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Spectral Studies on Single Crystal $BaBr_2$—Sn Phosphor

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The absorption spectra at 300 K, the emission and excitation spectra at 77 K and 300 K of $BaBr_2$—Sn phosphor have been studied. The complicated structure observed in the absorption and excitation spectra was connected with transitions to the components of the $^1P_1$, $^3P_1$ and $^3P_2$ excited states in tin centers which preserve the symmetry of the basic lattice. There has also been observed a complicated structure of the emission spectrum at 77 K, which unlike all alkali earth halide phosphors observed so far, manifests itself also in the visible region of the spectrum.

(Keywords: Absorption; Alkali earth; Emission; Phosphor)

Spektroskopische Untersuchungen an Einkristallen des $BaBr_2$—Sn-*Phosphors*

Die Absorptions-, Anregungs- und Emissionsspektren des Phosphors $BaBr_2$—Sn wurden bei 77 K und 300 K gemessen. Die komplizierte Struktur der Absorptions- und Anregungsspektren ist mit Übergängen zu Komponenten der Anregungszustände $^1P_1$, $^3P_1$ und $^3P_2$ des Sn^{2+} unter der Annahme zu verknüpfen, daß die Zinnzentren die Symmetrie des Grundgitters beibehalten. Für 77 K ist auch das Emissionsspektrum von komplexer Natur, was bis jetzt bei keinem Erdalkalihalogenid—Phosphor im sichtbaren Bereich beobachtet wurde.

Introduction

Recently, the s^2-configuration activators incorporated in alkali earth halides are becoming the subject of investigation[1–5]. It has been established that the bivalent activators Sn^{2+} and Pb^{2+} in $BaCl_2$ and $SrCl_2$ have absorption and excitation spectra which are similar to those of KCl—Sn and KCl—Pb. But in the emission spectra of the first phosphors several bands situated in the shortwave region are observed. Data about alkali earth bromide phosphors are lacking in literature for the present.

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Experimental

The phosphor $BaBr_2$—Sn was prepared by the *Bridgman* method. $BaBr_2$ was dried by melting in vacuum and a subsequent heating up to 250 °C in an atmosphere of HBr. The activator was incorporated as $SnBr_2$, also previously dried. The investigations were carried out on quenched single crystal plates of dimensions $10 \cdot 10 \cdot 0.7$ mm. The activator concentration was determined by atomic absorption analysis and it was found to be 25 ppm. The measurements were done in metalic cryostate at 77 K and 300 K. The absorption spectrum at 300 K was measured by means of a Cary 14 R spectrophotometer. The excitation and emission spectra were measured by a method described in [4,5].

Table 1

λ_I (nm)	Peak Position	
	in Excit. Spectra	in Abs. Spectra
350, 425, 500	208 nm	—
425, 500	220–230 nm	222 nm
500	240 nm	240 nm
425	245 nm	—
350, 500	250 nm	250 nm
500	257 nm	—
350, 425, 500	268 nm	268 nm
350, 425, 500	278 nm	expanded deformation
350, 425, 500	290 nm	293 nm
425, 500	305 nm	expanded deformation

Results

Fig. 1 shows the excitation spectra for different regions of the emission spectrum at 77 K as well as the absorption spectrum at 300 K. A comparatively good correspondence between the absorption and excitation spectra is observed, but the latter has a better expressed structure. The peak positions are given in the Table, where λ_I is the wave length of the emission for which the excitation spectrum has been studied.

The bands in the spectra can be divided into two groups. The bands of the longwave group are well separated in the excitation spectra of the visible emission, while in the absorption spectrum only one weak non-symmetric band is observed. In the excitation spectrum for the emission at 350 nm, the most longwave band at 305 nm does not appear. In all excitation spectra, one can observe deformation between 220 nm and 230 nm, which corresponds to the well resolved band at 222 nm in the absorption spectrum.

One can observe in the region of 235-280 nm in the excitation spectra five bands, which are of different relative intensity and do not correspond well in spectral position to the bands of the absorption spectrum.

In the most shortwave region, 200-220 nm, one can observe a band which is most intensive by excitation of the 425 nm emission. It probably corresponds to the great rise of absorption below 210 nm.

