

## OPTICAL PROPERTIES OF $Pb^{+}(1)$ CENTERS IN $BaLiF_3$ CRYSTALS\*

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A new perovskite crystal,  $BaLiF_3$  doped with lead was subjected to  $e^-$  irradiation. A metal related color center involving the  $Pb^{2+}$  ion emitting at 880 nm was identified. The excitation spectrum at 70 K shows that there are three bands peaking at 744, 487 and 305 nm (also present in the absorption spectrum) that are responsible for this emission. These bands, either in relative transition magnitudes and energy positions, are the expected ones for the lead perturbed color center,  $Pb^{+}(1)$ , the isoelectronic specie of the laser active  $Tl^0(1)$  center.

### 1. INTRODUCTION

WITH THE DISCOVERY of metal perturbed color centers as laser active media, a new class of lasers has been found. The prototype of such a laser medium is the  $KCl:Tl^0(1)$  center [1]. It consists of a substitutional metal ion, that has a deeper attractive potential for the electron with respect to the crystal ions. Besides, it is one of the nearest neighbors of an F center. The F electron is shared partially with the metal ion, in such a way that the center is a neutral Tl atom perturbed by an adjacent vacancy. Since then, a great effort has been applied to develop similar laser active media, either using Tl as a dopant or elements of the isoelectronic family. Besides In and Ga, other isoelectronic centers involving double ionized ions based on Pb (like the  $Pb^{+}(1)$  center), in other hosts, were developed. In the latter case, the doubly ionized ion ( $Pb^{2+}$ ) is isoelectronic to the  $Tl^+$  ion, both presenting an outer closed  $s$  shell. When incorporating the extra electron, it will occupy a  $p$  level, ( $6p$ ), for the both cases. Therefore, the model assumed of a  $p$  electron outside a positive core is applied either for the  $Pb^{+}(1)$  or the  $Tl^0(1)$  center. In particular, the perovskite  $KMgF_3$  crystal doped with  $Pb^{2+}$  when irradiated and with subsequent formation of the  $Pb^{+}(1)$  center showed tunable laser action in the near infrared [2]. These results showed that the  $Pb^{+}(1)$

centers are more stable than the  $Tl^0(1)$  centers. A troublesome fading in the lasing process was, however, observed. This seems to be explained by the fact that in  $KMgF_3$  crystals doped with  $Pb^{2+}$ , the impurity substitutes for the  $K^+$  ion which requires an additional charge compensating defect, probably a cation vacancy. By irradiating the crystals, complexes of  $Pb^{2+}-F$  centers are created and the F center electron is partially shared with the  $Pb^{2+}$  ion due to the large ionization energy of the  $Pb^+$  ion (15 eV). This complex ( $Pb^+$ -anion vacancy) is the laser active  $Pb^{+}(1)$  center. The fading process could be due to the removal of the anion cation vacancy pair through local heating by the pumping light [3]. In this case, the problem can be solved by suitable choice of a host matrix where the  $Pb^{2+}$  substitutes for a divalent ion. Studies have been performed in alkaline-earth fluorides doped with  $Pb^{2+}$  in which the authors succeeded in creating the  $Pb^{+}(1)$  center with a strong emission [4, 5] but laser action was not obtained due to an excited state absorption process [6].

In this paper we present the first fundamental spectroscopic results of lead center defects obtained by irradiating crystals of  $BaLiF_3.Pb$  at liquid nitrogen temperature with electrons of 1.5 MeV. This crystal is an inverted perovskite [7] which has the same structure of the  $KMgF_3$  crystal and nearly the same lattice parameter with the advantage that it can easily incorporate the  $Pb^{2+}$  in a divalent cation position because of the similarity between the  $Ba^{2+}$  and  $Pb^{2+}$  radii. Its structure can be seen in Fig 1. The

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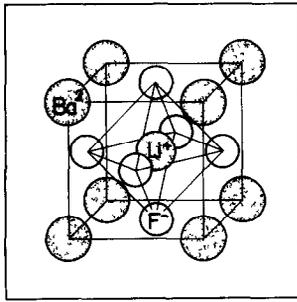


