Growth and properties of epitaxial Ce-doped YAG and LuAG films for scintillators

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Abstract. We have studied the growth and properties of the Ce³⁺-doped epitaxial garnet films. The single crystalline films were prepared by liquid phase epitaxy. Various fluxes were used with the goal to reduce the flux-related impurities, which could have a negative influence on the optical and scintillation properties. Crystallographic properties, film morphology and emission properties were studied in detail.

1. Introduction

Thin epitaxial films of Ce³⁺-doped Y₃Al₅O₁₂ (yttrium aluminum garnet, YAG) and Lu₃Al₅O₁₂ (lutetium aluminum garnet, LuAG) are promising candidates for 2D scintillation imaging screens with submicrometer resolution, where they can replace polished thin plates of single crystals [1]. Here we report on films grown by the liquid phase epitaxy. The advantage of epitaxial films compared to Czochralski (CZ) grown single crystals is much lower growth temperature (Tg ~ 1000 °C) and consequently lower structural disorder and lower number of intrinsic crystal defects [2, 3]. Furthermore, higher content of Ce³⁺ ions can be incorporated into the garnet lattice [4]. This is of fundamental importance in order to obtain reasonable light yield from films of micrometer thickness. On the other hand, various impurities can enter the lattice from the flux and other factors (such as substrate orientation, film-substrate lattice match, morphology of film-substrate interface, flux composition, purity of starting chemicals, possible second phases) can have a negative impact on the emission and scintillation properties of films. The films prepared from the standard PbO-B₂O₃ flux have very good structural and surface properties, however, they contain divalent and tetravalent Pb and Pt ions [5]. As a result, a variety of point defects are created, which result in electron traps or appearance of the slow component in the luminescence decay of Ce³⁺ centers [6]. Moreover, shallow electron traps due to the antisite Lu₆Al defects (which are typical for single crystals grown from the melt at high temperatures) are the most probable origin of the submicrosecond slow component in the scintillation decay [7].

Recently, we have shown that the Ce-doped garnet films prepared from the lead-free BaO-based flux exhibit excellent optical and emission properties and much higher Ce concentration can be achieved in garnet films compared to Czochralski grown crystals [4]. However, the BaO flux suffers from high viscosity, which has negative effect on the film surface morphology. The aim of this work is study of crystallographic, surface, optical and emission properties of epitaxial garnet films prepared...
from various fluxes. An important question is the morphology of both the film surface and film/substrate interface, which may be critical especially in micrometer thick films.

2. Growth of epitaxial garnet films

The single crystalline epitaxial garnet films were grown by the isothermal dipping liquid phase epitaxy (LPE) onto single crystalline YAG and LuAG substrates of (111) and (110) crystallographic orientation. Starting raw materials of 5N purity were used. Several series of Ce-doped YAG and LuAG films were grown from various fluxes, namely, PbO-B$_2$O$_3$, BaO-B$_2$O$_3$-BaF$_2$, and MoO$_3$-Li$_2$MoO$_4$ fluxes were used. We refer these fluxes here as PbO flux, BaO flux, and MoO$_3$ flux, respectively. The growth temperature was in the range from 930 to 1080 °C and the growth rates were from 0.04 to 1.8 µm/min in dependence on used flux and melt composition. The epitaxial films prepared from the PbO and BaO fluxes were grown from supercooled melt at undercooling 3 – 60 K, the films from the MoO$_3$ flux were grown at a temperature gradient. Details of LPE growth from PbO and BaO fluxes were published elsewhere [4]. The thickness of films was in the range from 2 to 24 µm. Ce concentration in films was from 0.04 to 0.8 at. % depending on the growth conditions and used melt. All the films show an intense green luminescence.

The epitaxial films prepared from the PbO flux exhibited excellent crystallographic properties, see the next sections, and high quality smooth surface. Films with superior luminescent properties were obtained from the BaO flux. The photoluminescence decay curves do not indicate any energy loss or quenching of luminescence. Besides, due to higher segregation coefficient of Ce ions, higher Ce content can be achieved in films grown from the BaO flux compared to the Czochralski single crystals. However, high viscosity and high surface tension of this flux resulted in more complicated film growth and worse surface morphology.

