

Article



Regularities of Manganese Charge State Formation and Luminescent Properties of Mn-Doped Al₂O₃, YAlO₃, and Y₃Al₅O₁₂ Single Crystalline Films

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Abstract: In this work, three sets of single crystalline films (SCF) of Al₂O₃:Mn sapphire, YAlO₃:Mn perovskite (YAP:Mn), and Y₃Al₅O₁₂:Mn garnet (YAG:Mn), with a nominal Mn content of 0.1%, 1%, and 10 atomic percent (at.%) in the melt-solutions, were crystallized by the liquid phase epitaxy (LPE) method onto sapphire, YAP and YAG substrates, respectively. We have also calculated the average segregation coefficient of Mn ions for Al2O3:Mn, YAP:Mn and YAG:Mn SCFs with Mn content in the melt-solution in the 0.1–10% concentration range, which was equal to 0.1, 0.14 and 0.2, respectively. The main goal of the conducted research was the spectroscopic determination of the preferable valence states of manganese ions which were realized in the SCFs of sapphire, perovskite and garnet depending on the Mn content. For this purpose, the absorption, cathodoluminescence (CL), photoluminescence (PL) emission/excitation spectra and PL decay kinetics of Al₂O₃:Mn, YAP:Mn and YAG:Mn SCFs with different Mn concentrations were studied. Based on the CL and PL spectra, we showed that Mn ions, depending on the Mn content in the melt-solution, are incorporated in Al₂O₃:Mn, YAP:Mn and YAG:Mn SCFs in the different charged states and are located in the different crystallographic positions of the mentioned oxide lattices. We have observed the presence of the luminescence of Mn⁴⁺, Mn³⁺ and Mn²⁺ valence states of manganese ions in CL spectra in all SCFs under study with 0.1 and 1% Mn concentrations. Namely, the Mn⁴⁺ ion valence state with the main sharp emission bands peaked at 642 and 672 nm, related to the ${}^{2}E \rightarrow {}^{4}A_{2}$ transitions, was found in the luminescence spectra of the all studied Al₂O₃:Mn SCFs. The luminescence of the Mn²⁺ valence state was found only in YAP:Mn and YAG:Mn SCFs, grown from melt solution with 1% Mn content, in the emission bands peaked at 525 and 560 nm, respectively, related to the ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ transitions. The PL and CL spectra of YAP:Mn and YAG:Mn SCFs with the Mn content in the 0.1-1% range show that the main valence state of manganese ions in these films is Mn^{3+} with the main emission bands peaking at 655 and 608 nm, respectively, related to the ${}^{1}T_{2} \rightarrow {}^{5}E$ transitions. Meanwhile, higher than 1% Mn content in the melt solution causes a strong concentration quenching of luminescence of all Mn centers in Al₂O₃:Mn, YAP:Mn and YAG:Mn SCFs.

Keywords: Al_2O_3 ; YAP and YAG oxides; Mn dopant; single crystalline films; liquid phase epitaxy; Mn^{4+} , Mn^{3+} and Mn^{2+} valence states; luminescence

1. Introduction

Nowadays Mn-doped Al₂O₃-Y₂O₃-based oxides are widely considered as potential laser media, holographic recording materials, luminescence converters of white lightemitting diodes (WLEDs) and materials for thermo- and optically-stimulated luminescent (TL and OSL) dosimetry [1,2]. All the mentioned applications may be realized using single crystals and powders of Mn-doped simple oxides, perovskites and garnets [3,4]. Namely, the crystals and powder ceramics of Mn-doped Y-Al garnets and perovskites can be explored also as potential solar cells, photodetectors, holographic recording materials [3,4]



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and WLED converters [5]. However, significantly less information exists about the crystallization and properties of Mn doped crystalline films of oxide materials, sintered using different methods. This fact inspires us to study the luminescent properties of manganese ions also in single crystalline films (SCFs) of the well-known Al₂O₃-Y₂O₃ based oxides with different crystalline structures (Al₂O₃ sapphire, YAlO₃ perovskite (YAP) and Y₃Al₅O₁₂ garnet (YAG)), grown by the liquid phase epitaxy (LPE) method [2,6].

