Time-resolved spectroscopy of exciton states in single crystals and single crystalline films of YAlO₃ and YAlO₃ : Ce

V Babin¹, V Gorbenko², I Kondakova³, T Kärner¹, V V Laguta³,⁴, M Nikl⁴, S Zazubovich¹ and Yu Zorenko²,⁵

¹ Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia
² Ivan Franko National University of Lviv, Gen. Tarnavsky 107, 79017 Lviv, Ukraine
³ Institute for Problems of Material Science, NAS, Krijianovskogo 3, 03142 Kiev, Ukraine
⁴ Institute of Physics AS CR, Cukrovarnicka 10, 16253 Prague, Czech Republic
⁵ Institute of Physics, Kazimierz Wielki University in Bydgoszcz, Weyssenhoffa sq. 11, 85-090 Bydgoszcz, Poland

E-mail: vladimir.babin@ut.ee and svet@fi.tartu.ee

Received 16 May 2011, in final form 17 June 2011
Published 14 July 2011

Abstract
Luminescence characteristics of single crystals (SC) and single crystalline films (SCF) of YAlO₃ and YAlO₃ : Ce are studied at 4.2–300 K under photoexcitation in the 4–20 eV energy range. The origin and structure of the intrinsic and impurity defects responsible for various exciton-related emission and excitation bands are identified. The ≈5.6 eV emission of YAlO₃ SCF is ascribed to the self-trapped excitons. In YAlO₃ SC, the dominating 5.63 eV and 4.12 eV emissions are ascribed to the excitons localized at the isolated antisite defect Y₃⁺Al and at the Y₃⁺Al defect associated with the nearest-neighbouring oxygen vacancy, respectively. The thermally stimulated release of the electrons, trapped at these defects, takes place around 200 K and 280 K, respectively. The presence of Y₃⁺Al-related defects and isolated oxygen vacancies (AlO₅ units) in YAlO₃ SC is confirmed by NMR measurements. The formation energies of various Y₃⁺Al-related defects are calculated within the density functional theory. The influence of various intrinsic and impurity defects on the luminescence characteristics of Ce³⁺ centres is clarified.

1. Introduction

Single crystals (SC) of Ce³⁺-doped yttrium- or lutetium-aluminium perovskite YAlO₃ (YAP) or LuAlO₃ (LuAP) were found to have favourable scintillation characteristics especially for medical applications [1, 2] which stimulated intense studies of this material. Luminescence characteristics of Ce³⁺ centres, as well as energy transfer and defect creation processes in YAP:Ce SC or LuAP:Ce SC were intensively studied [1–6]. The crystals grown from the melt at high temperatures (1900–2000 °C) contain antisite (e.g. Y₃⁺Al-, Ce³⁺Al-type) and vacancy-related defects which can negatively influence the scintillation characteristics of YAP:Ce SC. The concentration of these defects is strongly suppressed in the YAP single crystalline films (SCF) prepared by the low-temperature liquid phase epitaxy (LPE) method [7]. However, during the preparation of the SCF with the use of PbO-containing flux, lead ions are introduced into the SCF. As a result, various lead-related centres appear with the luminescence in the UV spectral range [8–10].

The luminescence of undoped YAP SC has been studied for more than 30 years (see, e.g. [7–9, 11–17] and references therein). The two emission bands observed at 5.9 eV (FWHM = 0.7 eV) and 4.2 eV (FWHM = 0.9 eV) under excitation in the exciton absorption region were ascribed to the self-trapped excitons (STE) and recombination processes, respectively [12–16]. In [7–9, 17] the role of antisite defects of the type of Y₃⁺Al in the formation of intrinsic luminescence centres was considered. After that, the highest energy intrinsic emission of YAP SC was concluded to arise from the Y₃⁺Al defect itself [7], or the exciton localized near the Y₃⁺Al defect [8, 9], or the STE [17]. In [17] the 5.28 eV emission was ascribed to...
the exciton localized near the \( Y_{3+} \) defect, while the emission bands located in the 3.0–4.5 eV range, to the excitons localized near various vacancy-related defects.

Thus, in SC and SCF of YAP, several types of intrinsic defects can exist. This reduces the efficiency and speed of energy transfer from the host lattice to \( Ce^{3+} \) centres. Photo-thermally stimulated disintegration of various exciton states into electron and hole centres and their subsequent tunnelling recombination can result in the appearance of slow luminescence decay components. The overlap of intrinsic emission bands with the absorption bands of \( Ce^{3+} \) can allow for an effective energy transfer from the defect-related centres to \( Ce^{3+} \) ions which negatively influences the scintillation response of \( Ce^{3+} \)-doped YAP.

