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Luminescence and decay kinetics of Pb^{2+} center in $LiCaAlF_6$ single crystal host

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The Pb-doped $LiCaAlF_6$ single crystals were grown using the micro-pulling-down method. The temperature dependences of photoluminescence characteristics were studied to reveal the kinetic processes in the excited state of Pb^{2+} luminescence center. A simple three-level phenomenological model applied to the decay time temperature dependences shows that energy separation between the metastable $^3P_0$ and the radiative $^3P_1$ states of Pb^{2+} center is relatively high, about 180 meV ($\sim$1470 cm^{-1}). Induced absorption spectrum after UV illumination at 500 K points to slight ionization of the Pb^{2+} excited state and creation of the color F-center with an absorption peak located around 260 nm.

1. Introduction

Due to the development of new generation of monitoring techniques in the field of safety measures there is a need for new scintillating materials for neutron detection. Such materials should meet several essential requirements: contain ^6Li or ^{10}B isotopes as regular lattice ions, have low density to be insensitive for background gamma rays and show reasonably fast scintillation response [1]. Among new single crystal materials studied for this purpose the Pb^{2+}-doped $LiCaAlF_6$ (LiCAF) crystal has been briefly reported [2]. The LiCAF single crystal host is not fragile and non hygroscopic. Recently, this host has received a lot of attention for its use in a solid-state laser [3,4] as well as scintillation applications when doped with Ce^{3+} [5]. Eu-doped LiCAF was considered both for scintillator [6] and dosimetric [7] materials applications. Furthermore, this material was intensively studied because it demonstrates superior transmittance in the UV and VUV wavelength regions, which is highly required for application as window materials for optical lithography [8,9]. Extensive research on improving LiCAF growth procedure and its optical properties has resulted in industrial-size production of high quality crystals [10].

The Pb^{2+} luminescence center belongs to the so-called ns^2 ions such as Tl^+, Pb^{2+} and Bi^{3+}, which have been studied for several decades and attractive luminescence properties have been found [11]. The lower-lying $^3P_0$ and $^3P_1$ excited state levels are responsible for the luminescence features. The transition from the $^3P_0$ to the ground $^1S_0$ state is J–J forbidden and only weakly allowed by phonon interaction so that it is characterized by long radiative lifetime of the order of milliseconds. The transition from the $^3P_1$ to the ground $^1S_0$ state is partially allowed due to the spin–orbit coupling which mixes the spin-allowed $^1P_1$ level with $^3P_1$ level. Such mixing results in radiative lifetime of the order of hundreds of nanoseconds [12]. The $^3P_0$ level is usually called metastable, while the $^3P_1$ level is often referred to as radiative. The $^3P_1$ and $^3P_0$ levels are close enough to obtain the thermal population of the $^3P_1$ level from the $^3P_0$ at higher temperatures.

The aim of this work was to study the optical and luminescence properties and the temperature dependence of photoluminescence decay time of the Pb^{2+} center in the LiCAF host. Application of the simple two-level phenomenological model on the decay time temperature dependence data provides a deeper insight into the excited state dynamics of the Pb^{2+} luminescence center.

2. Sample preparation and experimental procedures

Single crystals were grown by the micro-pulling-down method adapted for the growth of fluoride crystal [13]. Starting materials

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were prepared from the stoichiometric mixture of 99.99% pure LiF, CaF_2, PbF_2 and AlF_3 powders produced by Stella Chemifa Corp. They were thoroughly mixed and charged into the carbon crucible for as-melting. The growth chamber was first evacuated to 10^{-4} Torr. The crucible was then heated to 400 °C and kept at the temperature for about 1 h in order to remove oxygen traces caused by moisture of raw materials and adsorbates on the chamber surface. Following the baking procedure, the chamber was further evacuated down to 10^{-5} Torr. After the baking, the growth chamber was filled with 1:1 mixture of high purity Ar (99.9999%) and CF_4 (99.999%) until reaching an ambient pressure. Finally, the crucible was heated to the target material melting temperature of about 800 °C and left at the temperature for 1 h. As-melted materials obtained by described procedure were used for subsequent crystal growth experiments. We use platinum wire for seeding during all crystal growth runs. The pulling-down rate was 0.1 mm/min.

Samples of as-grown crystals were ground into powders. To identify the obtained phase, a powder X-ray diffraction (XRD) analysis was carried out at room temperature (RT) in air with a RIGAKU RINT Ultima diffractometer using Cu Kα X-ray source (40 kV, 40 mA). The chemical composition was examined by electron probe micro-analysis (EPMA) using a JEOL JXA-8612MX. Samples were cross-sectioned and analyzed in radial direction using 10 μm electron probe.

