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SPECTROSCOPY AND THERMOLUMINESCENCE OF LuAlO₃:Ce

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The present status of the LuAlO₃:Ce scintillator is reviewed. Scintillation mechanism of this material is based on capture by Ce³⁺ of holes and then electrons from their respective bands. Results of spectroscopic and thermoluminescence experiments are presented to support this model.

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1. Introduction

Scintillation properties of LuAlO₃:Ce (LuAP) crystals were first reported by Lempicki et al. [1]. The interest in this material is derived from the high light yield (above 20000 photons/MeV), high density (8.34 g/cm³) and short decay time (about 18 ns). These properties result in one of the highest figures of merit of any known scintillator and put LuAP in the forefront when high counting rates, fast timing, good stopping power, and energy resolution are of importance [1, 2]. Taking into consideration that this material is not fully optimized yet, and there is evidence that its performance may be highly improved [3, 4], it becomes exceptionally desirable to understand the physics which governs its behavior.

2. Materials and experiments

LuAP samples were cut from boules grown by Litton Airtron by the Czochralski method. Detailed description of the growth process was presented in [1]. Crystals were optically clear and single-phase. Ce doped specimens were colorless with Ce concentrations 0.035 and 0.11 mole% (as measured by spark source mass spectrometry). Color of nominally undoped specimens was slightly orange with level of unintended Ce contamination below 0.4×10^{-4} mole%.

Excitation spectra were acquired using synchrotron radiation at Brookhaven National Synchrotron Light Source (BNSLS). Emission spectra were taken under optical (at BNSLS), γ -ray (100 μ C Ru-Rh source, 0.5–2.9 MeV), and X-ray (8 keV) excitation. X-ray excited luminescence spectra were acquired using “transmission” geometry; sample was excited from one side, and emission gathered from the other one. Decays were obtained under pulsed synchrotron light at BNSLS. Thermoluminescence measurements were performed at Delft University, using facilities described in detail in [5] and [6]. Various sources were used for irradiation: ^{60}Co γ -source (1.2 kGy/h), X-ray tube with Cu anode (3.6 kGy/h) and Hg standard lamp.

3. Experimental results and discussion

Room temperature emission spectra of undoped and Ce-doped specimens, taken under γ and X-ray excitation, are presented in Fig. 1. Trace *a* shows the

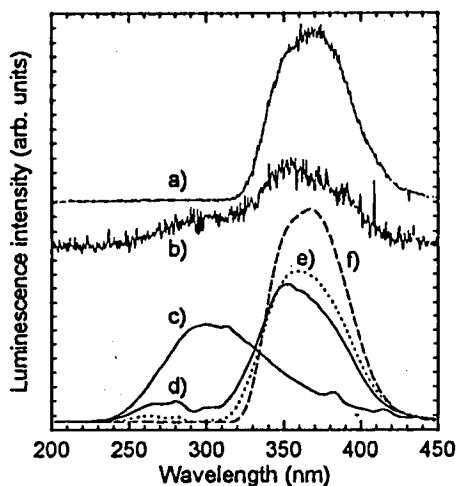


Fig. 1

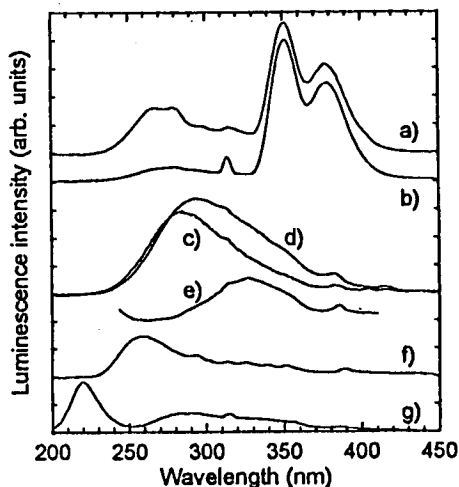


Fig. 2

Fig. 1. Room temperature emission spectra of LuAP under γ (*a, b*) and X-ray (*c-f*) excitation: *a* — 0.035 mole% Ce doped sample, *b* and *c* — undoped sample, *d* — 0.035 mole% Ce doped sample, 0.5 mm thick, *e* — 0.035 mole% Ce doped sample, 1 mm thick, *f* — 0.11 mole% Ce doped sample, 1 mm thick.

