Radiation-induced sensitisation in alkali halides

1990 J. Phys.: Condens. Matter 2 7233

(http://iopscience.iop.org/0953-8984/2/34/016)

J. Phys.: Condens. Matter **2** (1990) 7233–7239. Printed in the UK

Radiation-induced sensitisation in alkali halides

B T Deshmukh, S M Patey and S V Moharil
Department of Physics, Nagpur University, Nagpur 440 010, India

Received 21 August 1989, in final form 12 April 1990

Abstract. LiF-TLD 100 exposed to ionising radiations and then suitably annealed shows an enhanced thermoluminescence response for the second exposure. Several models have been proposed to explain this phenomenon which has been termed 'radiation-induced sensitisation'. In this paper it is shown that the sensitisation is observed only in LiF and KCl doped with impurities having limited solid solubilities. It is proposed that the sensitisation occurs owing to the redistribution of the impurities during the thermal annealing of the exposed samples.

1. Introduction

LiF-TLD 100 phosphor, after high γ exposure and partial annealing, exhibits enhanced thermoluminescence (TL) sensitivity. This has been termed radiation-induced sensitisation (Cameron and Zimmerman 1965). A number of models have been proposed to explain this phenomenon. The merits and demerits of these models have been discussed in detail (Stoebe and Watanabe 1975, Lakshmanan *et al* 1979, 1985, Jain 1980, Sagastibelza and Alvarez-Rivas 1981, Moharil and Kathuria 1982). The discussions have indicated that, of all the suggested models, only two have not yet met total contradiction. The track interaction model of Attix (1975) attributes the sensitisation to the increased recombination probabilities in the sensitised samples. When the phosphor is exposed to γ-rays, electrons and holes are trapped in the tracks of the secondary radiation. During read-out the trapped charges can recombine in their own tracks, and radiative recombinations lead to TL. For heavy exposures, tracks intersect and thus the trapped charges can recombine outside their tracks, leading to a 'supralinear' response. Not all the defects anneal out during the TL read-out; some of the defects are left behind. For the subsequent exposure, more defects are available for recombination and fraction of the trapped charges, leading to TL increases. All the experimental results on radiation-induced sensitisation in LiF-TLD 100 could be explained on the basis of this hypothesis after assuming reasonable model parameters (Moharil 1983). The model of Sagastibelza and Alvarez-Rivas (1981) is entirely different. They have attributed TL to the thermal release of halogen atoms from interstitial positions and their subsequent radiative recombinations with excess electron colour centres. Sensitisation has been attributed to the increased number of trapping sites created during pre-exposure. During the post-irradiation annealing, traps are emptied but the trapping sites are not destroyed. Thus the exposure to ionising radiation results in the filling as well as the creation of traps.

Both the models appear quite general. As the basic defect creation processes are the same for all alkali halides, one would expect from the above models that the radiation-induced sensitisation need not be characteristic of LiF-TLD 100 alone, but sensitisation of more or less magnitude might be observed in pure LiF as well as in the other alkali halides. Glow curves of pure LiF and LiF-TLD 100 have often been compared, but sensitisation has not been studied for pure LiF or any other alkali halide. In this paper we report some experiments on finding out whether there is radiation-induced sensitisation in other alkali halide phosphors, which might throw light on the mechanism of sensitisation.

2. Experimental details

Crystals of pure and doped KCl were grown from melt by the Czochralski method. The impurity concentrations stated refer to the amounts added to the melt. Crystals of size 5 mm × 5 mm × 0.5 mm approximately were cleaved from the as-grown blocks for TL measurements. They were exposed to γ-rays from a ^{60}Co source. Post-irradiation annealing and heating to record the glow curves were performed on a small, directly heated plate. A temperature programmer was used for linear heating. A heating rate of 150 K min^{-1} was used. The temperature was recorded with the help of a chromel–alumel thermocouple spot welded below the depression in the heater plate in which the samples were placed, and a millivolt recorder. TL emission was detected with an RCA photomultiplier (931 B), amplified and then recorded on the second channel of the same millivolt recorder as mentioned earlier. To establish the correctness of the procedure, the known results for LiF–TLD 100 were reproduced with this set-up.

