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Effect of Thermal Pretreatment on the Thermoluminescence of KCl Crystals

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Thermal pretreatment was found to enhance the thermoluminescence of x-colored KCl crystals. The effect was found to penetrate into the crystal by diffusion from the outer surfaces. It is affected by the atmosphere surrounding the heated crystal, and it seems also to be structure sensitive. For some crystals the enhancement in the thermoluminescence was by a factor as high as 4000 when the number of quanta emitted during the thermoluminescence was about the same as the number of F electrons bleached during this process.

INTRODUCTION

IT was found in previous work[1] that some peaks in the glow curve of x-colored KCl crystals increased enormously in intensity after the crystal had been subjected to many cycles of x-irradiation, heating and recooling to liquid-air temperature.

The coloring properties are known[2,3] to depend largely on the previous heat-treatment of the crystal. On the other hand, it was also reported that crystals are easier to color after they have been exposed to x-rays and bleached by exposure to daylight.[4] The behavior of the glow peaks, as mentioned above, could, therefore, be expected to be due to both the thermal treatment and the x-irradiation.

It was the aim of the present work to investigate this matter in detail, and to find out what part in the enhancement of the glow peaks is due to the x-irradiation, and what part should be assigned to the heat treatment.

The results as described below showed clearly that only the heat treatment produced the enhancement in the intensity of the glow peaks.

It seemed reasonable that the enhancement in the thermoluminescence might be associated with an increase in the darkenability of the heat treated crystals. Absorption spectra have, therefore, also been taken. Only a small increase in the F darkenability was found for the heat-treated crystals. The increase in the V_1 band (when the crystal was x-colored at liquid-air temperature) was more pronounced, and the main effect was the appearance of new absorption bands, not observable in the spectra of thermally untreated crystals. The role of these new centers in the enhancement of the thermoluminescence is yet not clear, and the matter is now being investigated.

EXPERIMENTAL

The specimens used in the present work were synthetic KCl crystals grown by Harshaw Chemical Company. These were supplied in blocks of larger dimensions, from which plates about 7×6×1 mm were cleaved.

The thermal treatment was carried out with the crystal (and thermocouple) in a test tube inside the electric furnace. In experiments aimed to examine the effect of the atmosphere surrounding the heated crystal, the thermocouple was kept in nearest access to the sealed tube containing the heated crystal in the desired atmosphere.

On the termination of the desired heating period the crystals were usually cooled rapidly to room temperature by immersion into carbon tetrachloride. Later, however, it was found that slower cooling in the open air did not affect the resulting glow curves and color bands. Some sets of experiments were, therefore, carried out by slower cooling, which avoided possible fracture of the crystals while being quenched.

The cryostat, detector, and recording devices as well as the x-ray apparatus and irradiation procedure were described previously.[5]

Absorption spectra were recorded using a Beckman DK spectrophotometer. A cryostat to fit this apparatus was built for this purpose.

The rate of warming-up used for obtaining the glow curves was kept at about 10°/min throughout the

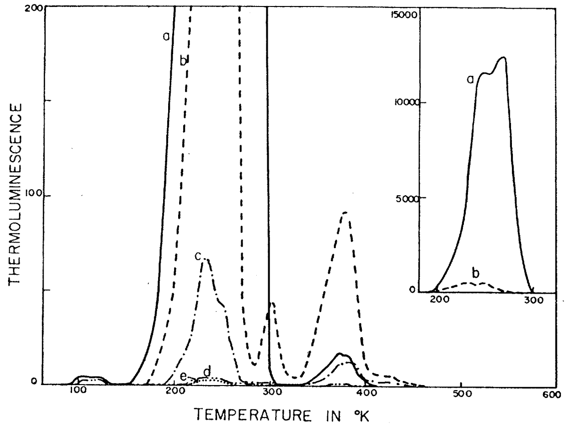

FIG. 1. Effect of thermal pretreatment on thermoluminescence of KCl crystals. Heating temperature—500°C; heating times: a—360, b—45, c—15, d—5 minutes. e—an untreated crystal. X-irradiation—5 minutes at 14 ma 50 kvp from a copper target.