Fig. 1 Crystalline structure of  $BaLiF_3$ . The dashed larger circles represent Ba ion site.

crystal has cubic symmetry where both cations occupy sites of local symmetry  $O_h$  but with different coordination numbers  $n$ . For the Ba ions  $n = 12$  and for Li ions  $n = 6$ . The fluorine ions occupy the center of the cube face and have  $D_{4h}$  symmetry. The  $Pb^{+}(1)$  center consists of a  $Pb^{+}$  ion which replaces a Ba ion near an anion vacancy so that the center is along the  $\langle 110 \rangle$  direction and has a local symmetry  $C_{2v}$ . With the results of optical measurements of absorption, emission and excitation spectra we have been able to identify the  $Pb^{+}(1)$  centers in this new matrix.

## 2 EXPERIMENTAL

### 2.1. Sample preparation and experimental arrangements

The  $BaLiF_3$  Pb crystals used in this experiment were grown [7] by using the Czochralski growth method and were doped with 0.14 mol% of lead as indicated by atomic spectrographic emission analysis of the grown crystals. Samples 1.5 mm thickness were sealed in aluminum foil and irradiated by electrons of 1.5 MeV (30 up to 130 MRad irradiation range) at liquid nitrogen temperature. This was accomplished by placing the crystals in a copper boat floating in a liquid nitrogen pool under the electron beam. After the irradiation, the crystals were stored at liquid nitrogen temperature to avoid centers degradation.

The absorption spectra were performed using a double beam Cary 17D spectrophotometer. For the spectroscopic measurements at low temperatures, a helium closed circuit refrigerator cryostat was employed.

The schematics of the emission and excitation apparatus is shown in Fig. 2. The light source is a 300 W xenon, high pressure lamp, focused into a 0.25 m long Ebert monochromator (Jarrel-Ash Div) and is modulated by a mechanical chopper. The detection system is composed by a second monochromator (Kratos, model GM 252), a 780 nm long pass color glass filter to avoid light scattering, an S-1

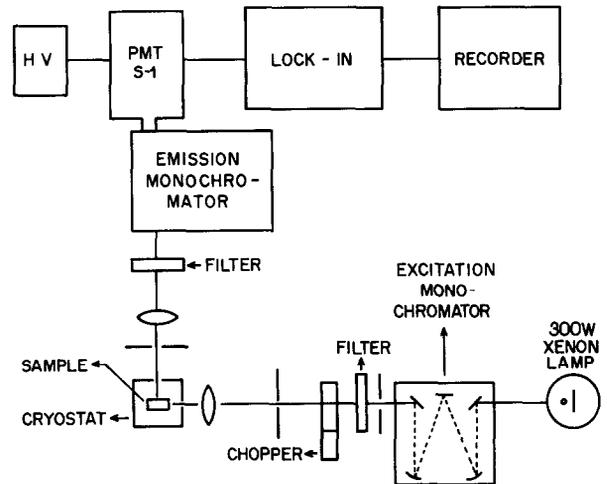


Fig. 2. Schematic diagram of the emission and excitation apparatus. The modulated monochromatic light from the source impinges on the sample, and the luminescence is analyzed at  $90^\circ$  with respect to the incident light. The emission light passes through a monochromator and is detected by a photomultiplier.

photomultiplier and a lock-in amplifier. The results were recorded in an  $X-t$  chart recorder.

### 2.2 Experimental results

Figure 3 and 4 summarizes the experimental results. Figure 3(a) shows the absorption spectrum measured at 10 K of a sample exposed to 127 MRad (irradiation temperature 77 K). The band gap for the  $BaLiF_3$  crystal is nearly 9 eV. The absorption bands related to  $Pb^{2+}$  ions occur at wavelengths shorter than 210 nm (5.90 eV), therefore, the measured absorption spectrum for longer wavelengths is due only to other irradiation induced color centers. After the irradiation, the spectrum shows essentially two regions of absorptions bands: in the long wavelength region there are two weak overlapping bands [with peaks at 735 nm and 660 nm, shown in the insert of Fig 3(a)] and an isolated band at 475 nm. In the ultraviolet region, strong absorptions occur at 304 and 210 nm. These UV absorptions originate from the composition of several peaks, due not only to  $Pb^{2+}$  ions (A band) or association of  $Pb^{2+}$  with radiation induced color centers, but also due to F and F aggregate centers. In a first approximation, the band peaking at 210 nm (5.90 eV) is composed by, at least, two bands. From the literature [8] it is known only that the F center absorbs at 280 nm but, on the basis of the similarity with LiF and  $KMgF_3$  crystals, it is expected that the F aggregate centers might absorb in the UV region.