Some samples were coloured electrolytically. Crystals of size 15 mm × 10 mm × 10 mm were used. Colouration was performed at 800 K under an electric field of the order of 100 V cm^{-1}.

3. Results and discussion

Figure 1 shows glow curves for LiF-TLD 100 exposed to 2.58 × 10^{-2} C kg^{-1}. TL in the sensitised sample (i.e. the sample exposed to 25.8 C kg^{-1} followed by annealing at 625 K) is much more than that in the 'virgin' sample. The dosimetry peak is enhanced about six-fold. This agrees with the results on LiF-TLD 100 in the literature (Lakshmanan *et al* 1979), thus establishing the correctness of the experimental procedure.

Figure 2 shows the results of the experiments performed on finding whether pure KCl shows sensitisation or not. Prior to irradiation the crystals were annealed and quenched from 600 K. (These annealed samples will be referred to as 'virgin' samples.) The glow curve of the virgin sample for an exposure of 2.58 × 10^{-2} C kg^{-1} contains prominent glow peaks at around 395, 410 and 450 K, and a shoulder rising above the background thermal emission at around 540 K. For higher exposures, the relative height of the 460 K peak is greater. For sensitisation, a sample was exposed to 51.6 C kg^{-1}, heated at the rate of 150 K min^{-1} up to 600 K and then quickly cooled to room temperature by switching off the power to the heater plate. This was then exposed to 2.58 × 10^{-2} C kg^{-1} and the glow curve was recorded (figure 2(*b*)). It is seen that TL in this sample is similar to that in the virgin sample, but somewhat reduced; there is no

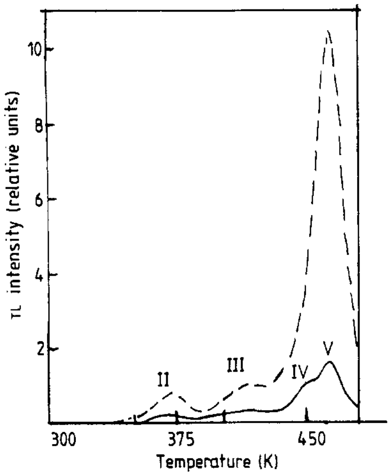

Figure 1. Radiation-induced sensitisation in LiF-TLD 100 as shown by the glow curves of LiF-TLD 100 exposed to 2.58×10^{-2} C kg^{-1}: ——, virgin sample; – – –, sensitised sample. The roman numbers show the conventional labelling of the different glow peaks.

sensitisation at all. The experiment was repeated several times, but in no case was sensitisation observed.

The results in figure 2 show that 'sensitisation' is not necessarily exhibited by all alkali halide phosphors. Attempts were therefore made to find out whether doped KCl shows any sensitisation. Figure 3, curve A, shows the glow curve for KCl:Ca (100 ppm) crystals exposed to 2.58×10^{-2} C kg^{-1}. Glow peaks can be seen at around 355, 385, 415 and 500 K. These crystals were also annealed at 600 K prior to irradiation. Glow curves were also recorded for the sensitised samples. The sensitisation treatment is the same as that tried for pure KCl. It is seen (figure 3, curve B) that all the glow peaks are enhanced after the sensitisation. The sensitisation factor is close to 3 if peak heights are compared. The area under the glow curve is about 2.6 times larger for the sensitised sample than for the virgin sample. The results could be reproduced and, when the experiment was repeated several times, sensitisation of nearly the above-mentioned magnitude was always observed.

Sensitisation is thus seen for doped KCl, but not for pure KCl. Further experiments were performed to see whether F centres that might remain after the post-irradiation annealing play any role in sensitisation. A KCl:Ca crystal was coloured electrolytically with a pointed cathode. The sample thus contains only F centres and no electron-deficient centres. A piece of size 5 mm × 5 mm × 0.5 mm was cleaved from the uniformly coloured portion and exposed to 2.58×10^{-2} C kg^{-1}. The glow curve of this sample is also included in figure 3 as curve C. It is seen that the glow curve structure has changed as a result of this treatment. There is a prominent peak at around 470 K with a shoulder at 500 K. The overall area under the glow curve is about the same as for the corresponding area for the virgin sample. It is thus clear that no sensitisation results when excess F centres are present. (Because of overlap of the 470 K peak, emission at around 500 K also appears enhanced. However, this is not due to the sensitisation; it appears to arise because of redistribution among traps or the creation of new trap corresponding to the 470 K peak.)

