Growth and scintillation characteristics of CeF₃, PrF₃ and NdF₃ single crystals

Kiyoshi Shimamuraᵃ,⁎, Encarnación G. Villoraᵃ, Satoshi Nakakitaᵇ, Martin Niklᶜ, Noboru Ichinoseᵃ

ᵃKagami Memorial Laboratory for Materials Science and Technology, Waseda University, 2-8-26 Nishiwaseda, Tokyo 169-0051, Japan
ᵇHokushin Corporation, 2-3-6 Shirite, Yokohama 230-0003, Japan
ᶜInstitute of Physics AS CR, Cukrovarnicka 10, Prague 162 53, Czech Republic

Received 11 November 2003; accepted 15 December 2003

Abstract

CeF₃, PrF₃ and NdF₃ single crystals with 1 inch in diameter have been grown under CF₄ atmosphere by the modified Czochralski technique. PrF₃ exhibited a single sharp emission at about 400 nm, with a light intensity comparable to that of BGO and a decay time of 510 ns. Lu-doping was effective to increase the luminescence efficiency of CeF₃.

© 2003 Elsevier B.V. All rights reserved.

PACS: 81.10.—h; 29.40.Mc

Keywords: A2. Czochralski method; B1. Rare-earth compounds; B2. Scintillator materials

1. Introduction

Lanthanide ions, due to their characteristic sharp absorption and emission bands in the ultraviolet, visible and infrared wavelength region, originated by f–d and f–f transitions, have been widely investigated as dopants for compounds used in luminescence devices, such as fluorescent lamps, scintillators and lasers. Among the lanthanide ions, Ce³⁺, Pr³⁺ and Nd³⁺ are of particular interest for scintillation crystals, as they can be efficient activator ions [1]. Ce³⁺-doping has been extensively studied, since it usually shows a fast dipole allowed d–f luminescence, with typically 10–50 ns decay time. Pr³⁺ and Nd³⁺ ions can show also a fast luminescence if a multiphonon relaxation from the lowest 5d level to a lower lying 4f level does not take place. In the recent years, a renewed interest in Pr³⁺ is emerging, since this ion can be a sensitizer for the 172 nm Xe discharge emission [2,3]. Photon cascade emission (PCE) of the Pr³⁺ ion, originated in sequential f–f transitions ($^1S_0 \rightarrow ^1I_6$ at approximately 400 nm followed by $^3P_0 \rightarrow ^3H_4$ at approximately 490 nm), can yield to quantum efficiencies larger than 1. High efficiency would enable the substitution of Hg (emission at 248 nm) in present fluorescence lamps by the novel gas Xe.

Scintillation characteristics of CeF₃ single crystals have been reported [4,5]. It showed promising
scintillation characteristics, such as short decay time and high radiation resistivity, however the luminescence efficiency of the Ce³⁺ ion was intrinsically limited. Instead, Ce³⁺ ions is being used as activator in many different host materials. Although Pr- and Nd-doping have also been investigated [6], to our knowledge, single crystals of the binary PrF₃ and NdF₃ have not been studied yet.

CeF₃, PrF₃ and NdF₃ are isostructural (tysonite, with the space group P3c1) with very similar lattice parameters. Their melting points are between 1400 and 1500 °C [7], and do not show any structural phase transition upon cooling down to room temperature. On contrast, most of the other rare earth trifluorides (REF₃) exhibit a transition from hexagonal to orthorombic. Initial growth studies of REF₃ go back to the 1960s. Single crystals of maximum 5 mm in diameter could be grown under HF or He atmosphere by the Czochralski (CZ) [8–10] and the Bridgman [11–13] techniques. The growth of CeF₃ single crystals by the Bridgman technique was substantially improved in the early 1990s by the use of higher purity raw material and more “oxygen-free” growth conditions.

