CONTROLLED PRODUCTION OF $Pb^+(1)$ CENTERS IN $BALiF_3$:Pb: Pb^{2+} DOPING CONCENTRATION DEPENDENCE

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The optical properties of potentially laser active media, the $Pb^+(1)$ centers in special, have been investigated, in the $BaLiF_3$:Pb fluoroperovskite. The $Pb^+(1)$ center results from the interaction between Pb^{2+} impurities with color centers. In this work we present a $Pb^+(1)$ center production study in electron irradiated $BaLiF_3$:Pb with the purpose of achieving significative defect concentrations of this center. Three parameters were investigated: impurity concentration, temperature and dose of electron irradiation.

INTRODUCTION

Laser action of $Pb^+(1)$ centers in $KMgF_3$:Pb crystals was previously reported[1]. The $Pb^+(1)$ center can be described as a Pb^+ ion (resulting from an electron capture, produced in the irradiation process, by a Pb^{2+} ion) in the field of a neighbor anion vacancy. Under intense pumping, however, a troublesome fading of the laser emission in this crystal was verified[2]. This seems to be explained by the fact that the Pb^{2+} ion substitutes on the K^+ ion site which requires an additional charge compensating defect.

In this work we describe the production of $Pb^+(1)$ centers in the inverted fluoride perovskite of $BaLiF_3$:Pb in which Pb^{2+} ion substitutes on the Ba^{2+} site. These centers present an emission at 880 nm (77 K)[3]. This emission can be excited by three absorption bands, centered at 744, 487 and 305 nm (77 K). The fundamental transition presents the classical relaxation processes and therefore this center shows the ideal four levels simple optical cycle. The corresponding decay time was measured[4] in the temperature range of 10-300 K. In this range of temperatures, the decay time is nearly constant and equal to 1.25 μs and therefore, the quantum efficiency is unity. The emission cross-section was evaluated as $\sigma_e = 4.0 \times 10^{-18}$ cm^2 (77 K).

In order to submit the $Pb^+(1)$ center to laser action tests, in resonant cavities, it was necessary to obtain significative defect concentrations. Since $Pb^+(1)$ centers result from the interaction between Pb^{2+} impurities with color centers we have investigated, in this work, the defect formation as a function of three parameters: impurity concentration, temperature and dose of electron irradiation.

EXPERIMENTAL

The $BaLiF_3$:Pb crystals used in this experiment were grown by Baldochi, by using the Czochralski growth method. Samples with 0.5 to 1 mm thickness, doped with 0.14, 0.20, 0.53 and 1.08 mol% of Pb^{2+}, were irradiated by high energy electrons (1.5 MeV and 0.3 mA) at 173 and 300 K. We have chosen doses of 250, 500 and 1000 KGy. After the irradiation, the crystals were stored at liquid nitrogen temperature to avoid centers degradation. The defect center production was monitored by absorption

spectra measured at 77 K, using a double beam Cary 17D spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 summarises the absorption spectra measured for different Pb^{2+} concentrations. Each curve corresponds to the absorption coefficient K (cm^{-1}) in function of the wavelength. The upper graphic shows the results for irradiation at 173 K; the lower graphic shows the same for irradiation at 300 K. In these cases the radiation dose was fixed at 250 KGy.

The lowest energy absorption band for the Pb^{2+} ions occur at 204 nm (A band), therefore the measured absorption spectra for longer wavelengths is due only to the other irradiation induced color centers. After irradiation, the spectra show essentially two regions of absorption bands. In the ultraviolet region the strong absorption originates from the composition of several peaks due not only to F and F aggregate centers but also due the association of Pb^{2+} with radiation induced color centers[5]. The efficiency of Pb^{2+} as an electron[6,7] and a hole[8] traps is well known from KCl:Pb irradiation experiments, so it is reasonable to expect the formation of Pb^{+}, Pb^{0} and Pb^{3+} centers. All these centers are expected to absorb near the Pb^{2+} A absorption band.