Process of doping by magnesite ions the pure crystals of various oxides can create different charge states of Mn ions (2+, 3+ and 4+). This mainly depends on the condition of crystallization and the content of the atmosphere during the growth procedure. Also, the post-growth treatment, as well as the charge state of co-dopants are involved in this process [2–4,7]. In the literature, we can find some articles, which describe the theoretical prediction of the behaviour of Mn ion in sapphire and perovskite crystal lattice [8,9]. The absorption and luminescence of different states of Mn ions in sapphire, perovskites and garnets were recently studied in the works [1,2,7]. In this work, we perform the comparative study of the absorption and luminescent properties of Al₂O₃:Mn, YAP:Mn and YAG:Mn SCFs depending on Mn content in a wide (0.1–10 mole%) concentration range. The study's specific purpose is to determine the optimum valence states of manganese ions which are realized in Al₂O₃, YAP and YAG SCFs, grown by the LPE method, depending on the Mn concentration in the mentioned range.

Crystal Structure Oxides under Study

Sapphire is a single crystal represented by the chemical formula Al_2O_3 . The sapphire host belongs to the R3c space group with the lattice parameters a = 0.4789 nm and c = 1.2991 nm. In the sapphire unit cell, the O atoms are bonded to four Al atoms and the Al atoms are bonded to the six closest oxygen atoms creating AlO_6 octahedrons (Figure 1a). For this reason, all valence states of Mn ions can be localized in octahedral sites of sapphire host instead Al cations.



Figure 1. Scheme of the crystal structure of sapphire Al_2O_3 , (**a**), $YAlO_3$ perovskite (**b**) and $Y_3Al_5O_{12}$ garnet (**c**) (see [1,8] for details).

The general formula for perovskite is ABO₃, where A and B are core cations. The three-dimensional structure of the perovskite consists of B cations that are surrounded by octahedrons made of oxygen that are connected by corners (Figure 1b). The A atom is in the corner of the cube with the coordinates, the B type atom is in the center (1/2, 1/2, 1/2) and the oxygen atoms are in the central positions with coordinates (1/2, 1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2). The perovskite crystallizes in the cubic structure of Pm3m. Due to the mentioned features of perovskite structure, the large Mn²⁺ ions can be localized in

the cub-octahedral sites, when the smallest Mn³⁺ and Mn⁴⁺ ions preferably substitute the octahedral positions of the perovskite host.

The chemical formula of the garnet host is $[A]_3[B]_2[C]_3O_{12}$, where [A], [B] and [C] represent the cation in the dodecahedral, octahedral and tetrahedral sites, respectively (Figure 1c). All the oxygen anions always occupy tetrahedral sites. The dodecahedral [A] site can be occupied by the following ions: Y^{3+} , Lu^{3+} , Tb^{3+} , Gd^{3+} , Ca^{2+} , Mg^{2+} , and Sr^{2+} ; the octahedral [B] site can be occupied by Al^{3+} , Ga^{3+} , Cr^{3+} , Y^{3+} , Mg^{2+} , Fe^{3+} , In^{3+} , Sc^{3+} ; the tetrahedral [C] site can be occupied by Al^{3+} , Ga^{3+} , Si^{4+} , Ge^{4+} . For net charge neutrality, the mix of cations in [A], [B], and [C] sites is changed and restricted by the relationship between ionic radius and valence states. Inside one unit cell, 160 atoms are located. The lattice constant of YAG is around 12 Å. Due to the flexibility of the garnet host, we can expect that the different states of Mn ions can be well separated in the respective positions: Mn²⁺ ions mainly in the decahedral sites, Mn³⁺ ions in the tetrahedral sites and Mn⁴⁺ in the tetrahedral sites.

However, all of the above-mentioned assumptions about Mn ions distribution on the different positions of sapphire, perovskite and garnet hosts are not general and always need experimental confirmation.

2. Materials and Methods

In this work, we have performed an investigation of absorption and luminescent characteristics of Mn ions in the Al_2O_3 :Mn, YAP:Mn and YAG:Mn SCFs, grown by the LPE method from the melt solutions based PbO-B₂O₃ flux in the relatively similar conditions of crystallization. The parameters of SCF growth are shown in Table 1. In the case of Al_2O_3 :Mn SCF crystallization, the Bi_2O_3 oxide was added also as a part of flux components (around 30%) for stabilization of the conditions of film growth. The total content of film-forming components in the melt solution was 3.5–5 mole%. The concentration of MnO₂ activating oxide in the melt solution was 0.1, 1.0 and 10 mol% concerning the film-forming components. However, due to low segregation coefficients of Mn ions at SCF crystallization growth, being equal to 0.08, 0.14 and 0.2 for the growth of Al_2O_3 :Mn, YAIO₃:Mn and Y₃Al₅O₁₂:Mn SCFs, respectively (Table 1), the real content of Mn in the mentioned films was correspondingly 0.008–0.8 at.%; 0.014–1.4 at.% and 0.02–2 at.%.

