

# Electronic Excitations and Defects in New Laser Crystals $\text{APb}_2\text{X}_5$ ( $\text{A}=\text{K}, \text{Rb}$ ; $\text{X}=\text{Cl}, \text{Br}$ )<sup>1</sup>

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**Abstract** – The paper presents the results of a time-resolved low-temperature (8 K) vacuum ultraviolet spectroscopy study of a low-phonon-frequency, nonhygroscopic host crystal family  $\text{APb}_2\text{X}_5$  ( $\text{A}=\text{K}, \text{Rb}$ ;  $\text{X}=\text{Cl}, \text{Br}$ ). Time-resolved photoluminescence (PL) spectra in the energy range from 1.2 eV to 4.1 eV, time-resolved PL excitation spectra in the broad energy range from 3.7 eV to 20.6 eV, effectivity and decay kinetics of PL were measured for  $\text{APb}_2\text{X}_5$  single crystals using synchrotron radiation. Research results of the excitonic states and the processes of the radiative relaxation of electronic excitations in pure crystals were presented. Variety of the channel of the radiative relaxation of host electronic excitations was observed. This variety mainly can be related with the peculiarity of the electron lattice structure.

## 1. Introduction

Search for new matrices for solid-state lasers, generating in mid IR spectral region [1] led to occurring new family of the rare earth ions doped (potassium, rubidium)-lead double (chloride, bromide)  $\text{APb}_2\text{X}_5$ : RE ( $\text{A}=\text{K}, \text{Rb}$ ;  $\text{X}=\text{Cl}, \text{Br}$ ) crystals, which are promising new materials emitting in wide spectral region from UV up to mid IR. The  $\text{APb}_2\text{X}_5$  crystals have low hygroscopicity, good mechanical properties and low phonon spectrum. A friable structure gives an opportunity for variation of composition and properties of the crystals and discovers prospects of their use as matrices, doped by rare earth ions [2].

Present study touches upon the problem of researching excitonic states and luminescence for pure  $\text{APb}_2\text{X}_5$  crystals. This study continues cycle of researches, commenced in [3–7], the purpose of which is study the excitonic states, processes of radiative relaxation of electron excitations and energy transfer both for pure and rare earth (RE) ions doped  $\text{APb}_2\text{X}_5$  crystals by means of time-resolved low temperature luminescence VUV spectroscopy method under selective synchrotron radiation (SR) excitation.

## 2. Experimental details

All the examined  $\text{APb}_2\text{X}_5$  crystals were grown by Stockbarger method in the Institute of Mineralogy &

Petrography. The samples were prepared in the form of plane-parallel plates  $7\times 7\times 1$  mm<sup>3</sup> in size with polished laser-quality surfaces. Time-resolved and steady-state photoluminescence (PL) spectra in the energy range from 1.2 eV to 4.1 eV, PL excitation spectra and reflectivity in the broad energy range from 3.7 eV to 20.6 eV, and the decay kinetics of PL were measured for  $\text{APb}_2\text{X}_5$  single crystals at the SUPER-LUMI station of HASYLAB using SR [8]. Measurements were carried out at  $T=8$  K using helium cryostat, providing the vacuum, which is not worse than  $7\times 10^{-10}$  Torr. The 0.3 m ARC Spectra Pro-300i monochromator and either R6358P (Hamamatsu) photomultiplier, or CCD camera were used as a registration system.

## 3. Results and Discussion

Monotonic exponential rise, corresponding to the fundamental absorption edge of the crystals, of the absorbance at 80 K begins in the range of 3.3–3.5 eV for bromides and 4.0–4.1 eV for chlorides. At temperature increasing it is observed a typical shift of the fundamental absorption edge to the range of smaller energy (red shift). In Fig. 1 fragments of the reflection spectra, measured in the fundamental absorption edge range of the  $\text{APb}_2\text{X}_5$  crystals at different temperature are presented. From this figure we may conclude that the reflection spectra of the  $\text{APb}_2\text{X}_5$  in 3.7–4.7 eV range contain the peaks, position of which depends on composition of A- and X-crystal components. Typical shape of the reflection spectra, temperature dependences allows us to relate these peaks with manifestation of large radius excitons. Analysis of the excitonic peaks position, carried out in the framework of the Wannier-Mott's hydrogen-like model [9,10], allows to determine energy gap  $E_g$  and exciton binding energy  $R$ , (Table 1).

