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## Luminescence of orthorhombic $\text{PbF}_2$

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**Abstract.** The results of a study of luminescence in orthorhombic and cubic monocrystals of  $\text{PbF}_2$  are presented in this paper. The luminescence properties of the orthorhombic structure phase of  $\text{PbF}_2$  are quite different from those of the currently well known cubic  $\text{PbF}_2$ , but correlate very well with the properties of  $\text{PbCl}_2$  and  $\text{PbBr}_2$ , which also have the orthorhombic structure. The explanation of the observed results on the basis of the self-trapped exciton model is suggested.

### 1. Introduction

An extremely dense ( $\rho \simeq 8 \text{ g cm}^{-3}$ ) crystal of  $\text{PbF}_2$  is a very attractive material for use as a scintillator. However, its usefulness is reduced because of the absence of scintillations detectable at room temperature. The inactivity of  $\text{PbF}_2$  results from the fact that its luminescence existing at liquid helium temperatures is rapidly quenched upon raising the temperature [1, 2]. The reasons for this quenching are not clear yet. A too rich spectrum of luminescence with many different bands, observed by different authors, made it difficult to give a united interpretation of the processes in this material. Firstly only one band of emission was observed in this material [1], then two [3] and three bands [2] all having the excitation in the exciton position region and thus claiming to the role of fundamental intrinsic states. In this paper we propose the new interpretation of the results observed earlier, which is based on taking into account the possibility for  $\text{PbF}_2$  to be in two different structure modifications under normal conditions: cubic and orthorhombic. Our results allow us to suggest a generalized picture for excitonic states in the series of related compounds with the orthorhombic crystal structure:  $\text{PbF}_2$ ,  $\text{PbCl}_2$  and  $\text{PbBr}_2$ .

Up to now spectroscopically studied  $\text{PbF}_2$  crystals (except in [4, 5], which will be discussed below) were treated as having the cubic structure. The crystals with only the cubic structure can be produced using the Bridgman method for growing bulk monocrystals of  $\text{PbF}_2$ . However, at temperatures lower than  $310^\circ\text{C}$ , the cubic phase is quasistable [6] and the transformation to the stable, orthorhombic phase may occur, and actually does under some conditions. This possibility must be taken into account because, as will be shown below, it affects significantly the luminescence spectrum of the studied samples.

The samples with low-temperature, orthorhombic structure may be grown using the low-temperature synthesis technology—the deposition from solution at room (or slightly higher) temperature. This is a common technology for the production of raw material powder of  $\text{PbF}_2$ . However, the properties of the powder may significantly differ from those of the bulk monocrystals. Thus, the spectroscopic study of the orthorhombic  $\text{PbF}_2$  powder

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might give unreliable results. The basis for our study was that we had found another method to prepare the orthorhombic phase. We found that immersing in water facilitates the phase transformation [7]. Exposure to water at room temperature makes it possible to fully transform the initially cubic crystals of 2–3 mm in size into an orthorhombic structure within a few hours. This cannot be a growth process, but only a phase transformation. Thus, the process of new impurity introduction is absent. This gave us the opportunity to study the luminescence of the same sample in different phase states. In addition, we were able to compare the luminescence results taken from our samples with those obtained on small-size orthorhombic  $\text{PbF}_2$  crystals grown from a solution [8].

## 2. Experimental details

The cubic structure samples of  $\text{PbF}_2$  were transformed to the orthorhombic form in twice-distilled water. After the transformation they had porous structure and looked like pieces of sugar with the same external dimensions as previously. Under the microscope they looked like a thin-plate compact consisting of transparent thin plates connected to each other. According to the x-ray diffraction analysis, the transformed samples were purely orthorhombic and did not contain the cubic phase. The orthorhombic  $\text{PbF}_2$  crystals grown from solution were thin plates  $\simeq 2 \times 2 \times 0.05$  mm in size.