Table 1. Growth conditions of Al₂O₃:Mn, YAP:Mn, and YAG:Mn SCFs. h—SCF thickness, f—velocity of SCF growth; T—SCF growth temperature.

Type of SCF	Mn Content, Mole%	Mn Segregation Coefficient	Substrate	Flux	h, µm	T, °C	f, µm/min
Al ₂ O ₃ :Mn	10%		Al ₂ O ₃ SC	$PbO + B_2O_3 + Bi_2O_3$	11	950	0.8
	1%	0.08	Al_2O_3 SC	$PbO + B_2O_3 + Bi_2O_3$	5	930	1.6
	0.1%		Al ₂ O ₃ SC	$PbO + B_2O_3 + Bi_2O_3$	14	945	2.14
YAO3:Mn	10%		YAO3 SC	PbO	14.7	1020	0.18
	1%	0.14	YAO ₃ SC	PbO	29	999	1.23
	0.1%		YAO ₃ SC	PbO	19	1012	2.2
Y ₃ A ₅ O ₁₂ :Mn	10%		Y ₃ A ₅ O ₁₂ SC	PbO	3.7	980	0.19
	1%	0.2	Y ₃ A ₅ O ₁₂ SC	PbO	24.8	985	0.22
	0.1%		$Y_3A_5O_{12}$ SC	PbO	60	983	0.21

The photos of Al₂O₃:Mn, YAlO₃:Mn and Y₃Al₅O₁₂:Mn SCFs, selected for optical investigations, are presented in Figure 2a–c, respectively.

It is worth noting that a peculiarity of the doping with manganese of SCFs of the mentioned oxides is the creation of different charge states of Mn ions (2+, 3+ and 4+) depending on the condition of the LPE growth, content of flux as well as the charge state of co-dopants [3,7]. Apart from the Mn ions, all SCFs under study can also contain the Pb²⁺ and Bi³⁺ (only in the case of Al₂O₃:Mn films) as well as Pt⁴⁺ trace impurity in the concentration range below 100 ppm, coming into SCFs as components of flux

and Pt crucible, respectively. The presence of Pb^{2+} ions in SCFs gives the possibility of charge compensation for Mn^{4+} by Pb^{2+} ions and Mn^{2+} by Pt^{4+} ions, respectively. The charge compensation of Mn^{2+} and Mn^{4+} ions is also possible due to the creation of the $Mn^{2+}-Mn^{4+}$ pairs.



Figure 2. Al₂O₃:Mn (**a**), YAP:Mn (**b**), and YAG:Mn (**c**) SCFs grown from melt solution with a nominal Mn content of 10%, 1%, and 0.1% (from left to right, respectively).

The valence state of manganese ions is influenced also by their location in the respective positions of oxide hosts. Mn^{4+} ions predominantly occur in the octahedral coordination (Al³⁺ sites) in sapphire [1], perovskite [2,3] and garnet [7] whereas relatively large Mn^{2+} ions dominantly localized in cub-octahedral and dodecahedral coordination's (Y³⁺ sies) in perovskite [2] and garnet [7]. Mn^{3+} ions can be localized predominantly in the octahedral positions of perovskite and garnet hosts [7,8]. The preferred manganese state in the SCFs under study is also strongly influenced by the Pb²⁺ flux and Pt⁴⁺ crucible-related dopants, especially at low Mn dopant levels [3,7].

The content of the SCF samples under study was measured using IXRF 500 and LN2 Eumex detectors at a KSM–6400 JEOL electron microscope (JEOL, Tokyo, Japan). The absorption spectra of the SCFs in the 190–1000 nm range were measured using a Jasco V-730 UV-Visible Spectrophotometer (Jasco Corporation, Tokyo, Japan) at room temperature (RT). The RT cathodoluminescence (CL) spectra were measured using a KSM–6400 JEOL electron microscope equipped with a Stellar Net spectrometer and with a TE-cooled CCD detector working in the 200–1120 nm range. The RT photoluminescence (PL) excitation and emission spectra and the decay curves of the Mn luminescence, were measured by an Edinburg FS5 spectrofluorometer. Excitation was performed by a 150 W CW Ozone-free xenon arc lamp and an R928P photomultiplier with a spectral coverage of 200–900 nm, was used for luminescence detection.

3. Results

3.1. Absorption Spectra

RT absorption spectra of Al₂O₃:Mn, YAP:Mn and YAG:Mn SCFs, grown from the melt solution with nominal 0.1, 1and 10% Mn content, are shown in Figure 3.

