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2008 J. Phys.: Condens. Matter 20 085203

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On the role of dislocations and aggregates in UV induced afterglow luminescence of KCl:Eu at low temperatures

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Received 4 July 2007, in final form 22 December 2007

Published 1 February 2008

Online at stacks.iop.org/JPhysCM/20/085203

Abstract

Afterglow (AG), thermoluminescence (TL) and photoluminescence efficiencies in KCl:Eu were investigated in samples annealed at 773 K with high Eu- v_c dipole concentration, samples aged at 373 K with high aggregate concentration and plastically deformed samples enriched with dislocations. AG and TL efficiencies increase significantly for samples with high concentration of aggregates. Plastically deformed samples show a greater efficiency of AG and TL compared to undeformed samples. However, the formation of aggregates during the ageing procedure is strongly reduced in deformed samples. Furthermore, the low temperature peaks in the TL glow curve are absent in deformed and aged samples. We interpret these results as evidence for the participation of dislocations in the AG process and ascribe the relatively high AG efficiency of aggregates to a preferential formation of aggregates along dislocations.

1. Introduction

Potassium chloride doped with europium (KCl:Eu) shows a persistent luminescence after ionizing or UV (maximum around 225 nm) irradiation at low temperature (around 20 K), which has a nonthermally stimulated component known as afterglow (AG). This component is distinct from that of a thermally stimulated process in that the luminescence of this component decays according to a power law, $I(t) = I_0 t^{-\alpha}$, while the luminescence of a thermally stimulated process decays exponentially, $I(t) = I_0 \exp(-\lambda t)$. Furthermore, the decay rate of AG characterized by α does not depend on temperature T (the intensity I_0 , however, could depend on temperature) while the decay rate λ of a thermally stimulated process increases with temperature according to $\lambda = \nu \exp(-E/kT)$, where ν is a frequency factor, E an activation energy and k Boltzmann's constant. Traditionally, AG in alkali halides has been explained by recombination of electrons and holes through a tunnelling process of the electron from an electron trap to a trapped hole [1]. The filling of electron and hole traps takes place during the irradiation. Recently an alternative model has been proposed for AG in UV (225 nm) irradiated KCl:Eu that was described in terms of F and H centres and based on the migration of H centres along

dislocations [2]. F-H centre pairs are the principal radiation products in KCl. However, since the energy of the UV radiation is not sufficient to create F-H centre pairs in the bulk, it has been proposed that the F-H centre pairs in UV irradiated KCl:Eu are created near Eu impurities, for which a lower creation energy is assumed [2, 3]. The alternative model for AG in KCl:Eu [2] assumes that an H centre created during the irradiation returns—if not trapped at a defect—to its point of creation, where its F centre partner resides. The recombination of the H-F centre pair causes the AG. Furthermore, it is assumed that the H centre migrates along a dislocation to explain the shape of the AG decay curve and the supposed mobility of H centres at 20 K. With these assumptions the parameter α in the AG decay $I(t) = I_0 t^{-\alpha}$ was estimated to be $\alpha = 3/2$ for pulsed irradiation and $\alpha = 1/2$ for long irradiation periods [2, 4]. According to this model, the presence of a dislocation near an Eu defect is thus an absolute requirement for AG. One of the objectives of the present paper is to evidence the participation of dislocations in the AG process. Related to this is the observation that in heavily aged samples the AG efficiency is much greater than in quenched samples [5]. This has been associated with the formation of precipitated phases like the Suzuki phase and metastable precipitated EuCl_2 -like plate zones parallel to the {310} and {111} planes, although

it is not clear how these phases affect the AG efficiency. In this paper we make it plausible that the relatively high AG efficiency of aggregates is due to a preferential formation of aggregates along dislocations. For these purposes we investigated the effect on AG of small aggregates created by a relatively short ageing procedure and of dislocations created by plastic deformation.

