The luminescence microspectroscopy of Pr^{3+} -doped LiBaAlF_6 and $\text{Ba}_3\text{Al}_2\text{F}_{12}$ crystals

S.I. Omelkov^{a,b,*}, V. Kiisk^a, I. Sildos^a, M. Kirm^a, V. Nagirnyi^a, V.A. Pustovarov^b,
L.I. Isaenko^c, S.I. Lobanov^c

^a Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

^b Ural Federal University, Mira St. 19, 620002 Yekaterinburg, Russia

^c Institute of Geology and Mineralogy SB RAS, Russkaya St. 43, 630058 Novosibirsk, Russia

HIGHLIGHTS

- ▶ During crystal growth of Pr-doped LiBaAlF_6 , $\text{Ba}_3\text{Al}_2\text{F}_{12}$ was formed as a by-product.
- ▶ Microspectroscopy techniques allowed to study the two crystal phases separately.
- ▶ The Pr^{3+} concentration was found to be much higher in $\text{Ba}_3\text{Al}_2\text{F}_{12}$.
- ▶ The possible reasons of $\text{Ba}_3\text{Al}_2\text{F}_{12}$ formation while growth of $\text{Pr}^{3+}:\text{LiBaAlF}_6$ are discussed.

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ABSTRACT

The combined luminescence and Raman-scattering microspectroscopy technique allows separate spectroscopic studies on several crystal phases in mixed compounds. A mixed sample of LiBaAlF_6 and $\text{Ba}_3\text{Al}_2\text{F}_{12}$ doped with Pr was studied. The Pr^{3+} concentration was found to be much higher in the $\text{Ba}_3\text{Al}_2\text{F}_{12}$ phase. Several non-equivalent Pr^{3+} centers are present in both compounds, however, only in $\text{Ba}_3\text{Al}_2\text{F}_{12}$ there are several non-equivalent crystallographic positions of Ba. In LiBaAlF_6 non-equivalent Pr^{3+} centers appear because of complicated scheme for charge compensation of $(\text{Pr}_{\text{Ba}}^{3+})^+$. Possible reasons of $\text{Ba}_3\text{Al}_2\text{F}_{12}$ formation in the process of $\text{Pr}^{3+}:\text{LiBaAlF}_6$ growth are discussed. An excess of LiF in melt is assumed to produce $(\text{Li}_{\text{Ba}}^+)^-$ antisite defects as a charge compensation for $(\text{Pr}_{\text{Ba}}^{3+})^+$ substitution.

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1. Introduction

Complex fluorides are optical materials known for wide variety of their applications. One group of such compounds is formed on the basis of the well-studied LiAEAlF_6 ($\text{AE} = \text{Ca}, \text{Sr}$ or Ba) crystals. Eu-doped LiCaAlF_6 (LiCAF) is reported to be a highly sensitive material for thermoluminescence dosimetry (Shiran et al., 2004). The Ce^{3+} (Gektin et al., 2002) and Eu^{2+} (Shiran et al., 2003) activated LiCAF crystals were recognized as promising scintillators, while LiSrAlF_6 (LiSAF) was studied in a view of potential application for neutron detection (Yanagida et al., 2011). LiCAF and LiSAF are colquiriite type crystals with quite simple cubic structure. Well developed preparation techniques are used for their growth.

However, the development of new multicomponent fluoride-based compounds is connected with certain difficulties. Among them is the sophisticated growth process, especially for doped materials. It is caused by multiple factors like phase diagram complexity, possible oxygen contamination, AlF_3 volatility, difference in sizes of dopant and host ions, charge compensation requirements and many others. These factors lead very often to the formation of two or more different phases (compounds) within one sample. For example, an excess of 0.5 wt % of AlF_3 introduced in the course of SrAlF_5 growth to compensate AlF_3 volatility produced AIOF inclusions (Vasiliev et al., 2009). The search for proper growth conditions to obtain single-phase compounds is very time consuming, which is not acceptable in modern materials technology.