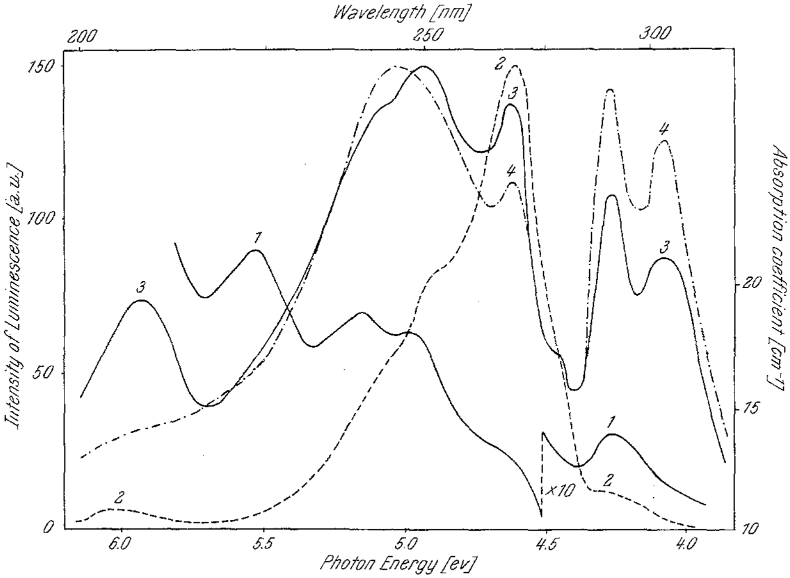


Fig. 1. Absorption spectrum (curve *1*) at 300 K and excitation spectra at 77 K, measured at: 350 nm (*2*), 425 nm (*3*), 500 nm (*4*)

The emission spectrum of the phosphor studied is complicated. For 77 K it consists of several bands located in the wide region 300-600 nm (Fig. 2 and Fig. 3). In the region 300-400 nm (Fig. 2) two bands are observed at 315 nm and 340 nm, the intensity of which depends on the wave length of the exciting light. Such a dependence is also established in the visible part of the spectrum (Fig. 3). By excitation at 205 nm, the most considerable differences in the shortwave side of the emission curves are observed. At 300 K, only one visible band exists in the spectrum. Its spectral position and halfwidth depend on the wave length of the exciting light (Fig. 4). The emission spectrum obtained by excitation at 303 nm (in the most longwave region of the absorption spectrum), irrespective of the temperature, consists of one band (Fig. 5) which moves in the longwave direction with decrease of temperature.

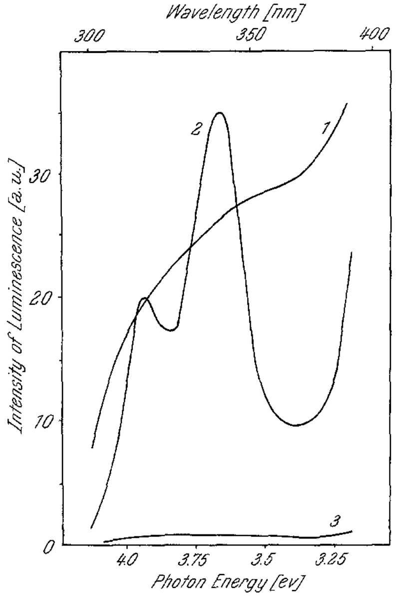


Fig. 2. Emission spectra at 77 K in the region 300-400 nm excited with: 205 nm (*1*), 250 nm (*2*), 303 nm (*3*)

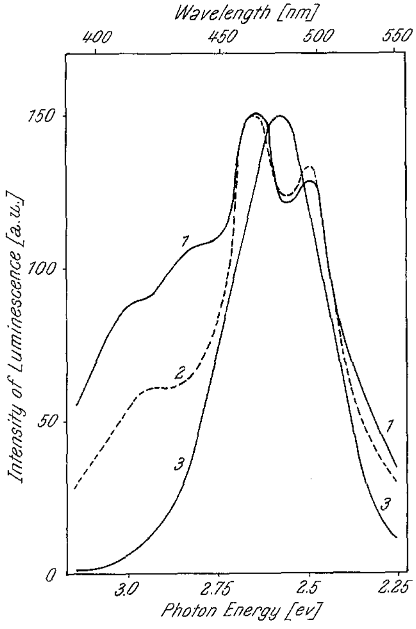
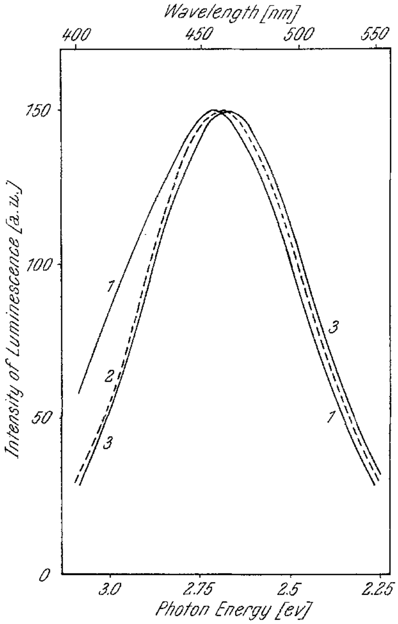