However, the origin of the defect-related states as well as the processes responsible for the luminescence of undoped YAP is not clear as yet. In different papers, different data are reported regarding the positions of the exciton, defect-related and impurity-related excitation bands in the exciton absorption region (see, e.g. table 1). Therefore, their detailed comparison is not always possible. In this work, the characteristics of the processes responsible for the luminescence of undoped YAP were measured with a heating rate of 5 K min\(^{-1}\) after x-ray irradiation of a sample at 70 K for 30 min (40 kV, 15 mA). The sample located in an Oxford Instruments OptistatCF (Continuous Flow) helium cryostat was cooled and heated by He exchange gas. The heating rate was controlled with an ITCS205 temperature controller. The luminescence was registered using a Hamamatsu H8259-01 photon counting head.

Nuclear magnetic resonance (NMR) spectra of \( ^{89}Y \) and \( ^{27}Al \) were measured in a magnetic field \( B = 9.4 \text{ T} \), corresponding to Larmor frequencies of 19.607 MHz and 104.264 MHz for \( ^{89}Y \) and \( ^{27}Al \), respectively. Both single pulse and solid echo pulse sequences with phase cycling were used. Due to the long spin–lattice relaxation time, the repetition time between pulses for yttrium was about 45 min. Magic angle spinning (MAS) \( ^{27}Al \) NMR spectra were measured at spinning rates 10 and 14 kHz.

2. Experimental details

The SC of undoped and \( Ce^{3+} \)-doped YAP were grown in CRYTUR Ltd, Turnov, Czech Republic, by the Czochralski method in a molybdenum crucible and studied in [3, 6]. The SCF of undoped YAP and YAP: \( Ce \) were prepared in Lviv University, Ukraine, by the LPE method from PbO–B\(_2\)O\(_3\) flux in a platinum crucible [7–9, 17] and investigated in [10]. The undoped YAP SC was used as a substrate. The YAP: \( Ce \) powder QM58/N-S1 with an average crystallite size of 6–8 \( \mu \text{m} \) was synthesized at Phosphor Technology Ltd, UK, through a solid-state reaction and was not melted in the process of the preparation. Our XRD measurements showed that it has a perfect orthorhombic perovskite structure. \( Ce \) concentrations in YAP: \( Ce \) SCF (estimated from the comparison of the absorption coefficients of these two samples at the same photon energy) were, with respect to Y content, 0.50 at% and 0.61 at%, respectively.

The luminescence characteristics were studied at 10 K under excitation by the synchrotron radiation at SUPERLUMI station (HASYLAB at DESY, Hamburg, Germany) with time windows 1–9 and 96–149 ns. The excitation spectra of different emissions were measured in the 4–20 eV energy range under exactly the same conditions and corrected for the spectral dependence of excitation intensity. The emission spectra were measured using the monochromator ARC 0.3 m Spectra Pro300i, detected with the photomultiplier Hamamatsu R6358P, and were not corrected. The spectral width of the slits was 15 nm. The experiments at low temperatures were carried out with the use of a closed-cycle refrigerator.

Thermally stimulated luminescence (TSL) glow curves were measured with a heating rate of 5 K min\(^{-1}\) after x-ray irradiation of a sample at 70 K for 30 min (40 kV, 15 mA). The sample located in an Oxford Instruments OptistatCF (Continuous Flow) helium cryostat was cooled and heated by He exchange gas. The heating rate was controlled with an ITCS205 temperature controller. The luminescence was registered using a Hamamatsu H8259-01 photon counting head.

3. Results and discussion

As the emission spectra were not corrected, their maxima positions and FWHM differ from the true ones, especially

| Sample | Exciton | Exciton emission (eV) | Defect emission (eV) | Lowest energy exciton band (eV) |
|--------|---------|-----------------------|----------------------|-------------------------------|
| YAP SC | STE     | 5.69 [17]             | —                    | 7.89 [17]                     |
|        | \( ex^{0}_{Y_{3+}} \) | 5.9 [12]; 5.69 [8]; 5.28 [17]; 5.63 | —                   | 7.88 [8]; 7.95 [16]; ≈7.9 |
|        | \( ex^{0}_{Y_{3+}-V_{O}} \) | 4.12 | 2.45 [29] | 7.65; 7.13 |
|        | \( ex^{0}_{Ce^{3+}} \) | 4.2 [22] | — | 7.67 [17]; 7.6 [13]; 7.52 [8] |
|        | \( ex^{0}(Ce^{3+}-Y_{3+}) \) | No | Ce\(^{3+}\) | 7.80 [9]; 7.9 |
| YAP SCF | STE | ≈5.6 | — | 7.91 [17]; 7.83 |
|        | \( ex^{0}(Pt^{4+}) \) | 4.16 | — | ≈7.6 |
|        | \( ex^{0}(Pb^{2+}) \) | 4.19 [8] | — | 7.59 [8] |
|        | \( ex^{0}(Pb^{2+}) \) | No | 3.63 [8] | 7.66 |
|        | \( ex^{0}(Pb^{2+}-V_{O}-Y_{3+}) \) | No | 3.15 [10] | 7.74 |
|        | \( ex^{0}(Ce^{3+}) \) | No | 7.80 [9]; 7.9 |

