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Thermoluminescence Properties of Some Alkali Halides

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Thermoluminescence curves of KI, KI:Tl, NaBr:Tl, KBr, KBr:Tl, NaI, NaF, and LiCl have been recorded after exciting the samples with low-energy cathode rays at liquid oxygen temperature. By using suitable filters and photomultiplier tubes, the thermoluminescence was recorded for different spectral regions and it was found that the high-temperature peaks are rich in ultraviolet emissions. The dependence of thermoluminescence on thermal treatment of the sample has been studied for KI. The changes in the absorption bands of some of the color centers, during thermoluminescence, have been investigated by simultaneously measuring diffuse reflectance. It has been found that glow peaks are accompanied by changes in color centers.

INTRODUCTION

THERMOLUMINESCENCE experiments have been employed by a number of workers to determine the trap depths in different phosphors. The exact nature of the trapping mechanism responsible for the glow peaks is still obscure, and the relationship between trapping centers and color centers has not yet been established in most cases. In the present work, thermoluminescence of some alkali halides has been studied, employing a comparatively high rate of heating (7–10°C/sec) because it was found that if the rate of heating is kept low, the details of the thermoluminescence, especially on the high-temperature side, are lost. The diffuse reflectance of some of the samples for radiations corresponding to the color centers has been recorded along with the thermoluminescence.

EXPERIMENTAL

The alkali halide sample was taken in powder form (pure reagents of E. Merck and Company) and mounted as a thin film on the silver bulb[1] of the sample holder. Thallium-activated samples were prepared by mixing a weighed amount of thallium compound with the alkali halide and melting the mixture in an electric furnace. The demountable cathode-ray tube is the same as that used for the study of afterglow.[2] The sample was excited to saturation at liquid oxygen temperature, with cathode rays (10 kv) operated from a rectifier power unit, and the electrons were made to strike the sample by deflecting them with the help of a small magnet suitably placed outside the tube; this bending was done to minimize the damage to the sample by the negative ions. Heating was started immediately after stopping the excitation, and thermoluminescence was recorded with a photomultiplier tube (R.C.A. 931 A, 1P28, 1P22) feeding a Moll-type galvanometer. A rotating photographic drum records the movements of this galvanometer and also those of another connected to a copper-constantan thermocouple, fixed to the sample holder. When studying the spectral nature of the glow peaks, the two galvanometers were connected to separate photomultipliers, responding in different spectral regions (filters were used when necessary), so that during the same run, emissions in different regions could be recorded.

Bose[1] has already reported similar work on NaCl, NaCl:Tl, KCl:Tl. In the present paper studies of KI, KI:Tl 2.5%, NaBr, NaBr:Tl 2.5%, KBr, KBr:Tl 2.5%, NaI, NaF, and LiCl are reported. The trap depth (E), in electron volts, has been estimated with

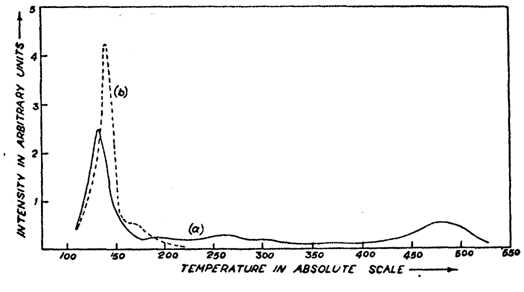

FIG. 1. Thermoluminescence curves of potassium bromide a and sodium iodide b, after irradiating the samples at liquid oxygen.

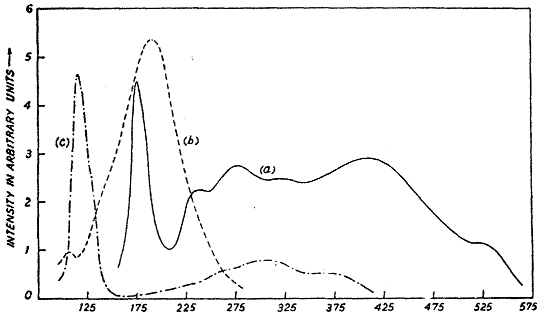

FIG. 2. Thermoluminescence curves of potassium bromide a, thallium-activated potassium iodide b, and lithium chloride c.

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[1] H. N. Bose, Proc. Phys. Soc. (London) **B68**, 249 (1955).

