



TEMPORAL DEPENDENCE OF THE EMISSION BAND OF $Pb^{+}(1)$ COLOR CENTERS IN $BaLiF_3:Pb$ CRYSTALS

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Abstract— $Pb^{+}(1)$ centers in $BaLiF_3$ crystals were created by high energy electron irradiation of lead doped crystals. The lowest energy emission band of these centers peaks at 880 nm at 77 K, and it is the counterpart of the $KMgF_3:Pb^{+}(1)$ laser emission. The $Pb^{+}(1)$ centers in both hosts show an asymmetric emission band shape. We have measured the emission decay time of these centers in the temperature range of 10–300 K. In this range of temperatures, the decay time is constant and equal to 1.25 μs and, therefore, for this simple optical cycle, the quantum efficiency is unity. By analyzing the low temperature time evolution of the emission band, it is then seen that the asymmetry is maintained, therefore it is a characteristic of the $Pb^{+}(1)$ centers in the $BaLiF_3$ crystal.

Keywords: A. optical materials, D. luminescence, D. optical properties, D. color centers, $BaLiF_3$.

1. INTRODUCTION

$Tl^0(1)$ centers in KCl crystals are prototypes of a class of laser active materials, i.e. neutral Tl atoms perturbed by an adjacent anion vacancy [1]. Isoelectronic centers involving double ionized ions, based on Pb [like $Pb^{+}(1)$ centers] were studied with the aim of identifying new laser active materials. In particular, the perovskite $KMgF_3$ crystal doped with Pb^{2+} , submitted to electron irradiation and subsequent formation of the $Pb^{+}(1)$ center, showed tunable laser action in the near infrared [2]. However, a troublesome fading in the lasing process was observed. $Pb^{+}(1)$ centers can be described as a complex Pb^{+} -anion vacancy. In the $KMgF_3$ crystal, the Pb^{2+} substitutes for the K^{+} ; therefore, an additional charge compensation (cation vacancy) is required to maintain electrical neutrality. The presence of the cation vacancy near the $Pb^{+}(1)$ centers induces an instability during the optical pumping cycle that leads to a subsequent destruction of the center, by removal of the anion-cation vacancy pair. Therefore, this instability could be solved by a suitable choice of a host matrix, where the Pb^{2+} ion substitutes a divalent ion.

We have been able to create $Pb^{+}(1)$ centers in a new Pb^{2+} doped perovskite crystal, $BaLiF_3$, by electron beam irradiation at low temperature [3]. These centers show an emission band peaking at 880 nm, at 77 K, which can be excited by three absorption bands centered at 744, 487 and 305 nm. These transitions are the expected ones as predicted by the crystal field

theory developed for the $Tl^0(1)$ center [4]. The $BaLiF_3$ crystal is an inverted perovskite whose crystal structure can be seen in Fig. 1. Both Pb^{2+} and Li^{+} ions occupy sites of local symmetry O_h but with different coordination number n_c . For the Ba^{2+} site, n_c is 12 and for the Li^{+} , n_c is 6. This crystal has the same structure of the $KMgF_3$ crystal and nearly the same lattice parameter. Its advantage is that it can easily incorporate the Pb^{2+} ion in a divalent cation position because of the similarity between the Ba^{2+} and Pb^{2+} radii. In this paper we studied the time dependence of the fundamental emission band of $Pb^{+}(1)$ centers, i.e. the temperature dependence of its decay time and its time resolved spectroscopy.

2. EXPERIMENTAL

The $BaLiF_3:Pb$ crystals used in this experiment were grown by using the Czochralski growth method [5] and were doped with 0.14 mol% of lead as indicated by atomic spectrographic emission analysis of the grown crystals. Samples with thickness of 1.4 mm were subjected to 1.5 MeV electron irradiation, at liquid nitrogen temperature (dose of 20 μA min/cm²) as previously described [3].

The experimental set-up used to measure the decay time and the emission spectrum time evolution is shown in Fig. 2. The excitation light source is a nitrogen pumped dye laser (5 ns of pulse duration), tuned at 632 nm. The detection system is composed by

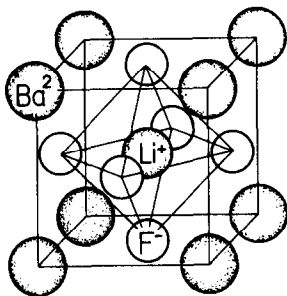


Fig. 1. Crystalline structure of BaLiF_3 . The dashed larger circles represent Ba ion sites.

a standard 0.5 m Ebert-type monochromator (Jarrel-Ash Div.) and by a S-1 photomultiplier. The detected signals were amplified by a large bandwidth PAR 115 amplifier and analyzed by a PAR 162 box-car integrator equipped with a 164 type preamplifier. The trigger was synchronized by the electronic response of an S-20 photomultiplier to the laser excitation light through an optical fiber. The results were recorded in an X - Y plotter for the decay time curves and in a X - t plotter for the time resolved spectroscopy. For the low temperature measurements, the crystal was placed in a cold finger cooled by a closed cycle helium cryocooler (LTS 21 type, Lake Shore Cryotronics).

