On the Shortwave Emission of Ga-activated Single Crystals of $BaCl_2$

V. Tabakova
Institute for Physics at the University of Münster, BRD

R. Trifonova
Institute for Foreign Students, Sofia, Bulgaria

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The luminescence of $BaCl_2$-Ga single crystals at temperatures down to liquid helium under excitation with different energies is studied. The emission consists of several bands, the intensities of which depend on the temperature and the exciting energy. The excitation spectra of the different emission bands measured at 4 K, 78 K and 293 K are also reported.

The results indicate the coexistence of centres of different structure and composition. The Jahn-Teller effect might also take place.

Key words: Luminescence, Barium chloride, Emission, Excitation.

1. Introduction

During the last years, the optical properties of tin, lead and indium activated $SrCl_2$, $BaCl_2$ and $BaBr_2$ [1–8] have been studied.

In our previous work we have obtained the emission data of the $BaCl_2$-Ga phosphor at 300 K and 78 K excited by 4.87 eV light [9]. These data show that by decreasing the temperature to 78 K the comparatively symmetrical emission band at 300 K, measured in the region 3.54–2.25 eV, grows in a complicated way, and that the intensity of the emission decreases greatly. In the excitation spectrum a band with a maximum at 5.16 eV is observed.

The present work is a continuation of our previous studies on the emission of $BaCl_2$-Ga in a wide UV-spectral range at different temperatures and at different energies of the exciting light.

2. Experimental Procedure

Single crystals of $BaCl_2$ were obtained by the Bridgman method. $BaCl_2$ (Suprapur, Merck) was first heated in vacuum for 4 hours at 120 °C and then dried for 8 hours at 450 °C in an atmosphere of dried HCl. Single crystal plates were cut in $10 \times 10 \times 8$ mm dimensions. The activation was made by heating the plates at 700 °C in vacuum in the presence of gallium metal during 4 hours. After that, the plates were polished in order to remove part of the surface and emitting centres formed on it.

Before the measurement the crystal plates were quenched. We used a metal cryostat and a Cary 14R with accessory 1442 for the emission measurements. All necessary corrections in the emission spectra were made using a standard lamp – Wi/17. For the excitation, a deuterium lamp (200 W Original Hanau) and a monochromator from Bausch & Lomb with a slit-width of 0.75 mm were used. The intensity distribution of the deuterium lamp was measured by means of rhodamine B.

3. Results

The emission spectra of $BaCl_2$-Ga, excited by 4.86 eV light are given in Figure 1. It is obvious that above 3.54 eV two bands are present at 78 K. In Fig. 2 the emission in the short-wave region and the temperature interval 4–293 K is given. At low temperatures (< 145 K) two well resolved bands are observed. They have a complex structure, which is clearly seen at 145 K. The emission intensity above 3.54 eV decreases strongly with decreasing temperature.

The results obtained in the wide spectral interval 4.59–2.25 eV led us to measure the excitation spectra of the emission at 4.35 eV, 3.87 eV and 3.18 eV at dif-

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Reprint requests to Dr. V. Tabakova, Institute for Foreign Students, Assen Veltchev St. 27, Sofia 1111, Bulgaria.

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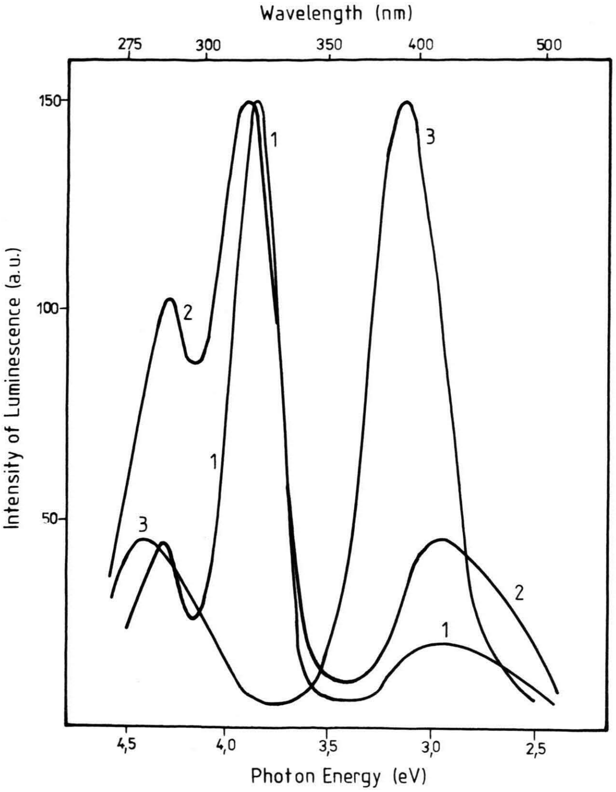

Fig. 1. Emission spectra, excited with 4.86 eV at 1: 16 K, 2: 78 K, 3: 293 K.

