Luminescence and scintillation characteristics of YAG:Ce single crystalline films and single crystals

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ABSTRACT

The detailed comparative analysis of luminescent and scintillation properties of the single crystalline films (SCF) of YAG:Ce garnet grown from melt-solutions based on the traditional PbO-based and novel BaO-based fluxes, and of a YAG:Ce bulk single crystal grown from the melt by the Czochralski method, was performed in this work. Using the ²⁴¹Am (α -particle, 5.49 MeV) excitation we show that scintillation yield and energy resolution of the optimized YAG:Ce SCF is fully comparable with that of the YAG:Ce single crystal analogue.

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1. Introduction

Ce³⁺-doped single crystals (SC) and single crystalline films (SCF) of Y₃Al₅O₁₂ (YAG) and Lu₃Al₅O₁₂ (LuAG) garnets are considered for fast scintillator applications. The YAG:Ce and LuAG:Ce SC are characterized by large (up to 0.2 and 0.6 at.%, respectively) content of Y_{Al} and Lu_{Al} antisite defects (AD) (Ashurov et al., 1977). The AD presence is the consequence of high-temperature (~ 2000 °C) growth of bulk SC of these garnets from melt by the Czochralski or Bridgman methods and energetically favourable creation of such defects (Kuklja, 2000; Stanek et al., 2006). The Y_{Al} and Lu_{Al} ADs in YAG:Ce and LuAG:Ce SC play the role of emission centers in UV range (Zorenko et al., 2007a) and trapping centers (Nikl et al., 2005). These centers participate in the excitation of the Ce³⁺ luminescence and are responsible for large amount of slow components in scintillation decay of YAG:Ce and LuAG:Ce SCs (Nikl, 2005; Zorenko et al., 2007b). Due to low temperature of growth by the liquid phase epitaxy (LPE) method, the YAG:Ce and LuAG:Ce SCFs can in principle possess better scintillation properties as compared with the corresponding SC due to the absence of Y_{Al} or Lu_{Al} ADs. However, the SCF grown from the PbO-based flux are contaminated by lead ions which negatively influence their light yield (LY) and timing characteristics (Babin et al., 2007).

Recently, the detailed comparative analysis of scintillation properties of LuAG:Ce SC and SCF was performed (Prusa et al., 2008) and positive influence of the novel BaO-based flux on scintillation characteristics of the Ce-doped YAG and LuAG SCFs was reported (Kucera et al., 2008). In this work, the luminescence and scintillation properties of the YAG:Ce SCF grown by LPE from PbO- and BaO-based fluxes and bulk YAG:Ce SC grown by Czochralski method were compared.

2. Samples and experimental methods

The YAG:Ce SC was grown in Crytur Ltd (Czech Republic) by Czochralski method from the melt in oxygen-free reduction atmosphere. The YAG:Ce SCF with a thickness of 13–55 μ m were grown in University of Lviv (Ukraine) by LPE method on YAG substrates from melt-solution (MS) based on PbO–B₂O₃ and BaO–B₂O₃–BaF₂ fluxes (labeled later as YAG:Ce (PbO) and YAG:Ce (BaO) SCF, respectively) at temperatures within 960–1025 °C. The growth conditions of these SCF are presented in Table 1. A SCF growth rate of 0.48–1.33 μ m/min in the case of using the PbO-based flux was significantly larger with respect to that of 0.045–0.075 μ m/min in the case of using the BaO-based flux (Table 1).

The Ce content in YAG:Ce SCF was determined using SEM JEOL 6420 equipped by a JXA-8612 MX setup. For the YAG:Ce (PbO) SCF, grown from MS with CeO₂ content of 6.2 and 10 mole %, the Ce concentration in SCF was 0.032 and 0.073 at.% (C3 and 42-7 samples, respectively, Table 2). Thus, the segregation coefficient of

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Table 1

Conditions of growth of YAG:Ce SCF by LPE method from the PbO–B₂O₃ and BaO–BaF₂–B₂O₃ fluxes.

Molar ratios in melt-solution	PbO–B ₂ O ₃	BaO–BaF ₂ –B ₂ O ₃
BaCO ₃ /BaF ₂ /B ₂ O ₃		0.4/0.4/0.2
PbO/B ₂ O ₃	12	
R ₂ = [Y ₂ O ₃]/[Al ₂ O ₃]	0.28	0.49
R ₃ = $\Sigma R_2O_3/BaCO_3 + BaF_2 + B_2O_3$	0.028	0.143
R ₄ = [CeO ₂]/[ΣR_2O_3]	0.062–0.1	0.053–0.1
Temperature of growth, T _g , °C	960–1000	950–1025
Velocity of substrate rotation ω , rev/min	100	100
SCF growth rate f _p , μ m/min	0.4–1.5	0.045–0.075
SCF thickness, μ m	13–55	3.5–9.0

