^+ + hv (2.9 eV). \quad (3)

At still higher temperatures a third broad but faint emission has also been observed; no detailed explanation has yet been given.

The effect of an electric field on the radioluminescence and the thermoluminescence of KI : Tl has been scarcely studied. In 1966 Parfianowitch et al. [5] have observed an increase of the radioluminescence under an alternating electric field at 300 °K. Later Denks and Leiman [6] have found at the same temperature a partial quenching of the photoluminescence excited in the C band, which they show to be a direct ionisation of the excited state. Looking at the thermoluminescence glow curves Grigor'ev et al. [7] have reported a partial quenching of the 170 °K peak only, without giving satisfactory explanations.

In this report we present a more systematic and detailed study of the influence of a static electric field on the radio- and thermoluminescence processes in KI : Tl between 4°K and 300°K (section 3). The effects are strongly dependent on the ionising irradiation doses (section 4, 5) and can be qualitatively explained in the framework of a charge transfer model.

2. Experimental procedure

The KI crystals used for these experiments were purchased from K. Korth (BRD) and doped either with 200 ppm or 1000 ppm of thallium in the melt. They were first cleaved at approximately 10 × 10 × 1 mm^3, then heated at 400 °C and quenched on a copper block. They were clamped on a sample holder which consisted mainly of two frame shape copper electrodes covered by a fine metallic net (100 μm mesh). The first one was fixed and electrically grounded to a variable temperature cryostat (Oxford Instrument L 1085). The high voltage (Brandenburg 807 R, 0–30 kV) was applied to the second mobile electrode which was clamped to the first one by isolated springs and screws specially designed to insure also a good thermal contact. The crystals were usually mounted in a direct contact with the electrodes. However sometimes a blocking electrode configuration, realized by inserting a thin Mylar foil between the net and either one of the two surfaces of the crystals, was also used. The temperature was carefully measured with a Gold Iron–Chromel thermocouple connected to a digital multimeter (Keithley 610). The excitation sources consisted either in a small β source (Sr 90, 8 mCi) or an X-ray generator (Mueller 150 Be tube with a W anticathode) usually operated at 150 kV, 5 mA and filtered by a 1 mm Cu foil. The luminescence was analyzed either by a set of filters (broad band or interference) or by a Leitz prism monochromator and detected with an EMI 6256 S photomultiplier followed by a micro microammeter (Keithley 410 and a recorder (Moseley 680).
3. Electric field effects

KI crystals doped with 200 ppm Tl and irradiated at $T = 77\ ^\circ\text{K}$ with the $\beta$ source or X-rays of extremely low intensity emit a radioluminescence (RL) with the following characteristics:

(a) Almost 90% of its intensity is intrinsic ($h\nu = 3.27\ \text{eV}$) and corresponds to the radiative recombination of self-trapped excitons. The remaining 10% is characteristic of the Tl impurity ($h\nu = 2.92\ \text{eV}$).

(b) The intensity of each emission band increases with time to eventually saturate after a long irradiation time.

![Fig. 2. Time (or irradiation dose) dependence and temporary d.c. electric field effect on the total radioluminescence of a 200 ppm Tl doped KI crystal $\beta$-irradiated at $77\ ^\circ\text{K}$.](image)

![Fig. 3. Temporary d.c. electric field on the thermoluminescence glow curves (constant heating rate of $3.5\ ^\circ\text{K}\ \text{min}^{-1}$) of a 200 ppm Tl doped KI crystal previously $\beta$-irradiated for 30 min at $T = 77\ ^\circ\text{K}$.](image)
The temporary application of a d.c. electric field causes a decrease $\Delta I$ of the intensity in both spectral regions; the ratio $|\Delta I/I|_{\text{RL}}$ is however a decreasing function of the irradiation dose. The effect disappears after a long irradiation time, i.e. when the intensity of the radioluminescence becomes stationary (fig. 2).

On the other hand the effect of the field on the thermoluminescence glow curves (TL) measured between 77 °K and 200 °K shows that the first peak at 105 °K is not affected, but that the intensity of the 170 °K peak is always depressed (fig. 3). The $|\Delta I/I|_{\text{TL}}$ ratio is constant throughout the peak for a given value of the field and is in-

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**Fig. 4.** Thermoluminescence glow curves measured without electric field in a 200 ppm Ti doped KI crystal $\beta$-irradiated at $T = 77$ °K under the following conditions: —— without d.c. electric field; —.—.— with d.c. electric field ($E = 30$ kV cm$^{-1}$) (constant heating rate of 3.5 °K min$^{-1}$).

**Fig. 5.** Thermoluminescence glow curves measured with a constant heating rate of 3.5 °K min$^{-1}$ in a 200 ppm Ti doped KI crystal, $\beta$-irradiated at $T = 77$ °K without electric field: —— TL measured without d.c. electric field; —.—.— TL measured with d.c. electric field ($E = 30$ kV cm$^{-1}$).
dependent of the field polarity, of the type of the electrodes and of the direction of observation with respect to the field. It, however, decreases with the irradiation dose to eventually disappear after a long irradiation. Results are similar with an a.c. field (50 Hz).