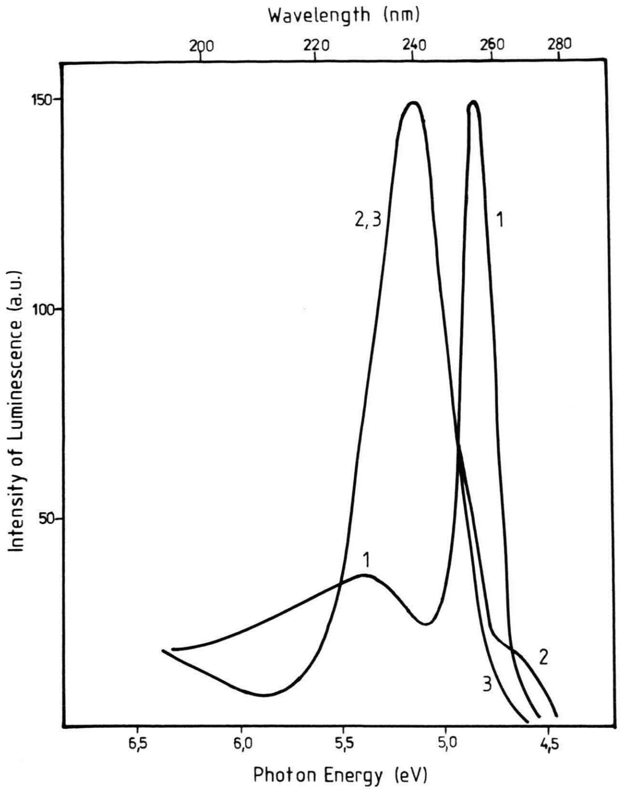

Fig. 3. Excitation spectra of the emission at 1: 3.87 eV (at 4 K), 2: 4.35 eV (at 4 K), 3: 3.18 eV (at 293 K).

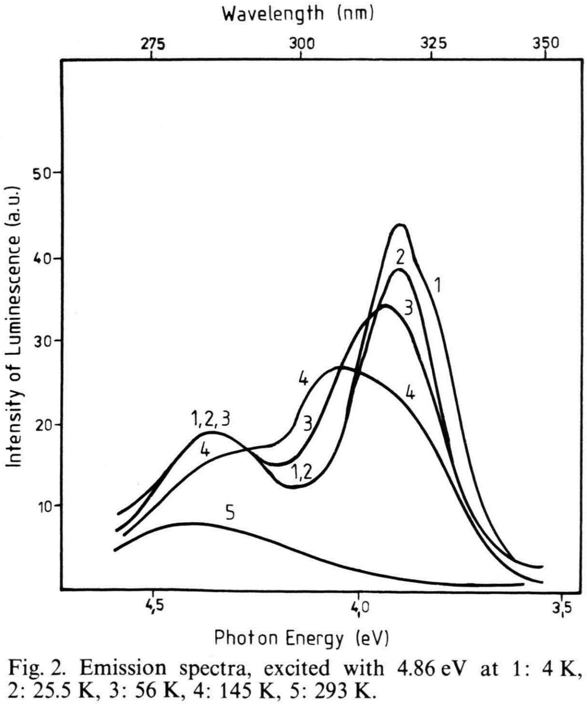

Fig. 2. Emission spectra, excited with 4.86 eV at 1: 4 K, 2: 25.5 K, 3: 56 K, 4: 145 K, 5: 293 K.

