

Effect of quenching on the thermal glow curves from X-ray irradiated KCl and KCl:Pb single crystals

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Thermal glow curves of quenched KCl, both pure and doped with PbCl_2 , have been studied. Quenching from 650°C enhances the glow output by a much larger amount than can be explained on the basis of enhancement of F -centre formation in quenched samples. Further, the glow peaks which are associated with divalent impurities and the first stage of colouration are also intensified by quenching. However, electrolytic colouration (which involves quenching) diminishes the integrated light output, when the coloured crystal is exposed to X-rays and warmed up. Heat-treatment of electrolytically coloured KCl crystals between 110 and 300°C induces a gradual increase of the colloid band at the cost of the existing F -band. In the case of KCl:Pb electrolysis produces F -band along with various forms of Pb (such as Pb^0 and Pb^-); but subsequent heating does not produce colloid centres in this sample. On the basis of these results it is concluded that, (i) quenching increases emitting centres where electrons and holes recombine during thermoluminescence, (ii) recombination efficiency of electrons and holes may also increase due to quenching. A new peak at 285°C in the thermal glow curve of quenched KCl has been observed.

1. Introduction

The effects of quenching from a high temperature (650°C) on the optical and electrical properties of alkali halides has been studied by various workers [1-4]. Thermoluminescence of pure KCl quenched from a high temperature has also been reported [5]. Enhancement of X-ray induced luminescence of NaCl, after heat-treatment, has been studied by Rexer [2, 3] and later by Spicer [4]. While Rexer assumed the heating effect results from diffusion of oxygen in the crystal, Spicer suggested removal of atoms at the surface of the crystal; this leaves a positive ion vacancy, which is followed by migration of the vacancy and a hole from the surface of the crystal into the interior [1]. In order to explain the enhancement of TL from quenched KCl, Halperin *et al* [5] adopted the mechanism of Spicer. Nakajima, however, concluded from his measurements on quenched LiF single crystal that heating in air introduces anions (such as OH and CO_2) into the lattice and the

enhancement of TL intensity is less in this case than that of the samples heat-treated in argon [7].

Jain and Mehendru [8] did not observe any appreciable change in the TL of additively coloured and subsequently X-rayed KCl crystals, although colouration is always accompanied by quenching. Topa and Yuste [9] suggested the formation of Pb^- centres in electrolytically coloured KCl:Pb. If TL is associated with divalent impurity ions serving as emitting centres [6] it is reasonable to expect radical changes in the thermal glow curves, both in the peak positions and in intensity, when the doped sample is either quenched from a high temperature or electrolytically coloured prior to TL measurement.

2. Experimental

"Pure" and lead-doped single crystals are grown from BDH AnalaR grade salts by the Kyropoulos method. The amount of impurity added to the

melt is indicated in the parenthesis. X-irradiation is from a Philips sealed tube (Cu-target). A Beckman model DU spectrophotometer has been used for measuring absorptions, and for TL, the output of a IP28 photomultiplier tube and a thermocouple response are recorded with the help of a cathode follower and a recorder [10]. In all TL measurements the heating rate used is $60^{\circ}\text{C min}^{-1}$. Electrolytic colouration in pure and doped KCl are produced by usual method of placing the sample between a flat platinum anode and a sharp cathode, and heating at a temperature of about 650°C .

3. Results

Fig. 1 gives the TL of as-grown KCl, electrolytically coloured KCl and KCl quenched from 650°C . All the samples have been exposed to X-rays at room temperature (30°C) for fifteen minutes. While the first two varieties give glow peaks around 110°C , 185°C and 245°C , quenched KCl yields TL peaks at 140°C , 190°C and 235°C ; in addition there is a new peak at 285°C , hitherto unreported. Quenched samples show greatly enhanced glow output, whereas the opposite effect is observed in electrolytically coloured crystals (which are always quenched from the temperature of colouration).