The spectroscopic studies were performed from room to liquid helium temperature using a cryostat with windows. The set of spectroscopic equipment included a Monospec 60 monochromator and a photomultiplier. The luminescence was observed from the excited surface in the  $90^\circ$  configuration. To excite the luminescence, radiation of an EMG 102 MSC pulsed excimer laser on KrCl ( $\lambda = 222.9$  nm,  $h\nu = 5.563$  eV,  $\tau \simeq 14$  ns) was used. To measure the pulsed signal produced by the photomultiplier, an SR250 boxcar averager was used. To measure the reflectance, the emission of a deuterium lamp was used.

## 3. Experimental results

The radiation used produces excitation almost into the level of free excitons in  $\text{PbF}_2$ . The positions of the exciton levels were defined from the reflection spectra (figure 1). The results for the cubic samples (figure 1(a)) correlate with those in [1]. In the orthorhombic  $\text{PbF}_2$ , the exciton position is  $E \simeq 5.8$  eV at liquid helium temperature and shifts to low energies with increasing temperature (figure 1(b)).

Figure 2(a) shows the luminescence spectrum of cubic  $\text{PbF}_2$ . Cubic monocrystals from four different sources (containing, therefore, different microimpurities) were tested in this work. Nevertheless, the spectra appeared similar. An intensive band with  $E = 4.0$  eV and a weak one with  $E = 3.2$  eV were detected. The lifetime of the emission with  $E = 4.0$  eV ( $\tau \simeq 200$   $\mu\text{s}$  at  $T \simeq 2$  K) correlates with that in [2].

Especially important is the fact that the luminescence was excited on the surfaces produced by cleavage. If the studied crystals are prepared using optical treatment they will contain a mechanically damaged surface layer. To get a 'real' surface, etching must be used. However, a water containing etchant can stimulate a phase transformation in the near-surface area (optical treatment is also in the presence of water). The luminescence spectrum of crystals prepared in such a way contains weak emission with  $E \simeq 2.2$  eV (figure 2(b)). The relative intensity of this emission may vary from crystal to crystal.

The transformation from the cubic to orthorhombic phase might be stimulated also by mechanical stress [4, 5, 6]. Figure 2(c) shows the luminescence spectrum of the stressed

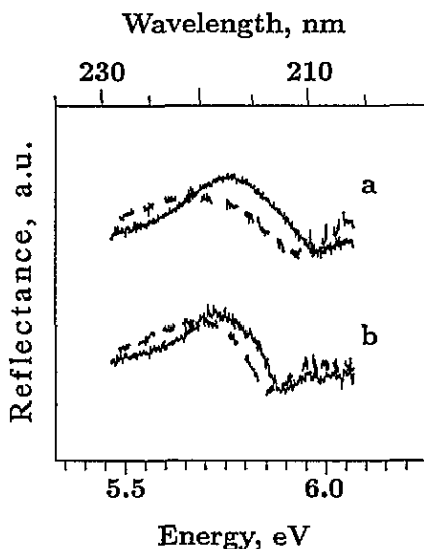


Figure 1. Reflection spectra of  $PbF_2$  with cubic (a) and orthorhombic (b) structure at different temperatures: 5 K—solid curve, room temperature—dashed curve.

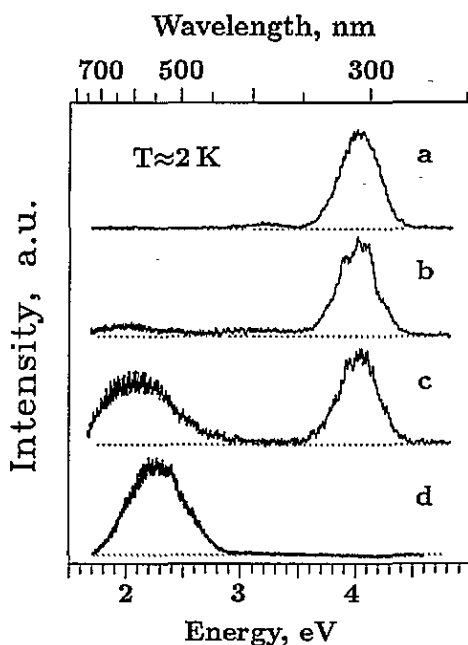


Figure 2. Luminescence spectra of  $PbF_2$  with cubic (a), mixed—'cubic + orthorhombic' (b), (c) and orthorhombic (d) structure.

sample. X-ray diffraction testing detects the presence of both cubic and orthorhombic phases in the volume of such a sample. When studying the luminescence, in addition to the band  $E = 4.0$  eV, emission with  $E \approx 2$  eV appears in this sample too.

