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Thermoluminescence and colour centres in KI: particle size effect

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Abstract. Differences in the colouration characteristics of single crystals and powders of KI are reported. The F-centre concentration decreased very quickly with decreasing particle size. The thermoluminescence (TL) intensities were not correlated to this decrease. F centres were also found to be quite unstable in powders. This is attributed to the interaction of moving dislocations. The TL intensities were correlated with the reduced stability of F centres in powders.

1. Introduction

Irradiation by ionizing radiation produces colour centres in alkali halide single crystals. Recombination of oppositely charged colour centres during subsequent warming leads to thermoluminescence (TL). Good correlation has been observed between colour centres and TL in single crystals.

Colour centres have mostly been studied in single crystals, while applications such as dosimetry of the ionizing radiations using TL more often involves measurements on powders. It is generally believed that the mechanism of colour-centre production as well as TL will be similar for powders and single crystals. Indeed, similar colour centres and TL have been observed in LiF and NaF single crystals.

On the other hand, it is well known that KI is prone to photo-decomposition on exposure to γ-rays, the decomposition becoming prominent for powders. Thus, while for KI single crystals, irradiation results into production of both F- and V-type centres, fine powders of KI develop a brown colour following such irradiation which is characteristic of the tri-iodide absorption. Pode *et al* (1989) have studied the dependence of iodine liberation upon irradiation on the particle size.

In this paper, we report the dependence of the nature of the 'radiolysis' products and TL on the particle size.

2. Experimental details

Single crystals of KI were grown from the melt in air using the Czochralski method. GR-grade powder from Merck was used as the starting material. It was observed that the growth was possible only in 'dry' (humidity less than 20%) atmosphere when the melt was 'clear'. In a humid atmosphere the melt was dark and it always solidified in a white mass having a marble-like appearance. Once the crystals were grown, they were relatively more stable to humidity. Only prolonged exposures to a humid atmosphere (humidity around 40%) turned them smoky. All the experiments were performed during the dry season when the relative humidity was much below 40%.

The crystals were exposed to γ-rays from a ^{60}Co source. Some crystals were crushed and sieved to yield fine particles of more or less well defined size. These were also exposed to γ-rays. To study the effect of reversing the crushing–irradiation sequence on the colouration characteristics, some crystals were exposed to γ-rays and coloured powders were obtained by crushing these crystals.

Optical spectra were measured with a CZ VSU 2P spectrophotometer with 45/o reflectance attachment for the powders. The TL glow curves were recorded with a routine set-up consisting of a small programmable heater, a photomultiplier (Hamamatsu 931 B), an amplifier and a two-channel plotter to record the photomultiplier tube, PMT, current and the sample temperature.

3. Results and discussion

Figure 1 shows the optical spectra of KI single crystals and powders exposed to γ-rays in the range 400–900 nm. A prominent F band peaking at 710 nm is seen for the single crystal. For powders the Kubelka–Munk function $F(R) = (1 - R)^2/2R$, where R is the reflectance, is plotted as a function of wavelength. A prominent F band is again seen at around 710 nm. With decreasing particle size, this band decreases. The absorption in the violet region also increases at the same time. This is the tail of the tri-iodide absorption band peaking at 354 nm (Hersh 1957a, b). It is thus seen that, with the decreasing particle size, the nature of the 'radiolysis' product changes. The F-centre concentration decreases while the tri-iodide centre concentration increases. These changes are so pronounced