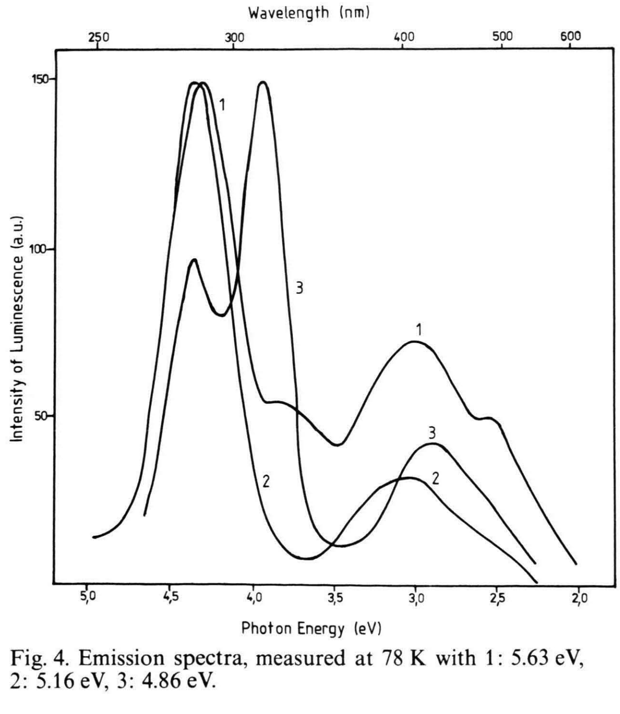

Fig. 4. Emission spectra, measured at 78 K with 1: 5.63 eV, 2: 5.16 eV, 3: 4.86 eV.

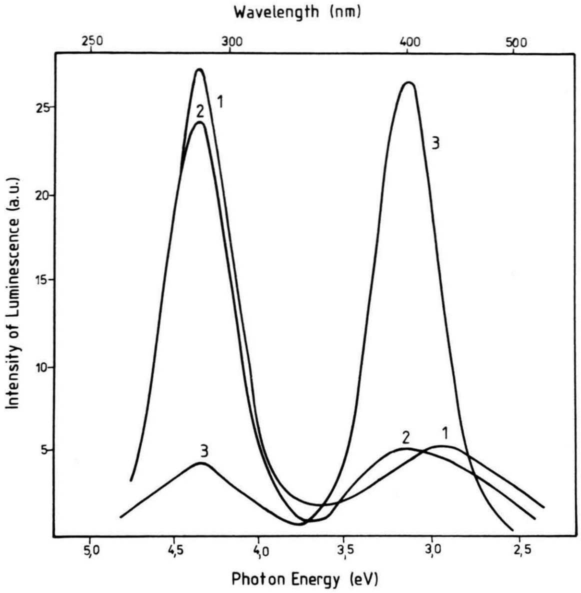

Fig. 5. Emission spectra, excited with 5.16 eV at 1: 4 K, 2: 78 K, 3: 293 K.

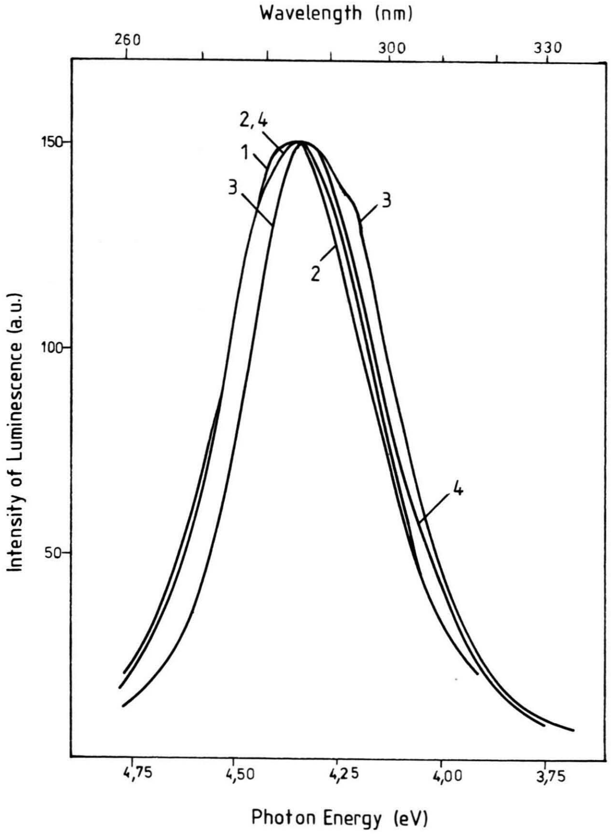

Fig. 6. Emission spectra, excited with 5.16 eV at 1: 4 K, 2: 16 K, 3: 25.5 K, 4: 78 K.

Table 1.