Ce ions is 0.004–0.007. The Ce concentration in YAG:Ce (BaO) SCFs, grown from MS with CeO₂ content of 5.2 mole % (Ba5 sample) and 10 mol.% (B10 and B12 samples) was equal or even below of the detecting limit of our apparatus (≥ 0.01 at. %). Thus, the segregation coefficient of Ce ions in the case of using the BaO-based flux does not exceed the values of 0.001–0.002 which is in contradiction with the results (Kucera et al., 2008), where higher Ce segregation coefficient was found in both YAG and LuAG SCF grown from BaO-based flux. The reason of such a contradictory result is not clear and deserves further studies.

The content of Ce and Pb flux dopants in the SCF is also strongly influenced by the growth temperature T_g and increase with decreasing T_g value and vice versa (Kucera et al., 2008). Therefore, we have used relatively high temperatures above 950 °C (Table 1) for growth of YAG:Ce (PbO) SCF. The content of Pb ions in such SCF usually appeared below the detection limit of the apparatus, but in some SCF, grown at low temperatures, namely C3 sample, was of about 0.01 at. %.

The CL spectra were measured at 300 and 80 K with the setup based on a DMR-4A monochromator and a FEU-106 PMT under the pulsed e-beam (9 keV, 100 μ A) excitation (duration of pulse 2 μ s, repetition frequency 3–30 Hz). The decay kinetics of the Ce³⁺ luminescence was measured using the Spectro-fluorometer 199S (Edinburgh Instrument) equipped by TBX-04 PMT detection module (IBH Scotland) under excitation by the M-5000 ns coaxial hydrogen-filled flashlamp. The N_{phels} photoelectron yield was measured using Hybrid DEP PPO 475B PMT under excitation by α -particles of ²⁴¹Am (5.5 MeV) and ²³⁹Pu (5.15 MeV) sources with shaping times of 0.5–10 μ s.

3. Results and discussion

The CL spectra of YAG:Ce SC and SCF at RT are shown in Fig. 1a. Apart from the intensive Ce³⁺ luminescence in the 2.75–1.75 eV range with maximum at 2.235 eV, the CL spectra of YAG:Ce SC contain the low-intensity UV emission band arising due to the AD presence (Fig. 1, curve 1). This band in RT range presents a superposition of the luminescence of excitons localized around Y_{Al} AD and the luminescence of Y_{Al} AD in the bands peaked at 4.14 and 3.75 eV, respectively. The shape of the latter emission band is

Table 2

Scintillation properties of YAG:Ce SCF in comparison with YAG:Ce SC under excitation by α -particles of ²⁴¹Am (5.49 MeV eV) source.

Samples	SCF thickness (μ m)	FWHM FW(1/5) (%)	N _{phels} yield per MeV (phels)	N _{phels} (SCF) to N _{phel} (SC)
YAG:Ce (PbO) 42-7	58	11.5 (15.4)	386.8	111.1
YAG:Ce (PbO) C3	55	18.5 (29.1)	100.3	28.8
YAG:Ce (BaO) Ba5	2.5	15.3 (22.9)	202.3	58.1
YAG:Ce (BaO) Ba12	1.56	30.9 (42.2)	126.2	36.2
YAG:Ce SC	1 mm	11 (17.2)	348.2	100

Fig. 1. (a) – CL spectra of YAG:Ce SC (1), YAG:Ce (PbO) (2) and YAG:Ce (BaO) (3) SCF at 300 K. The part of spectra of YAG:Ce SC in the UV range is multiplied by a factor of 10. Position of the Ce³⁺ absorption band is marked; (b) – CL spectra of YAG:Ce (BaO) SCF at 80 K (1) and 300 K (2).

strongly distorted by the Ce³⁺ absorption bands peaked at 3.52 eV. Opposed to YAG:Ce SC, the emission bands related to Y_{Al} AD are diminished in the CL spectra of YAG:Ce (PbO) and YAG:Ce (BaO) SCFs due to the absence of Y_{Al} AD and only Ce³⁺ luminescence is observed (Fig. 1, curves 2 and 3). The different positions of the onset of the Ce³⁺ emission band in CL spectra of YAG:Ce SC and both SCFs (Fig. 1a, curves 1–3) are caused by varying reabsorption of Ce³⁺ luminescence by the Ce³⁺ absorption band peaked at 2.69 eV.

The CL spectra of YAG:Ce (PbO) and YAG:Ce (BaO) SCF at 80 K show the emission of self-trapped excitons (STE) in the band peaked at 4.79 eV (Fig. 2b). In CL spectra of YAG:Ce (BaO) SCF the

Fig. 2. Decay kinetics of the Ce³⁺ luminescence in YAG:Ce (PbO) (1, 2) and YAG:Ce (BaO) (3) SCF at 530 nm under excitation at 340 nm and at RT.