Fig. 2. Luminescence spectra of 0.11 mole% Ce doped (*a, b*) and undoped (*f-g*) LuAP samples under optical excitation: *a* — 161 nm, 13 K, *b* — 153 nm, 13 K, *c* — 161 nm, RT, *d* — 152 nm, RT, *e* — 217 nm, 13 K, *f* — 180 nm, 13 K, and *g* — 148 nm, 13 K.

γ -excited luminescence of Ce doped (0.035 mole%) sample. This spectrum is dominated by a single band centered at about 365 nm, which is a clear case of Ce^{3+} *d-f* emission [1]. However, after more detailed examination, one can find an additional (about two orders of magnitude weaker) band at about 280 nm. This band is somewhat stronger in case of nominally undoped sample *b*, but yet scintillation

of this sample also consists mostly of Ce^{3+} emission. X-ray excited luminescence of the same sample *c*, on the contrary, does not demonstrate distinguishable cerium emission, showing instead an intense, wide, asymmetrical band peaking at about 300 nm (host emission), Gd^{3+} line at 314 nm and some Tb^{3+} lines. It is worth noting that Gd and Tb contaminations in this material are only 0.7 and 0.2 weight ppm, respectively, which suggest efficient energy transfer to these ions. X-ray excited luminescence spectrum of Ce-doped sample *d* shows intense Ce^{3+} emission and some remains of 300 nm band. One can observe dips in host emission band at 275, 292 and 310 nm which clearly correspond to bands in Ce^{3+} luminescence excitation spectrum (presented in Fig. 3). Host emission diminishes with increasing sample thickness (*e*) and Ce content; it vanishes almost completely for sample doped with 0.11 mole% of Ce (*f*). These observations leave no doubt that cerium absorption is responsible for deformation of 300 nm band. Although it may indicate of nonradiative energy transfer from host emission to Ce^{3+} ions, we will show later that scintillation mechanism of $\text{LuAP}:\text{Ce}$ is not based on this process.

Luminescence spectra under selective optical excitation are presented in Fig. 2. Traces *a* and *b* present low temperature spectra of 0.11 mole% Ce doped sample excited by 160 and 153 nm light, respectively. Both spectra display host as well as Ce^{3+} emission, but their relative intensities depend on the excitation wavelength. Despite of surface excitation, an effect of deformation of host emission by cerium absorption is also evident, particularly in the first spectrum. Under 153 nm excitation a Gd^{3+} emission line at 314 nm is also observable. Room temperature (RT) spectra of the same sample will not be presented here since they do not reveal any additional features, except that splitting of Ce^{3+} doublet (${}^2F_{5/2}$ and ${}^2F_{7/2}$) is no longer observed. Luminescence spectra of undoped sample let us see an undistorted shape of host emission, which in fact appears to be superposition of a few different ones overlapping each other. Excitation at around 160 nm reveals the strongest of these emissions peaking at about 280 nm (13 K) and at 285 nm (RT) (*c*). Decreasing the excitation wavelength to 152 nm results in admixture of an additional emission on the long-wavelength side of 285 nm band (*d*). At 13 K, using 217 nm excitation light, it becomes possible to isolate this new emission as a band centered at about 330 nm (*e*). Furthermore, at low temperature one can obtain two extra emissions which are not visible otherwise. An excitation at 180 nm exposes an emission peaking at about 260 nm (*f*) and at 148 nm results in an emission band at 220 nm (*g*). Both emissions are about an order of magnitude weaker than 280 nm band, but while the 220 nm band is observable in undoped as well as in intentionally Ce doped samples, the 260 nm luminescence seems to disappear in doped crystals. It is worth noting that in undoped YAlO_3 , an yttrium analog of LuAP , bands corresponding to our 220 and 280 nm emissions have been observed and investigated quite intensively in the past [7-9].