Figure 2(d) shows the luminescence spectrum of the orthorhombic  $PbF_2$  produced by the transformation in water. The same spectrum was observed for the samples grown from

solution. A slightly broader but similar band with  $E \simeq 2.2$  eV was observed on samples isostatically transformed using a method like that described in [5].

The bands  $E = 4.0$  eV in figure 2(b) and figure 2(c) look like a compound band. This may be due to the distortions in the interfaces which separate the different structure phase areas on the studied surfaces. For the aims of this paper it is important that the spectra in figure 2 display the qualitative changes in the luminescence of different  $\text{PbF}_2$  samples. The luminescence intensities differ slightly for different samples. In figure 2 they are normalized.

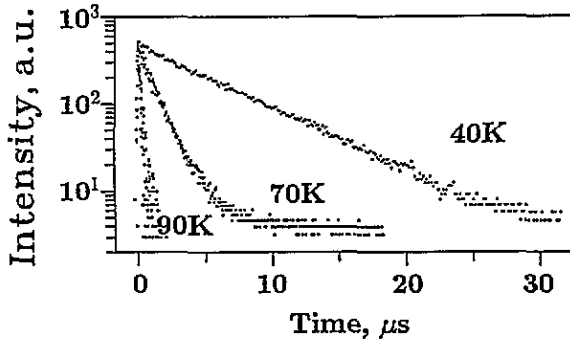


Figure 3. Decay curves of luminescence of orthorhombic  $\text{PbF}_2$  at different temperatures.

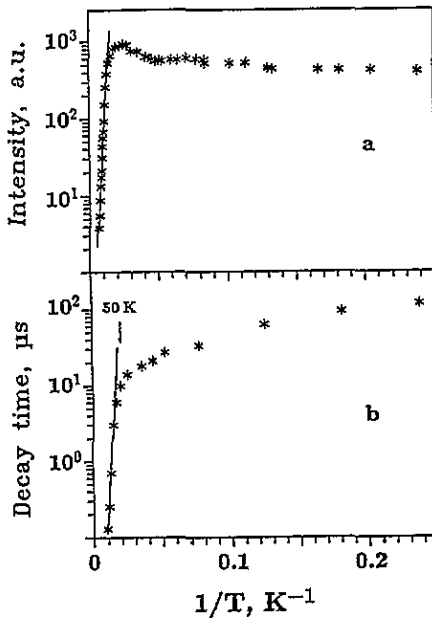


Figure 4. Temperature dependences of the intensity (a) and lifetime (b) of the emission in orthorhombic  $\text{PbF}_2$ . The fall-off regions of both dependences are approximated by an exponent with the same index ( $E_Q = 55$  meV).

The shape of the luminescence band  $E = 2.2$  eV observed in the water transformed samples does not significantly change with increases in temperature up to 150 K. Decay dependences are approximately single exponential (figure 3) and do not change (significantly) within the band width. Figure 4 shows the temperature dependences of the

integral intensity (figure 4(a)) and lifetime (figure 4(b)) of this emission.

#### 4. Discussion

The fact that the same luminescence bands appear in the spectra taken from orthorhombic crystals of different origin shows the fundamental nature of this emission. We treat the band with  $E = 2.2$  eV as radiative recombination of self-trapped excitons (STEs) in orthorhombic  $\text{PbF}_2$ . A similar band was observed earlier [3, 2], but was attributed in [2] to the presence of uncontrolled impurities. That fact that water facilitates the phase transformation together with the fact that water is present in the process of optical sample preparation allow us to suggest another reason for the registration of band  $E = 2.2$  eV in these papers. It is the presence of the orthorhombic phase in the initially cubic samples that explains, in our opinion, the spectra in [2, 3]. We observe a similar result on the samples prepared using optical treatment (figure 2(b)).