To test whether sensitisation is caused by all the impurities, similar experiments were performed on KCl:F and KCl:Na crystals also. Figure 4 shows the glow curves of KCl:F crystals exposed to 25.8 C kg^{-1}. A prominent glow peak is seen at around 375 K. For sensitisation, crystals were exposed to 51.6 C kg^{-1} and then annealed at 545 K. Some

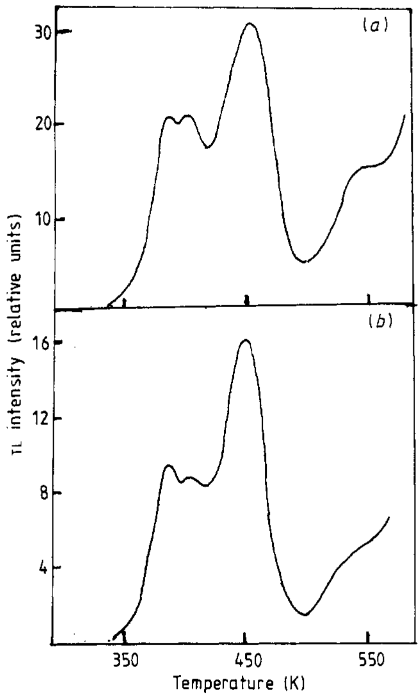

Figure 2. Absence of sensitisation in pure KCl as shown by the glow curves for KCl crystals exposed to 2.58×10^{-2} C kg^{-1}: (*a*) virgin samples; (*b*) samples pre-exposed to 51.6 C kg^{-1} and then annealed at 600 K.

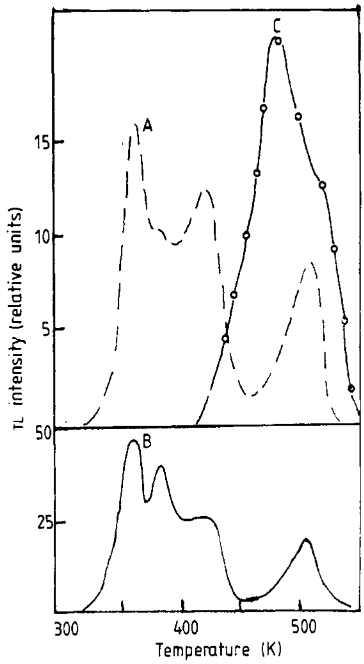

Figure 3. Glow curves of various KCl:Ca crystals exposed to 2.58×10^{-2} C kg^{-1}: curve A, crystals annealed at 600 K before irradiation (virgin crystals); curve B crystals for curve A exposed to 51.6 C kg^{-1}, annealed at 600 K and cooled to room temperature and then given the exposure; curve C, crystals coloured electrolytically to contain F centres.

crystals were also pre-annealed at 545 K to study the effect of heat treatment alone received during the sensitisation. No change in the glow curve structure or the intensities was found after the sensitisation or heat treatment. Negative results were obtained for KCl:Na also (figure 5) for which the glow peaks are at around 375, 400, 425 and 525 K. In fact, TL decreased after the sensitisation treatment.

It is felt that the absence of sensitisation in pure KCl and KCl doped with Na and F is peculiar to the sensitisation treatment used, and some suitable pre-exposure and post-irradiation annealing may yield sensitisation for these phosphors also. This is not true. We tried various pre-exposures ranging between 8.5 and 516 C kg^{-1} and various post-irradiation annealing treatments starting from the temperature which would remove TL resulting from pre-exposure (450–675 K). In none of these experiments could sensitisation be observed for these phosphors and hence the detailed results are not given here.