PL of the  $\text{APb}_2\text{X}_5$  crystals at 8 K contains the broad nonelementary bands in energy range of 1.6–2.9 eV, spectral profile and maxima position of which depends both on composition of A- and X-crystal components and excitation energy (Fig. 2). Ultraviolet PL band at 3.65 eV was observed only for KPC crystal (Fig. 2). This band is observed only at temperature

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below 15 K. Two fast exponential components ( $\tau_1 = 0.77$  ns,  $\tau_2 = 3.5$  ns) and millisecond component are selected in decay kinetics of this band.

In the excitation spectra some peculiarities are seen in the range of the maxima of the excitonic absorption and energy gap  $E_g$  (Fig. 3–4).

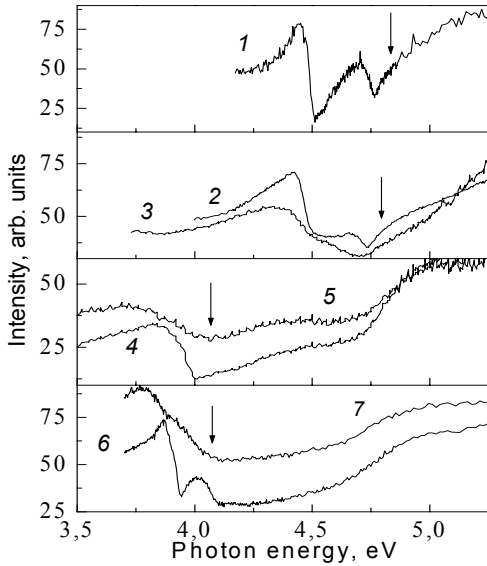


Fig. 1. Fragments of the reflection spectra of the crystals RPC – (1), KPC – (2,3), RPB – (4,5), KPB – (6,7), measured in the fundamental absorption edge region at 8 K (1,2,6), 80 K (4) and 290 K (3,5,7). Arrow indicates energy  $E_g$

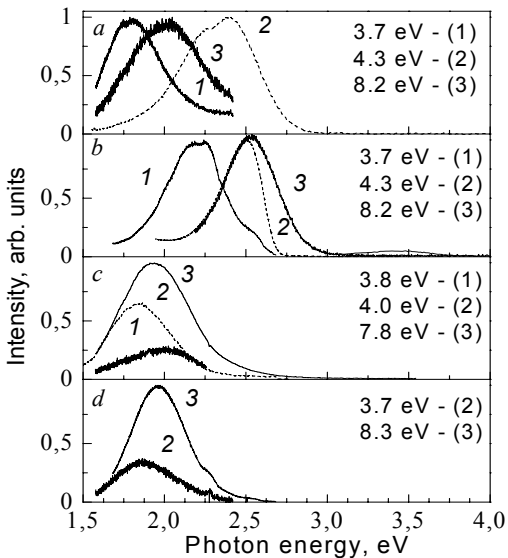


Fig. 2. Normalized PL spectra at  $T=8$  K of the crystals RPC – (a), KPC – (b), RPB – (c), KPB – (d), measured at different excitation energies

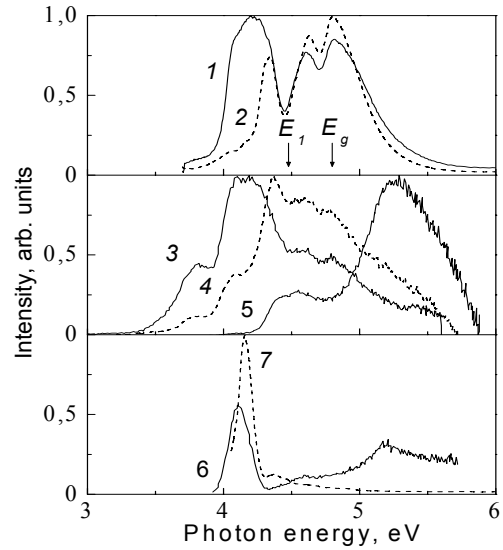


Fig. 3. Normalized excitation spectra of the PL bands at 2.0 – (1,3), and 2.3 – (2), 2.2 – (4), 2.75 – (5), 3.3 – (6) and 3.65 eV of the KPC crystal at  $T=8$  K (1,2,7) and 80 K (3–6)