A doped crystal of KCl:Pb ($2.4 \times 10^{-2}\text{ mol}\%$) gives three glow peaks at 110 , 140 and 240°C

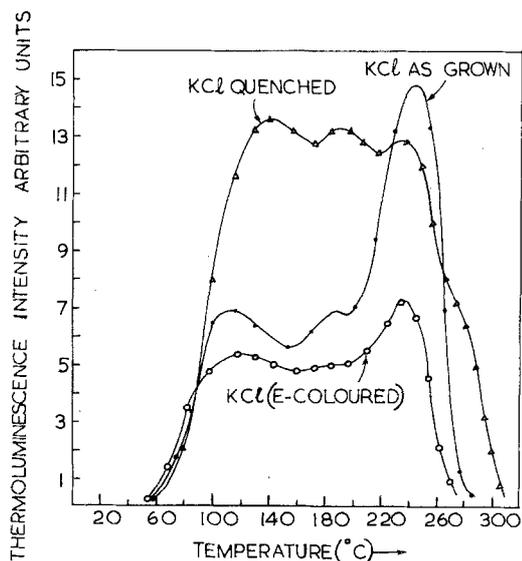


Figure 1 TL of as-grown KCl, electrolytically coloured KCl and KCl quenched from 650°C . All the samples have been exposed to X-rays (30 kV, 10 mA for 15 min) at room temperature (30°C). The rate of heating is $60^{\circ}\text{C min}^{-1}$.

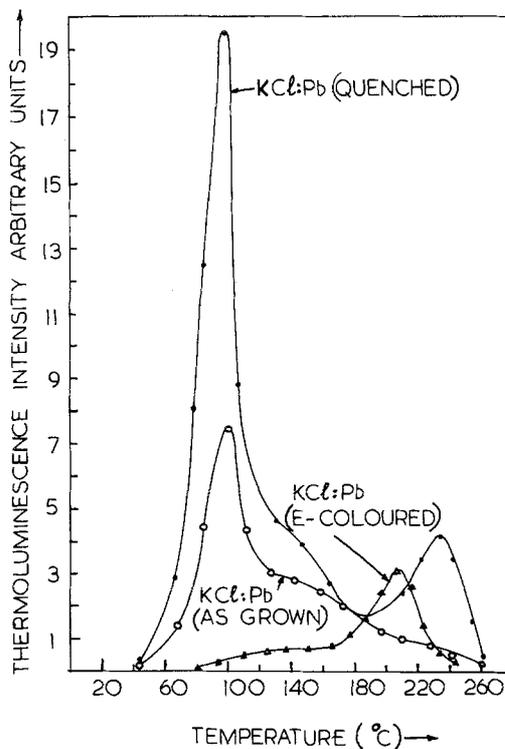


Figure 2 TL of as-grown KCl:Pb, KCl:Pb quenched from 650°C and KCl:Pb electrolytically coloured. All the samples are exposed to 30 kV, 10 mA X-rays for 15 min at room temperature. TL for as-grown and quenched samples are plotted after four times reduction in scale. The rate of heating is the same as in Fig. 1.

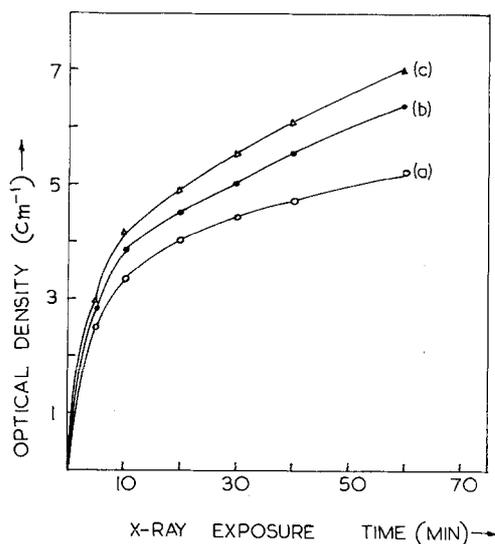


Figure 3 F-centre growth curves under 30 kV, 10 mA X-ray irradiation of (a) as grown KCl, (b) KCl quenched from 650°C , (c) KCl electrolytically coloured. In the last case increase in optical density due to fresh F-centres produced by X-rays has been plotted.