By exciting the crystal at 730 nm a near infrared

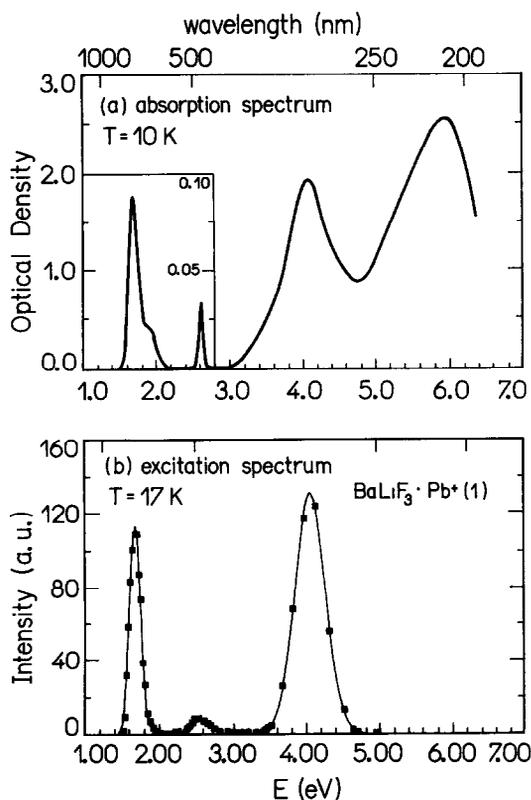


Fig. 3. (a) Optical absorption spectrum of the irradiated (127 MRad)  $\text{BaLiF}_3 \cdot \text{Pb}$  crystal. Note the change in the vertical scales showing that the strength of the transition in the near infrared and red are much smaller. (b) Excitation spectrum with the monitoring wavelength set at 880 nm. There are three excitation bands that correspond to the absorption spectrum of 3(a)

emission at 880 nm (1.41 eV) is observed, as shown in Fig. 4. This emission is asymmetric and could be fitted by two Gaussian curves in the same way as it was done for the optical emission of  $\text{Pb}^{2+}$  ions in  $\text{KMgF}_3$  [9]. There are other emission bands weaker than that peaking at the 880 nm which will not be discussed here. In order to determine the absorption responsible for this emission, the excitation spectrum was measured at 17 K, the emission being monitored at 880 nm. The sample in this case was irradiated with 32 MRad. This excitation spectrum [Fig 3(b)] was corrected considering the detector, excitation source and grating responses. Three excitation bands peaking at 744, 487 and 305 nm are observed, which can be identified with the 735, 476 and 305 nm absorption bands. The minor mismatch with the excitation peaks is probably due to normalization errors and wavelength calibration, since there are no other significant bands in this region. The excitation spectrum was also taken by monitoring the emission

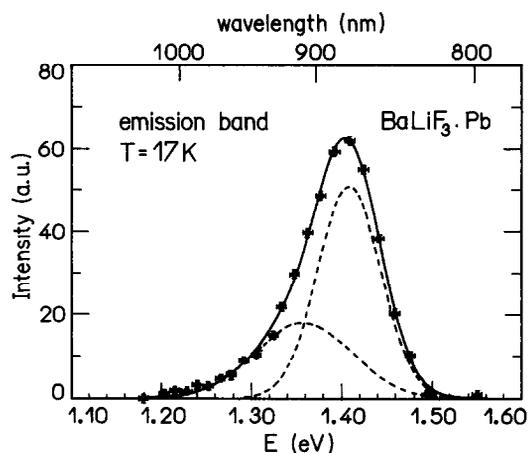


Fig. 4. Emission spectrum of the irradiated  $\text{BaLiF}_3 \cdot \text{Pb}$  (32 MRad). The excitation light wavelength is 730 nm. Temperature is 17 K.

at a different wavelength (960 nm) within the emission band. The spectrum obtained is essentially the same, showing that if the emission is really described by two Gaussian components, both should be originated by the same defect.