In order to eliminate the charged impurities (typical for the PbO melt) and to improve the melt viscosity (drawback of the BaO melt) we used, as a novelty, the MoO$_3$ based flux. This flux has essentially zero volatility, low reactivity with the Pt crucible, low viscosity and provided films with smooth surface. The surface morphology was comparable with films grown from the PbO flux, however, the growth rate are rather small, < 0.1 µm/min, and concentration of Ce ions in films was smaller compared to films grown from other two fluxes.

In this work we will study in more detail also the garnet films grown onto various substrates, which differ in lattice constant. Namely, Ce:LuAG films were grown either on LuAG substrates – we shall refer this growth as homoepitaxial (the lattice constants of the substrate and film are virtually the same, ∆a < 0.02 %). The Ce:LuAG films grown on YAG substrates we refer as heteroepitaxial (the lattice mismatch is rather high, ∆a = 0.8 %).

3. Properties of epitaxial films

We have studied the crystallographic properties of the LPE films using the X-ray diffraction (XRD), the surface morphology and surface profiles using the optical microscopy and the interferometric surface profiler ZYGO. Optical properties were studied using the optical absorption spectroscopy, luminescence emission and excitation spectroscopy, and Ce$^{3+}$ photoluminescence decay was studied, too. Scintillation characteristics and photoelectron yield of the films are published elsewhere [8].

3.1. X-ray diffraction

The crystallographic structure of the LPE films was studied by means of XRD on PANalytical high-resolution X-ray diffractometer XPert Pro MRD (Cu K$_{\alpha 1}$ peak). The X-ray beam was conditioned using the x-ray mirror followed by four bounce Bartels monochromator (4xGe220). Diffracted beam was registered using a three-bounce channel-cut analyser (Ge220) and proportional point detector.

We shall first discuss homoepitaxially grown films – Ce:YAG films grown on YAG substrates and Ce:LuAG film on LuAG substrates. The diffraction profile of a symmetric 444 diffraction of a Ce:YAG film (with ~0.13 at.% of Ce) grown on YAG substrate from the PbO flux is shown in figure
1. Lower intensity of substrate diffraction is due to radiation absorption in 11 µm thick film. From the position of the 444 diffraction peak in this sample, 2θ = 52.7583(1) deg, the lattice constant in the direction normal to the film surface was determined as a⊥ = 12.0114(1) Å. The measured lattice constant of the YAG substrate was aS = 12.0093(1) Å. The increased lattice parameter of films corresponds to doping of large Ce3+ ions (ionic diameter 1.143 Å), which are substituted for Y3+ ions (1.016 Å) in dodecahedral sites.

On the other hand, the XRD of Ce:LuAG films shows, that the measured lattice parameter of films is even lower than that of LuAG substrates. This can be explained due to increased number of antisite LuAl defects in LuAG substrates, which is several times higher than that in YAG substrates. Namely, due to the small ionic radius of Lu3+ ions (0.975 Å), some part of these ions occupies octahedral sites instead of regular Al3+ ions, and these defects increase the lattice parameter of LuAG substrates compared to the stoichiometric crystal. In epitaxial films, however, the concentration of these antisite defects is presumed to be much smaller [2, 6, 7] due to much lower growth temperature of films compared to that of the Czochralski grown crystals.

Observed halfwidths of 444 diffraction peak in epitaxial film, 12 ang. sec, are comparable to those of substrate, 10 ang. sec, giving evidence of high crystallographic quality of the epitaxial films.

![Image](image.png)

**Figure 1.** Diffraction profile of 444 diffraction (Cu-Kα1) of 10.7 µm thick Ce:YAG film grown on YAG substrate from the PbO-flux, L and S are respective diffractions from layer and substrate.