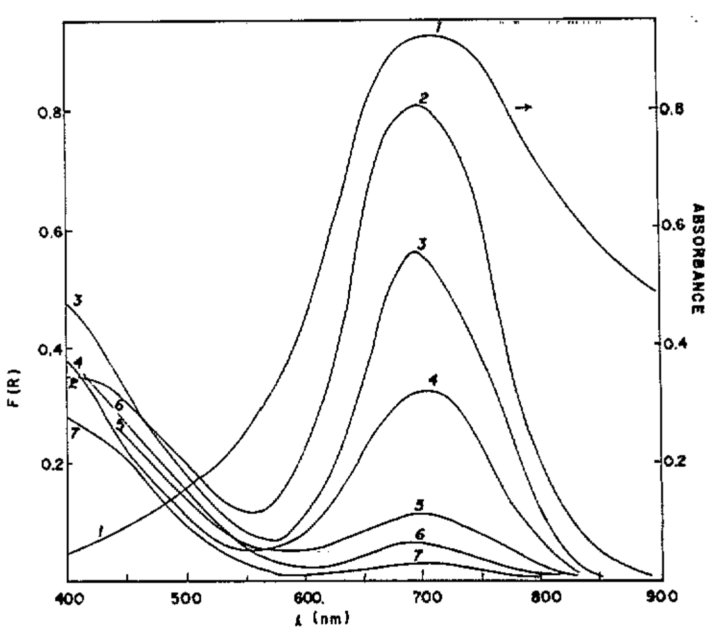

Figure 1. Optical spectra of a KI single crystal and fine powders of various sizes exposed to γ-rays for various particle sizes: curve 1, single crystal; curve 2, 850–1000 μm; curve 3, 710–850 μm; curve 4, 425–500 μm; curve 5, 300–355 μm; curve 6, 250–300 μm; curve 7, 210–250 μm.

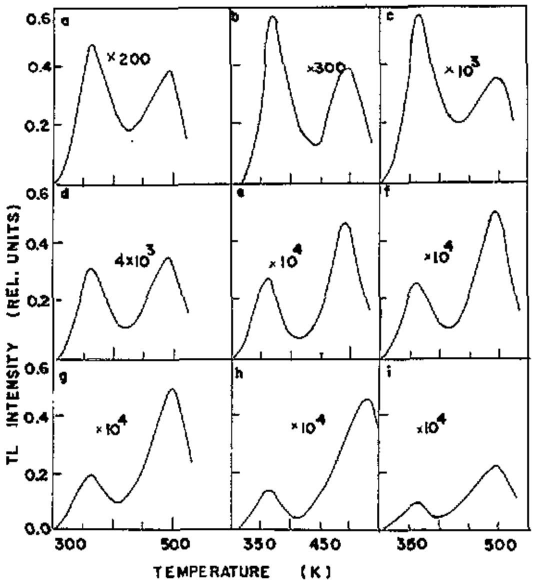

Figure 2. The TL glow curves of KI powders exposed to 490 C kg^{-1} for various particle sizes: (a) single crystal; (b) 850–1000 μm; (c) 710–850 μm; (d) 500–710 μm; (e) 425–500 μm; (f) 355–425 μm; (g) 300–355 μm; (h) 250–300 μm; (i) 210–250 μm.

that they can be observed 'visually'. The single crystals develop a blue colour while the powders assume a brownish tinge. The difference between the 'radiolysis' products was observed when powders were exposed to γ-rays. If the crystals are coloured and then crushed into powders, then these powders contained F centres and no predominance of the tri-iodide absorption was found. Even in this case, there is difference between the behaviours of F centres in crystals and powders. F centres in single crystals are stable while those in powders decay within 24 h (Deshmukh *et al* 1984).

The TL in KI originates in the radiative recombinations of V-type (interstitial halogen) centres with F centres (Mariani and Alvarez-Rivas 1978). It is expected that the changes in colouration characteristics of powders in comparison with crystals will be reflected in the TL also.

Figure 2 shows the glow curves of KI single crystals and fine powders exposed to 490 C kg^{-1}. In all the glow curves, two glow peaks at around 370 and 500 K can be seen. With decreasing particle size we find that the height of the 370 K peak increases up to 425–500 μm (figure 3, curve a) and then decreases. A more or less similar behaviour was observed for the 500 K peak (figure 3, curve b).

In the context of figure 1, it is surprising to note that there is no large decrease in TL intensities with decreasing particle size. The F-centre concentration shows a marked monotonic decrease (figure 3, curve c), while the TL initially increases with decreasing particle size and then again decreases below 400 μm. Similar results were obtained for lower exposures also (figure 3, curves d–f).