[2] H. N. Bose and J. Sharma, Proc. Phys. Soc. (London) **B66**, 371 (1953).

TABLE I. The temperatures T_G in °K of the glow peaks and the estimated trap depths E in electron volts are given, as estimated by the approximate formula of Randall and Wilkins, assuming $s=10^{9\pm1}$ sec^{-1}.

KI		KI(Tl)		NaBr		KBr(Tl)		KBr(Tl)		KBr(Tl)		NaI		NaF		LiF		LiCl	
T_G	E	T_G	E	T_G	E	T_G	E	T_G	E	T_G	E	T_G	E	T_G	E	T_G	E	T_G	E
112	0.20	106	0.19	133	0.24	104	0.19	176	0.32	165	0.30	140	0.25	174	0.31	131	0.25	116	0.21
118	0.21	140	0.25	194	0.35	117	0.21	235	0.43	200	0.36	170	0.31	316	0.57	143	0.26	121	0.22
120	0.22	190	0.34	255	0.45	131	0.24	281	0.51	286	0.53			370	0.67	200	0.36	131	0.23
158	0.29			300	0.54	137	0.25	330	0.60	363	0.66			463	0.84	254	0.46	270	0.48
176	0.32			480	0.87	173	0.31	415	0.75	520	0.94			540	1.0	290	0.53	300	0.54
235	0.43					253	0.46	525	0.95					673	1.22	430	0.78	367	0.66
						320	0.58												

the help of the approximate formula of Randall and Wilkins[3]:

$$E=21kT_G,$$

where k is the Boltzmann constant, T_G the temperature of maximum glow, and the frequency factor s is assumed to be $10^{9\pm1}$ sec^{-1}.

RESULTS AND DISCUSSIONS

The records of the glow curves for sodium bromide, sodium iodide, potassium bromide, potassium iodide with thallium, and lithium chloride, are reproduced in Figs. 1 and 2. Similar records were obtained for all the compounds referred to earlier. Table I gives a summary of the data pertaining to the temperatures of the glow peaks and the trap depths as estimated from all these records.

An examination of the records shows that, in general, the glow peaks emitted at low temperatures are sharper than those emitted at higher temperatures.

Figure 3 is one the simultaneous records of thermoluminescence for the visible and ultraviolet emissions. It is observed from this and other similar records that, in most cases, the traps released at higher temperatures are comparatively rich in ultraviolet emissions; similar results have also been reported by Bose[1] in the case of potassium chloride and sodium chloride phosphors.

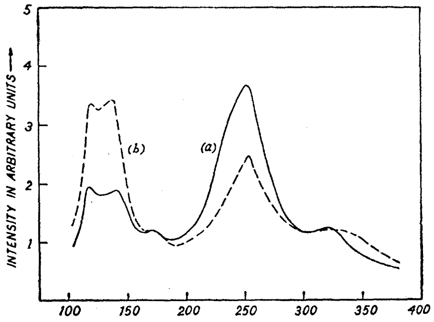

FIG. 3. Thermoluminescence curves of thallium-activated potassium bromide simultaneously recorded with the 1P28 photomultiplier across Wood's glass a and with the 931 A photomultiplier without any filter b showing that the high-temperature peaks emit more ultraviolet rays.

It has been reported earlier[4] that the fluorescence spectra of potassium iodide extends from 660 mμ to 330 mμ, consisting of two distinct regions 660–470 mμ and 470–330 mμ, respectively. However, for temperatures above 120°K the shorter wavelength band is absent. Measurement of the decay curves at different temperatures shows that at the temperature 120°K, the decay constant of afterglow suffers a sudden change. It is also found that the glow peak at this temperature is very rich in blue emissions; this should indicate a close association between the emitting centers responsible for blue emissions and the trapping mechanism corresponding to the glow peak at 120°K.

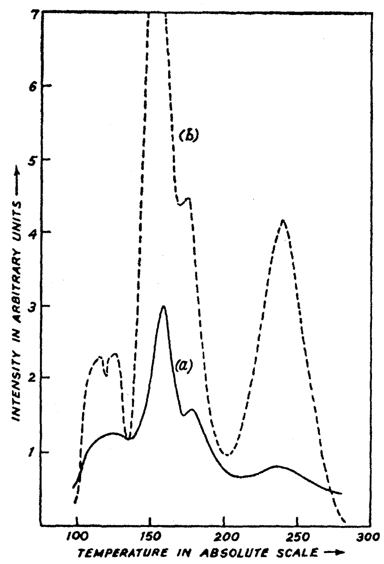

FIG. 4. Thermoluminescence curves of potassium iodide with the same sensitivity level of the photomultiplier. The curve (a) is the first record with a fresh sample; the curve (b) is the second record showing a marked increase in thermoluminescence output, due to irradiation followed by heating.