3. RESULTS

Figure 3 shows the 880 nm emission radiative decay

time as a function of the temperature. The measurements were taken in the 10–300 K temperature range. It is then observed that the decay time remains nearly constant in this temperature range. The measured decay time value is $1.25 \pm 0.1 \mu\text{s}$.

The time evolution of the emission spectrum was measured at the fixed temperature of 20 K. Three spectra were taken and are shown in Fig. 4. The first one was taken immediately following the laser trigger pulse (t_0); the other two at subsequent intervals of $5 \mu\text{s}$ each ($t_0 + 5 \mu\text{s}$ and $t_0 + 10 \mu\text{s}$). In all of them, it is clearly seen that there is a strong emission band, centered at 880 nm, asymmetric, and a much smaller one centered at 780 nm. These two bands show a different time dependence concerning their relative amplitude (their decay time is then different), therefore this emission must be due to another species, also excited by the 632 nm light.

Note that the 880 nm band is sharper at the shorter wavelength side and this feature is maintained in all the time resolved spectra.

4. DISCUSSION

Due to the heavy dosages of e^- irradiation, F centers and their aggregates are expected. These centers show fast decay times ($\leq 100 \text{ ns}$) and therefore, in the time range studied, it will be easily recognized due to the dramatic change in their emission intensity.

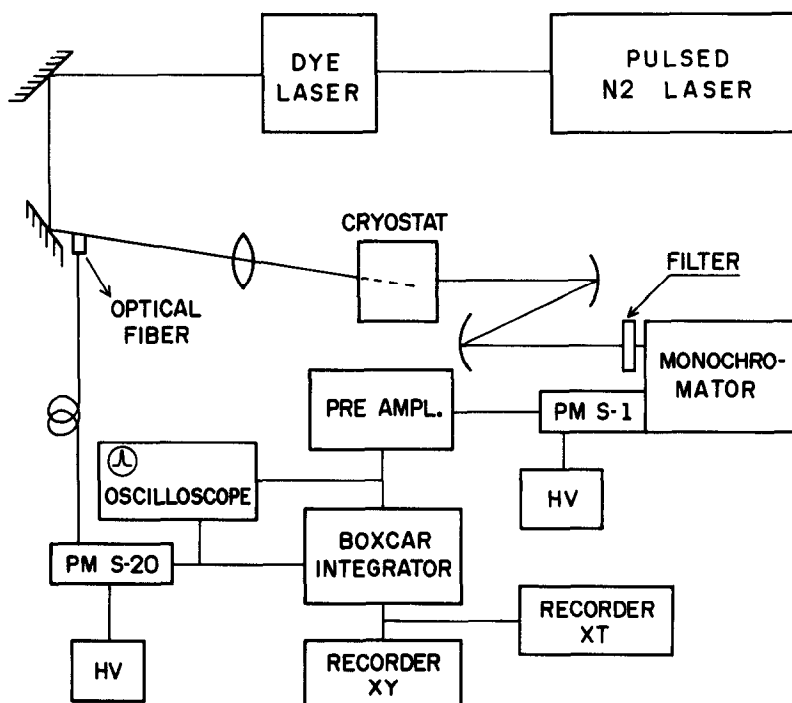


Fig. 2. Schematic diagram of the decay time and time resolved spectroscopy apparatus. The wavelength of the excitation laser pulse is 632 nm.

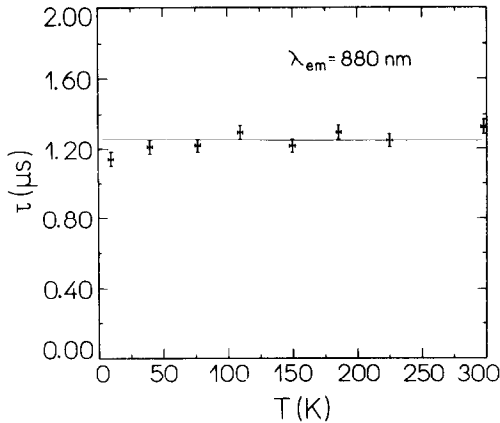


Fig. 3. Decay time behavior of Pb⁺(1) centers in BaLiF₃:Pb crystals as function of temperature.