Both emission and excitation measurements were taken for different temperatures between 17 and 300 K. A summary of the results obtained for the band peak energies and respective half maximum fullwidths for the temperatures of 17, 70 and 300 K are reported in Table 1. It is also shown the results available from the literature for the  $\text{Pb}^{+}(1)$  in  $\text{KMgF}_3$  crystals for the sake of comparison [10].

Figure 5 shows the temperature dependence of the half width of the emission band (5a) and the lowest energy excitation band (5b). The spread of the data values for high temperatures suggest a possible interference by other defects like Pb dimers or other aggregate centers. Although the emission band is slightly asymmetric, the width obeys the well known law  $W(T) = W(0) [\coth(\hbar\omega/2kT)]^{1/2}$  for a Gaussian curve. From the experimental results and the above expression we can infer the phonon energy that broadens the bands. They are  $\hbar\omega_e = 139 \pm 14 \text{ cm}^{-1}$  for the excited state and  $\hbar\omega_g = 120 \pm 7 \text{ cm}^{-1}$  for the ground state. These energies are close to the lowest transverse optical phonon mode of  $\text{BaLiF}_3$  [14]  $(142 \text{ cm}^{-1})$ , corresponding to the local perturbed phonon mode. The difference in the ground state local phonon mode is also expected, since the electronic wavefunctions are quite different for both states. Therefore we can evaluate an average value of number of phonons involved in the optical cycle from the mean energy phonon value and from the

Table 1 Transition energies of the three excitation bands A<sub>3</sub>, A<sub>2</sub> and A<sub>1</sub> and the emission band E<sub>e</sub> for the centers Pb<sup>+</sup>(1) and Tl<sup>0</sup>(1) The halfwidths δν<sub>1</sub> and δν<sub>e</sub> and crystal field parameters γ<sub>a</sub> and γ<sub>e</sub> for the lowest energy excitation and emission bands respectively are also given. The energies are given in eV and temperatures in K degrees

Crystal	T	A <sub>3</sub>	A <sub>2</sub>	A <sub>1</sub>	δν <sub>1</sub>	γ <sub>a</sub>	E <sub>e</sub>	δν <sub>e</sub>	γ <sub>e</sub>
BaLiF <sub>3</sub> . Pb	17	4.05	2.54	1.67	0.176	0.52	1.41	0.097	0.26
	70	4.05	2.54	1.68	0.210		1.40	0.103	
	300	4.00	2.54	1.60	0.362		1.38	0.187	
KMgF <sub>3</sub> Pb*	77	4.35	2.99	1.94	0.244	0.72	1.40	0.137	0.36
KCl: Tl**	77	2.23	1.72	1.19	0.169	0.40	0.82	0.083	0.20

\*From [10].

\*\*From [11]

experimental Stokes shift. We obtained S nearly 9 This value of the S factor explains why we could not observe zero phonon lines in the low temperature range investigated (10 K).

### 3. DISCUSSION

First of all, it should be mentioned that pure BaLiF<sub>3</sub> crystals, irradiated under the same conditions as used for the Pb doped crystals, did not show the 880 nm band emission described above This fact suggests that we are dealing with a center related to Pb ions. In order to investigate if the defect studied above corresponds really to the Pb<sup>+</sup>(1) center we have examined the spectroscopic data fit to the theoretical model of crystal field developed by Mollenauer and collaborators [11] for the Tl<sup>0</sup>(1) center in KCl. Both, Pb<sup>+</sup> and Tl<sup>0</sup> ions have the same electronic structure, [Xe]4f<sup>14</sup>5d<sup>10</sup>6s<sup>2</sup>6p<sup>1</sup>, with the ground and first-excited states of the single p electron, <sup>2</sup>P<sub>1/2</sub> and <sup>2</sup>P<sub>3/2</sub>, respectively, separated by a large spin-orbit splitting We are dealing thus with the same problem, namely one p electron perturbed by the field of a nearest anion vacancy This perturbing field has even and odd parity terms. As we can see schematically in the insert of Fig. 6, the even parity term of the perturbing field splits the states of the 6p manifold. Also, the odd crystal field component of the perturbed center, mixes in higher-lying even-parity states in the P manifold This mixing breaks the parity of the P derived wavefunctions and allows for moderate transitions probabilities (oscillator strength in the order of few percent) between the P derived levels (φ, ψ, χ) Figure 6 shows also the theoretical, normalized energy levels separations as a function of the normalized crystal field parameter. The energies are normalized to the spin-orbit splitting of the center in the crystal environ-