Fig. 3. Emission spectra at 77 K in the region 400-550 nm excited with: 205 nm (*1*), 250 nm (*2*), 303 nm (*3*)



ig. 4. Emission spectra at 300 K excited with: 205 nm (*1*), 250 nm (*2*), 303 nm (*3*)

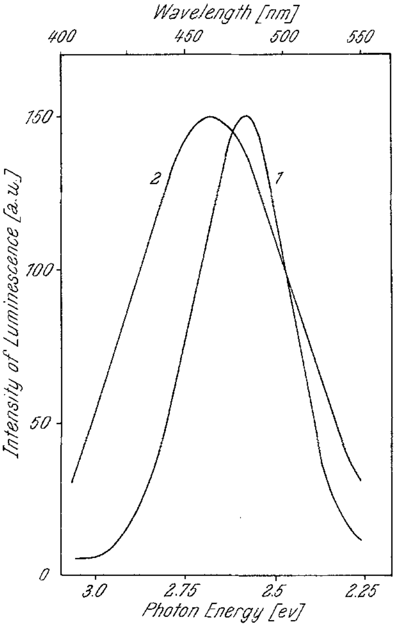


Fig. 5. Emission spectra excited with 303 nm at: 77 K (*1*), 300 K (*2*)

Discussion

We interprete the above results assuming that a type of center is formed in $BaBr_2$—Sn which has the rhombic symmetry of the host lattice. This assumption is based on the low concentration of the activators, and its electric charge being equal to that of Ba^{2+}; the quenching of the samples, the results from measurements of the excitation spectra for different regions of the emission. According to the *Bethe*'s theory[7], three bands corresponding to transitions to the components of the $^3P_1$ state (A band in the alkali halide phosphors) and three components of the C band (to the $^1P_1$ state) are to be expected. The components of the B band (vibration-induced transition to the $^3P_2$ state) can be three.

The two most longwave bands in the excitation spectra at 290 nm and 305 nm, to which an asymmetric absorption band at 293 nm corresponds, are supposed to be connected with transitions to the components of the $^3P_1$ state (A band). It can be assumed that below 77 K, a third band might be observed, corresponding to a transition to the third component of this state, just as is the case with the absorption spectrum of $BaCl_2$—Sn at 4 K.

The weak band at 278 nm in the excitation spectrum, which is nonresolved from the neighbouring more intensive shortwave band in the absorption spectrum, could be due by analogy with KBr—Sn, to a transition to the $^3P_2$ state (B_1 band). The well distinguished band at 268 nm (B_2 band) can be connected with a transition to another component of this state. Bands of similar behaviour are also observed in $BaCl_2$—Sn, and they are also considered to be B bands.

The intensive bands in the absorption and excitation spectra at 240 nm, 250 nm and 257 nm are supposed to be due to transitions to the components of the $^1P_1$ state. The band at 245 nm, which appears only in the excitation spectrum for the emission at 425 nm, although well shaped, does not appear in the absorption spectrum and can be interpreted as a result of superposition of the bands at 240 nm and 250 nm.

The bands at 222 nm in the absorption spectrum and at 208 nm in the excitation spectrum are assumed to be similar to the D and D′ bands in alkali halide phosphors. This assumption corresponds to the closer location of the D and C bands in KBr—Sn compared to KCl—Sn[6].

The great halfwidth of the emission band at 300 K and the different maxima in the spectrum at 77 K show that a great number of bands with commensurable intensity due to transitions to components of the different excited states are present in the spectrum even at 77 K (which is not the case with KBr—Sn and KCl—Sn). The emission band excited in the most longwave region of the absorption spectrum (303 nm) is considered to be due to a transition from the lowest lying components of the $^3P_1$ state.

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