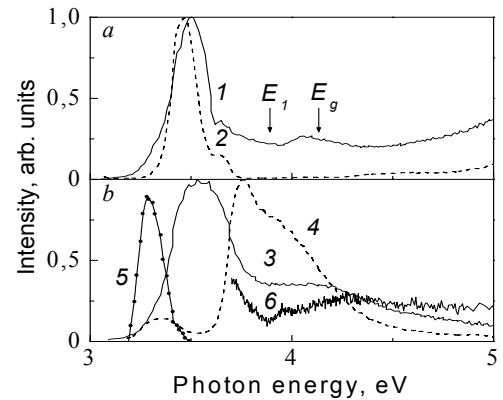


Fig. 4. Normalized excitation spectra of the PL bands at 2.0 – (1,3,6), 2.8 – (2), 2.2 – (4) and 2.9 eV – (5) of the RPB – (a) and the KPB – (b) crystals at  $T=8$  K (6) and 80 K (1–5)

Long-wave edge of the excitation spectra of the PL bands in range of 1.7–2.0 eV lies in the optical transparency range of the crystals, directly verging to long-wave fundamental absorption edge. At temperature increasing up to 80 and 300 K the efficiency of excitation in transparency range increases. It may indicate the presence of the thermostimulated processes with the participation of the impurity centers or lattice structure defects. PL bands in range of 2.0–2.4 eV are efficiently excited only in fundamental absorption range. Long wave edge of the excitation spectra of this PL coincides with the long-wave fundamental absorption edge. Excitation is efficient both in excitonic range and in the range of beginning band-to-band transitions.

Manifestation of the radiative decay of exciton is necessary to expect as typical narrow luminescence bands in the long-wave fundamental absorption edge range. We have not observed edge luminescence of the  $\text{APb}_2\text{X}_5$  crystals, however some bands of the low temperature PL spectra of these crystals have obviously an excitonic origin. Among of them is 3.65 eV short wave band in the KPC crystal and 2.9 eV weak band in the KPB crystal. These PL bands do not have an obvious relation with some kind of defects and are observed at low temperature.

Table 1. Excitonic parameters of  $\text{APb}_2\text{X}_5$  crystals

Crystal	$E_l$ , eV	$E_g$ , eV	$R$ , eV
$\text{RbPb}_2\text{Cl}_5$	4.51	4.83	0.32
$\text{KPb}_2\text{Cl}_5$	4.45	4.79	0.34
$\text{RbPb}_2\text{Br}_5$	4.0	4.22	0.22
$\text{KPb}_2\text{Br}_5$	3.87	4.12	0.25

For further discussion let's turn to the phase diagram of the self-trapped excitons (STE) (Fig. 5).

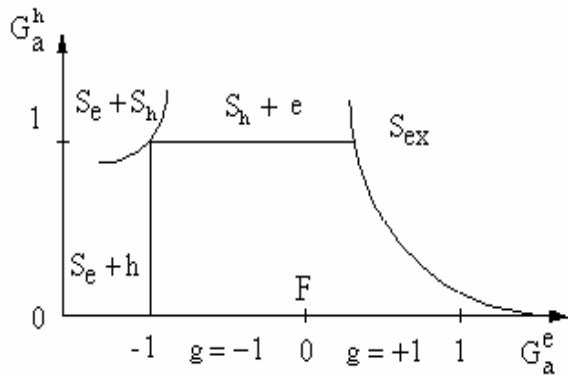


Fig. 5. Phase diagrams of the excitons in the acoustic phonon field

Sumi's theory [11] considers effects of strong exciton-phonon interaction and different states of the STEs within adiabatic approximation. Phase diagram is a dependence of value of the electron-phonon interaction  $G_a^e$  on value of the hole-phonon interaction  $G_a^h$ . For charge carriers self-trapping electron (hole)-phonon interaction should be  $G_a^{e(h)} \geq 1$ . Phase of free excitons (FE) is in the central part of diagram, for which values of  $G_a^e$  and  $G_a^h$  are small. Within strong interaction of electrons and holes with phonons we have two phases of STE, indicated as  $S_h + e$  and  $S_e + h$ . Herewith the base of STE is self-trapped hole (STH)  $S_h$  or self-trapped electron (STEL)  $S_e$  respectively.