In [2] there was also detected a band  $E = 4.4$  eV which was not observed in our experiment. This may be due to a different method of excitation. The excitation method we used—the discrete laser line—does not allow us to fully repeat the conditions produced in [2] (the excitation spectrum of band  $E = 4.4$  eV has a sharp maximum at  $E = 5.39$  eV). Thus, the intensity of this band may be too low under our conditions. On the other hand, the excitation spectrum of band  $E = 2.2$  eV has a tail in the region of our laser line. Hence, the excitation conditions for the observation of this band appear similar and the observed results coincide.

In the series of related compounds— $\text{PbF}_2$ ,  $\text{PbCl}_2$ , and  $\text{PbBr}_2$  (studied earlier as bulk monocrystals [1, 9])—lead fluoride drops out because it is initially synthesized with the cubic structure, whereas the others have the orthorhombic one [10]. Therefore, it is the luminescence of orthorhombic  $\text{PbF}_2$  that should be compared with the known spectroscopic data on  $\text{PbCl}_2$  and  $\text{PbBr}_2$  (table 1). The band  $E = 2.2$  eV in  $\text{PbF}_2$  may be related to 'blue emission' bands in  $\text{PbCl}_2$  and  $\text{PbBr}_2$ . The band  $E = 4.4$  eV (detected in [2]) may be related to 'UV emission' bands in  $\text{PbCl}_2$  and  $\text{PbBr}_2$ . It is the luminescence Stokes shifts determined from these bands which demonstrate the tendency expected in the series from  $\text{PbBr}_2$  to  $\text{PbF}_2$  (see table 1). All these bands have excitation spectra near the exciton positions in the corresponding materials [1, 2, 9]. The dependence of the intensity on the temperature we measured (figure 4(a)) correlates with those observed in  $\text{PbCl}_2$  and  $\text{PbBr}_2$  [1] too. Thus, the orthorhombic  $\text{PbF}_2$  luminescence results agree well with those observed for orthorhombic  $\text{PbCl}_2$  and  $\text{PbBr}_2$ .

Table 1. Spectral data for  $\text{PbBr}_2$ ,  $\text{PbCl}_2$  and  $\text{PbF}_2$ .

Material	$E_{\text{ex}}$ (eV)	uv emission		Blue emission	
		$E_{\text{UV}}^{\text{max}}$	$E_{\text{ex}} - E_{\text{UV}}^{\text{max}}$	$E_{\text{bl}}^{\text{max}}$	$E_{\text{ex}} - E_{\text{bl}}^{\text{max}}$
$\text{PbBr}_2$	4.0	3.3	0.7	2.75	1.25
$\text{PbCl}_2$	4.7	3.75	0.95	2.8	1.9
$\text{PbF}_2$ , orthorhombic	5.8	4.4	1.4	2.2	3.6
$\text{PbF}_2$ , cubic	5.8	4.0	1.8	3.2	2.6

The luminescence spectrum of cubic  $\text{PbF}_2$  differs greatly from that of the orthorhombic sample, but correlates very well with the luminescence of  $\text{Pb}^{2+}$  centres in cubic KBr, KCl [1], and NaCl [11]. When interpreting the weak band which corresponds to that we observed