2. Experimental details

The samples were cleaved from a single crystal of KCl doped with a nominal concentration of 200 ppm europium. The single crystal was grown by the Czochralski method at the *Instituto de Física de la Universidad Nacional Autónoma de México*. The size of the samples is typically $5 \times 5 \times 1$ mm. The uniaxial plastic deformation of the samples was performed at room temperature with a home-made hydraulic press. The force on the sample could be increased nearly linearly at a rate of about 0.1 N s^{-1} . The deformation was measured by the decrease of the thickness of the sample along the axis in the direction of the stress. For the thermal treatment to form $\text{Eu}-v_c$ dipoles, the sample was first wrapped in aluminium foil to protect it from environmental light and then placed in a furnace (Thermoline, model 1300) at 773 K for 1 h in air. Immediately after taking the sample out of the furnace, it was pressed against an aluminium block at room temperature, with a ball of aluminium paper. After this thermal quenching, all further handling was performed under red light. The sample was unwrapped and attached mechanically to the cold end of a two-stage cryogenic helium refrigerator (ADP, model DE-202). Also, an Au-constantan thermocouple for temperature measurements and a resistor for heating were attached to the cold end. The cold end, with all attachments, was enveloped in a vacuum tube for thermal insulation. At the level of the sample the vacuum tube had three quartz windows for optical access to the sample. The pressure of the vacuum inside the vacuum tube was maintained at about 2 Pa (2×10^{-2} mbar) during all measurements and ageing procedures. For the photoluminescence (PL), AG and thermoluminescence (TL) measurements, the enveloped cold end with the sample was placed into the sample compartment of a spectrofluorometer (SPEX, model Fluoromax) in such a way that the sample was positioned at the focal point of the excitation beam of the spectrofluorometer. The temperature of the photomultiplier of the spectrofluorometer was stabilized (at 15°C) to reduce background variations and care was taken to minimize stray light from the excitation source. AG and TL were measured after an irradiation with monochromated light (230 nm) from the spectrofluorometer's light source (150 W xenon lamp coupled to a monochromator) for 300 s. Ageing procedures were performed without moving the cold end (with the sample on it) from its position in the spectrofluorometer. The temperature of the cold end during the TL measurements and the ageing procedures was controlled by a home-made computerized temperature controller. The heating during the TL measurements started from 20 K at a rate of 0.1 K s^{-1} and continued until 300 K. All ageing procedures were performed at 373 K in vacuum over relatively short times (5 and 10 h).

3. Results

The PL, AG and TL emission spectra of the KCl:Eu samples immediately after quenching show an emission band around 419 nm associated with $\text{Eu}-v_c$ dipoles and dimers [5, 6]. During the ageing, the maximum intensity shifts to longer wavelengths. This process is ascribed to the conversion of $\text{Eu}-v_c$ dipoles and/or dimers to the Suzuki phase and/or small aggregates like trimers which emit around 427 nm [5, 6]. The aggregates formed in our experiment are mainly small aggregates, which was verified by measuring the temperature at which they dissolve during linear heating at a rate of 0.1 K s^{-1} . For the Suzuki phase this would be in the temperature range from 395 to 430 K, while in our case the aggregates dissolve in the temperature range from 430 to 460 K.