In order to explore the relaxation state of studied layers, asymmetrical reciprocal maps (RSM) were measured. The RSM around the asymmetric diffraction 664 suggests, figure 2, that homoepitaxially grown samples, i.e. Ce:YAG/YAG or Ce:LuAG/LuAG, showed pseudomorphic film on substrate (the intensities of scattered X-rays in the reciprocal space exhibit the same Qx coordinate in the RSM), i.e. the film lattice parameter in the plane was the same as that of substrate, a|| = aYAG. Since a⊥ differs < 2×10⁻⁴, any misfit dislocations are not expected in the film/substrate interface and a macroscopic elastic strain is present in the film.
Figure 2. Asymmetrical reciprocal map of 664 diffraction of Ce:YAG layer grown on (111) oriented YAG substrate from the BaO flux, thickness $t = 6.9$ µm, $S =$ substrate, $L =$ layer. A pseudomorphic layer was grown on substrate.

Figure 3. Asymmetrical reciprocal map of 664 diffraction of Ce:LuAG layer grown on (111) oriented YAG substrate from the PbO flux, $t = 13.3$ µm, $S =$ substrate, $L =$ layer. A relaxed layer was grown on substrate.
Quite different situation was observed for heteroepitaxial growth of Ce:LuAG film grown onto YAG substrate where the lattice mismatch is too large, \( \Delta a = 0.8\% \), for the pseudomorphic growth. In this case a relaxation of a film was observed and the lattice parameters of film and substrate differ. The RSM around the asymmetric diffraction 664 for Ce:LuAG/YAG system is shown in figure 3. The lattice parameter of Ce:LuAG film is virtually the same as that of LuAG crystal, \( a = 11.916 \) Å. Therefore the misfit dislocations that reveal misfit strain are expected in the film/substrate interface. The RSM of film diffraction is broad compared to the substrate and it shows that macroscopic defects are present in films. Nevertheless, the XRD proved that the films are of single garnet phase and the films exhibit a distinct 111 orientation.

3.2. Film surface and film-substrate interface properties

The film surface properties were studied using the optical microscopy and optical interferometry. The surface roughness of the films was measured by means of a noncontact 3D surface profiler Zygo, model New View 5022. It uses scanning white light interferometry to acquire ultrahigh z-resolution images. Typical surface profile of Ce:LuAG epitaxial film grown onto high quality LuAG substrate from the PbO flux is shown in figure 4a. Rather smooth surface was observed, see also figure 5a, and rms surface roughness is only a few nanometers.

**Figure 4.** The surface profile measured using the ZYGO interferometer. (a) Ce:LuAG film on LuAG substrate (homoepitaxial growth), smooth surface with rms surface roughness of \( \sim 2 \) nm is observed; (b) Ce:LuAG film on YAG substrate (heteroepitaxial growth, lattice misfit \( \Delta a = 0.09 \) Å), rms surface roughness \( \sim 200 \) nm.

**Figure 5.** Optical microscopy of the surface of Ce:YAG films grown on (111) oriented YAG substrate, magnification 300x. (a) Defect-free surface of a film grown from the PbO flux (for comparison, the sample edge is shown on the right side of the picture). (b) Triangular pits in a film grown from the MoO\(_3\) flux. Such pits are typical for 111 orientation and come from the substrate defects or defects induced during polishing of the substrate.
However, surface properties of epitaxial films are strongly dependent on crystallographic quality and final polishing procedure of used substrates. Any substrate defect, such as dislocation or inclusion, is replicated as a defect into the LPE film. Figure 5b shows triangular pits observed typically in films grown on 111 oriented substrates. These defects of $\mu$m dimensions come from the substrate defects, either intrinsic or induced during the polishing. In films grown from the PbO flux on high quality and well polished substrates such defects can be practically eliminated. However, increased number of these pits was observed in films grown from the BaO flux presumably due to high viscosity of this flux.

At heteroepitaxial growth (Ce:LuAG film on YAG substrate, where the lattice mismatch is 0.8 %), the rms surface roughness can be as high as several hundreds of nm, figure 4b, and surface of such films observed by naked eye is matte and strongly scatters light. In order to compare optical properties of these heteroepitaxial films with homoepitaxial ones, the uppermost surface 3 $\mu$m of films were polished out. After this repolishing a glossy surface was obtained. The transmission spectra of Ce:LuAG film grown on LuAG and YAG substrates from the PbO flux are presented in the next section, cf. figure 7.