ment. Also, it is shown in the insert, the diagram of the energy levels that gives rise to the level assignment.

The crystal field model permits us to describe the energies for the three lower levels as a function of the crystal field strength (Fig. 6) whose

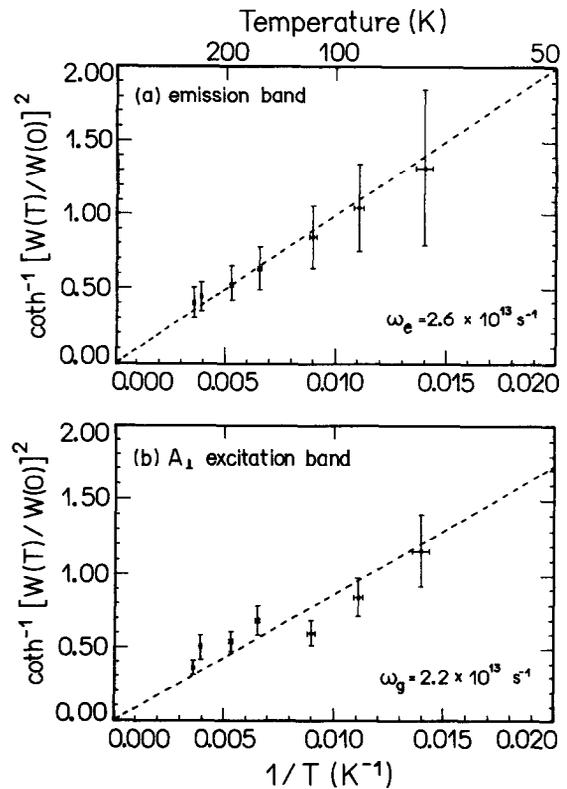


Fig 5. (a) and (b), shows the behavior of the fullwidth (W) at half maximum of the emission (a) and of the lowest energy excitation (b) bands of the Pb<sup>+</sup>(1) center in BaLiF<sub>3</sub>, as a function of the inverse of the temperature. The vertical scale is the arccoth [W(T)/W(0)]<sup>2</sup>

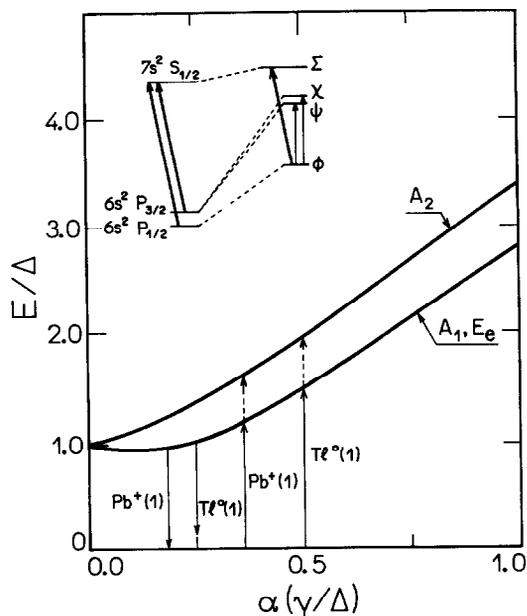


Fig. 6 Dependence of the normalized transition energy ( $E/\Delta$ ), on the crystal field normalized parameter,  $\alpha(\gamma/\Delta)$  for the  $A_1$  and  $A_2$  transition of  $\text{Pb}^+(1)$  center. The arrows show the fitting for the various isoelectronic centers. The insert shows the energy diagram plot for a free  $\text{Pb}^+$  or  $\text{Tl}^0$  (left side) and for the color center [ $\text{Tl}^0(1)$  or  $\text{Pb}^+(1)$ ] in the presence of crystal field.