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[1] Halperin, Braner, and Alexander, Phys. Rev. **108**, 928 (1957).
[2] E. Rexer, Z. Physik **106**, 93 (1937).
[3] H. Adler and F. Stegmuller, Acta Phys. Austriaca **11**, 31 (1957).
[4] See, for example, K. Przibram, *Irradiation Colours and Luminescence* (Pergamon Press, London, 1956), p. 45.
[5] A. A. Braner and A. Halperin, Phys. Rev. **108**, 932 (1957).

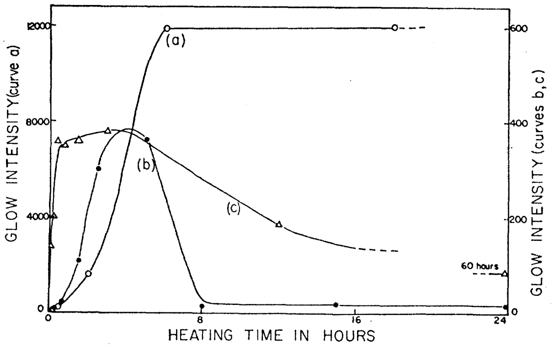

FIG. 2. Dependence of glow intensity on heating time for KCl crystal of different batches. The ordinate scale on the left belongs to curve a, and on the right to curves b and c.

present work. This resulted in a reduction of about 5% in the peak temperatures of the glow curves compared to those reported previously,[1] when the rate of warming was about 30°/min.

RESULTS

(a) Effect of Preheating on Thermoluminescence

The intensity of the peaks in the glow-curve of KCl crystals was found to be dependent on the thermal history of the crystals. Figure 1 shows glow-curves for different crystals all of them cleaved out of the same crystal block, but kept for different periods at 500°C. After the heat treatment, the crystals were mounted in the cryostat, cooled to liquid-air temperature and submitted all to the same x-ray dosages, after which the glow-curves were recorded. Curves a, b, c, and d in Fig. 1 were obtained for crystals heated for 360, 45, 15, and 5 minutes, respectively, while curve e belongs to a virgin crystal. The effect of the heat treatment is shown to be very strong in the temperature region of 200–300°K.[6] For the longer heating periods (curves a and b) the glow was very intense, and these glow-curves are given on a reduced scale to the right of Fig. 1. The effect was found to saturate, and the glow curve obtained for a crystal heated for 18 hours at 500°C was essentially the same as that obtained for one heated only for 6 hours (curve a, Fig. 1).

In the crystals of the batch just described the intensity of the glow peaks after heating the crystal to saturation increased by a factor of 4000 compared to the untreated crystal. The effect seems, however, to be structure sensitive, and crystals of other batches differed in behavior. This is shown in Fig. 2 in which the intensity at the maximum of the glow peak at about 250°K is plotted against the heating time for different sets of crystals, all the crystals of a given set being cleaved out of the same crystal block. Figure 2 (a) was obtained from the glow curves shown in Fig. 1, and Fig. 2 (b)—for a set of crystals cleaved from another block. The same intensity units were used for all the curves.

Comparison of curves 2(a) and 2(b) shows two main differences. First, the maximum intensity obtained is only about 350 in 2(b), compared to 12 000 in 2(a). In addition, in 2(b) there is a decrease in intensity for longer heating periods and after heating the crystal for 24 hours (at 600°C) the intensity was of the same order of magnitude as for the virgin crystal. To make sure that this effect is not incidental, another crystal (of another crystal block) was taken for a full set of measurements. In this case the crystal was first treated for 5 minutes at 550°C after which a glow curve was taken. Then the *same* crystal was submitted to additional periods of heat treatment, glow curves being taken at each step. Figure 2(c) shows the results. Here the intensity of the glow at a given step is plotted against the total heating time to which the crystal was submitted up to the given step. Again, the behavior is as in curve 2(b); i.e., a maximum in the glow intensity is reached, after which there is a decrease for additional heating periods.