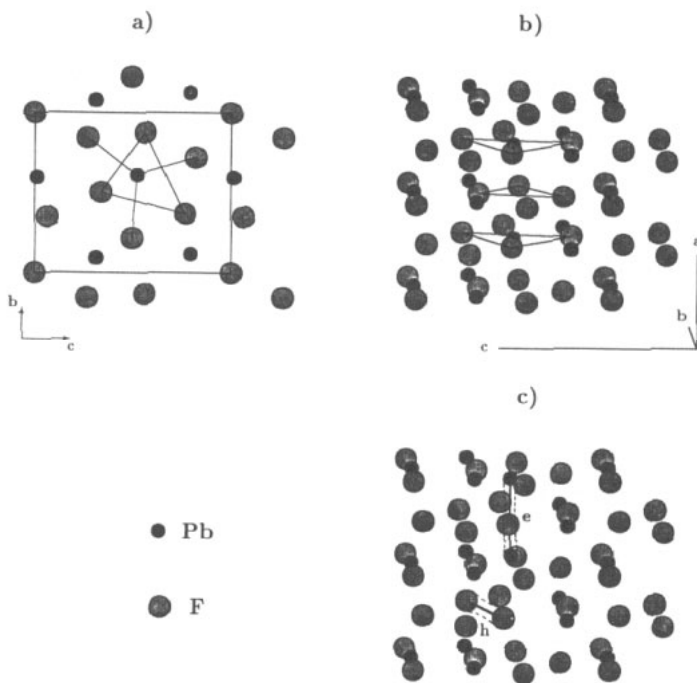
at  $E = 3.2$  eV (see figure 2(a)), the authors of [11] stressed its relation with the neighbouring pairs of lead ions. In  $\text{PbF}_2$  all lead ions have neighbours and the pairing may occur, but we believe this pairing has much more fundamental reasons. We suppose that in our case this emission is due to the self-trapped excitons in cubic  $\text{PbF}_2$ . The pairing of lead ions is the typical construction feature of the self-trapped excitations in the lead-halogen compounds, and the results of the presence of such pairing were detected recently in orthorhombic  $\text{PbCl}_2$  [12]. Here we will discuss the possible construction of the STE in orthorhombic  $\text{PbF}_2$ , which can explain the observation of band  $E = 2.2$  eV in our samples.

The pairing of halogen ions is a typical feature of the STE in the alkaline and alkaline earth halogenides [13]. The reason for this pairing is the self-trapping of the hole. The hole belongs to the  $p$  shells of halogens in these compounds. It is this fact (the  $p$  shells have well direction oriented wave functions) that is the basis of the pairing. The socialization of the hole between two nearest halogen ions is profitable thus decreasing the whole energy of the state. The large shifts of halogen ions from their regular positions occur as the result of such pairing [13].

In lead fluoride the situation, at first sight, is more complicated. Due to the results of the energy band structure calculations [14, 15, 16] in  $\text{PbF}_2$  both the conduction band (the first unoccupied band) and the top of the valence band (fully occupied band) are formed mostly of the electron shells of lead ions ( $p$  and  $s$  orbitals respectively). The halogen  $p$  levels lie deeper (but not much) in the valence band. Thus, at first the exciton in  $\text{PbF}_2$  may be treated as the excitation in the electron shells of the lead ion ( $\text{Pb}$  exciton), and this was used for the interpretation of the 'UV emission' band in  $\text{PbF}_2$  and other lead compounds [1, 2]. However, when taking into account the local structure relaxations, occurring near the excitation, another possibility may arise too. This is the self-trapped exciton, in which the electron is self-trapped on the lead pair and the hole is self-trapped on the fluorine pair. To make the appearance of this possibility clearer let us discuss the structure of orthorhombic  $\text{PbF}_2$ .

Figure 5(a) shows the well known projection along the  $a$  axis of the structure of orthorhombic  $\text{PbF}_2$  [17]. Along the  $a$  direction it consists of separate layers of ions. Each two layers construct the elementary cell. Figure 5(b) shows five sequential layers of the structure. All those ions which are given in figure 5(a) are also shown on figure 5(b). The bonds shown select the triangular groups of ions (one triangle of only fluorine ions and two triangles with the leads in the centres) which are important for the following discussion.