Table 1. Luminescence characteristics of perturbed and localized excitons and defects in YAP SC and YAP SCF at 10 K. The maxima positions obtained in this paper are shown in bold and labelled in the figures.
in the energy range >5 eV due to the decreasing sensitivity of the detection system with increasing emission energy. In YAP SCF, all the intrinsic and defect- or impurity-related emissions are most effectively excited in the exciton absorption region. The emissions of YAP SC are effectively excited in the band-to-band transition region as well. The positions of the excitation bands in the exciton region observed for various exciton emission bands as well as for the emission of Ce³⁺ centres in YAP SC and YAP SCF, and single and dimer Pb²⁺-based centres in YAP SCF are shown in table 1. It is evident that they are characteristic for each emission band studied.

3.1. Self-trapped and localized exciton luminescence in YAP single crystalline films

As mentioned above, the number of antisite and vacancy-related defects is strongly suppressed in SCF as compared with SC. Therefore, in the emission spectrum of YAP SCF, the STE band should be the dominating one. In the uncorrected emission spectrum of YAP SCF, measured at 10 K under excitation in the 8.40–7.95 eV range, the most intense band peaking at \( \approx 5.6 \) eV is observed (figure 1(a), curves 1–3) which should arise from the STE. The excitation band of this emission is located at about 7.83 eV (figure 2(a)) (see table 1). The band gap energy in YAP is \( E_g = 8.8 \) eV [18, 19].

In addition to the STE emission, a complex band is observed in YAP SCF, consisting of at least three components with maxima at 4.16 eV, 3.63 eV and 3.15 eV (figure 1(a), curve 4). The two latter bands arise from the single and dimer Pb²⁺-based centres [10]. A wide 4.16 eV emission, observed in [8] at 4.19 eV and ascribed to an exciton localized near a Pb²⁺ ion, is excited around 7.6 eV (figure 2(b)). The origin of the analogous (4.3 eV) emission in LuAG SCF was studied in detail [20]. By analogy with [20], we suggest that the 4.16 eV emission arises from an exciton localized near a Pt⁴⁺ ion whose presence in SCF is caused by the use of a platinum crucible during their preparation. In the excitation spectrum of the 3.63 eV emission of the single Pb²⁺-based centres, the 7.66 eV band is observed (figure 3(a)). In the excitation spectrum of the 3.15 eV emission of the dimer \{Pb²⁺–VO–Pb²⁺\} centres, the band located at 7.74 eV is present (figure 3(b)).
bands can arise from the excitons perturbed by the single and the dimer Pb\(^{2+}\)-related centres, respectively. The appearance of the intra-centre 3.63 and 3.15 eV emissions under excitation in the exciton 7.66 and 7.74 eV bands means that the excitation energy is effectively transferred to the corresponding lead centres. The different positions of the excitation band of the 4.16 eV emission as compared with those of the lead-related 3.63 and 3.15 eV emissions (table 1) confirm our conclusion that the 4.16 eV emission is not connected with lead ions.

### 3.2. Intrinsic luminescence of YAP single crystals

In the uncorrected emission spectrum of Y AP SC, the 5.63 and 4.12 eV emissions are observed (figure 1(b)). As mentioned in section 1, different interpretations are given for the highest energy intrinsic emission band [7–9, 13–17]. As in SC, containing numerous antisite and vacancy-related defects, the STE emission should be strongly suppressed, the 5.63 eV emission is surely connected with an antisite defect. In [17], a weak 5.28 eV emission was ascribed to ex\(^{0}\)Y\(^{3+}\)\(_{Al}\). However, this emission is not excited in the exciton absorption region (figure 1(b)). This is evident also from the complete coincidence of the excitation spectra shown in figures 4(a) and (b). The relative intensity of the 5.28 eV emission is much larger under x-ray excitation. By analogy with the \(\approx\)4.3 eV emission of LuAG [20], we suggest that the 5.28 eV emission arises from recombination processes.

The 4.2 eV emission found in [12] has been ascribed to the exciton-based centre [15, 16, 21]. This emission was also observed in the TSL spectra of undoped YAP SC [13, 16, 22] and ascribed [22] to an exciton localized around a single oxygen vacancy.

The results obtained indicate that the characteristics of the 5.63 and 4.12 eV emissions in YAP SC differ from the characteristics of the STE emission in YAP SCF. In the YAP SCF, these emissions are absent [8]. We conclude that both the 5.63 and 4.12 eV emissions arise from the excitons localized near Y\(^{3+}\)\(_{Al}\)-related defects. As the positions of their lowest energy excitation bands are different: the 5.63 eV emission is excited around 7.9 eV (figure 5(a)), while the 4.12 eV emission at 7.13 and 7.65 eV (figure 5(b)), it means that the defects responsible for these emissions are different as well. One can suggest that these emissions arise from an exciton localized near a single antisite defect: ex\(^{0}\)Y\(^{3+}\)\(_{Al}\) and from an exciton localized near the Y\(^{3+}\)\(_{Al}\) defect associated with an oxygen vacancy V\(_{O}\): ex\(^{0}\)\{Y\(^{3+}\)\(_{Al}\)–VO\}. The presence of Y\(^{3+}\)\(_{Al}\)–V\(_{O}\) defects in YAP SC has recently been confirmed by the ESR method [23] where the paramagnetic electron centres of the type of Y\(^{3+}\)\(_{Al}\)–V\(_{O}\) were detected in the irradiated crystals. Their emission band is located at 2.45 eV [24].