In the present work, we describe the growth characteristics of undoped and doped CeF₃, PrF₃ and NdF₃ single crystals by the modified CZ technique, expressly developed for the growth of fluoride materials [14–17]. The crystalline phase was determined by standard X-ray powder diffraction. Optical properties were studied by means of transmittance, X-ray luminescence and decay time measurements.

2. Experiment

Crystal growth was carried out in a CZ system with a 30 kW R.F.-generator. High purity powders (> 99.99%) of commercially available CeF₃, PrF₃ and NdF₃ were placed in a Pt crucible and heated at 1000 °C for a period of 12 h under vacuum (≈ 10⁻³ Pa). This vacuum level, obtained by a rotary and a diffusion pump, was necessary to eliminate effectively the water and oxygen present in the chamber and raw materials. Subsequently, high purity CF₄ gas (99.99%) was slowly flowed into the furnace and the powders were melted at about 1450 °C. After seeding, single crystals were pulled at 2 mm/h, while rotating the seed at 15 rpm. Additionally, it was observed that single crystals can be as well obtained by slow cooling down the melt inside the crucible, similar to the growth by the Bridgman technique. RE-solid solution experiments were carried out by the slow cooling method, after filling the crucible with the corresponding REF₃ powders. Following nominal compositions were prepared: 1 mol% RE:PrF₃ (RE = Nd³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺ and Tm³⁺), 5 mol% RE:PrF₃ (RE = Eu³⁺, Tb³⁺ and Dy³⁺), 5 mol% RE-CeF₃ (RE = Ho³⁺, Er³⁺, Tm³⁺ and Lu³⁺) and 10 mol% Lu³⁺:CeF₃. In the following, this solid solution crystals are denoted as RE-doped PrF₃ and CeF₃.

Absorption spectra were measured using a Shimadzu PC3101 UV/VIS/NIR. Luminescence spectra were obtained by a Spectrofluorometer 199S (Edinburgh Instruments) equipped with an X-ray tube as the excitation source for radioluminescence experiments.

3. Results and discussion

3.1. Crystal growth

An as-grown NdF₃ single crystal with 25 mm in diameter and 80 mm in length is shown in Fig. 1. It was transparent and red–violet in color, free from cracks and macrodefects. The symptom for foot-like spiral growth was observed at the tail part. The surface of the neck and shoulder of the crystal were covered by a black graphite based substance, which easily peeled off. CeF₃ growth proceeded in the same way and presented a similar behavior. The crystal was transparent, colorless and also macro defects free, as shown in the photo of Fig. 2.

All three materials had as a common feature a strong evaporation from the melt, condensing on the cooled chamber inner wall, however, contrary to the relative stable growth of CeF₃ and NdF₃, the growth of PrF₃ was of pronounced spiral character (Fig. 3), bending towards the direction
opposite to the crystal rotation, i.e. anticlockwise. The crystal was transparent and green in color, as well as macro defects free, however, the graphite contamination on the surface could not be so easily removed like in the case of CeF$_3$ and NdF$_3$.

Fig. 4 shows as an example a PrF$_3$ single crystal obtained by the slow cooling down of the melt in an open crucible.

X-ray powder diffraction patterns of the grown crystals are shown in Fig. 5. All peaks can be ascribed to the tysonite structure, indicating the single phase character of the crystals. Table 1 shows the estimated lattice parameters. The lattice parameter increased with the ionic radii.

3.2. Spiral characteristic

CeF$_3$, PrF$_3$ and NdF$_3$ are very similar from the chemical point of view; same space group, close ionic radii, bonding character and melting point. The difference in growth behavior can be interpreted regarding the optical properties. It is known that for materials with high melting temperatures, the temperature distribution within the growing crystal is affected by the crystal color, which can be either of intrinsic character or due to the presence of dopants and/or impurities. The origin is ascribed to a coupling between the radiation from the crucible and the crystal absorption [18,19]. According to the Wien’s displacement law [20], the wavelength of maximum emissive power $\lambda_{\text{max}}$ is given as

