

Emission Spectra of Crystal Phosphor BaCl₂-Pb

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Emission spectra of Pb²⁺ centres in barium chloride single crystals have been studied between 4 and 300 K by excitation with different wave lengths. Excitation spectra at 300 K have also been obtained by measuring the emission in the maxima of the shortwave and longwave bands. The results allow to conclude that the high energy emission band is due to the transition $|^3T_{1u} > \rightarrow |^1A_{1g} >$ in the activator ion. The more effective excitation of the low energy emission band observed in the shortwave region of the absorption spectrum and the complex nature of both bands are discussed.

1. Introduction

It is known that in the emission spectra of lead doped alkali halides two bands are present which can be excited in the "A" absorption band. The high energy emission band is connected in Ref. [1–6] with the transition $|^3P_1\rangle \rightarrow |^1S_0\rangle$ in dipole centres (Pb²⁺–V_k) which are formed at low activator concentration and quenching of the samples studied. With respect to the origin of the low energy band there are different opinions. In an earlier work it has been ascribed to the transition $|^3P_0\rangle \rightarrow |^1S_0\rangle$ [7], and later [5] to the transition $|^3P_1\rangle \rightarrow |^1S_0\rangle$. According to newer investigations of Trinkler [9] "A" luminescence of the lead-doped alkali halides is due to transitions from two types of Jahn Teller emitting minima of the $|^3P_1\rangle$ state. Marculescu et al. [10] suppose that there is a resonant energy transfer between lead centres, and they connect the low energy emission band with the transition $\mu |^1P_1\rangle + \nu |^3P_1\rangle \rightarrow |^1S_0\rangle$.

Studies of Pb as activator in alkaline earth chlorides have been carried out on sublimated phosphors [11] as well as on polycrystalline BaCl₂ samples with 5 mol% PbCl₂ [12]. Investigations on monocrystals have been performed so far only on Pb-doped strontium chloride [13].

2. Experimental Procedure and Results

The preparation of phosphors has been described in a previous work [14]. The emission and ex-

citation spectra were measured by means of a luminescence accessory Cary 1442, an optical metal cryostat, a Bausch and Lomb Monochromator together with a deuterium lamp and a photomultiplier EMI 6256.

Figure 1 shows the emission spectra from excitation with 257 nm light in the most intensive longwave absorption band at 4 K, 77 K, and 300 K. Just as with the alkali halides, two bands appear. Their spectral positions and halfwidths are given in Table 1.

The small halfwidth of the high energy band at 4 K allows to suppose that it is a single band. In accordance with this are the results given in Figure 2. But at 300 K this band is superposed by a shorter-wave band in the region 295–305 nm curve 3, Figure 1.

The longwave band is also complicated, and this is manifested not only at 300 K but even clearer at 4 K. It is possible that at 4 K the longwave shift is mainly due to the presence of a longwave component of this band. The deformation of curves 1' and 2' in the region of 450–470 nm indicates a superposition of one more longwave component in this region. Thus the longwave band in the spectrum is probably composed of 3 bands.

The intensity of the bands at 310 and 403 nm increases when the temperature goes down, and increase of the shortwave band is even higher. While at 300 K the longwave band is predominant, at 4 K it is about 40 times weaker than the shortwave band.

Figure 3 shows emission spectra at 4 K obtained by excitation in different absorption bands. The