The effect of pre-exposure on the sensitisation was studied for KCl:Ca also in the range 8.5–516 C kg^{-1}. The maximum sensitisation was observed for a pre-exposure of 51.6 C kg^{-1} and there was little sensitisation for the pre-exposures corresponding to the extremes of the stated range. These results are more or less the same as those obtained for LiF-TLD 100 (Lakshmanan *et al* 1979).

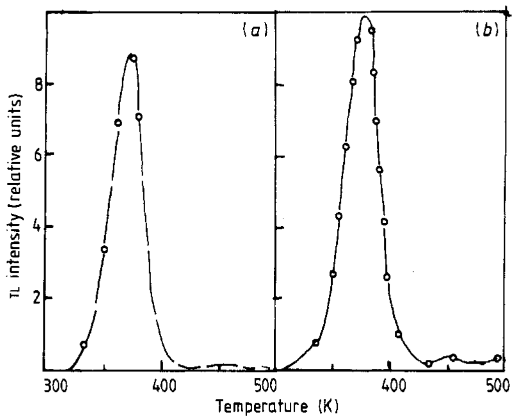

Figure 4. Absence of sensitisation in KCl:F (1 mol%) crystals (pre-exposure, 51.6 C kg^{-1}; test exposure, 2.58×10^{-2} C kg^{-1}): (*a*) crystals annealed at 545 K (virgin); (*b*) crystals for (*a*) exposed and then annealed at 545 K. Various pre-exposures and post-irradiation annealing treatments were tried, but in no case was sensitisation observed.

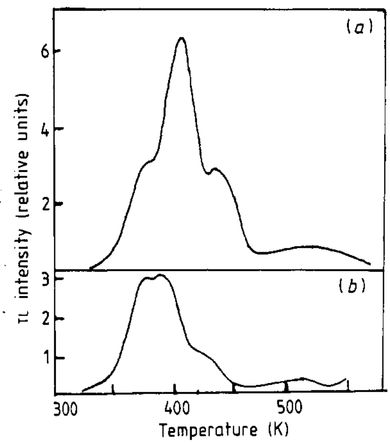

Figure 5. Absence of sensitisation in KCl:Na crystals (exposures, etc, same as in figure 4).

For LiF-TLD 100, supralinearity and sensitisation have often been linked together. In the track interaction model (Attix 1975, Moharil 1983) the supralinearity has been attributed to the increased recombination probability due to 'intersections' of the tracks and the sensitisation to a similar track interaction arising owing to pre-exposure. Experiments were therefore performed to study the supralinearity in different crystals, with the anticipation that these studies would help in understanding the mechanism of sensitisation, e.g. if we observe supralinearity in KCl:Ca but not in the other samples then the correlation between supralinearity and sensitisation would be established, which will indirectly support the track interaction model.

Figure 6 shows response curves for different samples. It is seen that the trend is rather common. A more or less linear response is observed up to 0.26 C kg^{-1} and then the response is more than linear. For exposures of around 51 C kg^{-1}, the response starts to drop. A similar response has been observed for LiF-TLD 100 also (Jain 1980). Thus, we fail to observe any correlation between the supralinearity and the sensitisation.

It is seen that the sensitisation has been observed in doped KCl and LiF but not in pure KCl. Again, not all impurities lead to sensitisation, but the sensitisation is observed in Ca-doped (KCl) and Mg-doped (LiF) phosphors. Any mechanism aimed at explaining the phenomenon must explain these facts.

A possible explanation of the results presented can be as follows. The alkaline-earth impurities have very limited solid solubilites. Thus, they exist in various forms (dipoles, dimers, trimers, higher aggregates, complexes with other defects, precipitate phases, etc) some of which are metastable. Thermal annealing, plastic deformation, etc, results in redistribution of the impurities. For this reason, the TL of alkaline-earth-doped alkali halides is extremely sensitive to preheat treatments (Chandra *et al* 1982, Joshi and Kekan 1974, 1980, Deshmukh and Moharil 1985). Radiation-induced sensitisation which seems