(Fig. 2). On quenching from 650°C all the peaks are greatly increased in intensity, the maximum enhancement occurring at 110°C. (It may be noted that TL for as-grown and quenched samples are plotted in Fig. 2 after a reduction in scale of $\times 4$). In the glow curve for electrolytically coloured KCl:Pb, only one peak of poor intensity at about 205°C is obtained, while the so-called impurity peak at 110°C [8] has been totally suppressed. Fig. 3 gives the *F*-centre growth curves under 30 kV, 10 mA X-irradiation of as-grown KCl (a), KCl quenched from 650°C (b) and KCl electrolytically coloured (c). In curve c, the increase in optical density due to fresh *F*-centres produced by X-rays has been plotted. It is clearly seen that the number of *F*-centres produced in the treated samples is comparable to, if not larger than, that in as-grown KCl.

The measurement of the isothermal decay of *F*-centres in KCl crystals coloured jointly by

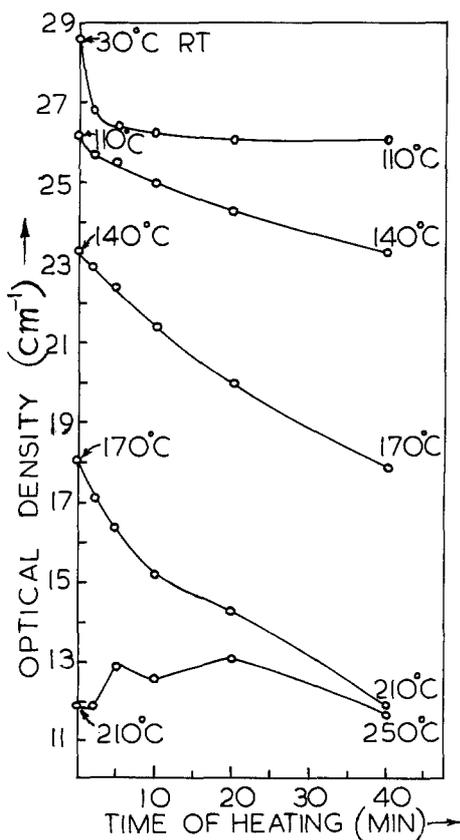


Figure 4 Isothermal bleaching of *F*-centres (OD cm^{-1} at 560 nm) in KCl coloured electrolytically followed by X-raying at room temperature. The absorption is measured at room temperature after the sample is kept at the stipulated temperature for a specified time and quenched.

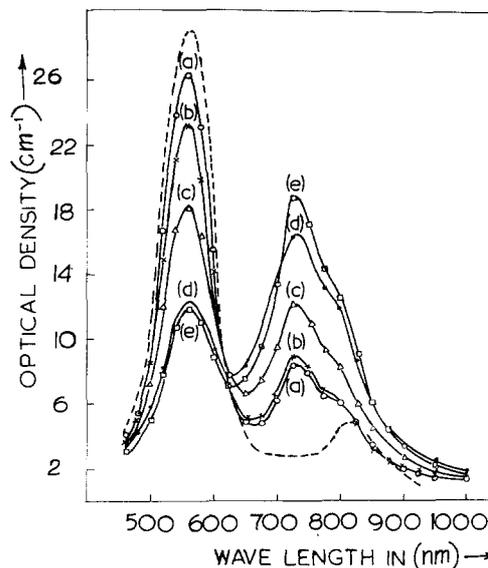


Figure 5 The effect of heat treatment on the absorption spectra of pure KCl coloured conjointly by electrolysis and X-rays (30 kV, 15 mA for 45 min). Curves (a), (b), (c), (d) and (e) are obtained after heating the sample at 110, 140, 170, 210 and 250°C respectively for 30 min each. The broken line gives the spectra before heat treatment is carried out.

electrolysis and X-rays has been carried out at various temperatures (Fig. 4). The results show that the *F*-centre concentration gradually decreases at all temperatures above 110°C. At 110°C (top curve, Fig. 4), the *F*-centre concentration attains a stable value in about 20 min.

The results of heat-treatment on the absorption of electrolytically coloured KCl and KCl:Pb single crystals have been depicted in Figs. 5 and 6. For KCl, the sample is coloured by electrolysis followed by X-rays and the optical absorption is measured at room temperature after the sample is kept at stipulated temperatures for half an hour and quenched (Fig. 5). The colloid band in this case gradually build up at the cost of the *F*-band. In case of electrolytically coloured KCl:Pb, however, similar heat-treatment at 300°C does not produce any colloid band; instead the optical absorption diminishes throughout the whole range of wavelength between 240 and 1000 nm (Fig. 6).

