DESTRUCTION MECHANISM OF COLOR CENTERS AND RECOMBINATION LUMINESCENCE IN NaCl-Cd CRYSTAL PHOSPHORS

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The authors have studied the origin of integral thermoluminescence peaks and the destruction mechanism of color centers during thermal relaxation of X-irradiated NaCl-Cd phosphors. The luminescence spectra have also been studied, and previous similar results are discussed.

Introduction

Thermal bleaching of radiation-induced color centers in alkali halide crystals has recently been used to study relaxation processes, absorption bands, and the kinetic characteristics of crystal phosphors [1]. This method has been combined with that of integral and spectral thermoluminescence to study nonstationary electron-hole and ionic processes leading to recombination luminescence in excited crystals [2-4].

Changes in emission spectrum during thermoluminescence occur in alkali halides [5-8] and have recently been intensively studied; we have shown [2] that the kinetics of thermoluminescence can explain the destruction mechanism of these color centers and also the origins of the thermoluminescence.

The present paper examines the destruction mechanism and nonstationary recombination luminescence in NaCl-Cd phosphors.

NaCl-Cd monocrystals (0.001 mole % Cd) were grown from the melt by the Kyropoulos method. The specimens were excited at 295 deg K by URS-55a apparatus with a BSV-Cu tube (unfiltered Cu radiation) V = 45 kV, I = 15 ma, t = 30 min). The absorption spectra were recorded with an SF-4 spectrophotometer. The thermoluminescence spectra were recorded automatically as in [2, 3]. We recorded the bleaching curves with an SF-4 spectrophotometer and an EPP-09 potentiometer recorder.

The emission spectra were corrected for the spectral sensitivity of the FEU-29 photomultiplier, the dispersion of the SF-4, and the nonlinearity of the scan. The crystals were heated at 0.3 deg/sec.

Results and Discussion

The absorption had maxima at λ_m = 215, 240, 345, and 465 mμ, which differed in strength; those for the F-centers were strongest, by those for the 215, 240, and 345 centers.

Fig. 1 shows bleaching of the absorption bands (curves 1) and the destruction rate of the corresponding color centers (curves 1').

The F-centers are destroyed relatively simply, with a single maximum rate at 420 deg K. The other centers are destroyed in at least two stages, with maxima in the ranges 360-370 deg K and 435-445 deg K.

Comparison with the integral thermoluminescence (TL) (curve 2, Fig. 1) may explain the origin of the various peaks (see also [2, 3]).

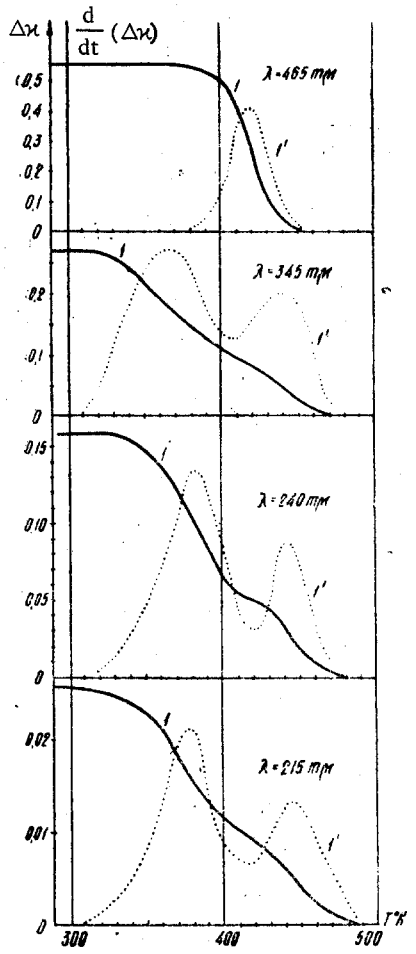
The integral TL curve of a NaCl-Cd phosphor has peaks at 380-390 deg K (I), 430 deg K (II), and 490 deg K (III). The Antonov-Romanovskii method [9] was used to determine the activation energies ε of the ionic liberation of charge carriers and recombination luminescence at 360-460 deg K, ie., for peaks I and II.

The rising branch of the TL curve for I gives ε = 0.3 eV; that branch for II, ε = 1 eV; and the falling branch for II, ε = 1.7 eV. At least three modes of destruction of color centers are needed to produce the strong peaks I and II.

Comparison of these activation energies with those of ionic processes in alkali halide crystals shows that the agents may be paired anion-cation vacancies (ε = 0.35 eV for displacement [10]) and single cation vacancies (ε = 1 eV [11]); ε = 1.7 eV may be associated with the displacement of more complex groups present at the start [12] or formed in the initial stages (ε = 0.3 and 1 eV, respectively).

Comparison of the TL curve with Fig. 1 shows which color centers yield charge carriers during destruction which then take part in radiative recombination. Peak I is connected with partial destruction of the 345, 240, and 215 centers, and II with that of the 465, 345, 240, and 215 ones. The weak third peak remains unexplained.