Exciting light (eV)	Peak position (eV)			
5.63 (at 78 K)	4.32	3.84	3.02	2.54
5.16 (at 78 K)	4.35		3.08	
4.86 (at 78 K)	4.32	3.94	2.94	2.60

ferent temperatures (Figure 3). Measurements of the excitation of the emission at 4.35 eV are made at 4 K and 78 K.

The position of the excitation maximum does not depend on temperature, but at 4 K we observed a deformation in the longwave region which is probably due to the presence of another weak band.

There are two well-resolved bands in the excitation spectrum of the 3.87 eV emission at 4 K. It is obvious that the excitation spectra of the 4.35 eV and 3.87 eV emission are similar; only the relative intensity of the bands is different: the shortwave band is more intensive in the excitation spectrum of 4.35 eV emission; in the excitation spectrum of 3.87 eV emission it is opposite. A structure is not observed in the excitation spectrum of 3.18 eV emission at 293 K. The character of the intensity distribution around the maximum of the excitation spectra of the emission bands 4.35 eV and 3.18 eV involves the existence of more closely situated bands which even at 4 K cannot be resolved. An analogous behaviour is observed for example in KCl doped with lead.

Detailed measurements of the emission by excitation with 5.63 eV and 5.16 eV were made at different temperatures. The results are given in Figs. 4 and 5. An exciting light of 5.63 eV is chosen in the excitation spectrum in order to exclude the excitation of emission bands with maxima at 4.35 eV and 3.18 eV. One can see in Figs. 4 and 5 that there are differences in the number of bands and their spectral position depending on the exciting light (Table 1). Especially complicated is the spectrum obtained by excitation with 5.63 eV.

Figure 6 presents the shortwave emission excited with 5.16 eV in the temperature interval 4–293 K.

4. Discussion

Replacing Ba^{2+} by Ga^+ in the $BaCl_2$ lattice requires the formation of charge compensating anionic vacancies (V_a^+). These vacancies can be situated in a different neighbourhood to the activator, and this explains the formation of different optical centers.

In the unit cell of the rhombic crystal lattice of $BaCl_2$ there are nine Cl^- around every Ba^{2+}. Seven of them are at equal distances and the other two are further removed from Ba^{2+}. With Ga^+ and V_a^+ as first neighbour, centre associates ($Ga^+V_a^+$) with C_1, C_s and C_{2v} symmetry can be formed. In our opinion it is logical that a larger quantity of centres with C_1 symmetry will be formed because there are 6 places of V_a^+ around Ga^+ with C_1 symmetry. The other two kinds of centre associates would be formed in smaller quantities.

Besides that, probably simple Ga^+ centres with C_{2v} symmetry are formed. The ratio of the ionic radii of Ga^+ and Cl^- (0.62) is much smaller than the minimal ratio which must be realised in the $BaCl_2$ lattice [10]. That is why one should also consider the formation of simple Ga^+ centres with higher symmetry (octahedral) especially during the activation of the $BaCl_2$ single crystals. This should lead to microregions with cubic symmetry in the rhombic $BaCl_2$ lattice.

The good quenching of the crystals done by us before every measurement and the multiple repetition of the obtained results give us reason to accept a stable statistical distribution of the different kinds of centres in the investigated phosphor.

The experimental results indicate that at least two types of Ga^+ centres, with absorption in the same spectral region, are formed in the phosphor. So it is very difficult to choose the energy which should excite only one of these centres.

In our opinion the emission (at exciting energy of 5.16 eV) at 4.35 eV and 3.08 eV (Fig. 5) is connected with one kind of these centres and the emission at 3.90 eV and 2.60 eV (Fig. 1) with an other one. The formation of two kinds of centres is confirmed by the excitation spectra of the investigated phosphor too. The observed temperature variation of the spectral distribution of the emission excited by 5.16 eV (Fig. 5) lets us assume that, similar to Ga^+-activated alkali halides [11], in the processes of emission of one type of centres the Jahn-Teller effect plays a role. The data given in Fig. 6 indicates the existence of different minima on the APES (Adiabatic Potential Energy Surface) of the lowest excited state of the activator in the mentioned centres. At excitation with higher energy photons (5.63 eV) a settlement of different minima on the APES of the excited states of centres with different symmetry could take place, which is the reason of the observed complicated spectrum in Fig. 6, curve 1. Additional investigations of the polarization of the emission, the life-time of the excited state and the absorption of $BaCl_2$-Ga would give more information about the composition and the symmetry of the emitting centres.

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