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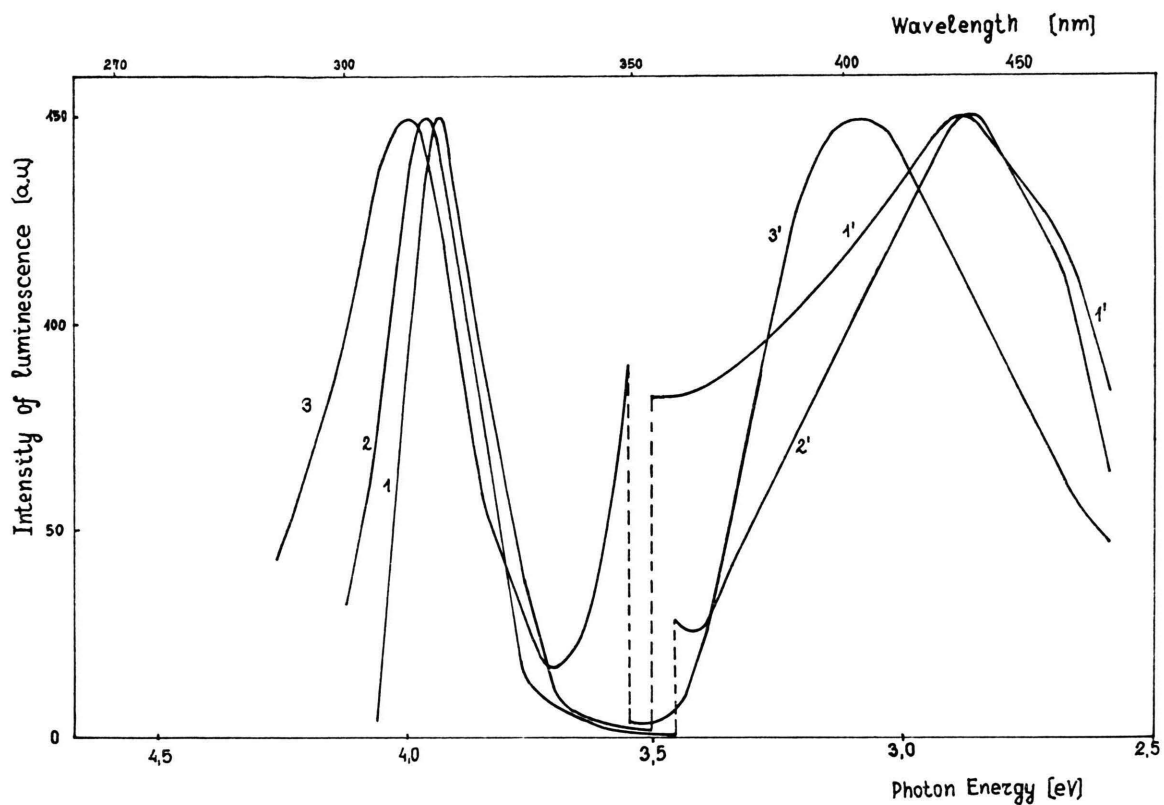


Fig. 1. Emission spectra by excitation with 257 nm at: 1,1'—4 K; 2,2'—77 K; 3,3'—300 K.

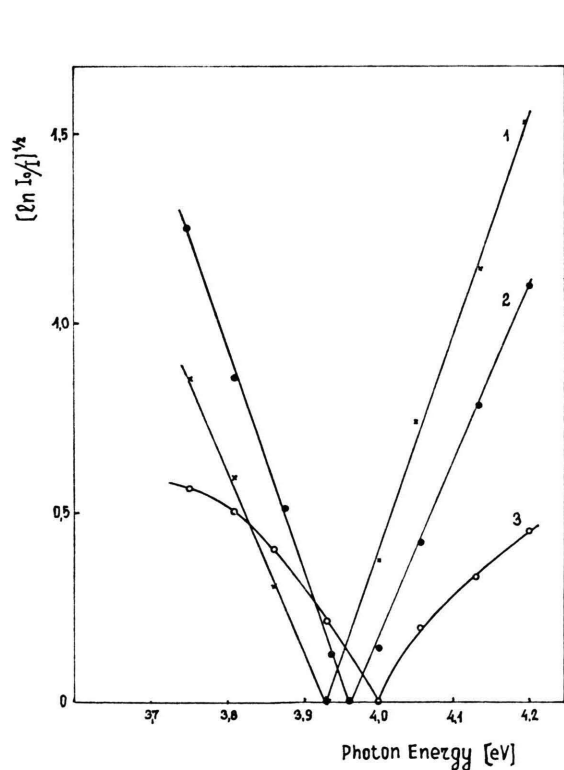


Fig. 2. Plot of $(\ln I_0/I)^{1/2}$ v.s. photon energy for the 315 nm emission band by excitation with 257 nm: 1—4 K; 2—77 K; 3—300 K. I_0 = intensity in band maximum.