The Al₂O₃, YAP and YAG band gaps are 9 eV, 8.2 eV and 7.8 eV, respectively [10]. Generally, the low-energy side of the fundamental absorption of the materials under study can be formed with the participation of lattice defects and impurities, namely by the absorption of excitons localized and bound with these defects and impurities. However, considering this work absorption of these materials in the 200–300 nm range (6.2–4.6 eV) is far from their fundamental absorption range. Secondly, the SCF of different oxides grown from the melt-solution at low (~1000 °C) using the LPE method, are almost free from the



antisemite's defects of Y_{Al} type and possess an extremely low concentration of oxygen vacancies due to the crystallization in an oxygen-containing atmosphere (air).

Figure 3. Normalized absorption spectra of Al₂O_{3:}Mn (**a**), YAP: Mn (**b**), and YAG:Mn (**c**) SCFs, grown from the melt solution with nominal Mn concentrations of 0.1, 1, and 10%.

The strong absorption band peaked at 252 nm in the spectra of all Al₂O₃:Mn SCFs (Figure 3a) is caused by the O²⁻ \rightarrow Mn⁴⁺ charge transfer transitions (CTTs) [11,12]. It looks most reasonable because the ionic radii of Mn⁴⁺ ions are equal to 0.53 Å, and are practically identical to Al³⁺ cation radii of 0.535 Å in the octahedral positions [10]. The absorption band at 209 nm in the spectra with large (1 and 10%) Mn content is due to metal-to-metal charge transfer transitions (CTTs) between the Mn²⁺, Mn³⁺, and Mn⁴⁺ ions, most probably due to Mn³⁺ \rightarrow Mn⁴⁺ CTTs. The absorption spectra of Al₂O₃:Mn SCFs consists also two resolved low intensive absorption band located at ~320 nm and 482 nm, related to ⁴A_{2g} \rightarrow ⁴T_{2g} spin-allowed transitions of Mn⁴⁺ ions, respectively. A weak absorption band peaked at ~380 nm can be attributed to the ⁴A_{2g} \rightarrow ²T_{2g} spin-forbidden transition of the Mn⁴⁺ ions. A low-intensive absorption band peaked at ~540 nm might be caused by the absorption of Mn³⁺ ions [13], and the intensity of this band increases as the Mn contents increase from 0.1 to 1 and 10%.

The absorption bands peaked at 230 nm and 285 nm in the spectra of all YAP:Mn SCFs (Figure 3b) most probably caused by the $O^{2-} \rightarrow Mn^{4+}$ and $Mn^{3+;2+} \rightarrow Mn^{4+}$ CCTs [7]. The positions of these bands are shifted in the long-wavelength range in comparison with respective bands in Al₂O₃:Mn SCFs due to a significantly large band gap of sapphire (9.0 eV) [14] in comparison with YAP (8.2 eV) [15]. The two weak absorption bands peaked at 346 and 429 nm, and are related to ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$, spin-allowed transitions of Mn⁴⁺ ions, respectively. Weak absorption bands peaked at ~562 nm might be caused by the absorption of Mn³⁺ ions [11]. Interestingly, the intensity of Mn³⁺ bands increases and Mn⁴⁺ bands decrease when the Mn concentration increases from 0.1 to 1 and 10%.

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Similarly to the absorption spectra of Al₂O₃:Mn and YAP:Mn SCFs, the band peaked around 209 nm in the absorption spectra of YAG:Mn (0.1 and 1%) may be caused by the $O^{2-} \rightarrow Mn^{4+}$ CTTs. Increasing the Mn concentration to 10% results in the appearance of the other two bands peaking at 233 and 267 nm. Most probably, the nature of these bands is connected with the formation of Mn³⁺ and Mn²⁺ states in these films. Namely, the band peaked at 233 nm can be related to the Mn³⁺ \rightarrow Mn²⁺ or Mn²⁺ \rightarrow Mn⁴⁺ CTTs when the band peaked at 266 nm can be assigned to the O²⁻ \rightarrow Mn⁴⁺ CTTs [7].

Such an assumption about the origin of various Mn related absorption bands in the spectra of Al₂O₃:Mn, YAP:Mn and YAG:Mn SCFs is confirmed by the results of CL spectra measurements, where the presence of different Mn states in the CL spectra depending on the activator content is well evidenced (Table 2).