An important issue is the morphology of the film surface and film/substrate interface. Large lattice mismatch between the Ce:LuAG film and YAG substrate at heteroepitaxial growth, $\Delta a = -0.09$ Å, is the main problem in obtaining films of high perfection. Of real importance, especially for thin films, is formation of a transient layer at the film-substrate interface. In the transient layer the chemical composition changes and a crucial issue is its contamination by impurity ions from the flux and presence of other defects. For low lattice mismatch $< 0.02$ Å, this transient layer is usually sharp and for homoepitaxial films its thickness is of the order of nanometers. For higher lattice mismatch the morphology of the transient layer is more complicated. Optical microscopy of edge of samples cleaved normal to the film-substrate interface is shown in figure 6. Sharp film-substrate interface is observed for homoepitaxial growth of the Ce:LuAG/LuAG system, where lattice constants of the film and substrate merge. Due to almost the same chemical composition, the optical contrast between film and substrate is very weak and the film-substrate interface is hardly observable. On the other hand at heteroepitaxial growth of Ce:LuAG/YAG system, where the lattice mismatch is rather high, the film-substrate interface is profound and oriented columnar like structure of the layer seems is observed. The morphology of the transient layer may be critical especially in micrometer thick films and detailed study of its structure is called for.

**Figure 6.** Edge of fractured samples observed in optical microscope; the arrows indicate the film/substrate interface. (a) Homoeptaxially grown Ce:LuAG film on LuAG substrate, lattice constants of the film and substrate are almost the same, $\Delta a < 0.02$ %, and sharp film-substrate interface is observed. (b) Heteroepitaxially grown Ce:LuAG film on YAG substrate, the lattice mismatch is rather high, $\Delta a = 0.8$ %, the film-substrate interface is profound. Both films were grown from the PbO flux.
3.3. Optical absorption and photoluminescence

Optical transmission measurements were performed in the spectral range from the ultraviolet to the near infrared, 200 – 1100 nm. Comparison of absorption spectra of Ce:YAG films grown from the PbO and BaO fluxes was published elsewhere [4]. We only mention here, that the Pb$^{2+}$ ions, always present in film grown from the PbO flux, give rise to the strong absorption below 280 nm and optical transparency of films grown from the BaO flux is better. In figure 7 the optical transmission spectra of homo- and heteroepitaxial Ce$^{3+}$:LuAG films grown either on LuAG or YAG substrates are compared. The Ce$^{3+}$ absorption bands are clearly resolved at 445 and 345 nm, but in the ultraviolet spectral range the Ce spectral bands are overlapped by Pb$^{2+}$ absorption. The absorption peak situated near 262 nm originates from Pb$^{2+}$ impurity ions [9, 6]. Owing to high undercooling (40–60 K) of the melt during growing of these two samples the relative concentration of lead ions is rather high, hundreds of ppm. The first results indicate that the content of Ce$^{3+}$ ions and also the lead ions is higher in heteroepitaxial films compared to homoeptaxial ones grown under the same conditions. Surprisingly very close relation of both the spectra in figure 7 is observed. We note that the transmission spectra were not normalized and the same intensity of 445 nm spectral band is accidental.

![Figure 7. Optical transmission spectra of epitaxial Ce:LuAG films grown on LuAG substrate (dashed line, sample 2LuC3, t = 8.9 µm) and on YAG substrate (solid line, sample 2LuC4y, t = 14 µm) grown from the PbO flux. Absorption peaks from Ce$^{3+}$ and impurity Pb$^{2+}$ ions are indicated. Transmission spectrum of Czochralski grown LuAG substrate is shown for comparison, dotted line. The surface of Ce:LuAG film grown on YAG was polished before measurements.](image)

The photoluminescence (PL) excitation spectra of Ce$^{3+}$ emission, $\lambda_{em} = 530$ nm, of Ce:YAG samples grown from the MoO$_3$ flux are displayed in figure 8a. The structure in the spectra comes from the Ce$^{3+}$ ions and it shows a close correspondence with the absorption curves in figure 7. In spite of strong absorption in the UV range, the Ce$^{3+}$ contributions in the PL excitation spectra at 220 – 270 nm are distinguished. The PL emission spectra at $\lambda_{exc} = 340$ nm are shown in figure 8b. Below 470 nm the PL emission has a negligible intensity.