$$\lambda_{\text{max}} T_{\text{m}} = b,$$

where $T_{\text{m}}$ is the melting point of the crystal in K and $b$ is a constant derived from the Planck’s radiation law [21]. In the case of a clean and polished platinum surface, $b$ can be set to 0.258 (cm K). Taking into account that the melting temperatures of CeF$_3$, NdF$_3$ and PrF$_3$ lie between 1400 °C and 1500 °C, the $\lambda_{\text{max}}$ of the heated Pt crucible is estimated to range within 1455–1542 nm. The absorption of all three materials in the near infrared is shown in Fig. 6. It is seen that PrF$_3$ presents a broad absorption between 1300 and 1700 nm, coincident with the wavelength region of maximum emissive power from the crucible. Instead, NdF$_3$ weakly absorbs between 1500 and 1800 nm and CeF$_3$ is practically transparent. These absorption bands correspond to excitations from the ground state to the $^3F_{4,3}$ and $^4I_{15/2}$ bands for PrF$_3$ and NdF$_3$, respectively. We interpret that the efficient heating of the growing
PrF$_3$ crystal, in contrast to NdF$_3$ and CeF$_3$, promotes an increase of the temperature near to the solid–liquid interface. This leads to a nonsymmetric melt flow and with it to the spiral characteristics [21]. The symptom for spiral growth in the case of NdF$_3$ appears after a relatively large crystal has been pulled, because of the much weaker coupling.

3.3. Absorption

Absorption spectra of the as-grown PrF$_3$, CeF$_3$ and NdF$_3$ singles crystals are shown in Fig. 7. Typical f–f transitions are indexed according to the well-known Dieke’s energy scheme. PrF$_3$ absorption at about 213 nm, which is assigned to the electric dipole forbidden transition from the ground state to the highest energy 4f$^2$ state of Pr$^{3+}$, $^3H_4 \rightarrow ^1S_0$. The dipole allowed 4f$^2$ -- 4f5d absorption band cannot be completely observed, since it lies out of the spectrometer range. In the case of CeF$_3$, the onset of 4f–5d absorption of Ce$^{3+}$ is situated below 280 nm without any shoulders at lower energies, which evidences the high quality and “oxygen-free” character of CeF$_3$ crystal [4]. Absorption spectrum of NdF$_3$ shows a rich collection of absorption lines related to f–f transitions of the Nd$^{3+}$ ion.

3.4. Emission

Fig. 8 summarizes the main features of the emission spectra after X-ray excitation. For clarity, the emission spectra are shown together with the emission of standard Bi$_4$Ge$_3$O$_{12}$ (BGO). PrF$_3$ shows three emissions at 269, 334 and 394 nm and a broad band around 290 nm, with relative integrated intensities 0.13, 0.03 and 0.84,
respectively. These emissions correspond to f–f transitions, from the \( ^1S_0 \) level to the \( ^1G_4, ^1D_2 \) and \( ^1I_6 \) multiplets, respectively. Photocascade emission, due to further radiative transitions from the intermediate levels to the lower and ground 4f\(^2\) states, \( ^3P_J \rightarrow ^2H_J \) and \( ^1D_2 \rightarrow ^3H_J \) (emission lines at about 480 and 600 nm, respectively), was not observed. The quenching of these emissions has been previously observed \([3,22,23]\). The decay characteristic of the dominant emission at 394 nm can be described by a single exponential function with 510 ns decay time, which is rather fast in comparison with most of the f–f radiative transitions within the group of RE ions, due to the forbidden character of these electric dipole transitions. The light yield of the 394 nm emission at room temperature amounted about \(1/7\) of that of BGO. This is to our knowledge the largest

reported for the Pr\(^{3+}\) ion, and it could arise interest for specific applications, since this narrow band emission coincides very well with the wavelength region where standard detectors exhibit a maximum efficiency.
Attempts to increase the emission efficiency by codoping with other RE ions, susceptible to efficient energy transfer from the Pr$^{3+}$ ions, have been unsuccessful in Pr$^{3+}$:YF$_3$ specimens [24]. RE-doping in the present work also suggests that Pr$^{3+}$ does not sensitize other RE$^{3+}$s. The lack of energy transfer can be interpreted by the fact that the first spin allowed f–d transitions of the tested RE-dopants are above that of Pr$^{3+}$ [1,25], so that hot electrons can deexcite firstly to the lowest 4f5d state of Pr$^{3+}$, and subsequently to the $^1S_0$ level.