Changing the deformation and irradiation sequence results in changes in the manifestation of deformation effects. In optical studies, it has been found that, if the crystals are coloured first and then crushed into powders, then these powders show predominantly F-centre colouration (blue). The crushed powders exposed to γ-rays, on the other hand, show predominant tri-iodide colouration (brown). Effect of changing the crushing–irradiation sequence on TL measurements was also studied.

Figure 4 shows the glow curves of KI powders obtained by crushing the irradiated (490 C kg^{-1}) single crystals. Again, we see two peaks at around 370 and 500 K. The

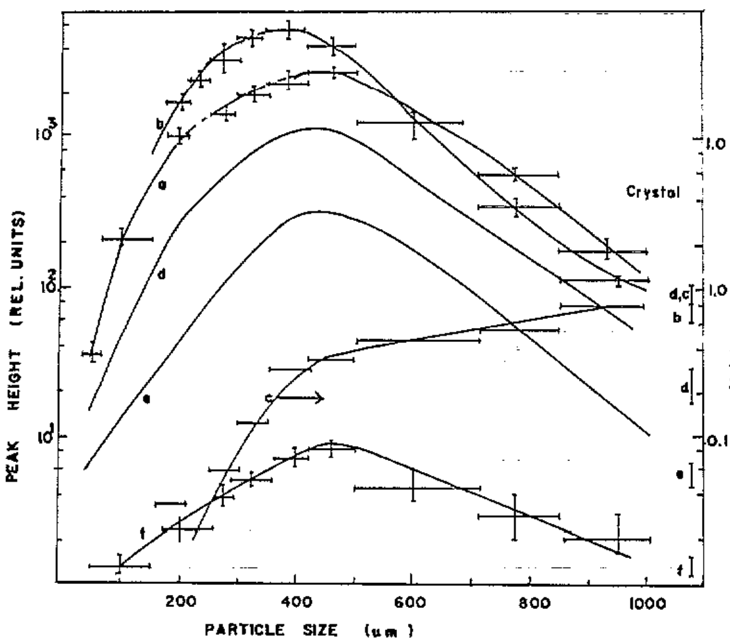

Figure 3. Variation in glow peak heights with particle size. The heights of the 370 K (curve a) and 500 K (curve b) peaks are plotted as a function of particle size for an exposure of 490 C kg^{-1}. A similar variation in the Kubelka–Munk function $F(R)$ at the peak of the F band is plotted in curve c. The heights of the 370 K peak for 390 C kg^{-1} (curve d), 195 C kg^{-1} (curve e) and 39 C kg^{-1} (curve f) are also plotted. Error bars are not shown on curves d and e to maintain clarity.

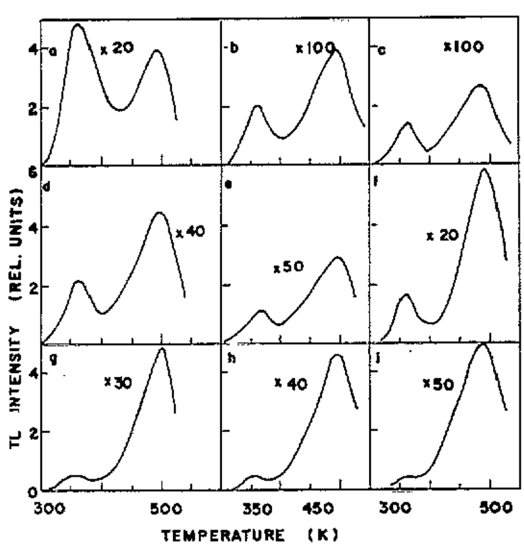

Figure 4. The TL glow curves of KI powders obtained by crushing the single crystals exposed to 490 C kg^{-1}: (a) single crystal; (b) 850–1000 μm; (c) 710–850 μm; (d) 500–710 μm; (e) 425–500 μm; (f) 355–425 μm; (g) 300–355 μm; (h) 250–300 μm; (i) 210–250 μm.