Under 8.3–8.4 eV excitation, the 5.63 eV emission intensity is constant up to 150 K and then decreases twice at about 220 K [3, 12]. The reduction in the 5.63 eV emission intensity is accompanied by the enhancement of the 4.12 eV emission [3]. In the YAP:Ce SC, the TSL peaks are observed at temperatures \(\approx\)200 K and \(\approx\)280 K (figure 6, solid line, see also [22]) corresponding to the thermal quenching of the 5.63 eV and 4.12 eV emissions, respectively. Due to the effective positive charge of an oxygen vacancy, the thermal stability of the electron centres based on Y\(^{3+}\)\(_{Al}\)–V\(_{O}\) defects should be larger as compared with the electron centres based on single Y\(^{3+}\)\(_{Al}\) defects. Therefore, the TSL peaks at \(\approx\)200 K and \(\approx\)280 K can arise from the recombination of electrons, thermally released from Y\(^{3+}\)\(_{Al}\) and Y\(^{3+}\)\(_{Al}\)–V\(_{O}\) traps, respectively, with the hole Ce\(^{4+}\) centres. Indeed, the thermal quenching of the 2.45 eV emission, caused by the electron release from Y\(^{3+}\)\(_{Al}\)–V\(_{O}\) traps, takes place just around room temperature [24]. The conclusion on the origin of the \(\approx\)200 K and \(\approx\)280 K peaks is also confirmed by the fact that these peaks are absent in the YAP:Ce powder (figure 6, dashed line). Indeed,
as this material was not melted at any preparation stage, the concentration of antisite defects in the YAP:Ce powder should be considerably lower as compared with the melt-grown YAP:Ce SC.

The existence of the defects of the type of \( Y_{\text{Al}}^{3+} - V_{\text{O}} \) was suggested also for \( \text{Y}_3\text{Al}_2\text{O}_12 \) \([25, 26]\). Clustering of \( \text{Ce}^{3+} \) ions with \( \text{Lu}_{\text{Al}}^{3+} \) antisite defect was observed by the ESR method in \( \text{Lu}_2\text{AlO}_12 : \text{Ce} \) SC \([27]\), and clustering of \( \text{Ce}^{3+} \) and oxygen vacancy was considered in \( \text{Lu}_2\text{SiO}_5 : \text{Ce} \) SC \([28]\). Thus, such defect clusters are repeatedly considered or evidenced in complex oxides to explain the observed characteristics. In contrast, the atomistic simulations \([29]\) found a negative binding energy for the \( \{ Y_{\text{Al}}^{3+} - V_{\text{O}} \} \) defect in \( \text{Y}_3\text{Al}_2\text{O}_12 \) and the authors concluded that these defects would not exist. However, despite the fact that there is no electrostatic attraction between \( Y_{\text{Al}}^{3+} \) and \( V_{\text{O}} \), one should take into account that a large \( Y^{3+} \) ion substitutes a much smaller \( \text{Al}^{3+} \) ion and, hence, the location of \( Y_{\text{Al}}^{3+} \) defect close to \( V_{\text{O}} \) can be preferable. Indeed, in section 3.3 the density functional theory (DFT) calculations of formation energies of various antisite-related defects in YAIo3 showed that the formation of the associate of antisite defect with oxygen vacancy is more preferable as compared with a single antisite defect.

3.3. Calculation of the \( Y_{\text{Al}}^{3+} \{ Y_{\text{Al}}^{3+} - V_{\text{O}} \} \) and \( Y_{\text{Al}}^{3+} \{ Y_{\text{Al}}^{3+} - \text{Ce}^{3+} \} \) defect formation energies

\textit{Ab initio} computations allow the determination of the total energy as a function of ionic coordinates and types of ions, and thus provide independent information about the microscopic structure of a defect and clarify some defect models.

The DFT calculations were performed by us within the local spin-density approximation (LSDA). We have used the all-electron full-potential local-orbital (FPLO) code version 7.00-28 \([30]\). In our scalar relativistic calculations, the exchange and correlation potential of Perdew and Wang \([31]\) was employed. The \( k \)-mesh gives the subdivision of the Brillouin zone along the three axes from which the \( k \)-space integration mesh is constructed. We have used the default value \( 12 \times 12 \times 12 \) for pure YAIo3 and \( 6 \times 6 \times 6 \) for supercells with defects. The defect energy was calculated using a 20-atom \( P_{\text{mnm}} \)-symmetry cell, where the lattice parameters were taken from x-ray diffraction data \([32]\).