Another set of experiments was carried out to examine the penetration of the thermal effect into the interior of the crystal. For this purpose, a crystal block of about one cubic centimeter was kept for two hours at 500°C. After cooling to room temperature, slices about 1 mm thick were cleaved from this block, and their glow curves after x-irradiation were compared. Results are shown in Fig. 3, in which curve a was obtained for the outer slice, curve b for the next cleaved plate, and curve c for the third (about 3 mm from the outer face). This

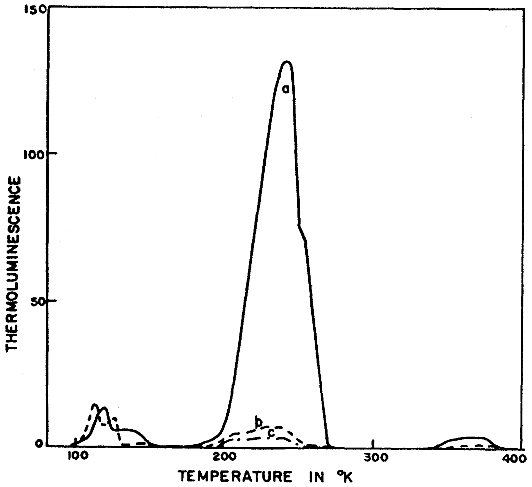

FIG. 3. Penetration of the heating effect into the crystal. a—for an outer slice cleaved from the heated crystal; b—next cleaved slice (about 1.5 mm from the outer surface); c—third cleaved slice (3 mm from outer surface).

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[6] Other peaks in the glow curve were much less affected by heat-treatment (e.g., the peaks below 400°K), while the glow peaks below 200°K seem not to be affected at all. The discussion is therefore limited to the peaks at about 250°K, and unless otherwise stated the term "glow intensity" will further be used for the maximum intensity in this temperature region.

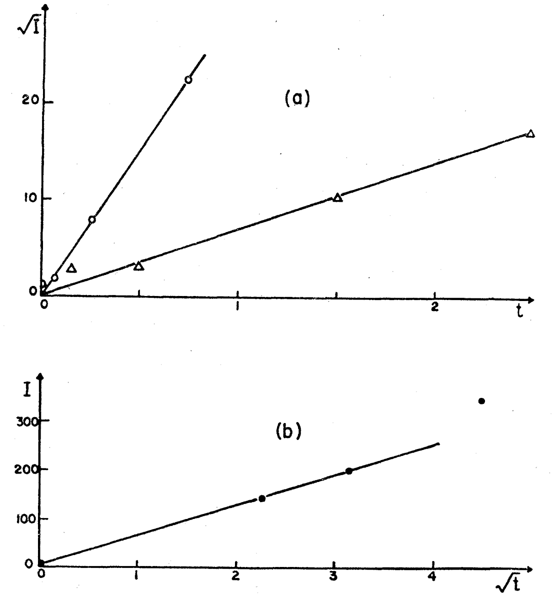

FIG. 4. (a) The curves 2(a) and 2(b) replotted with the square root of glow intensity ($\sqrt{I}$) as ordinate. (b) Curve 2(c) replotted with the square root of heating time as abscissa.

experiment indicates that the heating effect penetrates into the crystal by diffusion from the outer surfaces.

On heating at a given temperature the depth of diffusion into the crystal should grow with the square root of the heating time ($d \propto \sqrt{t}$). The thermoluminescence intensity seems, however, to rise for short periods of heating much faster than with $\sqrt{t}$, as is clearly seen in Figs. 2(a) and 2(b). The initial rise is shown to be proportional to t^2 in Fig. 4(a) in which the short period parts of Figs. 2(a) and 2(b) were replotted with the square root of glow-intensity ($\sqrt{I}$) in the ordinate.