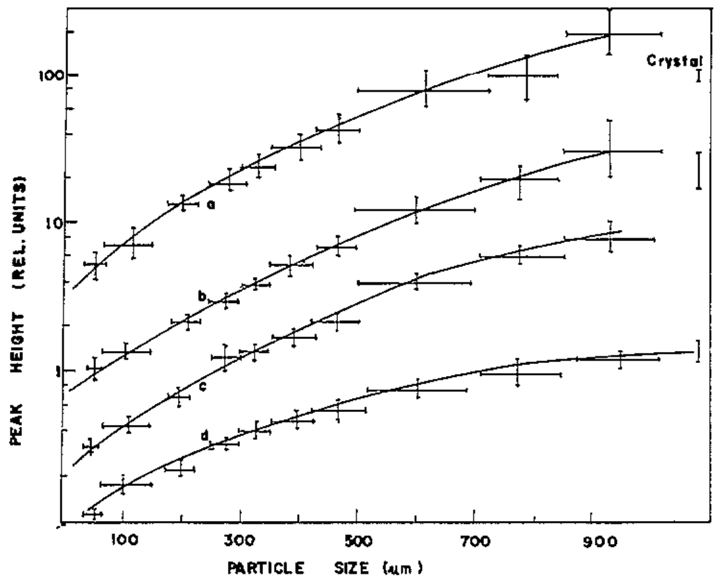

Figure 5. The height of the 370 K peak in particles obtained by crushing irradiated single crystals for various exposures: curve a, 490 C kg^{-1}; curve b, 390 C kg^{-1}; curve c, 195 C kg^{-1}; curve d, 39 C kg^{-1}.

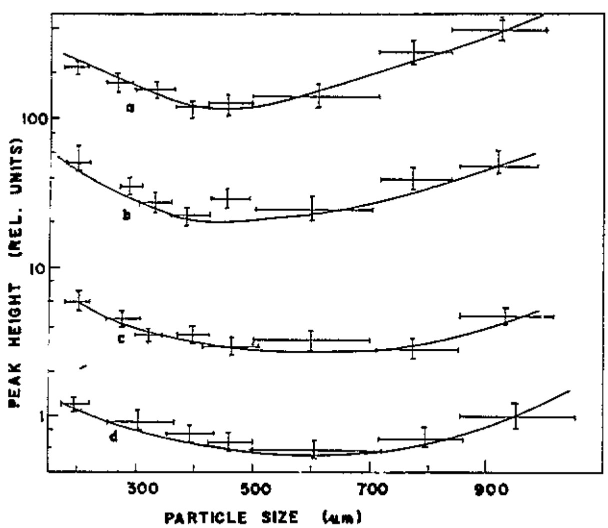

Figure 6. The height of the 500 K peak in powders obtained by crushing irradiated single crystals for various exposures: curve a, 490 C kg^{-1}; curve b, 390 C kg^{-1}; curve c, 195 C kg^{-1}; curve d, 39 C kg^{-1}.

former decreases with decreasing particle size (figure 5). The latter decreases initially but increases again for fine powders (figure 6). This is understandable, in view of the fact that deformations are known to favour high-temperature peaks in alkali halides

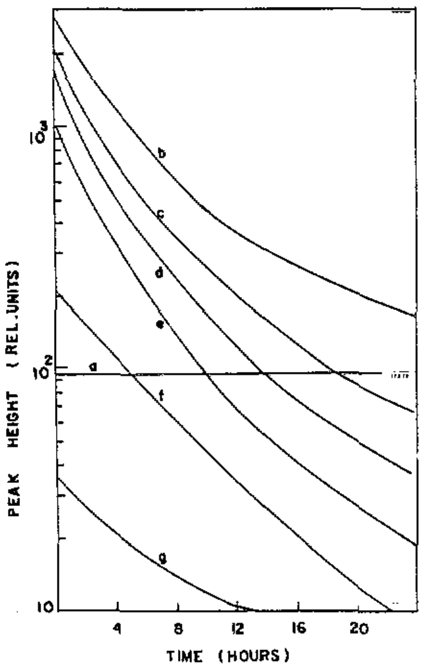

Figure 7. Typical curves for the decay of TL intensity in KI powders exposed to 490 C kg^{-1}, where the height of the 370 K peak is plotted as a function of storage time for various particle sizes: curve a, single crystal; curve b, 355–420 μm; curve c, 300–355 μm; curve d, 250–300 μm; curve e, 180–210 μm; curve f, 63–150 μm; curve g, 37–53 μm. A similar decay was observed for the 500 K peak also.