The self-trapping of the electron on the pair of lead ions was detected recently in orthorhombic  $\text{PbCl}_2$  [12]. It is the orientation of the pair along the  $a$  direction which follows from the results of EPR studies given in this paper. The additional self-trapping electron lies in the  $p$  shell of the leads thus producing the binding orbital between two lead ions (from upper and bottom triangles in figure 5(b)). However, only the orientation (the symmetry of the state) can be detected in the EPR studies, and not the real position of the lead ions in this state. We suppose that the large shifts of lead ions from their regular positions occur when the self-trapping of the exciton state occurs. The lead ion from the bottom triangle shifts somewhere closer to the position of the upper lead ion, thus producing a close pair and leaving its regular position empty (figure 5(c)). The absence of lead  $s$  electrons from the bottom fluorine triangle produces a local electron state situation like that in the alkaline and alkaline earth halogenides, thus leading to the possibility of fluorine ion pairing ( $V_K$  centre). The self-trapping of the hole on the fluorine pair is quite energy profitable [13] and can shift the level position very high into the forbidden gap. Thus, our model of STE in  $\text{PbF}_2$  can explain the large Stokes shift, which we detect in the luminescence of our samples (see table 1).



**Figure 5.** (a) (100) projection of the orthorhombic  $\text{PbF}_2$  structure. (b) Ion configuration around the site for the STE. (c) Suggested structure of STE in orthorhombic  $\text{PbF}_2$ . The bonds show possible pairs of lead (e) and fluorine (h) in the STE.

Because of the large space shifts of ions in our model there may exist an energy barrier on the local configuration energy curve between the two possible exciton states: the symmetric exciton (Pb exciton [1, 2, 3, 5, 9], on-site exciton) and the non-symmetric exciton (STE, off-site exciton). This barrier is due to the necessity for bottom lead ions to penetrate through the fluorine triangle (figure 5(b)). Perhaps that is why there can be simultaneously detected both bands: 'UV' and 'blue emission'. Large space separation of the charges (electron and hole) and material (lead pair and halogen pair) in the STE may be responsible for many special effects in lead halogenides. The temperature activated disintegration of the STE with further separation of the charges is responsible, we believe, for the temperature dependences of the intensity (quenching) and decay time of luminescence (figure 4). The disintegration of the STE with the separation of the different parts—the lead pair and the fluorine pair—may be the first step in the irreversible photochemical decomposition with the formation of colloidal lead particles observed in lead halogenides [18]. However, further studies of this object are required to confirm our model.

Thus, we consider the band with  $E = 2.2$  eV, observed in the luminescence of orthorhombic  $\text{PbF}_2$ , as having a fundamental, excitonic (not impurity assisted) origin. This emission (with the same spectrum profile) was detected on our samples under x-ray excitation too [19] (at room temperature), but with very weak intensity. The penetration of the 30 keV x-rays into the volume of the samples is not too deep. Thus, it is possible to observe the excited emission on our non-bulk-transparent, water transformed samples. Another case is the use of high-energy  $^{60}\text{Co}$  irradiation [5]. This radiation penetrates very deeply and it will be problematic to collect the excited emission. This may be why the



different spectrum of luminescence was observed in this work (at room temperature) on the isostatically transformed samples. Also a different spectrum was observed on the sample transformed to orthorhombic phase at high temperature and high pressure. This sample was transparent, but due to the method of preparation we believe it could have many point defects, which might affect the luminescence spectrum, making it broad and featureless (with weak integral intensity in addition). The presence of such defects may be derived from the view of the thermoluminescence spectrum of this sample [5]. Thus, the main reason for the non-detection of luminescence in this work we attribute to the temperature of observation (room temperature). At low temperatures we observe the emission on the samples prepared in a similar way (figure 2(c)).

## 5. Conclusions

The complex luminescence, observed in  $\text{PbF}_2$ , may be decomposed in two parts taking into account the possibility for  $\text{PbF}_2$  to be in two different structure modifications under normal conditions: cubic and orthorhombic. The observed luminescence properties of orthorhombic  $\text{PbF}_2$  correlate well with the properties of other orthorhombic lead halogenides. The suggested model of STE construction in  $\text{PbF}_2$  may explain the observed results.

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