Using the supercell calculations, we have first obtained the formation energy of \( \text{Y}_{\text{Al}} - \text{Al}_{\text{Y}} \) antisite defects by comparing the ground state total energy of a perfect cell with that of cells with single Y–Al interchanges. The structural parameters used are summarized in table 2. As can be seen from the table obtained using the LSDA calculations, the relaxed structure is close to the experimentally found one \([32]\) and is consistent with the density functional results published earlier \([33]\).

The calculated energies for different configurations of antisite defects are summarized in table 3. We found the antisite defect formation energies in the presence of the nearest-neighbouring oxygen vacancy as well as in the presence of a \( \text{Ce}^{3+} \) impurity ion. The formation of the antisite defect is more preferable in the cases where there is an oxygen vacancy nearby, which settles close to the direction \( \text{Al} – V_{\text{O}} – \text{Al} \). The formation energy of such a defect is 25% lower when compared with the energy of the antisite ion with an oxygen vacancy \( V_{\text{O}} \) in a farther environment.

We have also calculated the total energy for a supercell, in which a \( \text{Ce}^{3+} \) ion substitutes for a Y ion, and found that the antisite defect formation is facilitated when \( \text{Ce}^{3+} \) occupies the nearest \( Y^{3+} \) site (see table 3).

Our calculations have also shown that the ground state energy of the \( \text{Ce}^{3+} \)-doped YAP lattice with the oxygen vacancy...
near Ce$^{3+}$ is 0.25 eV lower than the energy of the lattice in which the oxygen vacancy is located far from the Ce$^{3+}$ ion.

In the case where Y$^{3+}$ substitutes for the Al ion near the oxygen vacancy, the Y$^{3+}$ ion must be shifted towards the vacancy because the Y$^{3+}$ ion is much larger than the Al$^{3+}$ ion. The total energy dependence on the displacement of an Y$^{3+}$ antisite ion is presented in figure 7. One can see that the calculation predicts the Y$^{3+}$ ion displacement from the Al position in the direction towards the oxygen vacancy by a distance of about 0.34 Å.

It should be noted that the calculations of the defects’ formation energies were performed for the ideal stoichiometric YAP lattice. Commercial YAP SC are usually grown with a small excess of Y ions that prevents the substitution of Al ions for Y sites. Therefore, in the general case, the probability of creation of different types of defects depends also on technological parameters which have to be taken into account under analysis.

3.4. Excitons perturbed by Ce$^{3+}$-related centres in SC and SCF of YAP : Ce

At 4.2 K, the emission spectrum of Ce$^{3+}$ centres in YAP : Ce consists of two components peaking at 3.30 and 3.55 eV (see, e.g. [3, 6]). In SC and SCF of YAP : Ce, the excitation spectra of the Ce$^{3+}$ emission in the exciton absorption region are considerably different (see also [7, 9]). The main exciton band is located at 7.7 eV in SC (figure 8(a)), but at about 7.9 eV in SCF (figure 8(b)). These bands are most probably arising from an exciton perturbed by a Ce$^{3+}$-related defect. As the main difference between SCF and SC is in the absence of antisite defects in SCF, we assume that the 7.9 eV band arises from an exciton perturbed by a single Ce$^{3+}$ ion, while the band around 7.7 eV, from an exciton perturbed by a Ce$^{3+}$ ion associated with the antisite defect Y$^{3+}_{Al}$ (see table 1). The preferable location of antisite defects close to Ce$^{3+}$ ions is confirmed by the calculations of the {$Y^{3+}_{Al}$–Ce$^{3+}$} defect formation energy (see section 3.3) and by the fact that in LuYAP : Ce and LuAP : Ce, where the content of antisite defects should be larger [34, 35], the above-mentioned difference in the excitation spectra in SC and SCF is also larger [9, 17, 35]. The presence of non-equivalent Ce$^{3+}$ centres in YAP : Ce and LuYAP : Ce has also been noticed earlier [6, 36].