Radioluminescence spectra of the CeF$_3$ crystal exhibited the typical Ce$^{3+}$ emission within 280–300 nm (Fig. 8). The relatively low intensity of the Ce-perturbed luminescence at lower energies provides further evidence for the high quality of the crystals. The decay time of CeF$_3$ at 290 and 340 nm was about 17 and 29 ns, respectively, which is in very good agreement with the reported values for the “regular” and “perturbed” Ce$^{3+}$ emissions in this material [26].

In the case of NdF$_3$, no emission could be observed in the visible wavelength region under X-ray excitation. It is expected that the emission occurs in the nearinfrared, at the well-known transition at about 1060 nm.

RE-doped PrF$_3$ crystals led to the same emission features and relative intensities of the three emission as in the case of undoped PrF$_3$ crystals, except for the fact that the broad band around

---

**Fig. 7.** Absorption spectra of CeF$_3$ (a), PrF$_3$ (b) and NdF$_3$ (c) at room temperature.

**Fig. 8.** Emission spectra of CeF$_3$, Lu:CeF$_3$, PrF$_3$ and BGO, after X-ray excitation at room temperature.
290 nm was not observed in the RE-doped crystals. The light yield of the doped crystals was lower than that of the undoped.

RE-doping in CeF$_3$ had similarities to the PrF$_3$ case. The intensity of the “regular” Ce$^{3+}$ site emission varied relative to the undoped one, without affecting the emission characteristic of Ce$^{3+}$. An exceptions was given by Tm-doping, whereas additional very weak emissions could be detected at 342, 357 and 444 nm. The light yield decreased after doping in the case of Ho$^{3+}$, Er$^{3+}$ and Tm$^{3+}$ (the values relative to the undoped being 0.36, 0.60, and 0.51, respectively). On contrast, a strong increase in light yield was observed for Lu$^{3+}$-doping. Addition of nominally 5 mol% Lu$^{3+}$ improved the light yield by approximately 50% (Fig. 8), yielding with it to an intensity comparable to that of standard BGO. Further increase in light yield was observed with the further increase in Lu concentration. Calibrated results will be shown in near future.

4. Conclusion

CeF$_3$, PrF$_3$ and NdF$_3$ single crystals with 1 inch in diameter have been grown under CF$_4$ atmosphere by the modified Czochralski technique. Although CeF$_3$ and NdF$_3$ single crystals could be grown stably, PrF$_3$ showed a marked spiral growth character, caused by the coupling between the peaking crucible radiation in the near infrared (estimated by the Wien’s law) and the strong absorption in this spectral region of the growing crystal. All crystals, however, could be grown as well in single crystalline form simply by slow cooling down the melt. NdF$_3$ did not emit in the visible, whereas PrF$_3$ exhibited a dominant sharp emission at 400 nm (corresponding to the intra-configurational $^1S_0 \rightarrow ^1I_6$ transition) in X-ray excited measurements, the decay time being 510 ns. No photon cascade emission from Pr$^{3+}$ was observed, as well as no radiative emission from the RE-dopants after a charge transfer process. Undoped CeF$_3$ presented the same features as high-quality crystals grown by the standard Bridgman technique. Lu$^{3+}$-doping in CeF$_3$ improved remarkably the light emission from Ce$^{3+}$ ion, and thus led to light yields comparable or even larger than that of BGO.

References