Absorption spectra were measured with UV–VIS–NIR spectrophotometer Shimadzu UV-3101PC at RT. The Spectrofluorimeter 199S (Edinburgh Instruments) was used for the luminescence experiments performed from liquid nitrogen temperature up to 500 K. An X-ray tube (radioluminescence spectra), steady-state hydrogen lamp (photoluminescence spectra) and pulsed xenon microsecond flashlamp and hydrogen-filled pulsed coaxial nanosecond flashlamp (photoluminescence decay) were used as excitation sources. Single grating emission monochromator and Peltier-cooled TBX-04 detection module (IBH Scotland) working in photon counting mode were used in the detection part. All the spectra were corrected for experimental distortions. Luminescence decay kinetics with the microsecond xenon flashlamp was measured using detection by multichannel analyzer in the scaling mode, while the decay kinetics measurements with the hydrogen-filled nanosecond flashlamp were performed using the time-correlated single photon counting method. Deconvolution procedures with the instrumental response (Spectra-Solve software of Ames Photonics Inc.) were used to extract true decay times.

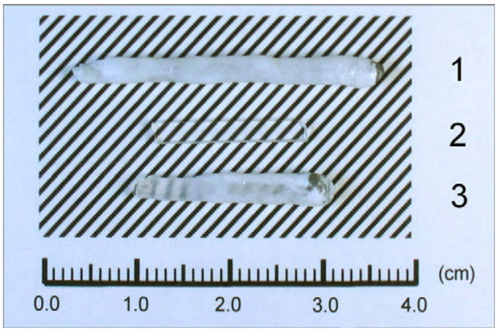

Fig. 1. LiCAF:Pb micro-pulling-down grown crystals: (1) 0.46 mol%, (2) 0.56 mol% (cross-sectioned and polished) and (3) 0.31 mol% Pb^{2+} in crystal, ((1) 1 mol%, (2) 5 mol% and (3) 10 mol% Pb^{2+} in the melt, respectively).

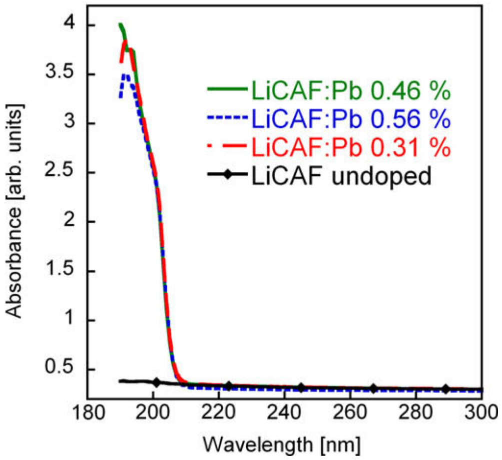

Fig. 2. Absorption spectra (RT) of undoped and Pb-doped LiCAF: 0.31, 0.46 and 0.56 mol%.

3. Results and discussion

Crystal growth of Pb-doped LiCAF was complicated by expected high volatility of PbF_2 during all stages of the process – preliminary baking, as-melting, final baking, melting and crystal growth itself. To compensate these losses, an excess amount of PbF_2 was added depending on the desired molar composition. From the initial compositions of 1.0, 5.0 and 10.0 mol% Pb-doped $LiCaAlF_6$, single crystals containing 0.46, 0.56 and 0.31 mol%, respectively, with quite uniform radial dopant distribution were produced. For details see [2].

A photo of the obtained crystals is given in Fig. 1. Surface of the crystals is rough and there are cracks at the very beginning, but their main body is quite transparent and crack-free, see No. 2 sample. Powder XRD performed on ground crystals manifest reflections pattern consistent with $P\bar{3}1c$ space group (JCPDS 73-2441).

The absorption spectra show complex Pb^{2+}-related absorption band at about 192 nm with the shoulder at 200 nm, see Fig. 2. No pronounced concentration dependence is found. This can be caused by variations in the optical quality of the crystal. Furthermore, the absorption peak is at the spectrophotometer limit (190 nm) and its high energy part could not be measured therefore. In fluoride matrices the lowest absorption transition (A-absorption band) of the heavy ns^2 ions (Tl^+, Pb^{2+}, Bi^{3+}) is situated in deep UV region within 200–250 nm [11,14]. Due to similar size of Ca^{2+} and Pb^{2+} ions, compared to Li^+ and Al^{3+} ones, and relatively isolated CaO_6 octahedron in LiCAF structure, even higher energy of this Pb^{2+} absorption transition is obtained in the present case peaking even below 200 nm.

Emission spectrum under the 204 nm excitation at RT and peaking at around 209 nm for the sample with 1 mol% Pb (0.46 mol% in crystal) is shown in Fig. 3. Excitation spectrum of the 209 nm emission is also displayed. Mutual position of maxima of both spectra indicates a small Stokes shift of about 0.2–0.3 eV (estimated value). This is probably due to the mentioned relative isolation and rigidity of CaO_6 octahedron in LiCAF structure as well as close values of Pb^{2+} and Ca^{2+} ionic radii in the 6-coordinated site.

In the radioluminescence spectra we observe well-shaped band at 208 nm, see Fig. 4, which resembles to the photoluminescence. There is some Pb-concentration dependence approximately proportional to the values obtained from chemical analysis of the crystals, in contrast to the absorption measurements. Due to the different interaction of UV/VIS light and X-rays with the sample, the radioluminescence measurements are less sensitive to crystal quality than the absorption ones, which is probably an explanation for the observation of such a trend. There are practically no other noticeable emissions up to 750 nm for any of the samples. Undoped LiCAF shows practically no emission at RT.