At room temperature, the 880 nm emission band envelope shows a nearly Gaussian profile. At low temperatures, it did not change its asymmetry during the investigated time range (approximately 10 time constants). In fact, at 20 K, as shown in Fig. 4, the emission band asymmetry remains in all emission

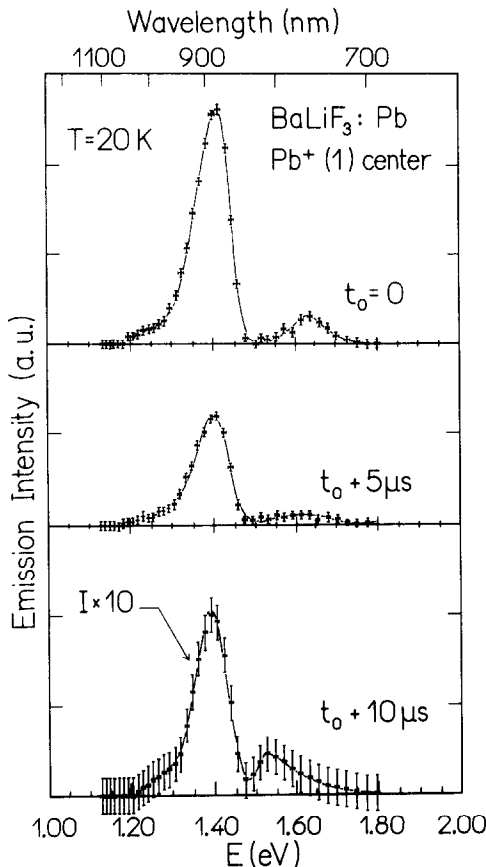


Fig. 4. Time resolved emission spectra of the 880 nm emission band in BaLiF₃:Pb crystals irradiated with high energy electrons. Temperature is 20 K. The wavelength excitation is 632 nm. The spectra were taken at $t_0 = 0$, $t_0 + 5$ and $t_0 + 10 \mu\text{s}$ after the beginning of excitation.

spectra and, besides, we do not observe any peak shift. This indicates that this asymmetry is a characteristic of the Pb⁺(1) center in the perovskite BaLiF₃ crystal and not to any other aggregate.

On the other hand, the very weak 780 nm emission band was detected only for some samples and for temperatures below 77 K. Besides, the intensity ratios between the 880 and the 780 nm emission bands are not preserved for the three spectra shown in Fig. 4. The 780 nm band intensity shows a different decay time than the Pb⁺(1) centers. Nevertheless, this band may correspond either to a modified Pb⁺(1) center, due the presence of neighbor Pb²⁺ ions, or to F center higher aggregates, since this emission is not observed for pure irradiated BaLiF₃ crystals.

The nearly constant decay time behavior for the temperature dependence of the 880 nm emission, likewise the one observed for the Tl⁰(1) centers, suggests a luminescent quantum efficiency of 1 for this emission. Therefore the luminescent decay time is the radiative decay time. We can thus evaluate [6] the emission cross-section σ_e for these centers using the expression:

$$\sigma_e = \frac{2}{\Delta\nu} \left(\frac{\ln 2}{\pi} \right)^{1/2} \frac{\lambda^2}{8\pi} \frac{1}{\tau_r n^2} \quad (1)$$

considering a nearly Gaussian shape of the emission band, where λ is the maximum wavelength band emission, $\Delta\nu$ is the full width at half maximum of the emission band, τ_r is the radiative decay time and n is the refraction index.

The refraction index for BaLiF₃ crystal is 1.544 and, at 77 K, the spectroscopy parameters for Pb⁺(1) centers are: $\Delta\nu = 0.103$ eV; $\lambda = 880$ nm (1.40 eV) and $\tau = 1.22 \mu\text{s}$. Using these values in eqn (1), we then have $\sigma_e = 4.0 \times 10^{-18} \text{ cm}^2$. At room temperature, $\Delta\nu = 0.187$ eV, $\lambda = 900$ nm (or 1.38 eV) and $\tau = 1.33 \mu\text{s}$ and therefore the emission cross-section is 50% smaller than the low temperature one ($\sigma_e = 2.1 \times 10^{-18} \text{ cm}^2$).

The oscillator strength f_1 for the relaxed state configuration of the emission can also be determined by the expression [6]:

$$f_1 = \frac{1}{8\pi^2} \frac{\lambda^2}{c r_0 \tau_r n} \left(\frac{3}{n^2 + 2} \right)^2 \quad (2)$$

where r_0 is the classical electron radius and c is the speed of light. The obtained value is $f_1 = 0.0029$.

5. CONCLUSIONS

Temporal characterization of the 880 nm luminescent emission of Pb⁺(1) centers in the BaLiF₃:Pb perovskite crystal is presented. These centers have

been investigated as potential candidates for laser active media. Luminescent decay time measurements showed a nearly constant temperature dependence. The mean value of it is 1.25 μ s. This suggests a unitary luminescent quantum efficiency that enables us to evaluate the emission cross-section for these centers as $4.0 \times 10^{-18} \text{ cm}^2$ (77 K). The corresponding oscillator strength is 0.0029, which is a characteristic of a weakly allowed transition.

Time resolved spectroscopy measurements show that the asymmetry of the 880 nm emission band, observed at low temperatures, is a $\text{Pb}^+(1)$ center characteristic in the BaLiF_3 crystals. This result is unexpected, because the BaLiF_3 is a cubic perovskite and no dependence on the particular Fluorine ion,

which is replaced by the anion vacancy, should occur.

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