We have studied the spectra of the thermoluminescence peaks and the changes in the spectra during thermal relaxation: as a rule, data from such studies are discussed without regard to the relation to the destruction of color centers



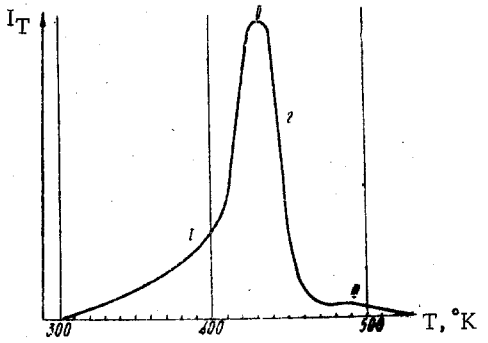


Fig. 1. Bleaching $\Delta\kappa(T)$ and integral thermoluminescence $I_T(T)$ for NaCl-Cd. (1) $\Delta\kappa(T)$; (1') $\frac{\partial}{\partial T}\Delta\kappa(T)$. The The bleaching was measured at the λ shown. (2) $I_T(T)$. (I, II, III) Thermoluminescence peaks.

and the subsequent recombination of the charge carriers.

Fig. 2 shows the thermoluminescence spectra of an X-irradiated NaCl-Cd phosphor. There are marked changes during thermal relaxation. The main feature near peak I is a short-wave band (λ_m = 350 mμ); other bands appear as the temperature approaches peak II (λ_m = 410, 450, and 550 mμ); in the peak III region the short-wave bands vanish, leaving bands with λ_m = 450 and 550 mμ, of almost identical intensity.

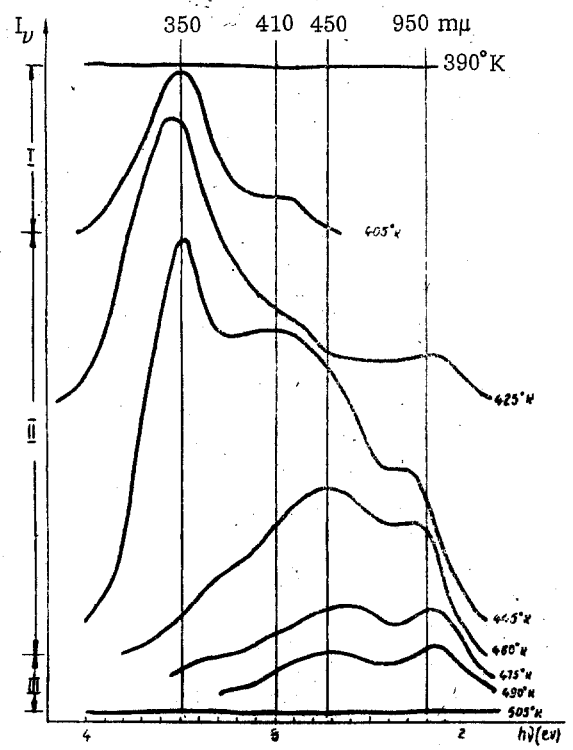


Fig. 2. Thermoluminescence spectra of NaCl-Cd at various stages.

These changes can be further examined from curves of spectral thermoluminescence (STL). Fig. 3 gives STL curves from the data in Fig. 2; the table compares the intensities with that of the 410 mμ band showing that the bands make different contributions to the three TL peaks.

Comparison with Fig. 1 shows that:

(a) The 345, 240, and 215 centers give mainly the 350 band near peak I;

(b) The 465, 345, 240, and 215 centers give the 350, 410, 450, and 550 bands near peak II;

(c) Unidentified centers give the 450 and 550 bands near peak III.

Thus each integral TL peak is formed by simultaneous destruction of several types of center and recombination of the liberated charge carriers.

The centers are destroyed by various ionic formations; in this sense, peaks I and II are not elementary [4].

These results, together with those in [2-4] for other alkali halides, lead to the following conclusions:

1. Each integral TL peak may be formed by destruc-

tion of several types of color center, followed by recombination of the liberated charge centers.

2. The centers may be destroyed during nonisothermal relaxation by ions drifting through the crystal, ionic vacancies, or groups of these.

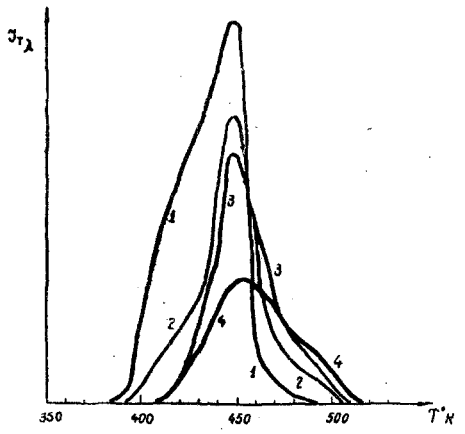


Fig. 3. Spectral thermoluminescence curves $I_{\lambda T}(T)$ of NaCl-Cd for wavelengths (mμ) of: (1) 350, (2) 410, (3) 450, (4) 550.

3. The complexity of recombination luminescence arises partly from the emission by centers of various types during capture or repeated capture of electrons at the corresponding localization centers.

4. The elementary or nonelementary nature of any integral TL peak is determined by the number of types of ion or vacancy which destroy the particular centers. An elementary TL peak is due to the destruction of several different types of center by ions or vacancies having a single ε.

Integral and spectral thermoluminescence, thermal bleaching, and photoluminescence together provide a useful method for studying the detailed mechanisms of liberation and recombination of charge carriers.

TABLE

T°K	$\frac{I_{350}}{I_{410}}$ %	$\frac{I_{410}}{I_{410}}$ %	$\frac{I_{450}}{I_{410}}$ %	$\frac{I_{550}}{I_{410}}$ %
410	333	100	0	0
445	133	100	86	40
490	0	100	157	185

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