The comparison of the excitation spectra of the slow and fast decay components of the Ce$^{3+}$ emission in the exciton region (figure 8) indicates that in YAP SC, unlike YAP SCF, a competition exists between the processes responsible for these components (see also [7–9]). Indeed, the excitation spectrum maximum of the fast component coincides with the excitation spectrum minimum of the slow component. A similar competition was observed in YAP : Ce SC between the processes of defects creation and excitation of the Ce$^{3+}$ emission in the exciton absorption region [6]. As the absorption/excitation bands of Ce$^{3+}$ are strongly overlapped with the intrinsic emission bands of YAP SC and SCF (figure 1), one can assume that the appearance of the slow components in the Ce$^{3+}$ emission decay is caused by the energy transfer from the corresponding defects to Ce$^{3+}$ ions. However, the excitation bands of the defect-related emissions (figures 2(b)–5) do not coincide with the excitation spectrum of the slow component of the Ce$^{3+}$-related emission in the exciton absorption region (figure 8). Only in the 7.6–7.7 eV range, can the slow component of the Ce$^{4+}$ emission in YAP SC arise from the above-mentioned energy transfer processes. Therefore, one can assume that the slow component of the Ce$^{3+}$ emission appears around 8.0 eV mainly due to the tunnelling recombinations between the electron centres and hole Ce$^{4+}$ centres produced as a result of the photostimulated disintegration of the regular exciton state. The tunnelling recombination processes in YAP were also considered earlier [22, 37]. In the energy range <7.5 eV, the slow component can appear in YAP SC due to the tunnelling recombinations in the pairs consisting of an antisite-defect-related electron

Figure 8. Time-resolved excitation spectra of the Ce$^{3+}$ emission measured at 10 K for (a) YAP : Ce SC and (b) YAP : Ce SCF (shown only in the 6–9 eV range).
centre and hole Ce³⁺ centre, both produced as a result of the photoionization of the higher energy excited states of Ce³⁺ or the photostimulated electron transfer processes [6].

A comparison of the lowest energy exciton bands in the excitation spectra of the lead-related emission (figure 3) and the Ce³⁺ emission (figure 8(b)) indicates that there is no energy transfer from the lead-induced centres to Ce³⁺-related centres. However, the energy transfer from Ce³⁺ to dimer lead centres can take place.

3.5. ⁸⁹Y and ²⁷Al NMR study

In the previous study [23] we have shown the high ability of NMR to detect the presence of Y₃Al antisite ions. In particular, SC ⁸⁹Y NMR measurements have shown the presence of Y₃Al ions in YAP SC in the concentration range 2–3%. It is expected that in the YAP powder the concentration of irregular Y ions should be much smaller than that in SC and NMR could prove this statement. However, unfortunately, ⁸⁹Y NMR in YAP powders is too weak and broad to resolve the irregular Y positions, and the MAS measurements for ⁸⁹Y are not possible due to the low Larmor frequency (19.6 MHz) and long spin–lattice relaxation time (45–60 min) of this nucleus.

In this work, we have performed the studies of ²⁷Al NMR in YAP ground SC and in the commercial YAP powder QM58/N-S1 with the aim to look for Al antisite defects. In YAP SC or powders, ²⁷Al static NMR spectra are too broad to resolve the spectral component responsible for Al at irregular positions. However, the application of MAS technique enables effective narrowing of the NMR linewidth, so that inequivalent positions of ions can be resolved in MAS spectra. ²⁷Al NMR spectra measured in the ground SC and in the commercial powder are shown in figure 9. ²⁷Al chemical shifts are quoted with respect to the octahedral AlO₆ resonance of Y₃Al₄O₁₂.

Figure 9. ²⁷Al static (inset) and MAS NMR spectra measured in ground YAP SC and commercial powder: (a) ground SC, spinning rate (SR) 10 kHz; (b) ground SC, SR 14 kHz; (c) powder, SR 14 kHz. The strong line at 10 ppm corresponds to resonance from regular Al ions in the AlO₆ octahedral coordination, while weak resonance at 50 ppm corresponds to Al in 5-fold coordination. The broad lines visible at spinning frequencies are quadrupole sidebands.

Static linewidth of the central 1/2 ↔ −1/2 transition is large, about 3.5 kHz, while the MAS linewidth is only 0.3 kHz. In addition to the strong central transition at 10 ppm, the MAS spectrum consists of broad quadrupole sidebands visible at spinning frequencies and a weak intensity line which appears in ground SC at both spinning rates. Its position, 50–55 ppm, suggests that this resonance can originate from Al ions in five-fold coordinated AlO₆ positions. It is well known (see, e.g. [38]) that ²⁷Al chemical shift strongly depends on the Al coordination number. In Al–O environments, the ²⁷Al chemical shifts occur at about 60–90 ppm and −10 ppm to 15 ppm for 4-coordinated and 6-coordinated Al, respectively. The isotropic chemical shifts of 5-coordinated Al in well-defined crystalline compounds fall between these two ranges at about 30–50 ppm. Therefore, the weak resonance at 50–55 ppm can originate from Al in the octahedral coordination where one of the six oxygen ions is missing, i.e., oxygen vacancies are detected. Our assignment agrees with the fact that this spectral component is undetectable in commercial powder which was sintered at a much lower temperature than the temperature used in bulk crystal growth (about 2000 °C). Therefore, the powder should contain a much lower concentration of oxygen vacancies. The formation of oxygen vacancy defects is crucially dependent on the preparation temperature and is an inevitable consequence of using both the high growth temperature and the reducing atmosphere of the bulk crystals grown from the melt by Czochralski, Bridgman or similar methods. The relative concentration of AlO₆ units (isolated oxygen vacancies) in SC was estimated from the integral intensities of NMR lines as 0.3–0.5%. However, the total concentration of oxygen vacancies is obviously larger as part of the vacancies is coupled to Y₃Al antisite ions and is not visible in ²⁷Al NMR.