Type of SCF	Mn Content in MELT Solution, Mole%	Registered Mn State in Absorption Spectra	Registered Mn State in CL Spectra	Other Emission Centers in CL Spectra
	0.1	Mn ⁴⁺	Mn ⁴⁺	Pb^{2+} , ex(Pb)
Al ₂ O ₃ :Mn	1	Mn ³⁺ , Mn ⁴⁺	Mn ⁴⁺	Pb^{2+} , ex(Pb)
	10	Mn ³⁺ , Mn ⁴⁺	Mn ³⁺ , Mn ⁴⁺	Pb^{2+} , ex(Pb)
	0.1	Mn ³⁺ , Mn ⁴⁺	Mn ³⁺	
YAO3:Mn	1	Mn^{2+} , Mn^{3+} , Mn^{4+}	Mn ²⁺ , Mn ³⁺	Pb ²⁺
	10	Mn^{2+} , Mn^{3+} , Mn^{4+}	Mn^{2+} , Mn^{3+} , Mn^{4+}	
	0.1	Mn ⁴⁺	Mn ²⁺ , Mn ³⁺ , Mn ⁴⁺	
Y ₃ A ₅ O ₁₂ :Mn	1	Mn ⁴⁺	Mn ²⁺ , Mn ³⁺ , Mn ⁴⁺	Pb ²⁺
	10	Mn^{4+} , Mn^{3+} , Mn^{2+}	Mn ²⁺ , Mn ³⁺ , Mn ⁴⁺	

Table 2. Registered absorption and emission centers in Al₂O₃:Mn, YAP:Mn and YAG:Mn SCFs.

It is necessary to mention here that all SCF under study, grown from PbO and Bi₂O₃-based fluxes exhibit two groups of absorption bands in the UV range peaking at about 200–220 nm and 230–267 nm. These bands can be caused by the absorption of Pb²⁺ and Bi³⁺ trace impurities [6,16]. Specifically, the Pb²⁺ and Bi³⁺ dopants can be responsible for the absorption bands peaking around 200–220 nm and 230–267 nm and are caused by the intrinsic ${}^{1}S_{0} \rightarrow {}^{1}P_{1}$ and ${}^{1}S_{0} \rightarrow {}^{3}P_{1}$ transitions of these ions [7,15]. All the mentioned bands are strongly overlapped with the absorption of Mn ions in the different valence states in the SCFs under study.

3.2. CL Spectra

In the context of electron excitation within a crystalline material, particularly when subjected to high-energy electron bombardment originating from a cathode source, certain noteworthy phenomena take place. They are essential to the understanding of luminescence processes. Firstly, when high-energy electrons impact a crystal, electrons residing in the lower-energy valence band undergo an elevation in energy levels, transitioning to the higher-energy conduction band. Subsequently, these high-energy electrons tend to promptly revert to their ground state within the valence band. However, during this process, their journey may be temporarily interrupted or delayed due to the presence of the traps. These traps can be intrinsic ones, connected with the structural defects inherent to the crystal lattice, and extrinsic traps, which arise from external factors such as impurities and dopant atoms. It is worth noting that there exist several pathways through which these excited electrons may return to their ground state, each bearing its level of complexity. The simplest pathway involves the direct recombination of the stimulated electrons with available holes in the valence band, bypassing interactions with traps altogether. In contrast, the second

pathway entails a more intricate course, wherein the electron embarks on a stochastic trajectory through the crystal lattice, eventually encountering one of the aforementioned traps. Subsequent outcomes can vary: the electron may revert to the ground state from the encountered trap, or it may engage with multiple traps, leading to the release of photons with differing wavelengths contingent upon the energy disparities involved. Notably, the intensity of cathodoluminescence (CL) phenomena often exhibits a direct correlation with the density of available traps within the crystal [17,18].

The CL spectra of Al_2O_3 :Mn, YAP:Mn and YAG:Mn SCFs, grown from the meltsolution with nominal Mn content in the 0.1–10% range are shown in Figure 4. Analysis of the obtained CL showed that Mn ions are incorporated in SCF in different charged states and are located in various crystallographic positions. In general, these results confirmed the above mentioned assumptions related to the presence of the Mn²⁺, Mn³⁺ and Mn⁴⁺ valence states in the SCFs under study. The integral CL intensity of all states of the manganese centres in Al_2O_3 :Mn, YAP:Mn and YAG:Ce SCF has a maximum in the 0.1–1% range of Mn concentration and then CL intensity strongly decreases with increasing the manganese content to 10%.



Figure 4. Normalized CL spectra of Al_2O_3 : Mn (**a**), YAP:Mn (**b**), and YAG:Mn (**c**) SCFs doped with 0.1% (1), 1% (2), and 10% (3) Mn ions.