transition energies can be written, according to Fockele *et al.* [12], as

$$A_1 = E(\psi - \phi) = \Delta[(1 - \alpha_a)^2 + 8\alpha_a^2]^{1/2},$$

$$A_2 = E(\chi - \phi) = (\Delta/2)[1 + 3\alpha_a] + A_1/2,$$

and the emission energy as

$$E_e = E(\phi - \psi) = \Delta[(1 - \alpha_e)^2 + 8\alpha_e^2]^{1/2},$$

where  $\Delta$  means an effective spin-orbit splitting,  $\gamma$  is the crystal field parameter and  $\alpha = \gamma/\Delta$ . The subscripts  $a$  and  $e$  correspond respectively to lowest energy excitation and emission bands.  $\phi$ ,  $\psi$ , and  $\chi$  indicate energy levels as shown in the insert of Fig. 6.

Ahlers *et al.* [12], supported by the model of Mollenauer *et al.* [11], proposed that  $\gamma$  is proportional to  $r^{-3}$  where  $r$  is the (impurity ion) - (anion vacancy) distance. This is valid for radially confined wavefunctions. Therefore, we can infer an approximate value for the crystal field parameter of the  $\text{BaLiF}_3$  (0.55 eV). Moreover, by a self-consistent criterion we can fit the values of the observed transition energies,  $A_1$  and  $A_2$  1.67 and 2.54 eV respectively and the result of this procedure is shown in Fig. 6. The best fitting of the observed transition energies  $A_1$  and  $A_2$  to the above expressions gives  $\alpha_a = 0.36$ ,  $\Delta = 1.45 \pm 0.09$  eV and  $\gamma_a =$

$0.52 \pm 0.05$  eV. For this  $\alpha_a$  the value of the reduced spin-orbit splitting  $\Delta$  is, correspondingly, 1.45 eV. On the other hand, it is known that the spin-orbit splitting of the free  $\text{Pb}^+$  ion is 1.746 eV, therefore,  $\Delta$  is reduced by 17% when the ion is incorporated in the  $\text{BaLiF}_3$  crystals. Recalculating the values of the absorption bands peaks positions for these two determined parameters  $\gamma_a$  and  $\Delta$  we obtain  $A_1 = 1.77$  eV and  $A_2 = 2.38$  eV, which fit rather well to the experimental values (within 10%). Using the same criterion for the emission transition energy we obtain  $\alpha_e = 0.18$  eV for  $\Delta = 1.45$  eV. Table 1 summarizes the results obtained for the  $\text{Pb}^+(1)$  center in  $\text{BaLiF}_3$  and for other isoelectronic centers. The crystal field parameter,  $\gamma$ , for the  $\text{Pb}^+(1)$  center is larger than that for  $\text{Tl}^0(1)$ . This is essentially due to the smaller distance between the cation and the anion vacancy in  $\text{BaLiF}_3$  than in the KCl (the distance cation-anion for  $\text{BaLiF}_3$  is  $r = 2.83$  Å, whereas for the KCl it is  $r = 3.15$  Å). According to the cubic dependence of the crystal field ( $r^{-3}$ ) on the cation-(anion vacancy) distance, we calculate the expected value of  $\gamma$  for  $\text{BaLiF}_3 \cdot \text{Pb}^+(1)$  that is 0.55. The obtained  $\gamma$  value from the experimental data is 0.52 (see Table 1). Therefore, the effective charge, in the  $\text{BaLiF}_3 \cdot \text{Pb}^+(1)$  crystal, is smaller than in KCl (that is approximately unity). Since the effective charge is not the same and the crystal field parameter is smaller in  $\text{BaLiF}_3$ , we expect a smaller effective charge for the  $\text{BaLiF}_3 \cdot \text{Pb}^+(1)$ . In fact, another evidence for this reduction is that the cation-(anion vacancy) distance for the  $\text{BaLiF}_3$  crystal is  $r = 2.83$  Å whereas for the  $\text{KMgF}_3$  crystal it is  $r = 2.82$  Å, i.e. essentially the same. Therefore, the difference in the crystal field parameter [0.72 for  $\text{KMgF}_3$  and 0.52 for  $\text{BaLiF}_3 \cdot \text{Pb}^+(1)$ ] should again be partially due to a smaller effective charge in  $\text{BaLiF}_3 \cdot \text{Pb}^+(1)$ . The value obtained for the effective spin-orbit splitting for  $\text{BaLiF}_3 \cdot \text{Pb}^+(1)$ ,  $\Delta$ , is 1.45 eV, this reduction (17%) is due to a small delocalization of the electron towards the vacancy.