Possible ²⁷Al resonance from Al₃Y antisite positions (12-fold Al coordination) is expected to be at chemical shifts −40 to −90 ppm. To the best of our knowledge, the actual values of the chemical shifts of 12-coordinated Al have not yet been reported because such crystalline compounds probably do not exist in a stable state. One can see from figure 9 that at the chemical shifts of up to −100 ppm, there are no resonances. This means that the concentration of Al₃Y antisite ions in SC is lower than the detection limits of about 0.05–0.1%. It is also worth mentioning that commercial YAP SC are usually grown with a small excess of Y ions that obviously prevents the substitution of Al ions for Y sites. Finally, our SC NMR measurements of the ²⁷Al quadrupole transitions also did not reveal any additional resonances related to possible Al₃Y ions.

4. Conclusion

The detailed study of luminescence characteristics of undoped and Ce³⁺-doped SC and SCF of YAP and the analysis of published data have allowed us to identify the origin and structure of the defects responsible for various localized exciton emission bands. In YAP SCF, the relatively weak ≈5.6 eV emission of the STE is the dominating one. The antisite defects of the type of Y₃Al³⁺ and Y₅Al³⁺−VO are absent. In YAP SC, the STE emission is practically absent, the 5.63 eV
emission is assumed to arise mainly from \( \text{ex}^{0}\text{Y}^{3+} \), while the 4.12 eV emission, from \( \text{ex}^{0}\{\text{Y}_{\text{Al}}^{3+}-\text{V}_{\text{O}}^{0}\} \). In x-irradiated YAP:Ce, the thermally stimulated destruction of the \( \text{Y}_{\text{Al}}^{3+} \) and \( \{\text{Y}_{\text{Al}}^{3+}-\text{V}_{\text{O}}^{0}\} \)-related electron centres takes place around 200 K and 280 K, respectively. The recombination of the released electrons with Ce\(^{4+}\) centres is accompanied by Ce\(^{3+}\) emission. The effective formation of \( \{\text{Y}_{\text{Al}}^{3+}-\text{V}_{\text{O}}^{0}\}\)-type defects in YAP single crystals is confirmed by theoretical calculations. The presence of \( \text{Y}_{\text{Al}}^{3+} \)-related defects and isolated oxygen vacancies (\( \text{AlO}_{5} \) units) in SC is confirmed by NMR measurements.

In the excitation spectra of various intrinsic, defect-related and impurity-related emission bands, regular and various perturbed exciton bands are identified. A comparison of their positions allowed us to clarify the influence of various defects on the appearance of undesirable slow components in the decay kinetics of Ce\(^{3+}\) luminescence, which negatively influence the scintillation characteristics of YAP:Ce. A conclusion is drawn that the slow decay is caused mainly by the tunnelling recombination of electron and hole centres created at the disintegration of the regular exciton states and the photoionization of Ce\(^{3+}\) ions. The contribution of the energy transfer processes between a defect and Ce\(^{3+}\) states is found to be smaller.

Acknowledgments

The work was supported by the projects of the Estonian (No 8678), Czech (No 202/08/0893 and GA AV IAA100100810) and Ukrainian (No SF-28F) Science Foundations as well as by the II-20052049 EC project of DESY, Hamburg. The authors are very much grateful to Paul Ripley (Phosphor Technology Ltd) for useful technological information.