In Fig. 3 we present RT excitation spectrum of Ce^{3+} luminescence in 0.11 mole% Ce doped LuAP . Bands at 215 and 230 nm in addition to those mentioned previously (at 275, 292 and 310 nm) are typical of the *f*-to-*d* transitions of the Ce^{3+} ion [1]. The intense excitation peak at 153 nm can be associated either with creation of band excitons or free electron-hole pairs, and consequently gives us an approximate evaluation of LuAP band gap as 8.1 eV. The broad band

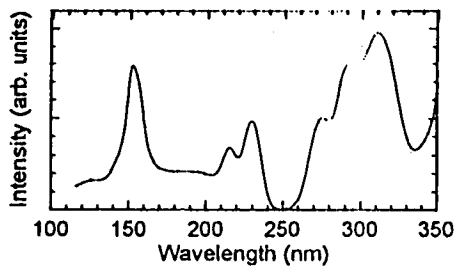


Fig. 3

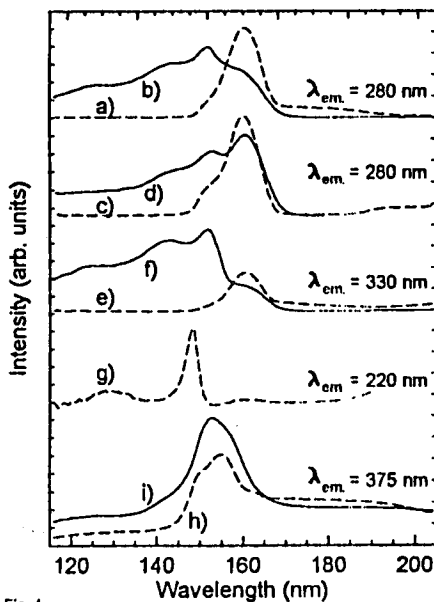


Fig. 4

Fig. 3. Room temperature excitation spectrum of Ce^{3+} luminescence of 0.11 mole% Ce doped LuAP.

Fig. 4. Excitation spectra of 0.11 mole% Ce doped and undoped LuAP. Solid and dashed lines represent spectra measured at RT and 13 K, respectively. Traces: *a*, *b*, *e*, *f*, and *g* represent spectra of undoped sample, while *c*, *d*, *i*, and *h* — Ce doped.

centered at about 180 nm, partially overlapping both 153 nm and higher energy Ce^{3+} $f-d$ bands, is most likely due to photoionization of Ce^{3+} ions.

Excitation spectra in the vicinity of band gap energies of Ce-doped and nominally undoped specimens are compared in Fig. 4. Traces *a* and *b* present excitation spectra of the 280 nm emission of undoped LuAP at 13 K and RT, respectively. Although the low-temperature (LT) spectrum consists of three bands, only 160 and 153 nm bands are in fact attributable to the 280 nm luminescence. The band centered at about 175 nm on the contrary belongs to 260 nm luminescence overlapping the 280 nm emission. The room temperature spectrum exhibits a strongly increased contribution of 153 nm band and new higher energy bands at about 142 and 125 nm, which suggests presence of thermally activated processes. Low-temperature excitation spectrum of 280 nm emission in 0.11 mole% Ce doped sample (*c*) is nearly identical to that of undoped sample. The only difference is lack of the 175 nm band (and consequently the 260 nm emission). A corresponding RT spectrum *d* consists of similar bands observed previously for undoped sample, but ratios of their intensities are different. In general the intensities of higher energy bands are decreased in comparison with the 160 nm band. Assuming that absorption of the 160 nm light creates band excitons, and the 153 nm light generates free $e-h$ pairs, it becomes evident that presence of Ce in the LuAP lattice does not

affect direct creation of free excitons, but to some extent prevents their formation from free band charge carriers. The mechanism of this "prevention" is most probably a competition for holes and electrons by Ce^{3+} ions which strongly supports scintillation model based on consecutive carrier trapping proposed by Wojtowicz in [10].