For the undeformed sample the effect of ageing on the PL, AG and TL emission spectra is shown in figure 1(a). In the PL spectra it is seen that after ageing the aggregate contribution around 427 nm is moderately increased at the cost of the dipole contribution around 419 nm. In the AG and TL emission spectra, however, a strong increase of the intensity and a pronounced shift from dipole to aggregate emission is observed. This difference in behaviour of the spectra of the PL on the one hand and the spectra of the AG and TL on the other could be interpreted as if the AG and TL are more efficient in the vicinity of aggregates than in the vicinity of dipoles [5]. An alternative interpretation, favoured by us, would be that more aggregates than dipoles participate in the AG and TL, compared to the participation in the PL. Figure 1(b) shows similar measurements but now for a sample that was 5% plastically deformed before the ageing procedures. The time to perform the deformation was about 1 h, which was not sufficiently long to prevent crack formation. Nevertheless, the sample remained in one piece. The deformation of the crystal implies the displacement and generation of dislocations [7, 8]. After annealing the deformed sample, the $\text{Eu}-v_c$ dipoles are distributed homogeneously over the crystal volume. Since this crystal contains more dislocations than the undeformed sample, we may expect an increase of the number of $\text{Eu}-v_c$ dipoles along dislocations. It is seen that the AG immediately after the deformation increases significantly with respect to that of the AG of the undeformed sample (compare AG for 0 h of figures 1(a) and (b)) and furthermore that the emission spectrum of the AG in the deformed sample is dominated by the dipole emission around 419 nm. After ageing the intensity of AG and TL does not change much, but the participation of aggregates becomes more evident. In another sample, also about 5% deformed but during a much shorter period (only a few seconds causing the formation of cracks and the fracture of the sample into two pieces), the participation of aggregates in the PL, AG and TL emission spectra was almost absent. In the latter sample we expect a larger content of dislocations and a larger degree of entanglement between dislocations than in the slowly deformed sample, suggesting that the aggregation depends on the dislocation content and/or the degree of entanglement.

Figure 2 shows the TL glow curves of the undeformed sample, and of the deformed sample after subsequent ageing

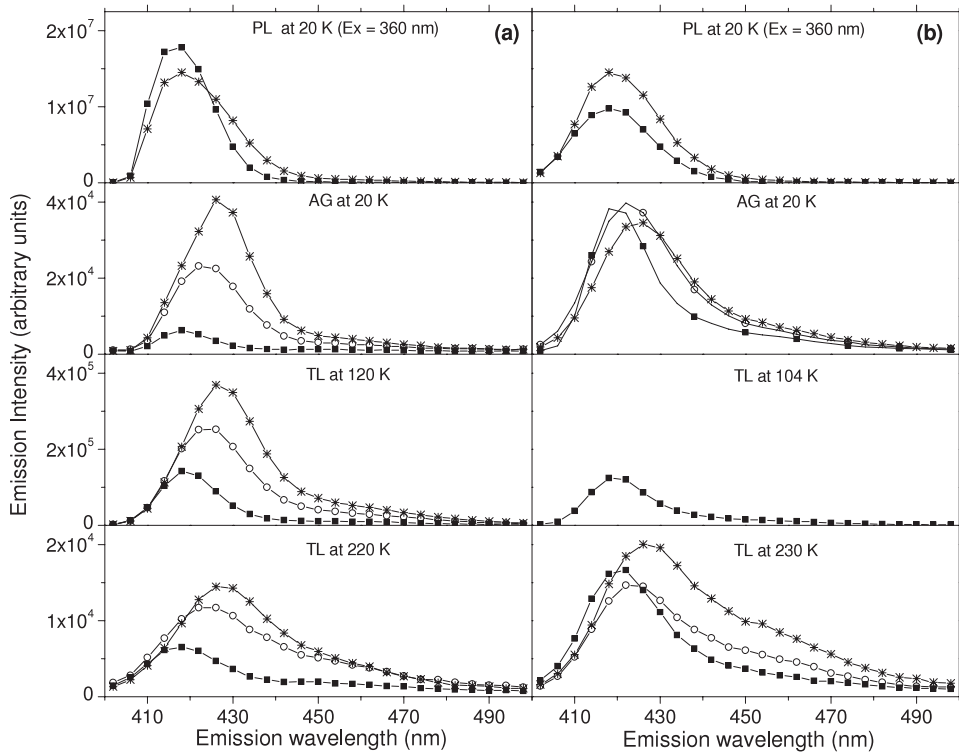


Figure 1. Emission spectra of PL, AG and TL of an undeformed KCl:Eu sample (a) and a 5% deformed sample (b). The deformation rate of sample b was about $5\% \text{ h}^{-1}$. The samples were repeatedly aged in vacuum at 373 K for a total period of 0 h (squares), 5 h (open circles) and 10 h (asterisks). Before the experiment the samples were annealed in air at 773 K for 1 h and quenched to room temperature. For the AG and TL measurements the irradiation wavelength was 230 nm and the irradiation period was 300 s. The heating rate during the TL was 0.1 K s^{-1} . The emission spectra of the AG correspond to the AG signal 30 s after the irradiation.

