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OPTICAL PROPERTIES

Luminescence of Gadolinium Gallium Garnet Epitaxial Films under Excitation by Synchrotron Radiation

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Abstract—The luminescence excited by synchrotron radiation in gadolinium gallium garnet single-crystal films grown by liquid-phase epitaxy from lead- and bismuth-containing solution melts on $Gd_3Ga_5O_{12}$ substrates is investigated. It is shown that the luminescence intensity in the visible range of the spectrum depends on the type and concentration of impurity ions passing from the solvent into the film.

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1. INTRODUCTION

In recent years, great interest has been expressed in the development of efficient x-ray scintillation screens with a high spatial resolution that heretofore could only be fabricated on the basis of films [1–3]. Single-crystal films with a thickness ranging from 0.1 to 100 μm, particularly those with a garnet structure, can be grown through liquid-phase epitaxy from a supercooled solution melt on isomorphous substrates [3–5]. In this technique, the most frequently used type of solvent is $PbO–B_2O_3$ or $Bi_2O_3–B_2O_3$.

The basic difference between epitaxial films and their bulk analogs grown, for example, according to the Czochralski technique, lies in the fact that impurity ions pass from the solvent into the film [6–8], so the film–air transition surface layer is enriched with these ions to the greatest extent [9–12]. In films, the impurity ions give rise to additional optical absorption as compared to that of the substrate. Specifically, in films grown on $Gd_3Ga_5O_{12}$ (GGG) from a lead-containing solution melt under insignificant supercooling, this additional absorption is attributed to the ${}^1S_0 \longrightarrow {}^3P_1$ electron transition of the Pb^{2+} impurity ions, whereas considerable supercooling brings about the appearance of additional absorption bands associated with both the pair intervalence transitions of the Pb^{2+} and Pb^{4+} ions ($Pb^{2+} + Pb^{4+} + h\nu \longrightarrow Pb^{3+} + Pb^{3+}$) and charge-transfer transitions ($O^{2-} + Pb^{4+} + h\nu \longrightarrow Pb^{3+} + V_O^{2-}$), where $h\nu$ is the quantum energy and V_O^{2-} is an oxygen vacancy [7]. In the latter case, the films turned violet. The additional absorption observed in the films grown on GGG substrates from a bismuth-containing solution melt is attributed to the ${}^1S_0 \longrightarrow {}^3P_1$ electron transition of the Bi^{3+} impurity ions [8].

The purpose of the present work was to compare the specific features of the luminescence excited by synchrotron radiation [13] in gadolinium gallium garnet films grown through liquid-phase epitaxy from lead- and bismuth-containing solution melts.

It should be noted that, after the epitaxial film is deposited on the surface of a single-crystal substrate, the intensity of the luminescence excited by synchrotron radiation increases significantly [14]. The specific features of the liquid-phase epitaxy of these films were discussed in our previous papers [7, 8].

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The growth conditions and parameters of the films under investigation are given in the table (where T_g is the growth temperature of the film, f_g is the growth rate of the film, and $2h$ is the total thickness of the film on both sides of the substrate). Samples *1* and *2* were grown from solution melts with different Gd_2O_3 contents (6.1 and 2.0 mol %, respectively [8]). It should be noted that, in contrast to samples *3–6* and *8*, which contained only Pb^{2+} ions as impurities, sample *7* contained both Pb^{2+} and Pb^{4+} ions (the valence of impurity ions was determined from the optical absorption spectra [7]). The luminescence spectra in the energy range 1.5–6.0 eV were investigated on the Superlumi experimental station (DESY, Hamburg, Germany) [15, 16]. The experimental station is installed on the synchrotron