This article describes an experimental method combining luminescence and Raman-scattering microspectroscopy, which are powerful tools to study samples containing several crystalline

* Corresponding author. Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia. Tel.: +372 7374787; fax: +372 7383033.

E-mail address: omelkov@ut.ee (S.I. Omelkov).

phases within one polycrystalline sample. It reduces significantly time waste for test sample preparation and is capable of indicating ways for further improvement of a growth procedure. We apply microspectroscopy methods to the LiBaAlF_6 (LiBAF) compound. It is homologous to the above-mentioned LiAlF_6 group but has a different, more complex structure described by Merkulov et al. (2008). The luminescence properties of undoped LiBAF single crystals have been studied by us (Omelkov et al., 2010). Wet chemical synthesis and luminescent properties of Ce- and Eu-doped LiBAF (Belsare et al., 2009a, b) have been briefly reported. In the present study, Pr^{3+} ions were chosen as a dopant. Pr^{3+} ions are known to exhibit photon cascade emission (PCE) – a subsequent emission of two or more photons under UV or VUV excitation (Sommerdijk et al., 1974; Piper et al., 1974). Depending on the crystal field strength of a host, Pr^{3+} ions can act as a scintillating activator, producing fast 4f-5d emission, or alternatively exhibit slow intraconfigurational 4f transitions. In ternary elpasolite compounds it has been shown that the crystal field on various sites can introduce multiple luminescence centers resulting in several d-f luminescence bands along with 4f emissions depending on excitation energy (Schiffbauer et al., 2005).

During Pr:LiBAF crystal growth, the $\text{Ba}_3\text{Al}_2\text{F}_{12}$ compound was formed as a reaction by-product. Conventional spectroscopy methods fail in analysis of such sample, where different phases can accommodate Pr^{3+} ions in microcrystals. In the present report, we demonstrate the power of microspectroscopy methods in distinguishing materials characteristics.

2. Experimental

2.1. Luminescence microspectroscopy

Luminescence microspectroscopy measurements were carried out at a home-assembled setup (Fig. 1) consisting of an Olympus BX41M microscope combined with an Andor iXon DU-897D camera for fluorescence imaging and an Andor SR303i spectrometer equipped with an Andor Newton DU970P-BV CCD for spectral measurements. For excitation the sample was side-illuminated by a laser beam from a pulsed tunable optical parametric oscillator (OPO) Expla NT142/1/UVB (frequency 20 Hz, pulse length 5 ns, spectral line width 5 cm^{-1}). The spot diameter on a sample was not smaller than $\sim 1\text{ mm}$ to prevent possible ablation. With a continuous-wave laser source (several fixed-wavelength lasers available) it is also possible to use the confocal excitation and focus

the spot down to several microns. The spectrometer was coupled to a microscope through a $50\text{ }\mu\text{m}$ silica fiber, enabling confocal detection with the spatial resolution of a few microns. The system can be equipped with a Linkam THMS350V heating/cooling stage for microspectroscopy experiments within the temperature range 77–600 K.

Ordinary luminescent spectroscopy setup for a few mm size samples was used in low-temperature time-resolved measurements. The sample was mounted into an immersion Utreks-type liquid helium cryostat (temperature range 5–300 K). The same excitation source was applied, but the detector was changed to an Andor DH-501 ICCD camera cooled by a Peltier thermoelectric device to -15°C , which allowed recording time-resolved emission spectra. For emission decay kinetics measurements the spectrograph was equipped with a Hamamatsu H8259-01 photon counting head. The signal from the head was processed by FAST ComTec MCA-3 multichannel analyzer card.

The Raman scattering microspectroscopy was performed using a Renishaw micro-Raman setup, where the argon laser (514.5 nm) is used as excitation source. The sample is illuminated and the scattered light registered through Leica confocal microscope.