The CL spectra of all Al₂O₃:Mn SCFs show the dominant luminescence of Mn⁴⁺ ions in the octahedral positions of the sapphire host in the two characteristic bands peaked at 678 and 695 nm, related to the ${}^{4}T_{2} \rightarrow {}^{4}A_{2}$ transitions. Rising the Mn content to 1 and 10% leads to the appearance of the additional band peaked at 805 nm, and another wide band peaked around 680 nm which is strongly overlapped with the Mn⁴⁺ luminescence. These last emission bands can be assigned to the Mn³⁺ luminescence, namely to the ${}^{5}T_{2} \rightarrow {}^{5}E$ radiative transitions.

The Mn³⁺ luminescence band peaked at 650 nm and is dominated in the CL spectra of YAP:Mn0.1% SCF [19,20]. This band and a bump at 820 nm are related to the ${}^{5}T_{2} \rightarrow {}^{5}E$ transitions of Mn³⁺ ions. Meanwhile, the increase of Mn content to 1% leads to the appearance of the weak Mn²⁺ luminescence in the cub-octahedral positions of perovskite host in the band peaked at 525 nm, assigned to the ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ transitions of Mn²⁺ ions.

The next increase of the Mn concentration to 10% results in the strong complicity of the CL spectrum of YAP:Mn SCF (Figure 4b, curve 3). Namely, in this spectrum, additionally to the luminescence of Mn²⁺ and Mn³⁺ ions in the respective bands, we observe also the luminescence of Mn⁴⁺ ions in the characteristic bands peaked at 677 and 730 nm, related to the ${}^{4}T^{2} \rightarrow {}^{4}A_{2}$ transitions, and emission in the infra-red bands peaked at 900 and 960 nm, most probably related to the luminescence of dipole Mn centres [2,3].

The shape of the normalized CL spectrum of YAG:Mn 0.1% SCFs in Figure 4c, demonstrates the dominant luminescence of Mn^{2+} ions in the dodecahedral position of garnet host in the band peaked at 605 nm, assigned to the ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ transitions, and the luminescence of Mn^{4+} ions in the tetrahedral garnet sites in the characteristic bands peaked at 646 and 676 nm, related to the ${}^{4}T_{2} \rightarrow {}^{4}A_{2}$ transitions. Most probably, the last band overlapped with the luminescence of Mn^{3+} ions in the octahedral sites of the garnet host in the weak band peaked at 730 nm, and is connected with the ${}^{5}T_{2} \rightarrow {}^{5}E$ transitions. Meanwhile, the increase of the Mn content to 1% leads to a notable increase in the contribution of the Mn^{3+} luminescence in the 730 nm band. For the highest Mn concentration 10%, mainly the Mn^{2+} , Mn^{3+} and weak Mn^{4+} luminescence in the respective bands are observed in the CL spectrum of the YAG:Mn10% sample.

It is important to note here, that apart from the luminescence of Mn related centers, the emission centers created by the Pb^{2+} flux-related impurity are well resolved in the CL spectra of all SCF samples under study. Namely, the emission bands peaked at 340 nm, 363 nm and 373 nm, related to the ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ radiative transitions of Pb^{2+} ions, are observed in the emission spectra of $Al_{2}O_{3}$:Mn, YAP:Mn and YAG:Mn SCFs, respectively. The emission of excitons around Pb ions (ex(Pb) centers) in the band peaked at 530 nm and is well separated in the emission spectra of $Al_{2}O_{3}$ SCF. However, the luminescence of ex(Pb) centers is not observed in the CL spectra of YAP:Mn and YAG:Mn SCFs (Figure 4b,c), due to strong overlapping with the luminescence of Mn related centers.

The CL spectra of some SCF samples under study show also the sharp-line luminescence of the rare-earth trace impurities from row charge components. Namely, the CL spectra of all Al_2O_3 SCFs exhibit the luminescence of Nd^{3+} ions in the characteristic 400 nm band, when in the spectra of the SCF YAP:Mn1% the luminescence of Gd^{3+} ions in the 313 nm band and Eu³⁺ ions in the bands peaked at 591, 611 and 711 nm is well resolved.

Finally, the dominant absorption and emission states of Mn ions in the SCFs under study, depending on nominal Mn content in the 1–10% range, are summarized in Table 2.

3.3. Photoluminescence Emission and Excitation Spectra

The PL emission and excitation spectra of the dominant valence states of Mn ions in SCF samples of sapphire, perovskite and garnet compounds with different Mn concentrations are shown in Figure 5. Namely, a fragment of Figure 5a consists of the PL emission and excitation spectra of Mn⁴⁺ in two Al₂O₃:Mn SCFs with different Mn contents of 0.1 and 1%. The observed dominant emission bands peaked at 679 and 695 nm corresponding to the ${}^{2}E \rightarrow {}^{4}A_{2}$ radiative transitions in Mn⁴⁺ ions. The excitation bands peaked at 319 and 407 nm are related to the ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ spin-allowed transitions of Mn⁴⁺ ions.