Coincidences between emission of some glow peaks and changes in color centers have already been reported[5–7] for potassium iodide, potassium chloride,

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[3] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 365 (1945).

[4] H. N. Bose and J. Sharma, Proc. Natl. Inst. Sci. India **16**, No. 1, 47 (1950).

[5] P. Pringsheim and P. Yuster, Phys. Rev. **81**, 293 (1950).

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

[7] J. Sharma, Phys. Rev. **85**, 692 (1952); **87**, 335 (1952).

sodium chloride, and lithium fluoride. Similar coincidences are observed for potassium bromide, sodium bromide, sodium fluoride and lithium chloride. Potassium bromide becomes blue on bombardment at liquid oxygen temperature, which obviously is due to development of *F*-centers (6300 A).[7] During the thermoluminescence experiment, this color disappears with the glow peak at 175°K. Sodium bromide does not show any visible coloration on excitation at liquid oxygen temperature, but becomes yellow after the emission of the peak at 250°K; this color disappears with the luminescence at 480°K. If the yellow color is produced by irradiation of the sample at 300°K, the color dies with the glow peak at 480°K.

In the case of sodium fluoride, excited at liquid oxygen temperature or at 300°K, no visible coloration is detected, obviously because the *F*-band is at 3400 A.[8] However, from an examination of Fig. 4, it is seen that the glow peak at 540°K is accompanied by the appearance of a red coloration (R_2 or *M*-band, 4150 A)[8] which in turn disappears with another glow peak at about 673°K. Thus the peaks at 540°K and at 673°K are associated respectively with the development and disappearance of the red color. Similarly, lithium chloride develops a reddish blue color with the emission of a feeble peak at 573°K. However, annihilation of this color takes place at a much higher temperature. The survey of the aforementioned coincidences leads to the conclusion that thermoluminescence peaks are associated with destruction of color centers. This conclusion is further supported by the fact that a corresponding shift in glow temperature is observed if the coloration is made more stable by exciting the phosphors at higher temperatures. For example, in potassium bromide, the blue color disappears with a glow peak at 175°K when excited at 89°K, whereas when excited at 300°K, not only is the color center produced more stable but also the thermoluminescence peak is shifted to 435°K.

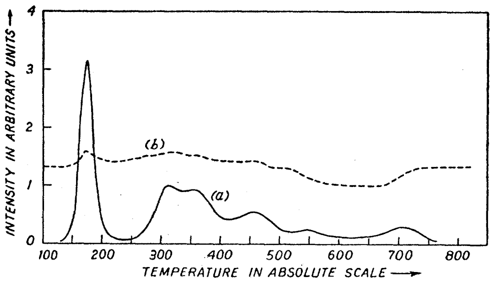

FIG. 5. Thermoluminescence and simultaneously recorded diffuse reflectance with blue light for sodium fluoride. The depression in the reflectance curve at 540°K marks a red coloration of the sample, while the rise in this curve at 700°K marks the disappearance of the red color, both the transitions being accompanied by thermoluminescence peaks.

The dependence of the thermoluminescence and fluorescence yields on the previous history of the sample was studied for potassium iodide and it was found (Fig. 5) that these are very much increased by strongly irradiating the sample at low temperature and heating it to 300°K. The samples were subjected to one or the other of the following treatments: (1) irradiating the samples at low temperature, (2) heat treatment at 300°K, and (3) combination of (1) and (2). No increase in thermoluminescence or fluorescence yield could be detected for either of the treatments (1) or (2), whereas, on the contrary, there was an appreciable increase for treatment (3). The following model is suggested to explain this result. The irradiation at low temperature produces various irregularities in the lattice, which gradually diffuse toward special sites and become stabilized. For a certain range of temperature these diffusion processes are favored without disturbing the stability of the irregularities. Consequently, irradiation, followed by heating, yields a large number of emitting and trapping centers in the case of potassium iodide.

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[8] H. F. Ivey, Phys. Rev. **72**, 341 (1947).