Another important feature is the identification of three absorption bands  $\phi \Rightarrow \psi$  ( $A_1$ ),  $\phi \Rightarrow \chi$  ( $A_2$ ) and  $\phi \Rightarrow \Sigma$  ( $A_3$ ) (see insert of Fig. 6). The last  $A_3$  is analogous to the free ion ( $\text{Pb}^+$ ),  $P \Rightarrow S$  transition, therefore it is strongly allowed. Therefore, it is expected that the oscillator strength of the  $\phi \Rightarrow \Sigma$  is larger than that of  $\phi \Rightarrow \psi$  and  $\phi \Rightarrow \chi$  transitions. This is exactly what is observed, as can be seen in Fig. 3(a) and 3(b).

#### 4 CONCLUSION

We were able to obtain, for the first time, lead related color centers in a new matrix,  $\text{BaLiF}_3$  crystals,

by irradiation with 1.5 MeV electrons Pb<sup>+</sup>(1) color centers were identified and studied by means of optical absorption, emission and excitation spectroscopy. In particular, there are three excitation bands corresponding to a unique emission band (peaking at 880 nm), that shows essentially the characteristics of the Tl<sup>0</sup>(1) center. Furthermore, the relative strengths of the excitation transitions (744, 487 and 305 nm) show a good fit to the model developed for the Tl<sup>0</sup>(1) center. The crystal field parameter and the spin-orbit energy splitting are also in good agreement with the expected values for this new host.

## REFERENCES

1. W. Gellerman, F. Luty & C.R. Pollock, *Opt Commun.* **39**, 391 (1981)
2. G. Hörsch & H.J. Paus, *Opt. Commun.* **60**, 69 (1986)
3. W. Flassak, A. Göth, G. Hörsch & H.J. Paus, *IEEE J Quantum Electron* **24**(6), 1070 (1988).
4. M. Fockele, F. Lohse, J.M. Spaeth & R.H. Bartram, *J Phys. Condens. Matter* **1**, 13 (1989)
5. F. Lohse, M. Fockele & J.M. Spaeth, *Cryst. Latt. Def. and Amorph. Mat.* **16**, 275 (1987).
6. J.M. Spaeth, R.H. Bartram, M. Rac & M. Fockele, *J. Phys Condens Matter* **3**, 5013 (1991).
7. S.L. Baldochi & J.Y. Gesland, *Mat. Res. Bull.* **27**, 891 (1992).
8. N. Kristianpoller & B. Trieman, *Rad. Effects* **72**, 201 (1983)
9. M. Missori & A. Scacco, *Solid State Commun.* **76**, 5 (1990)
10. M. Fockele, F. Lohse & J.M. Spaeth, *Israel. J. Chem.* **29**, 13 (1989)
11. L.F. Mollenauer, N.D. Vieira Jr & L. Szeto, *Phys. Rev.* **B27**, 5332 (1983).
12. M. Fockele, F.J. Ahlers, F. Lohse, J.M. Spaeth & R.H. Bartram, *J. Phys. C Solid State Phys.* **18**, 1963 (1985).
13. F.J. Ahlers, F. Lohse, Th. Hangleiter, J.M. Spaeth & R.H. Bartram, *J Phys. C Solid State Phys.* **17**, 4877 (1984).
14. A. Boumriche, P. Simon, M. Rousseau, J.Y. Gesland & F. Gervais, *J Phys Condens Matter* **1**, 5613 (1989).