3.4. Decay kinetics of photoluminescence

In order to obtain more detailed information on the role of impurities in the PL emission of epitaxial garnet films, we measured the PL decay kinetics. Decay curves were measured by single photon counting method, the samples were excited at 340 nm and the PL Ce$^{3+}$ emission was collected at 530 nm.
The PL decay curve for a typical Ce$^{3+}$ doped YAG films grown from the MoO$_3$ flux is shown in figure 9. The curve exhibit 1-exponential decay with $\tau \sim 58$ ns, which is in close relation with values obtained for high purity Ce-doped single crystals.

The decay curve from Ce:YAG and Ce:LuAG films grown from PbO and BaO fluxes were reported elsewhere [4]. We summarize only that detailed inspection of Ce decay curves of films grown from the PbO flux shows on some nonlinearity and a two-exponential fit provides better correspondence. This indicates a nonradiative transfer of part of energy between Ce$^{3+}$ and impurity ions or defect states.

The decay curve of Ce:YAG films grown from the lead-free BaO flux exhibit linear dependence over three orders of magnitude indicating 1-exponential decay and the decay time $\tau \sim 60$ ns. Therefore we can conclude that in films grown from a flux, which does not contain lead, the PL decay curves do not indicate any loss of energy in contrast to the films grown from the PbO flux.

Figure 8. Excitation spectra (left) measured at $\lambda_{\text{exc}} = 530$ nm and emission spectra (right) for $\lambda_{\text{em}} = 345$ nm of Ce:YAG epitaxial films grown from the MoO$_3$ flux with various concentration of Ce$^{3+}$ ions.

Figure 9. The Ce$^{3+}$ decay curve of Ce$^{3+}$:YAG film (1MC78) measured at 530 nm at room temperature, excitation at 340 nm. The solid line is convolution of the fitting curve I(t) with the instrumental response.
4. Conclusions
The garnet films were grown by the liquid phase epitaxy from three different fluxes: PbO-B$_2$O$_3$, BaO-B$_2$O$_3$-BaF$_2$, and MoO$_3$-Li$_2$MoO$_4$. The films grown from the PbO flux exhibit relatively high structural perfection and high quality surface. However, divalent Pb$^{2+}$ ions in concentrations 0.01 – 0.1 at. % (depending on the growth conditions and undercooling) are always incorporated into the crystal lattice. They cannot be easily charge compensated in YAG or LuAG and, as a consequence, lower emission efficiency is observed in such films. Quite the opposite, the films prepared from lead-free fluxes based either on BaO or MoO$_3$ do not contain any charged impurities, which influence the emission properties. However, the surface morphology of films grown from BaO is inferior due to high viscosity of the melt. The MoO$_3$ flux has low reactivity with the Pt crucible, low viscosity, and the films do not contain any solvent-related impurities, which would quench the luminescence. Very good emission properties of these films and one-exponential decay of 530 nm emission of Ce$^{3+}$ with 58 ns decay time were observed.

Important advantages of epitaxial films compared to Czochralski grown single crystals are, first, lower growth temperatures and, as a consequence, lower number of intrinsic crystal defects [2, 3] and, second, higher content of Ce$^{3+}$ ions (by a factor of 2-5), that can be incorporated into the garnet lattice, cf. ref. 4. This is of fundamental importance in order to obtain reasonable light yield from films of micrometer thickness. The films grown from the BaO or MoO$_3$ fluxes exhibit much higher purity and PL decay curves do not indicate any loss of energy in contrast to the PbO-grown films.

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