The PL emission and excitation spectra of YAP:Mn SCFs with a Mn content of 0.1 and 1% are presented in Figure 5b. The bumps in the emission spectra of these samples at 655 nm correspond to the ${}^{5}T_{2} \rightarrow {}^{5}E$ radiation transitions of Mn^{3+} ions. The luminescence band of Mn^{4+} ions peaked at 688 nm is related to the ${}^{2}E \rightarrow {}^{4}A_{2}$ transitions. The strong excitation band peaked at 340 and 406 nm mainly corresponds to the ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transitions of Mn^{4+} ions.

The PL emission and excitation spectra of YAG:Mn SCFs with a Mn concentration of 0.1 and 1% are shown in Figure 5c. The dominant emission band peaked at 608 nm and bumps at 730 nm are related to the ${}^{5}T_{2} \rightarrow {}^{5}E$ radiation transitions of Mn³⁺ ions. The emission band peaked at 680 nm corresponds to the luminescence of Mn⁴⁺ ions (${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transitions).



Figure 5. RT-normalized PL emission and excitation spectra of Mn⁴⁺ ions in Al₂O₃:Mn SCFs (**a**) and of Mn⁴⁺ and Mn³⁺ ions in YAP:Mn SCFs (**b**), Mn³⁺ in YAG:Mn SCFs (**c**), and Mn⁴⁺ ions YAG:Mn SCFs (**d**).

The excitation spectra of the Mn^{4+} luminescence in Al_2O_3 :Mn and YAG:Mn SCFs exhibit also the luminescence of Tb^{3+} trace impurity in the respective sharp bands in the UV and visible ranges corresponding to the ${}^5D_3 \rightarrow Hj$ transitions of Tb^{3+} ions.

3.4. Photoluminescence Decay Kinetics

The decay kinetics of the Mn^{4+} luminescence, registered at 679 nm in Al_2O_3 :Mn SCFs under excitation at 340 nm at RT, is shown in Figure 6a. The parameters of the respective approximation of the decay curves in the Al_2O_3 :Mn SCFs with different Mn contents are presented in Table 3. The decay curves in the initial part are non-exponential even for lower (0.1%) Mn concentration. An increase of Mn content from 0.1% up to 1% and 10% leads to a strong acceleration of the initial part of decay kinetics of the Mn⁴⁺ luminescence due to their concentration quenching and results in decreasing the respective t_1 and t_2 values However, the main components of the Mn⁴⁺ luminescence and their values do not change significantly in the 0.64–0.68 ms range.

The decay kinetics of the Mn^{3+} luminescence registered at 635 nm in YAP:Mn SCFs at RT is shown in Figure 6b. The details of the approximation of the decay curves for YAP:Mn SCFs with different Mn concentrations are presented in Table 3. The observed decay curves are strongly non-exponential for all Mn concentrations. Rising the Mn content from 0.1 do up to 1% and 10% leads to a strong acceleration of decay kinetics of the Mn^{3+} luminescence due to the concentration quenching. The decay time of the main component of the Mn^{3+} luminescence (t₃ value) is equal to 0.34 ms for YAG:Mn0.1% SCF and 0.26 ms for YAP:Mn1% SCF samples.



Figure 6. Decay kinetic time of Mn^{4+} luminescence in Al_2O_3 :Mn SCFs (**a**), Mn^{3+} luminescence in YAP:Mn SCFs (**b**), and Mn^{3+} and Mn^{4+} luminescence in YAG:Mn SCFs (**c**,**d**).

Table 3. Parameters of approximation of the decay curves are presented in Figure 4 for Al₂O₃:Mn, YAP:Mn and YAG:Mn SCFs with different Mn concentrations.

SCF Type	Mn Content,%	Mn State	A_1/t_1 , ms	$A_2/t_{2,}$ ms	A_3/t_{3_j} ms
Al ₂ O ₃ :Mn	0.1	Mn ⁴⁺	0.04 (5.9%)	0.64 (94.1%)	-
	1	Mn ⁴⁺	0.03 (2.8%)	0.33 (29.4%)	0.76 (67.8%)
	10	Mn ⁴⁺	0.026 (3%)	0.22 (24.8%)	0.64 (72.2%)
YAO3:Mn	0.1	Mn ³⁺	0.14 (27.4)	0.03 (6%)	0.34 (66.6%)
	1	Mn ³⁺	0.11 (25.6%)	0.06 (14%)	0.26 (60.4%)
Va A-Ota Mn	0.1	Mn ³⁺	0.17 (14.8%)	0.98 (85.2%)	-
	1	Mn ³⁺	0.17 (24.6%)	0.05 (3.3%)	0.47 (68.1%)
13/15012.1011	0.1	Mn ⁴⁺	0.066 (3.6%)	0.65 (34.6%)	1.16 (61.8%)
	1	Mn ³⁺	0.06 (40.5%)	0.265 (33.1%)	0.875 (26.4%)

