Crystal growth and scintillation properties of Ce-doped PrAlO$_3$

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Abstract

Using the micro-pulling-down method, the undoped and Ce$^{3+}$-doped PrAlO$_3$ single crystals were grown. Absorption spectra and luminescence characteristics under UV and X-ray excitations were measured at room temperature. Weak 5d–4f emission of Pr$^{3+}$ was found at 265 nm in the undoped sample. Energy transfer from the Pr$^{3+}$ sublattice to Ce$^{3+}$ ions seems plausible, but absence of efficient Ce$^{3+}$ emission was found and explained as due to the positioning 5d$_1$ relaxed excited state of Ce$^{3+}$ within the host conduction band.

Keywords: Ce-doping; Micro-pulling-down method; Oxides; Scintillator material

1. Introduction

Scintillator materials based on the Ce-doping are of persistent interest due to short decay time of the Ce$^{3+}$ emission center, which is within tens-of-ns range depending on the crystal host [1,2]. Wide commercial application of Ce$^{3+}$-doped YAlO$_3$, Gd$_2$SiO$_5$ and Lu$_2$SiO$_5$ in medical imaging systems, high-energy physics and industry [3–6] stimulates the search for new scintillating materials. Doping PrF$_3$ with Ce$^{3+}$ has been shown to be a novel approach to obtain potentially promising scintillator because of efficient energy transfer from the Pr$^{3+}$ subsystem to Ce$^{3+}$ ions via the $^1$S$_0$ level of Pr$^{3+}$ [7]. Furthermore, relatively easy doping of the Ce$^{3+}$ ion into a Pr-based crystal lattice with possibility to form a wide range of solid solutions is of practical importance.

Recently, successful crystal growth of PrAlO$_3$ by the Czochralski method and results of spectroscopic properties characterization have been reported, but no reasonable application of this material was proposed [8]. Undoped PrAlO$_3$ can hardly ever be used as a scintillator because of strong concentration quenching of the Pr$^{3+}$ 5d–4f emission. However, it also points to an enhanced energy migration over the Pr$^{3+}$ energy levels and the very interesting question appears – which level is the guiding one. It could be either the lowest 5d$_1$ state or energy penetrates immediately to the lower P or D f-levels of Pr$^{3+}$. If the former process is prevailing, quite efficient energy transfer to Ce$^{3+}$ may happen. Because both involved levels of Pr$^{3+}$ and Ce$^{3+}$ are d-levels, sufficient overlapping of 5d–4f emission of Pr$^{3+}$ with Ce$^{3+}$ excitation band is expected. If this concept works, it can save the migrating energy from Pr$^{3+}$ cations to Ce$^{3+}$ emission centers increasing luminosity.

In this paper, we show the results of Ce-doped PrAlO$_3$ crystal growth by the micro-pulling-down method (μ-PD) and characterization of its scintillation performance in the light of the potentiality of such a material to obtain a new fast scintillator of elevated density.

2. Experimental

Starting materials were prepared from the stoichiometric mixture of 4 N purity Pr$_6$O$_{11}$, Al$_2$O$_3$ and CeO$_2$ powders. Undoped and Ce-doped PrAlO$_3$ square-shaped single crystals were grown by the μ-PD method using an
iridium crucible with a die [9]. The crucible was heated inductively at a frequency of 20 kHz. Ir wire was used as a seed. Pulling rate was 0.05–0.1 mm/min. The growth atmosphere was a mixture of Ar + H₂ (3 vol%).

To identify the obtained phase, powder X-ray diffraction (XRD) analysis was carried out in air at room temperature (RT) with a Rigaku RINT Ultima diffractometer using Cu Kα X-ray source (40 kV, 40 mA). The chemical composition was analyzed by electron probe micro-analysis (EPMA) using JEOL JXA-8600 analyzer.

Plates of 4 × 4 × 1 mm were cut and polished for the optical experiments. Absorption spectra were measured by the UV–VIS–NIR spectrophotometer Shimadzu UV-3101PC at RT. Measurements of photoluminescence characteristics were performed within 80–450 K using liquid nitrogen bath optical cryostat of Oxford Instrument. The Spectrofluorometer 199S (Edinburgh Instruments) was used for the luminescence experiment. It was equipped with a steady-state hydrogen flashlamp and nanosecond hydrogen-filled flashlamp serving as the 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 within ns to ms time scale was measured at the same set-up using the nanosecond hydrogen-filled coaxial flashlamp and time-correlated single photon counting method. Deconvolution procedures (Spectra-Solve software of LASTEK) were used to extract true decay times in the situation where the decay curves were distorted due to a finite width of the instrumental response.