Fig. 3. Dependence of LY of YAG:Ce SCF (1) and YAG:Ce SC (2) on the shaping time of registration of scintillation response under excitation by α -particles of Am^{241} (5.49 MeV) sources.

additional low intensity band peaked at 3.5 eV is present. The origin of this band is not clear and might be connected with the formation of some defects of YAG host during the SCF growth from BaO-based flux.

The decay kinetics of the Ce^{3+} emission in YAG:Ce (PbO) and YAG:Ce (BaO) SCFs under excitation in the Ce^{3+} absorption band at 340 nm is shown in Fig. 3. The decay of the Ce^{3+} emission in YAG:Ce (PbO) SCF with small (below 0.01 at. %) lead content is a single-exponential with the decay time of 65 ns which is close to that in YAG:Ce SC. Increasing the lead content in SCF accelerates the decay of the Ce^{3+} emission in YAG:Ce (PbO) SCF (Fig. 3, curve 3 for C3 sample) which can be caused by the energy transfer from the Ce^{3+} ions to Pb^{2+} -based complex centers (Babin et al., 2009). The decay of the Ce^{3+} luminescence in YAG:Ce (BaO) SCF is close to the single-exponential course within one decade but may contain another slower components, the origin of which is not understood and has not been observed in another YAG:Ce (BaO) SCF samples in (Kucera et al., 2008).

The detailed studies of scintillation response under α -particle excitation by ^{241}Am (5.49 MeV) and ^{239}Pu (5.15 MeV) sources showed that N_{phels} LY of the best YAG:Ce (PbO) SCF (42-7 sample) is even slightly exceeding that of YAG:Ce SC sample (Table 2). Their energy resolutions are similar ($\sim 11\%$) under ^{241}Am (5.49 MeV) excitation (Table 2). The increasing lead content in YAG:Ce SCF (C3 sample) leads to the significant N_{phels} decrease and energy resolution deterioration (Table 2).

The dependence of N_{phels} on the shaping time of registration of scintillation response of the best YAG:Ce (PbO) SCF (42-7 sample) and reference YAG:Ce SC is shown in Fig. 3. In the latter sample the N_{phels} LY increases in the 0.5–10 μs time range by about of 8.5% while for YAG:Ce SCF this value is at least two time lower ($\sim 4.2\%$). The latter observation points to lower content of shallow electron traps in the YAG:Ce SCF with respect to YAG:Ce SC due to absence of the ADs as trapping centers in SCF scintillators (Nikl et al., 2005; Nikl, 2005). Thus, the PbO-based flux can be successfully applied for producing the YAG:Ce SCF scintillators with comparable or even better scintillation properties than those of the SC analogues.

N_{phels} of the best YAG:Ce (BaO) SCF (B5 sample) achieves the values of about 60% in comparison with YAG:Ce SC with energy resolution of about 15.3% (Table 2). The lower values of LY and energy resolution are caused by low (≥ 0.01 at.%) Ce concentration and small thickness in these SCFs. Considerably better scintillation performance of YAG:Ce (BaO) SCF with higher Ce content were

reported very recently (Prusa et al., 2009) though the problem of bad surface morphology and high dislocation density remains unsolved so that there is certainly the room for further BaO-based flux technology optimization.

4. Conclusions

Detailed comparison of the luminescent and scintillation properties of the YAG:Ce SCF grown by LPE from the PbO- and BaO-based fluxes and a bulk YAG:Ce SC grown from the melt by Czochralski method, was made. Apart the common Ce^{3+} luminescence in the visible range, the emission spectra of YAG:Ce SC at RT under high-energy electron excitation show also the complex emission band in UV range arising due to Y_{Al} antisite defect presence, which is absent in LPE-grown SCF.

N_{phels} photoelectron yield of the optimized YAG:Ce SCF, grown from the PbO-based flux, is slightly superior to that of YAG:Ce SC. The energy resolution of these SC and SCF samples is the same ($\sim 11\%$) under ^{241}Am (5.49 MeV) α -particle excitation. Therefore, the PbO-based flux can be successfully applied to manufacturing the YAG:Ce SCF scintillators with comparable scintillation figure-of-merit with respect to the SC analogues. N_{phels} of the best YAG:Ce SCF samples, grown from BaO-based flux, is about 60% of that of YAG:Ce SC, and energy resolution is of about 15.3%. Inferior performance is presumably caused by too low Ce^{3+} concentration in these SCF samples. The fundamental problem of the BaO-based flux is also very high viscosity and surface tension as well as rather low SCF growth rate in comparison with the growth from PbO-based flux.

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