Growth conditions and parameters of the epitaxial films under investigation

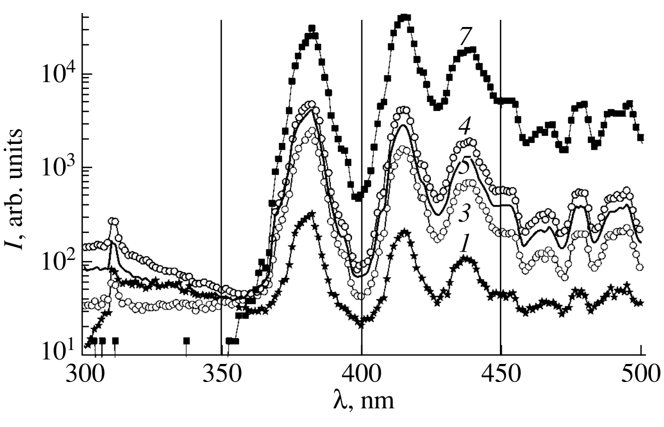
Sample	Solvent	Impurity	T_g, °C	f_g, μm/min	$2h$, μm	I_{382}, arb. units	I_{415}, arb. units	I_{438}, arb. units
1	Bi_2O_3–B_2O_3	Bi^{3+}	794	0.6	18.4	296	190	100
2	Bi_2O_3–B_2O_3	Bi^{3+}	912	0.8	22.8	2412	1474	697
3	PbO–B_2O_3	Pb^{2+}	1000	1.7	43.4	2342	1467	651
4	PbO–B_2O_3	Pb^{2+}	931	1.1	4.5	4461	3882	1751
5	PbO–B_2O_3	Pb^{2+}	931	0.8	3.1	3932	2608	1160
6	PbO–B_2O_3	Pb^{2+}	979	0.24	0.94	4629	2846	1302
7	PbO–B_2O_3	Pb^{2+}–Pb^{4+}	945	2.0	59	29059	38900	17232
8	PbO–B_2O_3	Pb^{2+}	929	0.19	11.5	3148	1988	898

radiation beamline of the DORIS III positron storage ring at DESY. All measurements of the luminescence spectra were performed without normalization to the instrument function.

3. RESULTS AND DISCUSSION

Under exposure to exciting synchrotron radiation, both the epitaxial films and GGG single crystals [17] turned dark, which was most likely caused by the defect formation. With the passage of time (a day later), the color of the samples under investigation partially disappeared.

The figure shows the luminescence spectra $I(\lambda)$ of the epitaxial films under investigation. It can be seen that the luminescence spectra contain a series of narrow bands. As in the case of GGG substrates [17], the most intense bands are centered at wavelengths $\lambda \approx 382$, 415, and 438 nm. These bands are associated with uncontrollable impurities or structural defects of the crystal lattice. The luminescence intensities at these wavelengths, namely, I_{382}, I_{415}, and I_{438}, are given in the table. The band with a maximum at a wavelength $\lambda \approx 313$ nm is attributed to the Gd^{3+} ions [18].



Luminescence spectra $I(\lambda)$ of the epitaxial films under investigation. The numbers of the curves correspond to the sample numbering in the table.

As can be seen from the figure and the table, the luminescence intensity of the epitaxial film at a particular wavelength can change by more than two orders of magnitude depending on the growth conditions (batch composition, growth temperature T_g, growth rate f_g). On the whole, the films grown from a lead-containing solution melt are characterized by a more intense luminescence under synchrotron radiation in the wavelength range covered than those grown from a bismuth-containing solution melt. Note that the films containing mixed-valence lead impurity ions (sample *7*) exhibit a more intense luminescence.

The concentration of lead impurity ions at the surface of the film is more than one order of magnitude higher than that in the bulk of the film, and these ions are in divalent and tetravalent states (in approximately equal proportion) [3]. Bismuth is not only a component of the solvent but also a garnet-forming element. As a consequence, the concentrations of Bi^{3+} ions at the surface and in the bulk of the film differ to a lesser extent [5].

4. CONCLUSIONS

Thus, the results obtained in this study of gadolinium gallium garnet epitaxial films grown from lead- and bismuth-containing solution melts on GGG substrates can be summarized as follows.

(i) Compared to the substrate, the presence of impurity ions in gadolinium gallium garnet epitaxial films does not substantially affect the position of the bands of the luminescence excited by synchrotron radiation.

(ii) The intensity of the luminescence excited by synchrotron radiation can be changed by more than two orders of magnitude by varying the growth conditions of the epitaxial film.

(iii) The films grown from a lead-containing solution melt exhibit a more intense luminescence under synchrotron radiation.

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