It is clearly seen in figure 1 that Pb^{2+} drastically suppresses the rate of F and F_2 centers creation (the F and F_2 absorption bands are observed at 260 and 420 nm in

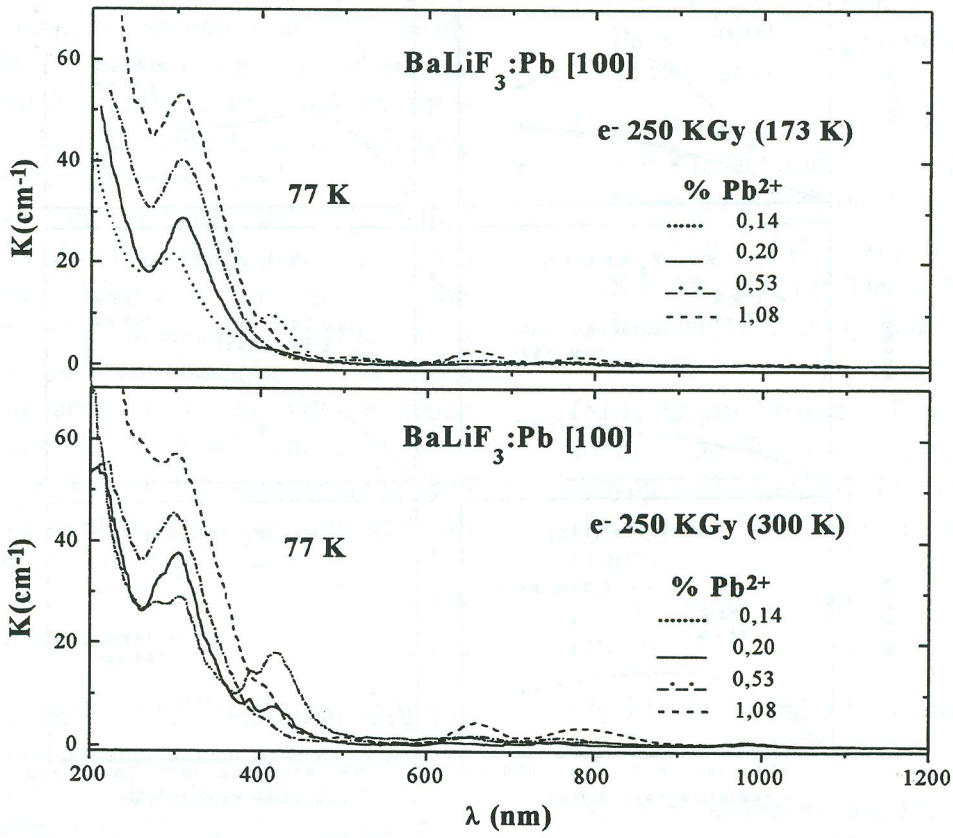

Figure 1: Optical absorption spectra of electron irradiated $BaLiF_3$:Pb crystals pulled in the [100] direction. The temperature irradiation was 173 K (upper picture) and 300 K (lower picture). The initial Pb^{2+} concentration is indicated in the figure.

irradiated pure $BaLiF_3$ cristals[5]). For Pb^{2+} concentrations above 0.20 mol% we cannot see anymore the F_2 absorption band. At room temperature irradiation we note an optical absorption growth near 280 nm. We could not observe this band in irradiated pure $BaLiF_3$, so it should be related to another kind of Pb^{2+}-color center complex. The band peaking at 303 nm (corresponding to the $Pb^{+}(1)$ third absorption band) became more intense with the increase of Pb^{2+} concentration.

In the visible region the absorption spectrum is more simple and corresponds mainly to the $Pb^{+}(1)$ centers and others species involving lead ions. The concentration increase results in a gradual shift of the lowest energy absorption of $Pb^{+}(1)$ centers, from 744 nm (0.20 mol%) to 760 nm (0.53 mol%) and finally 780 nm (1.08 mol %). The 660 nm absorption band increases with both the concentration and irradiation temperature. The increase of radiation dose did not induce a qualitative change of the experimental spectra. This means that no new defects were produced but only an intensity change of the absorption bands was observed.

The dose dependence for the visible absorption bands can be seen in more detail in figure 2. We observed an increase in the 660 and 780 nm bands with the increase of