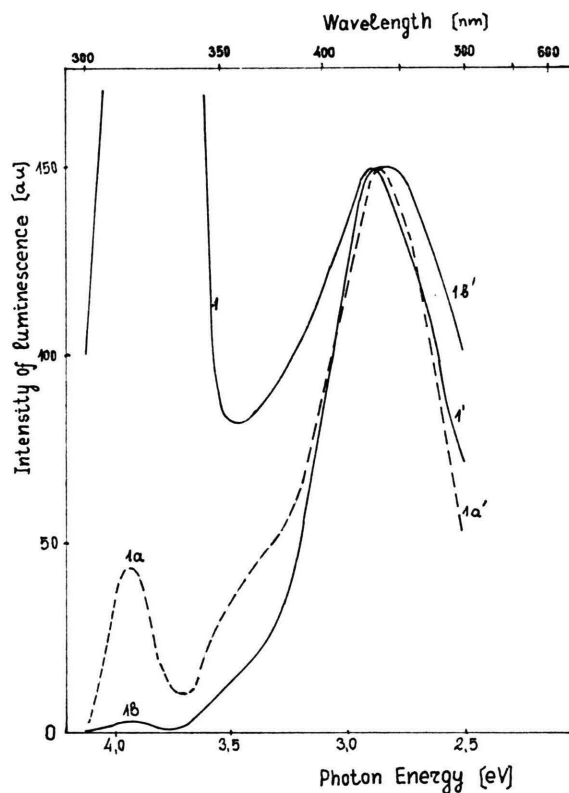


Fig. 3. Emission spectra obtained by excitation with: 257 nm—1,1'; 235 nm—1a,1a'; 215 nm—1b,1b'.

Table 1.

	Shortwave band			Longwave band	
	Peak position	Halfwidth	Intensity	Peak position	Intensity
4 K	315 nm—3.93 eV	0.20 eV	3000	431 nm—2.87 eV	70
77 K	313 nm—3.96 eV	0.23 eV	3000	435 nm—2.85 eV	50
300 K	310 nm—4.00 eV	0.30 eV	1.7	403 nm—3.07 eV	40

excitation in the most shortwave absorption band (215 nm) leads to the appearance of the longwave emission band (curve 1 b') of highest intensity. It can also be seen that in the region 350–370 nm a band appears which is most intensive by exciting at 235 nm.

Figure 4 presents the excitation spectra obtained in measuring the emission at 400 nm (curve 4') and at 310 nm (curve 4). As it can be seen from curve 4',

the longwave emission (3') can be excited not only in the region 257 nm but also with a great quantum yield in the region 200–240 nm. The maxima in the excitation spectrum 4' at 215 nm and 240 nm correspond to the absorption maxima at 214 nm and 235 nm. These absorption bands are only spurious at 300 K (curve 5), but they are well defined at 4 K [14]. The comparison of curve 4 and 4' shows that in the region 300–350 nm the longwave band 3' can be better excited than the shortwave band 3.