2.2. Samples preparation

The $\text{LiBaAlF}_6 \times \text{Ba}_3\text{Al}_2\text{F}_{12}$ mixed-phase compound was grown from the melt by the Bridgman method in a two-region furnace. Fluorides LiF, BaF_2 , AlF_3 , PrF_3 of 99.99% purity were taken as starting reagents. Pr concentration in melt was about 0.5 wt.%. The target compound LiBaAlF_6 melts congruentially at 840–860 $^\circ\text{C}$. An excess $\sim 0.5\text{ wt.}\%$ of AlF_3 was added to the original composition due to high volatility of this compound. The growth was carried out in a graphite container after a special treatment. The container was placed in a silica ampoule. All operations were carried out in a dry glove-box to avoid contamination with oxygen-containing impurities. To suppress the composition dissociation CF_4 gas was added into the reactor. The growth was performed at excess pressure (approximately 0.1 bar). Axial temperature gradient was $10^\circ/\text{cm}$, the ampoule pulling rate varied from 5 to 10 mm/day. XRD analysis has shown that the obtained polycrystalline agglomerate contained approx. 80% of LiBaAlF_6 and 20% of $\text{Ba}_3\text{Al}_2\text{F}_{12}$. The growth process and the lattice parameters of undoped LiBaAlF_6 crystals have been described by Merkulov et al., (2008), the crystal structure data of $\text{Ba}_3\text{Al}_2\text{F}_{12}$ have been presented by Kaiser and Babel (2004). An as-grown mixed phase sample was used in ordinary luminescent

Fig. 1. The scheme of a luminescence microspectroscopy setup.

Fig. 2. The sample prepared for microspectroscopy studies. Numbers enumerate different microsamples. The highlighted region is shown in Fig. 7.

spectroscopy measurements. For microspectroscopy studies the biggest monocrystalline pieces (max. size 100–200 μm) were extracted from the agglomerate and mounted in one layer on a black carbon sticker (Fig. 2).

3. Results and discussion

The low-temperature photoluminescence (PL) spectrum of the Pr-doped mixed phase $\text{LiBaAlF}_6 \times \text{Ba}_3\text{Al}_2\text{F}_{12}$ sample is presented by a series of lines in the region of 1.5–5 eV (Fig. 3). The emissions from both $(4f^2)^1S_0$ and $(4f^2)^3P_0$ states indicate that the photon cascade emission takes place, while no fast d-f emission is observed. The lines are inhomogeneously broadened, which cannot be explained only by crystal field splitting (normally it is only 300–500 cm^{-1} for 3F_2 level, see for example Antic-Fidancev et al. (1992)). The contribution to the emission spectra by different PL centers formed by the Pr^{3+} ions located in non-equivalent crystalline environment is highly probable.

Using OPO, the mixed phase sample was excited in the region of the $(4f^2)^3H_4 \rightarrow ^3P_0$ transition at $T = 10$ K, whereas the exact excitation energy varied from 2.575 to 2.611 eV. The 3P_0 state is not split by the crystal field, so each center has only one excitation line within this region. By monitoring the $^3P_0 \rightarrow ^3F_2$ emission with high resolution (better than 5 cm^{-1}), this experiment revealed a number of different inequivalent PL centers. As the 3F_2 state is split into up

Fig. 3. PL spectrum of the mixed phase sample, excited into $4f \rightarrow 5d$ band by synchrotron radiation ($E_{\text{exc}} = 6.70$ eV) at $T = 10$ K.

Fig. 4. PL emission spectra of different Pr^{3+} PL centers in a mixed phase sample at $T = 10$ K excited with laser beam into the $(4f^2)^3H_4 \rightarrow ^3P_0$ transition region (2.575–2.611 eV). Exact excitation energies (eV): 2.575 (1), 2.593 (2), 2.600 (3), 2.604 (4).

Fig. 5. Normalized PL emission spectra of the $\text{Pr}^{3+}(4f^2)^3P_0 \rightarrow ^3F_2$ transition in a mixed phase sample (M) and microsamples 1, 2 and 3 at $T = 290$ K, excited with laser beam at transition $(4f^2)^3H_4 \rightarrow ^3P_0$ (2.600 eV). Curves 2 and 3 are shifted by +1 and +2 units along intensity axis for better visibility.

to five Stark components, one could expect up to five lines in the emission spectra of a single PL center. The emission spectra of some of them are shown in Fig. 4.