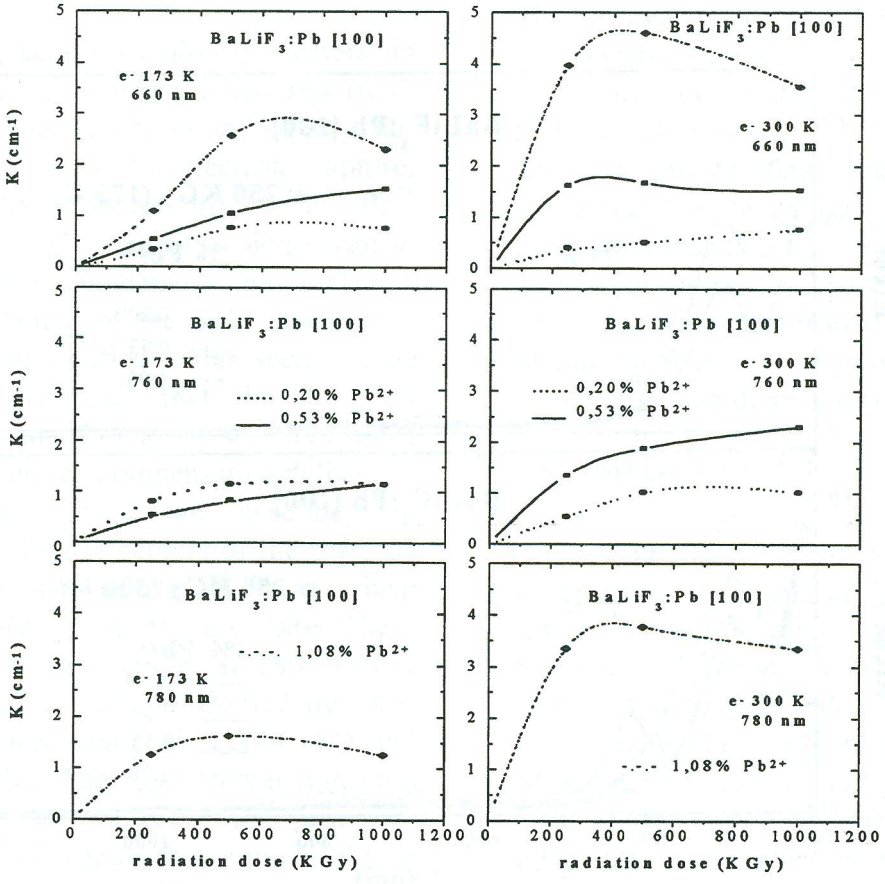

Figure 2: Dose dependence for the 660, 760 and 780 nm absorption bands. The irradiation temperatures were 173 K (for curves at left) and 300 K (for curves at right). Each curve corresponds to a initial Pb^{2+} ion specific concentration.

radiation dose until nearly 500 KGy. For higher doses it happens a little destruction of the defects. The similar behavior for both 660 nm defect in $BaLiF_3$:Pb and F_2^+ centers in pure $BaLiF_3$ (absorption band in 630 nm)[5] suggest that the first one may corresponds to a F_2^+ center absorption perturbed by a nearest Pb^{2+} ion. The 780 nm absorption band can involve Pb^{2+} dimmers.

As can be seen in figure 2, the absorption intensity of the 760 nm band is higher for crystals with 0.5 mol% of Pb^{2+} and irradiated at 300 K. In these conditions, the irradiation also produces the 660 nm band defects with equal or higher efficiency. It is not clear yet if this band interferes with the optical pumping cycle of the $Pb^+(1)$ centers. This defect can be produced in higher concentrations so it would be interesting to investigate itself as a potential laser medium. The optimum concentration of nearly isolated $Pb^+(1)$ centers is giving for crystals doped with 0.2 mol% of Pb^{2+} and irradiated at 173 K. In these conditions the resultant absorption coefficient is 1 cm^{-1}.

We can consider an hypothetical example of $Pb^+(1)$ centers pumping with a diode laser emitting in 797 nm. At this wavelength the absorption coefficient is nearly 0.4 cm^{-1}. By focusing a 4 W diode laser to an area of $10^{-4}cm^2$ we can reach pump intensities of 18 KW/cm^2. For these conditions and using the spectroscopic data for $Pb^+(1)$ centers we can estimate[5] an optical gain of 0.06 cm^{-1}.

CONCLUSIONS

The optimum concentration of $Pb^+(1)$ centers, concerning laser action tests, is achieved for crystals with nearly 0.2 mol% of Pb^{2+} irradiated at 173 K. For higher Pb^{2+} concentrations, until almost 0.5 mol%, the $Pb^+(1)$ center concentration is higher. However a simultaneous 660 nm defect is produced with equal or higher efficiency. This suggests that, in laser action tests, we should pump the $Pb^+(1)$ centers in the half band side of lowest energy. An estimate of the gain coefficient with a diode laser excitation gives 0.06 cm^{-1}. Hence, samples 8 mm thickness or higher must be employed in resonant cavity tests in order to achieve the usual laser threshold.

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