3. Results and discussion

Transparent and crack-free undoped and Ce-doped (1, 2 and 5 mol%) PrAlO₃ square-shaped single crystals (4 × 4 × 12 mm) were grown by the μ-PD method. Powder XRD performed on ground crystals revealed reflections patterns consistent with R3m space group (JCPDS 85-1069). No impurity phase was detected.

Results of EPMA demonstrated uniform Ce distribution in the samples with the effective segregation coefficient near unity. It should be noted here that for the Czochralski grown Ce-doped Lu₂SiO₅, Ce has low distribution coefficient and distribution itself is not uniform [10]. High pulling rates applied in the practice of the single crystal growth by the μ-PD method lead to the effective segregation coefficient near unity with uniform distribution of the dopant. On the other hand, similarity of the ionic radius of Pr and Ce is an extra advantage for this process.

Absorption spectra of the samples are given in Fig. 1. In the undoped PrAlO₃ the onset of 4f–5d absorption transition was found at about 250 nm and 4f-4f transitions to the ¹Pₓ (450–490 nm), ¹D₂ (595 nm) and ¹G₄ (~1000 nm) levels of Pr³⁺ as well. Ce³⁺ doping introduces 4f–5d transition of Ce³⁺ with the onset at about 340 nm.

In Fig. 2 the radioluminescence spectra of the undoped and two Ce-doped samples are presented. In the undoped sample, very weak and broad emission is found peaking at about 265 nm, which is strongly diminished in the Ce-doped samples. The latter samples show slightly increasing and rather flat emission round 400 nm. Finally, all the samples show four emission lines at about 490, 545, 585 and 615 nm of similar intensity in all of them. Taking into account the position of Pr³⁺ 5d–4f emission at about 245 nm [11] the broad emission band at 265 nm in PrAlO₃ can be ascribed to the same transition of Pr³⁺, which is strongly diminished due to concentration quenching. As this emission is overlapped with the Ce³⁺ absorption in the Ce-doped samples, the diminishing of the former can be interpreted as the energy transfer to the Ce³⁺ ions and increasing emission round 400 nm as the 5d–4f emission of Ce³⁺. However, extremely weak intensity of 400 nm...
emission and its rather flat shape indicate that very probably even the relaxed $^5d_1$ excited state of Ce$^{3+}$ lays within the conduction band of PrAlO$_3$ host and thus the ionization of excited Ce$^{3+}$ ion easily occurs resulting in the emission quenching, which is usual in this situation [12].

Four emission lines mentioned are most probably related to emission of accidental Tb$^{3+}$ impurity ($^5D_4$–$^7F_x$ transitions). It is interesting to note that the Tb$^{3+}$ $^5D_4$ level is in an approximate resonance with the Pr$^{3+}$ $^3P_0$ one, which can become populated during the energy relaxation process of the excited Pr$^{3+}$ ion and due to energy migration these Tb$^{3+}$ emission transitions can be fed. In Fig. 3 the emission band was further found round 300 nm, which shows the onset of the excitation towards 200 nm. In YAlO$_3$ a broad and structured emission within 250–500 nm was found and interpreted as the emission of an exciton localized around lattice defects [13] and due to great similarity the same assignment can be tentatively adopted also in this case.

4. Conclusions

Undoped and Ce-doped (1, 2 and 5 mol%) PrAlO$_3$ shaped single crystals were grown by the micro-pulling-down method. Crystal samples have uniform dopant distribution with the effective segregation coefficient near unity. Luminescence of both undoped and Ce-doped samples was found to be very weak. Broad band at 265 nm was ascribed to the 5d–4f emission of Pr$^{3+}$ and is strongly diminished due to concentration quenching. Energy transfer occurs from this band towards Ce$^{3+}$ ions. Only a very weak emission found round 400 nm in the Ce-doped samples was ascribed to 5d–4f emission of Ce$^{3+}$. Strong inefficiency of the latter was tentatively explained by the location of $^5d_1$ relaxed excited state of Ce$^{3+}$ in the conduction band of PrAlO$_3$. Weak emission at 300 nm was ascribed to the host lattice luminescence. Due to inefficient luminescence mechanism these materials are found unsuitable to be used for fast scintillators.

Acknowledgements

The authors acknowledge the financial support provided by the Japan Society for the Promotion of Science (JSPS), the Postdoctoral Fellowship for Foreign Researches Program (AN), the Czech projects MSMT, KONTAKT, ME871 and Institutional Research Plan No. AV0Z10100521 in Institute of Physics AS CR.

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