Sumi's theory predicted two more additional phases of STE:  $S_{ex}$  and  $S_h + S_e$ . If even electron-phonon or hole-phonon interactions separately is not enough for transition of electron or hole to the self-trapped state, but for exciton as a whole the self-trapping is possible due to adding deformations, created by electron and hole. So excitons  $S_{ex}$  was called "self-

shrunken" excitons (SSEs). It is impossible to create SSEs by recombination assembling method. These excitons are efficiently excited only in long-wave fundamental absorption edge range.

Such situation is possible when  $G_a^e > 1$  and  $G_a^h > 1$ , i.e. both electron and hole are self-trapped. If herewith deformation potentials of electron and hole have different signs ( $g = -1$ ), so excitonic tandem aside from Coulomb attraction in small distance it will feel the distraction of electron and hole through the field of created deformations. Herewith we may observe a balance state of STE. Such states of STE are called "dichotomy" of STE.

Within the framework of developed believes 3.65 PL band for the KPC crystal and 2.9 PL band for the KPB crystal are due to radiative annihilation of SSE, trapped at one  $\text{Pb}^{2+}$  cation. This is some analog of the single halide excitons in the alkali halide crystals (AHC) [9,10]. A number of typical properties of the SSE emission in the KPC crystals and single halide exciton luminescence in the AHC are identical.

The  $\text{APb}_2\text{X}_5$  crystals are comparatively new system, in which electron and hole self-trapping processes have not studied yet. We have no data on electron paramagnetic resonance (EPR) of STH and STEI in these crystals. However by means of luminescence spectroscopy method we can observe all basic typical manifestations of STH and STEI in  $\text{APb}_2\text{X}_5$  crystals [3–7], earlier found in  $\text{PbX}_2$  [10]. In our opinion PL bands in range of 2.0–2.5 eV, observed in the  $\text{APb}_2\text{X}_5$  crystals under excitation in the fundamental absorption range can be due to tunnel recombination between STH and STEI. Really, these bands are efficiently excited in the band-to-band transitions range; their thermal stability is in range up to 150–200 K, they are characterized by micro- and millisecond range decay kinetics.

On the grounds of above mentioned we may suppose that in researched crystals it is realized the case of both the strong electron-phonon and hole-phonon interactions, i.e. electron and hole are self-trapped. It is more likely that STH is  $(\text{X}_2)^-$  ion and STEI is  $(\text{Pb}_2)^{3+}$  quasimolecule, i.e. density of probability of electron finding is concentrated on two lead ions. It is necessary to study the  $\text{APb}_2\text{X}_5$  crystals by EPR method for proof of this model.

#### 4. Conclusion

$\text{AP}_2\text{X}_5$  crystals are comparatively new system, which is promising for using as active laser matrices, doped by RE ions.

Firstly, it was established that fundamental absorption edge of researched crystals is formed by excitonic states. Parameters of the excitons and minimum energy gap  $E_g$ , calculated according to Wannier-Mott's model, depend on kind of halide and alkaline metal.

Secondly, the luminescence of free excitons was not observed in low temperature PL spectra, but it was found

the luminescence of the relaxed excitons – self-shrunk, trapped at  $\text{Pb}^{2+}$  cation, and host luminescence with the considerable Stocks' shift. Host luminescence arises as a result of tunnel recombination of the STEs ( $\text{Pb}_2$ )<sup>3+</sup> and STHs ( $\text{X}_2$ ). It is necessary a radiospectroscopic research – search for an EPR's signal of the STEI and STH for direct proof of the suggested models.

Thirdly, presence of the efficient channel of the electron excitation self-trapping discovers the prospects of studying the processes of forming the radiation defects of lattice structure, arising due to sub-threshold mechanism – within decay of the electron excitations. Namely such mechanism of radiation defects forming is the most efficient for the AHC [9] and this mechanism can be manifested in the  $\text{APb}_2\text{X}_5$  crystals. This question is directly connected with practical application of these crystals as laser matrices.

And finally, in the low energy range of the PL spectrum it was revealed the bands, related with the radiative relaxation of the electron excitations near the lattice structure defects. Peculiarities of behavior of the electron excitations allow to suppose the presence of the efficient channel of energy transfer of the host electron excitation to impurity centers in these crystals, doped by RE ions.

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