The effect observed on the thermoluminescence glow peaks occurring between 230 and 330 °K corresponds to a small transient increase of their intensities; it is probably due to a local modification of the thermoluminescence kinetics (Gudden-Pohl effect) and will not be discussed in this report.

Although these temporary effects are important and easily observed, they do not allow us to give a clear insight of the physical mechanism involved in these processes. The following observations lead however to the idea that the radio and thermoluminescence electric field effects are intrinsic to the state of the crystal respectively during and at the end of the irradiation and more precisely to the charge state of the different defects present in it.

In fig. 4 we compare the thermoluminescence glow curves recorded after a 30 min β-irradiation realized respectively with and without a d.c. electric field at 77 °K. The second peak at 170 °K and to a lesser extent the very faint peaks observed for 200 °K < T < 300 °K, are enhanced. This clearly indicates that the application of the field during the irradiation at 77 °K has favoured the non-radiative trapping of free electrons on Ti⁺ sites (formation of Ti⁰) and on unknown traps at the expense of the radiative process. In fig. 5 we compare the thermoluminescence glow curves measured with and without an applied d.c. electric field after a 30 min β-irradiation at 77 °K. The first peak is unchanged but the second peak at 170 °K is globally depressed. We see again in this example that the application of the field has favoured a non-radiative recapture of free electrons (in this case those thermally ionised from Ti⁰ centres) on unknown traps at the expense of the radiative process (process (3), fig. 1(B)).

The fact that no marked variation occurs on the first glow peak ruled out the idea that a d.c. electric field has any influence either on the migration of the self-trapped holes, on their capture by the Ti⁰ recombination centres, or on the subsequent recombination process. The effect of the field can only act on charges coming from the conduction band, i.e. the electrons. A Schottky effect in the bound excited state of Ti⁺ is rather improbable: if it existed the effect would be temperature dependent. This was never observed experimentally since:

(a) The |ΔI|/|I₄| ratio is constant throughout the 170 °K glow peak.
(b) The |ΔI|/|I₄|, measured for a given irradiation dose is also constant between 4 °K and 77 °K.
(c) The intensity of the 412 nm photoluminescence (2.9 eV) excited in the 236 nm and 286 nm absorption bands does not change under an electric field between 77 °K and 200 °K.

Moreover the electric field does not change the activation energy of the processes (1) and (3) since in this case a temperature shift of the glow curves should have been observed.
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Fig. 6. Relative decrease of the second thermoluminescence glow peak as a function of the applied d.c. electric field in a 200 ppm Ti doped KI crystal, \( \gamma \)-irradiated at \( T = 77^\circ K \). Curve (1): \( \bigcirc \) 3 min \( \gamma \)-irradiation; heating rate \( 3.5^\circ K \) min\(^{-1} \); curve (2): \( \times \) 30 min \( \gamma \)-irradiation, heating rate \( 3.5^\circ K \) min\(^{-1} \); \( \bigoplus \) 30 min \( \gamma \)-irradiation, heating rate \( 0.6^\circ K \) min\(^{-1} \); \( \pm \) error.

We can reasonably assume that the recombination occurs with an initial capture of the electron via hydrogenic excited states close to the conduction band (due to the Coulombic potential of the positively charged recombination centres). Thus as in the case of n-type semiconductors [8], we can expect that in the presence of an external electric field, the electrons which have not had the time to make a transition from these levels to the bound emissive state will be easily retransferred into the conduction band. Therefore the ratio of the electron capture cross-section for positively charged recombination centres (such as \( V_K \), \( Ti^{2+} \) centres) to that of neutral electron traps (\( Ti^+ \) for instance) is a decreasing function of the applied field. This consequently enhances the rates of electron trapping at the expense of any radiative mechanism.

The relative variation \( |\Delta I|/I_{TL} \) as a function of the field strength is shown in fig. 6. This ratio is independent of the heating rate, i.e. of the intensity of the glow peak as long as the other experimental conditions remain the same. The irradiation dose (at low value only) has simply the role of a scaling factor.
4. 200 °K X-irradiation effects

The measurements of electric field effects on KI : Ti crystals have been completed and the interpretation has been confirmed by a systematic study as a function of the irradiation dose at 77 °K and 200 °K.

In the following experiments a sample was first X-irradiated for a given period of time at 200 °K and then immediately cooled down to \( T = 77 °K \). At this temperature it was submitted to a very small constant \( \beta \)-irradiation compared to the X-irradiation. The sample was then heated to 200 °K and the glow curves recorded. The thermoluminescence electric field effect was periodically sampled and measured accurately at well defined temperatures during a very short time (of the order of 1 sec) in order to minimize the recombination kinetic variations mentioned in the previous section. The whole cycle was repeated several times by choosing an X-irradiation dose higher than the prior ones.

As expected the intensity of the radioluminescence and of the glow curves are found independent of the X-irradiation but are only a function of the \( \beta \)-irradiation dose. However fig. 7 shows that the \( \text{IAI/IRL} \) and \( \text{M/ITL} \) ratios (more precisely the absolute values \( \text{IAI/IRL} \) and \( \text{M/ITL} \) since \( \text{RL} \) and \( \text{ITL} \) are constant for a given \( \text{I} \) dose) are decreasing functions of the X-irradiation dose.