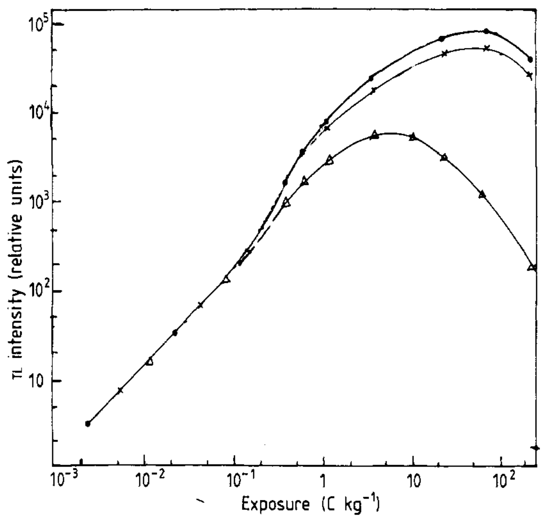

Figure 6. Response curves for various samples: ●, KCl:Na (390 K peak); ×, KCl:Ca (385 K peak); △, KCl:F (380 K peak). More or less similar responses were obtained for the other glow peaks also.

to be typical of these impurities also might originate in some sort of redistribution of the impurities. It is known (Taylor and Lilley 1982, Moharil and Kathuria 1988) that filled traps are much more mobile than empty traps. For this reason, the redistribution of impurities that leads to enhanced TL is not brought about by thermal treatments alone but results when exposed phosphors are thermally treated. The radiation-induced sensitisation thus may be due to the larger number of defect sites created by the redistribution of the sparingly soluble impurities arising during the thermal treatments of the exposed samples.

The data presented here include results on Ca and Mg impurities. Experimental results on other sparingly soluble impurities will be needed to test the above hypothesis and to draw a definite conclusion.

4. Conclusions

It is shown here that radiation-induced sensitisation is not necessarily correlated with supralinearity and does not originate in excess F centres. The sensitisation is not observed universally in all alkali halide phosphors. A mechanism which will apply generally to all alkali halides thus seems unwarranted. A mechanism based on the peculiar properties of the impurities may be adequate. From the results presented here, it appears plausible that the radiation-induced sensitisation is due to redistribution of impurities brought about by thermal treatment of the exposed sample. The role of the radiation may be to produce the impurity-related defects which are much more mobile than the corresponding defects in the unexposed sample. Further experiments would be needed to test these suggestions before drawing a definite conclusion. It would also prove interesting to see whether the other properties of LiF-TLD 100 not mentioned here, such as photo-transfer TL, are also characteristics of the impurities or whether they can be observed for all alkali halide phosphors.

Acknowledgments

The free samples of LiF-TLD 100 were generously provided by Ms Harshaw-Filtrol. The gift is gratefully acknowledged. We are also grateful to the Director, RST Cancer Hospital, Nagpur, for permitting the use of the γ exposure facilities.

References

Attix F H 1975 *J. Appl. Phys.* **46** 21
Cameron J R and Zimmerman D W 1965 *USAEC Report* C00-1105-102
Chandra B, Lakshmanan A R and Bhatt R C 1982 *Int. J. Appl. Rad. Iso.* **33** 1399
Deshmukh B T and Moharil S V 1985 *Bull. Mater. Sci. (India)* **7** 427
Jain V K 1980 *Phys. Status Solidi* **60** 351
Joshi R V and Kekan N L 1974 *J. Lumin.* **8** 338; *Z. Kristallogr.* **139** 153
—— 1980 *Radiat. Eff. Lett.* **57** 73, 99
Lakshmanan A R, Bhatt R C and Vora K G 1979 *Phys. Status Solidi* **53** 617
Lakshmanan A R, Chandra B, Bhatt R C, Hoffmann W and Spallek R 1985 *J. Phys. D: Appl. Phys.* **18** 1673
Moharil S V 1983 *Phys. Status Solidi* **79** 599
Moharil S V and Kathuria S P 1982 *J. Phys. D: Appl. Phys.* **15** L145
—— 1988 *Cryst. Latt. Defects Amorph. Mater.* **17** 405
Sagastibelza F and Alvarez-Rivas J L 1981 *J. Phys. C: Solid State Phys.* **14** 1873
Stoebe T G and Watanabe S 1975 *Phys. Status Solidi* **29** 11
Taylor G C and Lilley E 1982 *J. Phys. D: Appl. Phys.* **15** 2053