periods. From this figure it can be seen that before ageing (0 h) the glow curve of the deformed sample is quite different from that of the undeformed sample. Nevertheless, one can still distinguish the two temperature ranges of 50–160 K with a relatively intense complex of TL peaks and of 200–280 K with a less intense complex of TL peaks. The most pronounced effect of the ageing is that the TL of the lower temperature region disappears in the deformed samples except for some luminescence at the beginning of the readout, which is probably a residue of the AG.

4. Discussion and conclusions

Our observation that the dipole related AG emission increases significantly in deformed samples confirms the participation of dislocations in the AG process and is in agreement with the alternative model for AG and TL. In view of this model, the high efficiency of the AG of aggregates could be interpreted as a relatively high participation of aggregates in the AG, suggesting that aggregates are preferentially formed along dislocations. The mechanism for the formation of small aggregates would thus be that dipoles first arrive somewhere along a dislocation. That this is more likely than interactions with other dipoles in the bulk is a reasonable assumption because of the large interaction cross-section of dislocations. Once along the dislocation they migrate relatively fast and may interact with other dipoles along the

dislocation to form aggregates. Evidence for the preferential formation of aggregates along dislocations was recently found in europium doped NaCl and mixed KCl/KBr crystals, for which fluorescence microscope images show that Eu regroups in chains after aggregation [9, 10]. Dipoles and aggregates located along dislocations participate in AG and PL, but dipoles in the bulk participate only in PL. The PL signal is thus richer in dipole emission compared to the AG signal, which is in accordance with the observations.

The observation that in strongly deformed crystals the aggregation process seems to be slowed down is not well understood. At first sight one would expect that the rate of the aggregation process increases because of the high concentration of dislocations, along which aggregation occurs preferentially. A possible cause for the slowing down could be the high degree of entanglement of dislocations in the deformed samples so that a network of dislocations is formed. Such a network has been observed in KCl with a high concentration of dislocations [11]. Maybe the nodes of the dislocation network act as traps for $\text{Eu}-v_c$ dipoles preventing their migration and thus their aggregation. A related observation, also not well understood, is the disappearance of the TL peaks around 120 K in deformed samples after ageing. Maybe this effect could be explained by a competition between the trapping of H centres at (intrinsic) bulk defects close to dislocations (assumed to be related to the low temperature TL peaks) and the trapping of H

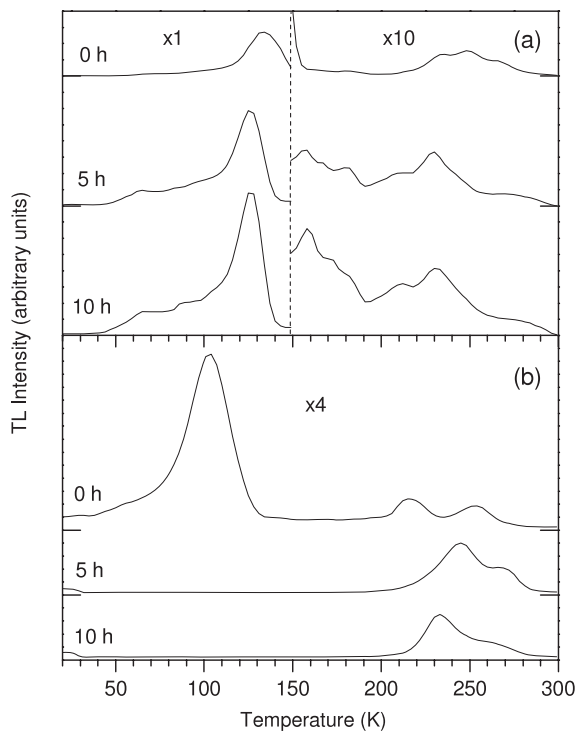
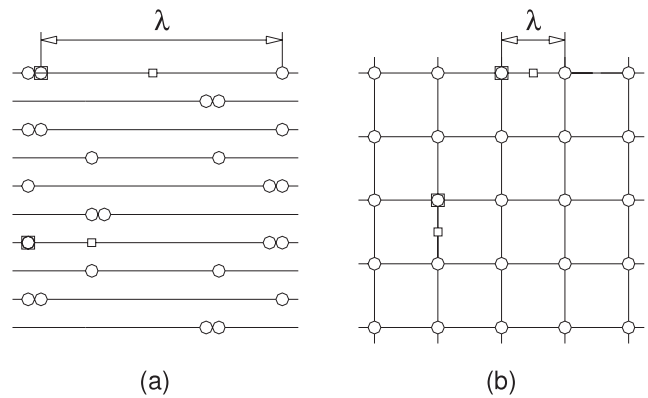