These results are readily explained in the framework of our model: the 200 °K X-irradiation fills little by little all the electron traps which are stable down to this temperature. The effect of the field on the electrons, available either during the \( \beta \)-irradiation at 77 °K or during the thermal release from \( \text{TI0} \) centres, will therefore be a decreasing function of the X dose. The number of traps filled by the X-irradiation at 200 °K is essentially proportional to \( S = f(T) \text{d}T \).

Fig. 7 shows clearly the anticorrelation of \( S \) with \( \text{IAI/IRL} \) and \( \text{M/ITL} \).

Fig. 7. Relative variation of the radioluminescence intensity \( \text{IM/IRL} \) (X) and of the 170 °K glow peak at its maximum intensity \( \text{I~I/II~} \) as a function of an X-pre-irradiation at 200 °K.

For each measurement the crystal is \( \beta \)-irradiated at LNT for 3 mm. The electric field is \( E = 30 \text{ kV cm}^{-1} \). The anticorrelation of \( S = \text{IAI/IRL} \text{d}T \) with the X dose, is also shown (A).
5. LNT irradiation dose effect

In these experiments the sample was either β- or X-irradiated at \( T = 77 \, ^\circ\text{K} \) during a given time, and then heated at a controlled rate up to a maximum temperature of \( 200 \, ^\circ\text{K} \). This temperature corresponds to the valley between the \( 170 \, ^\circ\text{K} \) peak and the faint ones. As in the prior experiments the thermoluminescence electric field effect was periodically sampled and measured during a very short period of time. The crystal was then cooled down rapidly to LNT and the whole cycle repeated again by choosing an irradiation dose 10 times higher than the previous one. The first two irradiations were done with the β source: it indeed allows an excitation approximately 600 times weaker than the X-irradiation (for the same laps of time). Fig. 8(A) shows in a double logarithmic plot the maximum intensity of the \( 170 \, ^\circ\text{K} \) glow peak as recorded for increasing irradiation dose (run(1) to (6)). For our experimental conditions, the height of the peak is almost a linear function of the irradiation dose, i.e. the irradiation dose. The crystal does not "remember" the previous irradiation for the thermoluminescence intensities between 77 and 200 \( ^\circ\text{K} \). This is verified for the run (6) and (7) (30 min β-irradiation): the experimental points fall right on the β-irradiation straight line, although 3 X-rays runs (5) to (5)) have been previously performed. Fig. 8(B) shows schematically the relative value of the electric field effect measured at the maximum glow peak intensity. For the first 6 runs the ratio diminishes with the irradiation dose. This clearly shows that, in this case, the crystal remembers all the prior irradiation effects, otherwise the \( |\Delta I/I|_{\text{TL}} \) ratio for run (6) should have been of the order of 10% instead of 3% as observed. Then, by heating the sample to \( T = 320 \, ^\circ\text{K} \) it appears that the intensity of the faint glow peaks (\( 230 \, ^\circ\text{K} < T < 320\, ^\circ\text{K} \)) is much greater than expected for a single 30 min β-irradiation. For run (7) the crystal is now completely regenerated, since the \( |\Delta I/I|_{\text{TL}} \) ratio is equal to the expected value (10%).

These results show again that the thermoluminescence electric field effects are essentially governed by the rates of non-radiative electron trapping processes.

6. Conclusions

This study is the first of a series undertaken in our laboratory to understand better the effects of an applied electric field on the radio and thermoluminescence of alkali halides doped with different impurities. In this report the case of KI : Ti was exemplified. Our observations have shown that the effects on the radio luminescence and the thermoluminescence are basically identical. The electric field acts only on electrons coming from the conduction band. Such electrons are available either during the ionising irradiation or during the heating up of a previously irradiated sample but in well defined temperature ranges. The electric field favours the non-radiative electron transfer on to specific traps by reducing the radiative processes.
Fig. 8. (A) Maximum thermoluminescence intensity of the 180 °K glow peak versus irradiation time. • after β-irradiation; o after X-rays irradiation. For runs (1) to (6) the crystal was heated to a maximum temperature of $T = 200$ °K, then heated to 320 °K for run (7). (B) Schematic diagram of the electric field effects on the 170° K thermoluminescence glow peak for each specific run (see text).
This suggests that the ratio of the electron capture cross-section for positively charged recombination centres to that of neutral (with respect to the crystal) electron traps is reduced by the field. The relative influence of these traps depends on their concentration and it decreases with the irradiation dose. Most of these traps are unstable between 200°K and 300°K, so that the crystal can be regenerated by heating at room temperature. Since the nature of these electron traps is still unknown, a quantitative explanation is as yet impossible. These traps may pre-exist in the crystal but can also be created by the ionising irradiation. The exact knowledge of their nature could be of great practical importance since several optical memory devices are precisely based on reversible inhibited cathodoluminescence mechanisms.

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References