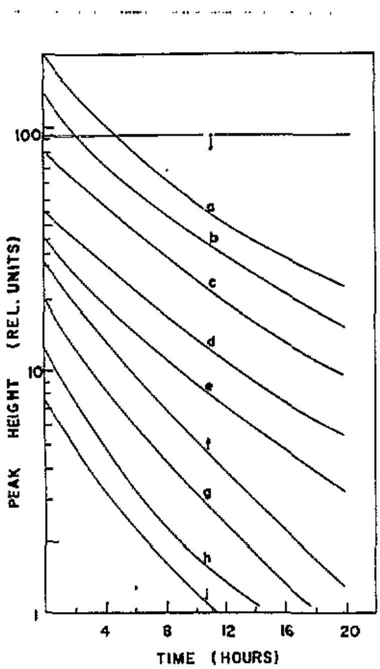

Figure 8. Typical curves for the decay of TL intensity in KI powders obtained by crushing the single crystals exposed to 490 C kg^{-1}, where the height of the 370 K peak is plotted as a function of storage time for various particle sizes: curve a, 850–1000 μm; curve b, 710–850 μm; curve c, 500–710 μm; curve d, 425–500 μm; curve e, 355–425 μm; curve f, 300–355 μm; curve g, 250–300 μm; curve h, 180–210 μm; curve i, 63–150 μm; curve j, single crystal. A similar decay was observed for the 500 K peak.

(Jain and Mehendru 1965). Thus, some colour centres will be bleached mechanically during crushing, and overall TL will decrease with decreasing particle size. However, the deformations introduced during crushing will favour the 500 K peak. Hence, the 370 K peak decreases rapidly with decreasing particle size while the 500 K peak shows an increase for finer sizes. Similar results were obtained for lower exposures also (figure 4(*b*)—(*d*)).

There is yet another interesting aspect of the differences between the colouration characteristics of the single crystals and powders. The colour centres in single crystals are stable while those in powders decay very quickly. The decay has been attributed to the interaction of moving dislocations with F centres (Deshmukh *et al* 1984). It is thus expected that, if the powdered samples are stored before recording the glow curves, then the TL intensities in powders would decrease with increasing storage time. The effect should be more prominent for finer particles. This was indeed found in both the irradiated powders and the powders of the irradiated crystals. All the glow peaks were found to decay with storage. Typical decay curves are shown in figures 7 and 8. The differences between the stability of colour centres in single crystals and powders are thus reflected in both the optical and the TL measurements.

Thus, we find that the colouration characteristics of KI powders and single crystals are different. Although the relative heights of glow peaks change with decreasing particle size, the overall TL intensities are not correlated with the changes observed in optical spectra of single crystals and powders. Since F centres are the only electron centres in pure KI responsible for TL, it was expected that the decrease in F-centre concentration would be reflected in the corresponding TL intensities. The differences between the stability of colouration in single crystals and powders, on the other hand, are very well reflected in the TL glow curves.

4. Conclusions

Thus, from the results presented earlier (Deshmukh *et al* 1984) and in this paper, we find that, in alkali halides such as LiF and NaF, the defects created by irradiation and the subsequent TL are similar in single crystals and powders. In KI, which is also an alkali halide, on the other hand, we find different 'radiolysis' products in single crystals and powders, and TL intensities not correlated to these differences. The stability (or rather the instability) of coloration, on the other hand, is correlated to the TL intensities. The problems posed by the results presented here may be considered as of only academic interest, but the solutions to these will definitely add to our knowledge of defect interactions, in particular, and of real solids, in general.

Acknowledgment

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