Figure 2. TL glow curves of an undeformed sample (a) and a deformed sample (b) after repetitive ageing at 373 K. The samples and procedures are the same as in figure 1. The unit of the TL intensity is the same for all TL measurements. With respect to this unit, the glow curves in (a) are scaled up tenfold after 149 K and the glow curves in (b) are scaled up fourfold over the whole temperature range.

centres at Eu related defects located along dislocations. An H centre migrating along a dislocation after its creation has some probability to escape from the dislocation and may be trapped at a bulk defect. The longer the mean free path along the dislocation the more probable this escape is. After the 773 K annealing of a deformed sample one has more impurity defects along dislocations but also more dislocations compared to an undeformed sample. The average impurity defect concentration along a dislocation (number of impurities per unit length) is not expected to change much with respect to the undeformed sample and thus the mean free path just after the annealing is expected to be similar for a deformed and an undeformed sample. However, after ageing, the extra arrived dipoles along dislocations in a deformed sample get trapped at nodes in the dislocation network so that a single dipole occupies two dislocations. Depending on the degree of entanglement this could reduce the mean free path significantly. Furthermore, dipoles along a dislocation with many nodes in a deformed sample do not aggregate so easily as dipoles along a dislocation in an undeformed sample, where they fuse without obstruction into aggregates. The concentration of Eu related defects along a dislocation in a deformed sample will thus be greater than in an undeformed sample. So, after ageing a deformed sample, one may expect a relatively short mean free path for the H centre along a dislocation due to the increased number of Eu related defects, so that the capture



- ○ Aggregate of two Eu- v_c dipoles in a dislocation
- F centre near a Eu- v_c dipole in a dislocation
- Eu- v_c dipole in a dislocation
- H centre in a dislocation

Figure 3. Schematic representation of a low (a) and a high (b) degree of entanglement of dislocations after ageing. The mean free path λ for a migrating H centre along a dislocation is much shorter for the case of a high degree of entanglement where all Eu- v_c dipoles are trapped in nodes than for the case of low degree entanglement where many Eu- v_c dipoles are fused into small aggregates. The H centres in the figure were created at the sites where the F centre resides. They can be trapped at a Eu related defect, escape from the dislocation or recombine with their corresponding F centre. Note that the concentration of Eu along dislocations (total number of Eu atoms along dislocations divided by the total length of dislocations) is the same for both cases but the Eu related defect (dipoles and aggregates) concentration is less in the undeformed sample.

of H centres at Eu related defects would be preferable (see figure 3).

In summary, we have evidenced that dislocations play an important role in the process of UV induced AG and TL in accordance with our previously proposed model. Also, we made plausible that the increased sensitivity of aggregates in AG stems from the relatively high concentration of aggregates along dislocations due to a preferential formation of aggregates along dislocations. The mechanisms behind the slowing down of the aggregation process in deformed samples and the disappearance of the lower temperature TL peaks in aged deformed samples are not well understood and need further investigation.

Acknowledgments

This work was supported by CONACyT through projects U40497-F and 37641-E and by PROMEP. We are grateful to J C Avila-Barrera and M Atondo for their technical support.

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