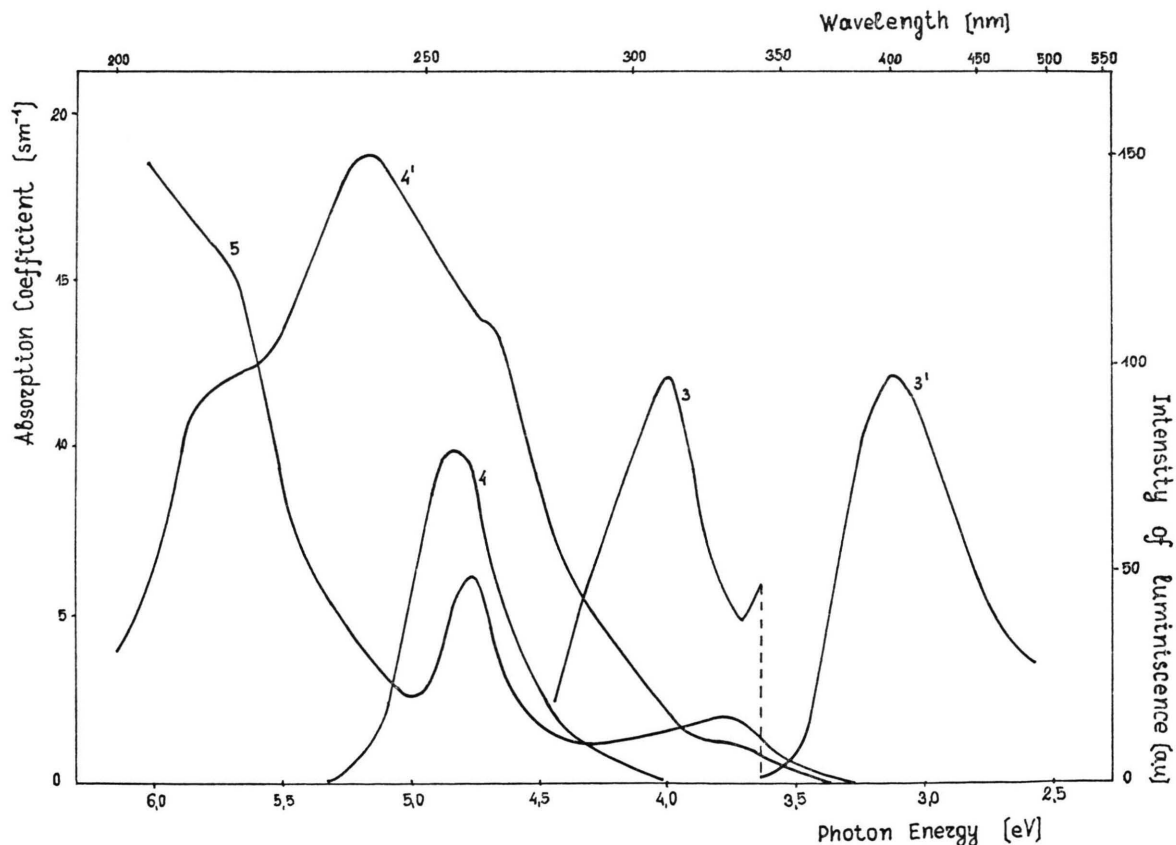


Fig. 4. Absorption, excitation and emission spectra at 300 K: 3,3' — emission spectrum by excitation with 257 nm; 4,4' — excitation spectra for 403 nm and 310 nm emission bands; 5 — absorption spectrum.

3. Discussion

The data on the dependance of the emission spectrum on the wave length of the exciting light as well as on the excitation and absorption spectra show that the high energy emission band at 310 nm should be ascribed to the transition $|^3T_{1u}\rangle \rightarrow |^1A_{1g}\rangle$ in the activator ion.

The more effective excitation of the longwave band in the shorterwave region of the absorption spectrum can be explained by the assumption that the Stokes shift between the absorption and emission bands which are due to the transitions $|^1A_{1g}\rangle \rightleftharpoons |^1T_{1u}\rangle$ is greater than the Stokes shift for $|^1A_{1g}\rangle \rightleftharpoons |^3T_{1u}\rangle$. Such a difference in the Stokes shift can be realized by an appropriate position of the potential curves corresponding to the $|^3T_{1u}\rangle$ and $|^1T_{1u}\rangle$ states.

The complex nature of the shortwave and long-wave bands is probably a result of the low sym-

metry of the centre determined by the low symmetry of the rhombic BaCl₂. This leads to splitting of the $|^1T_{1u}\rangle$ and $|^3T_{1u}\rangle$ states, which creates the possibility for several radiative transitions especially at low temperatures.

The comparison of our results with those of Bettinali *et al.* shows that there is a good coincidence in the positions of the spectral bands at 310 nm and 403 nm. The band at 350 nm is well expressed in the polycrystalline samples but in our case it only causes a deformation of the spectral curve at 340 – 380 nm. Probably this band is formed at the higher concentrations of the activator (5 mol%) in the polycrystalline samples studied [12].

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