The RT decay kinetics of the Mn³⁺ luminescence in the YAG:Mn (0.1 and 1%) SCFs under excitation in the CTT band peaked at 267 nm are presented in Figure 6c. The parameters of the respective approximation of the decay curves in the YAP:Mn SCFs with 0.1 and 1% of Mn concentration are showed in Table 3. The decay time of the main component of the Mn³⁺ luminescence in YAG:Mn0.1% SCFs is equal to 0.98 ms (Figure 5c, curve 1).

Rising the Mn concentration up to 1% results in the strong acceleration of decay kinetics of the Mn³⁺ luminescence in YAG:Mn1% SCFs due to the concentration quenching (Figure 6c, curve 2) and decay time of the main component of the Mn³⁺ luminescence decreases to 0.47 ms.

The decay kinetics of the Mn^{4+} luminescence in YAG:Mn SCFs at RT under excitation in a 330 nm band of Mn ions is presented in Figure 6d. The details of the approximation of the decay curves for YAG:Mn SCFs with different Mn contents are presented in Table 3. The main component of the Mn^{4+} luminescence in the YAG:Mn0.1 SCF sample (Figure 5b,d) has decay times vales $t_2 = 0.65$ ms and $t_3 = 1.16$ ms. Meanwhile, raising the Mn concentration to 1% results in the strong acceleration of decay kinetics of the Mn^{4+} luminescence in YAG:Mn1% SCF due to the concentration quenching (Figure 5c, curve 2) and decay times of the main component of the Mn^{3+} luminescence decrease to $t_2 = 0.265$ ms and $t_3 = 0.875$ ms (Table 3).

4. Conclusions

The regularities of manganese charge state formation and luminescent characteristics of single crystalline films (SCFs) of Mn-doped oxides with different crystallographic shapes, like sapphire Al_2O_3 :Mn, perovskite YAlO₃ (YAP:Mn) and garnet Y₃Al₅O₁₂:Mn (YAG:Mn), were investigated. The SCF samples were grown by the LPE method from the melt solutions based on the PbO-B₂O₃ flux onto undoped sapphire, YAP and YAG substrates, respectively. The MnO₂ in the 0.1–10 mole% concentration concerning the film-forming components was used as an activating oxide. Meanwhile, due to relatively small segregation coefficients, the real content of Mn ions in the SCFs of sapphire (0.1), YAP (0.14), and YAG (0.02) was significantly less and lay in the 0.001–1; 0.01–0.81 and 0.002–0.2 at—% ranges, respectively.

Changing the oxide host composition causes changes in the optical characteristics of the SCF materials under investigation. To characterize them, the absorption, cathodoluminescence (CL), and photoluminescence (PL) spectra, as well as the PL decay kinetics of Al₂O₃:Mn, YAP:Mn, and YAG:Mn SCFs with different Mn concentrations, were investigated. The measured spectra were analyzed to establish the preferred valence states of manganese ions realized in these SCFs of various oxides based on the Mn content.

Manganese ions were found in various valence states (Mn²⁺, Mn³⁺, Mn⁴⁺) in all of the SCFs studied. The valence states of manganese are greatly affected by changes in the host crystal lattice structure and dopant concentration in these three materials, as evidenced by the intensity difference in their absorption, CL, PL spectra, and PL decay kinetics.

We discovered that the valence of manganese ions is modified by their location in the aforementioned oxide hosts. Mn^{4+} ions predominantly occur in the octahedral coordination $(Al^{3+}$ sites) in sapphire, perovskite, and garnet whereas Mn^{2+} ions dominantly localized in the cub-octahedral and dodecahedral coordination $(Y^{3+}$ sites) in the perovskite and garnet compounds. Mn^{3+} state is predominantly observed in the SCFs of perovskite and garnets. The preferred manganese state in the SCFs under study is also strongly influenced by Pb^{2+} , especially at low 0.1% Mn dopant concentration levels.

The above mentioned results can be useful for consideration of the Mn-doped SCFs of oxides under study as prospective materials for developing thin-film dosimetric materials and combined (film/substrate) phosphors for photovoltaic devices as well.

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