References

[1] Lempicki A, Randles M H, Wisniewski D, Balcerzyk M, Brecher C and Wojtowicz A J 1995 IEEE Trans. Nucl. Sci. 42 280
[2] Nikl M 2000 Phys. Status Solidi a 178 595
[3] Babin V, Fabeni P, Krasnikov A, Nejezchleb K, Nikl M, Pazzi G P, Savikhina T and Zazubovich S 2007 J. Lumin. 124 273
[4] Weber M J 1973 J. Appl. Phys. 44 3205
[5] van Eijk C W E 2001 Nucl. Instrum. Methods Phys. Res. A 460 1
[6] Blazek K, Krasnikov A, Nejezchleb K, Nikl M, Savikhina T and Zazubovich S 2005 Phys. Status Solidi b 242 1315
[7] Zorenko Yu V, Voloshinovskii A S, Stryganyuk G M and Konstankevich I V 2004 Opt. Spectrosc. 96 70
[8] Zorenko Yu, Voloshinovskii A, Gorbenko V, Zorenko T, Nikl M and Nejezchleb K 2007 Phys. Status Solidi c 4 963
[9] Zorenko Yu et al 2007 Radiat. Meas. 42 528
[10] Babin V, Bichevin V, Gorbenko V, Makhov A, Mihokova E, Nikl M, Vedda A, Zazubovich S and Zorenko Yu 2009 Phys. Status Solidi b 246 1318
[11] Kuznetsov A I and Abramov V N 1978 Sov. Phys.—Solid State 20 399
[12] Kuznetsov A I, Abramov V N, Namozov B R and Uibo T V 1982 Tr. Inst. Fiz. AN Est. SSR 53 83 (in Russian)
[13] Kuznetsov A I, Abramov V N, Mürk V V, Namozov B R and Uibo T V 1989 Tr. Inst. Fiz. AN Est. SSR 63 19 (in Russian)
[14] Tomiki K, Kaminao M, Tanahara Y, Futemma T, Fujisawa M and Fukudome F 1991 J. Phys. Soc. Japan 60 1799
[15] Münk V, Kuznetsov A, Namozov B and Ismailov K 1994 Nucl. Instrum. Methods Phys. Res. B 91 327
[16] Lushchik Ch, Feldbach E, Friorap A, Kirm M, Lushchik A, Maaroos A and Martinson I 1994 J. Phys.: Condens. Matter 6 11177
[17] Zorenko Yu, Gorbenko V, Voloshinovskii A, Vistovskii V, Nikl M, Mihokova E and Nejezchleb K 2008 IEEE Trans. Nucl. Sci. 55 1186
[18] Kirm M, Lushchik A, Lushchik Ch and Zimmerer G 2000 Physics and Chemistry of Luminescent Materials PV 99-40, ed C Ronda et al (The Electrochemical Society Proceedings Series) (Pennington, NJ: The Electrochemical Society) p 113
[19] Tomiki K, Fukudome F, Kaminao M, Fujisawa M and Futemma T 1988 J. Lumin. 40/41 379
[20] Babin V, Bichevin V, Gorbenko V, Kink M, Makhov A, Maksimov Yu, Nikl M, Stryganyuk G, Zazubovich S and Zorenko Yu 2011 Phys. Status Solidi b 248 1505
[21] Pedrini C, Bottet D, Dujardin C, Moine B, Dafinei L, Lecoq P, Koselja M and Blazek K 1994 Opt. Mater. 3 81
[22] Fassoli M, Fontana I, Moretti F, Vedda A, Nikl M, Mihokova E, Zorenko Yu and Gorbenko V 2008 IEEE Trans. Nucl. Sci. 55 1114
[23] Laguta V, Nikl M, Vedda A, Mihokova E, Rosa J and Blazek K 2009 Phys. Rev. B 80 045114
[24] Grigorjeva L, Krasnikov A, Laguta V V, Nikl M and Zazubovich S 2010 J. Appl. Phys. 108 053509
[25] Springis M, Pujats A and Valbis J 1991 J. Phys.: Condens. Matter 3 5457
[26] Selim F A, Solodovnikov D, Weber M H and Lynn K G 2007 Appl. Phys. Lett. 91 104105
[27] Laguta V, Slipenyuk A M, Glinchuk M D, Bykov I P, Zorenko Yu, Nikl M, Rosa J and Nejezchleb K 2007 Radiat. Meas. 42 835
[28] Vedda A, Nikl M, Fasoli M, Mihokova E, Pejchal J, Dusek M, Ren G, Stanek C R, McClellan K J and Byler D D 2008 Phys. Rev. B 79 195123
[29] Stanek C R, Levy M R, McClellan K J, Uberuaga B and Grimes R V 2008 Nucl. Instrum. Methods Phys. Res. B 266 2657
[30] Kopernik K and Eschrig H 1999 Phys. Rev. B 59 1743
[31] Perdew J P and Wang Y 1992 Phys. Rev. B 45 13244
[32] Ross N L, Zhao J and Angel R J 2004 Phys. Rev. B 70 11148
[33] Zorenko Yu and Gorbenko V 2008 IEEE Trans. Nucl. Sci. 55 1114
[34] Stanek C R, Levy M R, McClellan K J and Uberuaga B and Grimes R V 2008 Nucl. Instrum. Methods Phys. Res. B 266 2657
[35] Zorenko Yu, Gorbenko V, Volozhnyak T, Mikhailin V, Kolobanov V, Spassky D and Nikl M 2008 IEEE Trans. Nucl. Sci. 55 1192
[36] Zorenko Yu, Gorbenko V, Volozhnyak T, Mikhailin V, Kolobanov V, Spassky D and Nikl M 2008 IEEE Trans. Nucl. Sci. 55 1192
[37] Asatryan H R, Rosa J and Mares J A 1997 Solid State Commun. 104 5
[38] Vedda A, Fasoli M, Nikl M, Laguta V V, Mihokova E, Pejchal J, Dusek M, Ren G, Stanek C R, McClellan K J and Byler D D 2008 Phys. Rev. B 79 195123
[39] Mackenzie J K D and Smith M E 2002 Multinuclear Solid-State NMR of Inorganic Materials vol 6 (Pergamon Materials Series) (Amsterdam: Elsevier) (imprint) p 271