Figure 4(b) corresponds to Fig. 2(c), now replotted with $\sqrt{t}$ as abscissa. The proportionality of the glow intensity to $\sqrt{t}$ instead of t^2 in the former cases, might be attributed to the difference in procedure as the same crystal was used now in successive cycles of heating, cooling, x-coloration, and glow-curve measurements. Accordingly, the time accumulated during several cycles was taken as the heating time instead of one uninterrupted heating period in the former experiments.

The effect of the temperature of the thermal treatment was also examined. Figure 5 shows the glow curves for three crystals (cleaved from the same crystal-block) treated similarly except that heating temperatures were 700, 600, and 500°C for crystals a, b, and c, respectively.

As long as the heating effect does not reach saturation, the glow intensity seems to rise with temperature faster than the diffusion depth which should be proportional to $\exp(-1/T)$.[7]

The value of the saturated glow intensity seems to be affected only slightly, if at all, by changing the temperature at which the crystal was preheated.

(b) Effect of the Surrounding Atmosphere

Essentially the same results were obtained by heating the crystals in a chlorine atmosphere instead of the open air.

The next step was to heat the crystal in high vacuum. At the beginning, when the crystal was heated in a glass tube evacuated down to nearly 10^{-5} mm of Hg, the intensity of the glow was again about the same as on heating in the open air. Later, the residual traces of air were flushed by pure argon which was re-evacuated before sealing the tube. This resulted in a pronounced reduction in the glow intensity. Two crystals heated for $2\frac{1}{2}$ hours at 500°C, but one in the open air and the other in argon at a pressure of about 10^{-5} mm of Hg showed relative glow intensities of 310 and 60, respectively.

Quite different results were obtained in an atmosphere of potassium vapor. Figure 6 shows for comparison the glow curves for an untreated crystal (curve a), for a crystal heated in the open air (curve b) and for one heated in potassium vapor at 500°C (curve c).[8] The difference between curves b and c is impressive. The treatment in potassium vapor removed completely all the glow peaks which appear in the virgin crystal, and two new glow peaks at 150 and 180°K appear

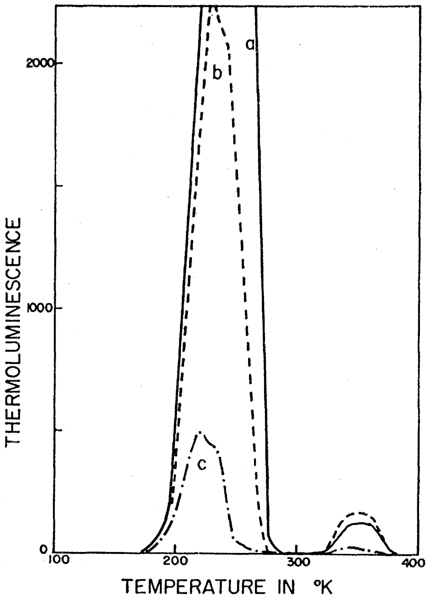

FIG. 5. Temperature dependence of the heating effect. Crystals were heated for one hour, a—at 700°C, b—at 600°C and c—at 500°C.

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[7] See, for example, N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948), p. 34.

[8] The comparatively low temperature of the heat treatment in potassium vapor was not enough for considerable additive coloration of the crystal, which showed only slight traces of coloration after this treatment.

The effect of the heat treatment in potassium vapor is not as stable as that obtained by heat treatment in the open air. While the latter lasts for many months (and probably for many years), the effect of heat treatment in potassium vapor is considerably reduced on keeping the crystal for a few weeks at room temperature in the open air, when glow curves are again nearly the same as for a virgin crystal.