The detailed analysis of these centers is out of the scope of the present paper. The corresponding study is in progress and will be published elsewhere. We will note only that the centers can be divided into two groups. The first group shows all the characteristic features of the Pr^{3+} emission in many different crystalline hosts:

Fig. 6. Raman scattering spectra recorded at $T = 290$ K. Microsamples are numbered according to Fig. 2. Curves 1 and 3 are shifted by +1 and +2 units along intensity axis for better visibility.

Fig. 7. An optical image (left) and the image of PL emission (right) of the highlighted region on the sample (see Fig. 2). The microsamples 1 (top) and 2 (bottom) are visible.

very narrow excitation and emission lines (about 10 cm^{-1} FWHM, see Fig. 4, curves 3,4) with the decay constant $\tau = 30\text{--}50 \text{ }\mu\text{s}$. The second group displays broader emission lines (curves 1,2) with $\tau = 1\text{--}2 \text{ }\mu\text{s}$. At $T = 290 \text{ K}$ due to the broadening of the excitation peaks all centers are excited simultaneously within the $2.575\text{--}2.611 \text{ eV}$ excitation range and hence no strong differences in emission spectra can be observed (see Fig. 5, curve labeled “M”).

Three crystallites (microsamples) were selected for further studies from the sample prepared for microspectroscopy (see Fig. 2). Their Raman scattering spectra were recorded and compared with that of a LiBAF single crystal (see Fig. 6). No measurements with polarized light were performed due to unknown orientation of the microsamples. It is clearly seen from Fig. 6 that the spectra of samples 2 and 3 resemble that of undoped LiBAF single crystal, while phonon spectrum of sample 1 is different. That is, the samples 2 and 3 are constituted mostly of LiBAF compound, while the sample 1 is most probably $\text{Ba}_3\text{Al}_2\text{F}_{12}$. To our best knowledge no Raman or infrared absorption spectra have been reported up to now for latter material. The background rising towards higher energy in curve 2 is likely to be a luminescence signal from some defect centers.

The PL of the same microsamples was further studied at a PL microspectroscopy setup at room temperature. All microsamples were illuminated simultaneously by an OPO laser beam in the region of the $(4f^2)^3\text{H}_4 \rightarrow ^3\text{P}_0$ transition of Pr^{3+} ions ($2.575\text{--}2.611 \text{ eV}$). The PL image of microsamples 1 and 2 shown on Fig. 7 did not depend on excitation energy within this region.

It is clearly seen that hardly any emission from the sample 2 (LiBAF) is visible, while sample 1 ($\text{Ba}_3\text{Al}_2\text{F}_{12}$) displays a strong light output. The spectrum of sample 1 emission did not change significantly with excitation energy in the region studied (see Fig. 5). The ratio of the intensities in the maxima of curves 1 and 2 is 13:1. The sample 3 shows the same light output as the sample 2. Due to the wide-area excitation used, some light scattered from the sample 1 was registered in the spectrum of sample 2. However, for the sample 3 this effect is negligible as it resides further away from strongly emitting samples. One can observe many overlapping bands in the PL spectrum of samples 2 and 3 (LiBAF) due to the presence of different Pr^{3+} PL centers formed by Pr^{3+} ions in non-equivalent crystalline environments. Mainly one kind of the Pr^{3+}

PL centers is responsible for the emission in sample 1 ($\text{Ba}_3\text{Al}_2\text{F}_{12}$). However, it is highly probable that there are other centres in lower concentration, as three non-equivalent crystallographic Ba^{3+} sites are available in $\text{Ba}_3\text{Al}_2\text{F}_{12}$.