4. Discussion

The increase in thermal glow is so large in quenched samples, that it cannot be explained on the basis of enhancement of *F*-centre concentration alone. The glow peak at 110°C has been associated with impurities [8] and the thermal glow is most

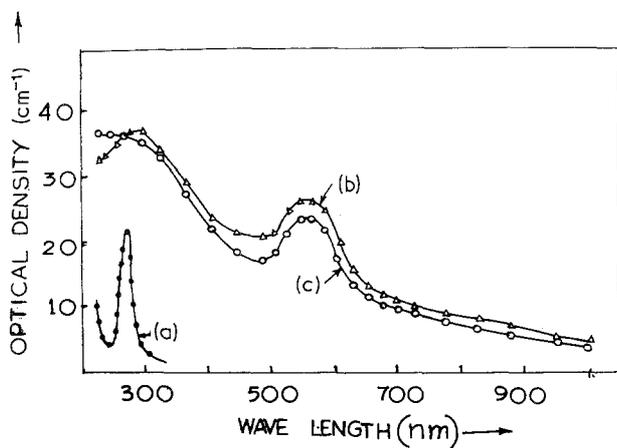


Figure 6 The effect of heating at 300°C for 1 h on the absorption bands produced by electrolysis of KCl:Pb crystal. The curve (a) gives the spectra before electrolysis, (b) after electrolysis, while (c) gives the spectra after heat treatment.

prominent here. It may be noted that even in most of the so called pure samples, unintentional divalent impurities are always present, as can be seen from electrical conductivity measurements [11]. If this is so, it is expected that quenching should increase emitting centres associated with divalent impurities; in other words, rapid cooling preserves the equilibrium distribution of the impurities and vacancies that exists at the higher temperatures, and aggregation of the impurities is prevented [12, 13]. In doped samples the enhancement of thermal glow is most prominent around the low temperature peak (110°C), which is associated with impurities. This confirms that quenching increases unassociated divalent impurities which act as emitting centres. Moreover, at a temperature of about 650°C positive ion vacancies accompanied by holes may diffuse from the surface into the interior [1]. This vacancy-hole combination may distribute inside the crystal in such a way that the recombination efficiency of electrons and holes may increase [5].

On electrolysis, some or most of the divalent positive ions capture electrons (Pb^{++} is converted to Pb^0 , Pb^-) [9] and as a result they no longer serve as emitting centres; also neutralization of electron-capturing centres may assist the process of colouration during X-ray irradiation. Fresh *F*-centres may be produced in this case by X-rays according to the mechanism suggested by Hersh [14], which is why the rate of *F*-centre formation by X-rays in electrolysed samples (Fig. 3) is comparatively higher than that in as-grown samples. The TL yield is, however, poor since the potential emitting centres (associated with intentional or unintentional divalent impurities) have been destroyed by electrolysis (Fig. 2).

At 110°C (top curve, Fig. 4), a saturation of *F*-centre concentration is attained quickly, since very small colloids are formed at this temperature, the normal temperature of colloid formation being around 300°C. At other temperatures, the slow and gradual destruction of *F*-centres observed for electrolytically and X-rayed KCl (Fig. 4) may indicate that coagulation occurs by diffusion of neutral potassium.

It is generally accepted that colloids are formed by heat treating additively or electrolytically coloured alkali halides at a temperature of about 300°C [15]. Fig. 5 shows that even at a low temperature of 100°C colloids may be formed in electrolytically coloured KCl crystals. Moreover, if heat treatment is carried out in the low temperature region of 110 to 250°C, no shift of the absorption maximum of the colloid band is observed. This means that no change in the size distribution of the colloidal centres takes place in this temperature region. It may be noted that the shift of the absorption maximum observed by Scott *et al.* [16] is due to heat treatment at higher temperatures.

The absorption band at 273 nm in Fig. 6 is due to Pb^{++} centres occupying potassium ion sites. On electrolysis, some or most of the Pb^{++} ions in KCl:Pb capture electrons and are converted to Pb^0 or Pb^- [9] and as a result the absorption band is practically destroyed. The presence of these neutral lead and other centres disturbs the formation of colloid centres upon heat treatment.

Acknowledgement

The author is greatly indebted to Professor H. N. Bose for helpful discussion and constant encouragement.

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Received 10 May and accepted 30 May 1977.