(c) Effect of x-Irradiation History

Crystals were subjected to very long exposures to x-irradiation in order to examine whether the irradiation history of the crystal affects its glow curves. The long x-irradiations were carried out with the crystals at room temperature just near the beryllium window of the x-ray tube. The irradiated crystals were bleached thermally by warming them up to about 600°K, and then subjected to 5 minutes of x-irradiation at liquid-air temperature, after which the glow curve was recorded.

The glow curves obtained with these crystals were essentially the same as for virgin crystals, and no effect of previous irradiation of up to 100 hours could be detected in the glow curves.

It was also of interest to examine the effect of prolonged x-irradiation on the enhanced glow of previously heat-treated crystals. The results were negative as far as no reduction in glow intensity was found after 100 hours of previous x-irradiation of heat-treated crystals. This was true for crystals thermally treated in the open-air as well as for those treated in potassium vapor. For the latter, the reduction with time of the glow peak at 150°K (see above) was found to be independent of the x-irradiation history.

DISCUSSION

Effects of thermal pretreatment on the optical properties of alkali-halide crystals were described by many investigators. Only a few, however, dealt with the effects on the luminescence of the crystals,[2,3,9] and still fewer deal with the effects on thermoluminescence.

Adler and Stegmuller[3] have found that the phosphorescence and thermoluminescence of NaCl crystals were enhanced by thermal treatment. Their thermoluminescence experiments were restricted to temperatures above room temperature, and the enhancement in thermoluminescence was examined only qualitatively. As to the origin of these effects the authors say that it should be attributed to the higher density of the *F* electrons, and to their higher mobility in the heat treated crystals.

Spicer[9] has examined the effect of thermal pretreatment on the intensity of the x-ray induced luminescence from NaCl crystals. It seems that the heating affects similarly both the x-ray induced luminescence and the thermoluminescence, and it seems worthwhile to compare some of our results to those reported by Spicer.

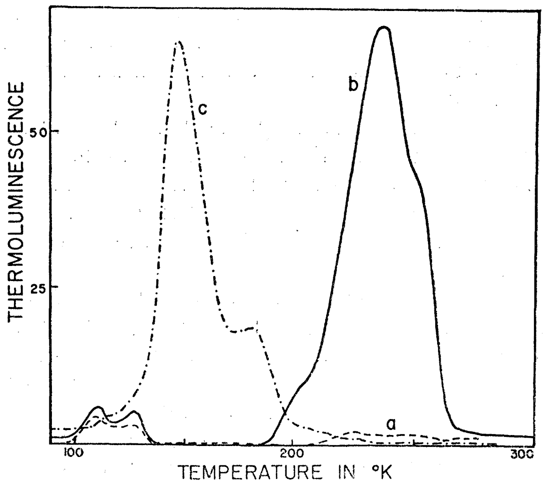

FIG. 6. Effect of preheating in various atmospheres. a—an untreated crystal; b—crystal heated 15 minutes at 500°C in the open air; c—heated for 14 hours at 500°C in potassium vapor.

In full agreement with our results Spicer found that the heating effects penetrate by diffusion from the outer surfaces into the crystal. On the other hand, according to Spicer the results differed very little for heating times varying between 1 minute and one hour which seems inconsistent with our results, unless we assume that in that case one minute was enough to bring the heating effect to saturation. Spicer has also found that prolonged x-irradiation reduced the heating effect, which again does not agree with our results.

Rexer[2,10] has investigated in detail the effects of preheating on the coloration and x-ray induced luminescence in NaCl crystals. Using the ultramicroscope he had shown that rough irregularities in the bulk of the crystal become finer and evenly distributed after prolonged heating of the crystal.

For direct measurement of the depth of penetration, Rexer made use of the afterglow in the heat effected regions of the crystal. Inner crystal slices cleaved from heat treated crystal blocks were used for this purpose. The penetration of the heating effect was then obtained by putting such a crystal slice, immediately after x-raying, in contact with a photographic plate, on which more intense blackening was obtained in points in close contact with those regions in the crystal which showed the enhanced afterglow.