The effective ionic radius of Pr^{3+} in an octahedral environment is 113 pm . Therefore, the most favorable positions for Pr^{3+} incorporation do not comprise the sites of Al^{3+} ions (67.5 pm) with the same charge. On the contrary, Ba^{2+} ions seem to be the most suitable for replacement by Pr^{3+} . The radius of the Ba^{2+} ion is 156 pm in an 8-coordinate position. The actual coordination number of Ba^{2+} ions is 12 in LiBAF and 10 or 11 in $\text{Ba}_3\text{Al}_2\text{F}_{12}$ depending on the crystallographic position. The Shannon radius of Ba^{2+} is 161 pm in LiBAF according to Merkulov et al. (2008). However, a big intensity difference of Pr^{3+} emissions shows that the concentration of Pr^{3+} ions is much smaller in LiBAF, than that in $\text{Ba}_3\text{Al}_2\text{F}_{12}$. This cannot be explained merely by the atomic radii difference, because the average interatomic $\text{Ba}^{2+} \leftrightarrow \text{F}^-$ distances are even slightly larger for LiBAF (300 pm) than for $\text{Ba}_3\text{Al}_2\text{F}_{12}$ ($280\text{--}290 \text{ pm}$). The reason for the formation of $\text{Ba}_3\text{Al}_2\text{F}_{12}$ in order to accommodate dopant ions lies, most probably, in the charge compensation requirements. One of the logical ways to compensate Pr in a Ba site ($\text{Pr}_{\text{Ba}}^{3+}$) in LiBAF is a Li vacancy (Li_v). Together with the smaller ($\text{Pr}_{\text{Ba}}^{3+}$) radius (comparing to a regular Ba^{2+}) it might lead to low stability of LiBAF with $(\text{Li}_v)^-$ and formation of $\text{Ba}_3\text{Al}_2\text{F}_{12}$ locally around the Pr^{3+} dopant. On the other hand, charge compensation is possible via $(\text{Li}_{\text{Ba}}^+)^-$, which causes the lack of lithium and shifts the melt composition towards $\text{Ba}_3\text{Al}_2\text{F}_{12}$ in the concentration diagram triangle $\text{LiF}\text{--}\text{BaF}_2\text{--}\text{AlF}_3$ (Al-Mansour and Wallrafen, 1993). In both cases, $(\text{Li}_{\text{Ba}}^+)^-$ defects may provide charge compensation in $\text{Pr}^{3+}\text{:Ba}_3\text{Al}_2\text{F}_{12}$. If these assumptions are correct, an excess of LiF added in the melt in the same amount as the PrF_3 dopant is an option to form Li_{Ba}^+ instead of Li vacancies in LiBAF, possibly preventing $\text{Ba}_3\text{Al}_2\text{F}_{12}$ formation.

4. Conclusions

The combined luminescence and Raman-scattering microspectroscopy technique allows separate spectroscopic studies on mixed phase compounds. A Pr-doped $\text{LiBaAlF}_6 \times \text{Ba}_3\text{Al}_2\text{F}_{12}$ mixed phase sample was studied. The Pr^{3+} concentration was found to be

much higher in the $\text{Ba}_3\text{Al}_2\text{F}_{12}$ phase. In both compounds several non-equivalent Pr^{3+} centers are present due to several non-equivalent crystallographic positions of Ba^{2+} in $\text{Ba}_3\text{Al}_2\text{F}_{12}$ and more complicated charge compensation scheme of $(\text{Pr}_{\text{Ba}}^{3+})^+$ in LiBaAlF_6 . The possible reasons favoring of $\text{Ba}_3\text{Al}_2\text{F}_{12}$ formation during growth of $\text{Pr}^{3+}:\text{LiBaAlF}_6$ include low stability of LiBAF with $(\text{Li}_v)^-$ providing charge compensation, or the lack of lithium in case $(\text{Li}_{\text{Ba}}^+)^-$ centers provide it. An excess of LiF in melt is proposed to produce additional $(\text{Li}_{\text{Ba}}^+)^-$ antisite defects as a charge compensation for $(\text{Pr}_{\text{Ba}}^{3+})^+$ substitution.

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