The dependence of the diffusion depth on heating time as well as on temperature was shown by Rexer to fit the diffusion process well.

Rexer has also shown that when care is taken to eliminate traces of air, the diffusion depth for crystals treated for the same time and at the same temperature is much smaller in vacuum compared to that in the

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[9] W. Spicer, Phys. Rev. **106**, 726 (1957).

[10] E. Rexer, Z. Physik **75**, 777 (1932); **106**, 70 (1937).

open air. This is in agreement with our results, and it seems that residual traces of air caused the heating effect to be the same in vacuum as in air in Spicer's experiments.[9]

The same reasoning might explain why Adler and Stegmuller[3] obtained the heating effect on heating the crystals in nitrogen, which they took as a strong argument against Rexer's assumption that the heating effect results from penetration by diffusion of oxygen into the crystal.

To prove this assumption, Rexer used a copper-doped NaCl crystal. On heating, he observed a black layer penetrating into the crystal. Rexer assumed that the black layer was formed by oxygen molecules which oxidized the copper inside the crystal.

This sounds reasonable. It seems, however, that more than one diffusion process is involved. Oxygen ions might tend to increase the number of chlorine-ion vacancies,[11] and thus increase the darkenability of the crystals. However, only, a small part of the enhancement of the luminescence might be attributed to an increase in the darkenability by the heat treatment. As already mentioned, absorption measurements have shown that the F centers and the V-type centers are enhanced only by a factor, say, of two to three, which is not enough to explain the increase in the thermoluminescence in the heat treated crystals.

We assume therefore that another diffusion process, namely the migration of potassium-ion vacancies and holes from the surface of the crystal into the interior,[12] helps in the enhancement of the luminescence. This is essentially what Spicer[9] has suggested as an explanation for the effect of heating on the x-ray luminescence.

The heating might be expected to cause the potassium-ion vacancies diffusing into the crystal to approach the neighborhood of chlorine-ion vacancies in the crystal, which would result in an increase in the probability of radiative transitions in the process of recombination of electrons and holes on warming the colored crystals.

The spectral distribution of the light emitted at each of the peaks in the glow curve has also been investigated in this laboratory.[13] An interesting result was that, although the glow curves of crystals heated in the open air were quite different from those of crystals heated in potassium vapor, the spectra were found to be composed of the same bands in both cases. This excludes the possibility of the luminescence being characteristic of oxygen or other foreign molecules which diffuse into the crystal during the heating process. On the other hand, on our assumption, according to which diffusion of vacancies into the crystal is responsible for the enhancement of the thermoluminescence, the spectral distribution should be the same no matter whether the diffusion process involved potassium-ion vacancies or chlorine-ion vacancies.

This is also in accord with the results of Dutton and Maurer,[14] who have shown that thermoluminescence results from recombination of holes released from V centers with electrons in F centers.

The efficiency of the recombination process is very low, and is usually of the order of 10^{-4}. The role of the diffusion in the heat-treated crystals might be to increase this efficiency by a suitable distribution of the hole and electron traps and probably also by supplying intermediate steps which seem to be necessary for the recombination process.

It is of interest at this point to note that for some of the heat saturated crystals described above [Fig. 1(a)], the number of quanta emitted during the glow process was about the same as the number of F centers bleached thermally during this process.

While the diffusion depth rises with the square root of the heating time, the thermoluminescence intensity was found to rise faster. This might be explained partly by the increase in darkenability of both the F and V centers in the heat-treated crystals. We have, however, to turn again to the assumption mentioned above as to the role of the diffusion process in increasing the efficiency of radiative transitions.

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[11] R. J. Ginther and R. D. Kirk, J. Electrochem. Soc. **104**, 365 (1957).

[12] See, for example, p. 56 of the review of F. Seitz, Revs. Modern Phys. **26**, 7 (1957).

[13] A. Halperin and N. Kristianpoller, J. Opt. Soc. Am. 48, 996 (1958).

[14] D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).