Traces *e* and *f* present excitation spectra of 330 nm emission in undoped sample at 13 K and RT, respectively. Since the 330 nm luminescence overlaps the long-wavelength slope of 280 nm band, the measured spectra exhibit mixed features characteristic of both emissions. Some evaluations are however possible. The LT spectrum shows an excitation band centered at 217 nm which definitely belongs only to 330 nm emission (217 nm band is beyond the wavelength range of Fig. 4, but its existence is confirmed by Fig. 2 *e*). The 160 nm light probably does not excite 330 nm emission (or at least does it insignificantly in comparison with excitation of 280 nm band), but shorter wavelengths again do it — the 148 nm excitation (Fig. 2 *g*) gives the 280 and 330 nm bands at similar intensity level (very weak yet). The RT excitation spectrum of 330 nm emission consists exclusively of bands observed previously for 280 nm emission, but shorter wavelength bands are more intense in comparison with this at 160 nm. In fact, if we subtract from this spectrum that measured for 280 nm emission, the result will not contain 160 nm band. This suggests that the origin of 330 nm luminescence may be entirely different from that of 280 nm one. While a large Stokes shift (≈ 3.3 eV) affirm trapped excitons as a source of the latter, the former may be caused by defect or impurity centers which can be excited themselves (at 217 nm) or act as radiative recombination centers.

The LT excitation spectrum of 220 nm emission of undoped LuAP (*g*) consists of two weak bands at 160 and 128 nm and an intense narrow band peaking at 148 nm. The 160 nm band is most probably artificial as a result of slight overlapping of emissions 220 and 280 nm. The slim shape of the 148 nm peak, together with a large Stokes shift (≈ 2.7 eV) proves the excitonic origin of the 220 nm luminescence. At RT the 220 nm band becomes unmeasurable. It is hard to believe that thermal quenching of the emission is responsible for that, more likely a low dissociation energy of excitons (before relaxation) is the reason. In Ce doped samples both 220 nm emission and its excitation spectra behave in the same way.

In order to complete a comparison we show the short wavelength parts of Ce^{3+} emission excitation spectra at 13 K (*h*) and RT (*i*). Both spectra have a similar shape with major band at about 153 nm, some contribution from photoionization, 160 nm, and higher energy bands. Note that an admixture of the 160 nm band is greater at 13 K, while the 153 nm band is much more intense at RT. An explanation of this behavior can be presumably found in prolonged lifetime of excitons and reduced mobility of band holes at low temperature.

In Fig. 5 we present selected luminescence pulse shapes under a synchrotron light excitation. Previous experiments with γ excitation resulted in scintillation pulse shape with an unmeasurable rise time (below 1 ns) followed by prompt decay with main time constant about 18 ns for both Ce-doped and nominally undoped samples of LuAP. The contribution of longer components was below 5% of zero-time amplitude. No faster components have been found. The decay

curve for Ce-doped sample has been published in [1]. An optical excitation in Ce^{3+} $d-f$ absorption bands (a) gives a pulse shape with no rise time and a single exponential decay with time constant equal (within an experimental error) to that measured under γ excitation. For 0.11 mole% Ce doped sample this remains true even for excitation in band gap absorption region. Traces b and c represent pulse shapes of 280 nm luminescence in undoped specimen at 13 K and RT, respectively. Both are characterized by single exponential decays; there is, however, a slight possibility that very long components may be hidden in the background. The difference of decay times (4.0 ns at 13 K and 3.1 ns at RT) indicates some thermal quenching of 280 nm emission. Room temperature decay times of the same emission in 0.035 (d) and 0.11 mole% Ce doped (e) samples are 2.9 and 2.6 ns, respectively, which indicate some quenching of the excitonic emission in presence of significant amounts of Ce in the LuAP lattice. Although this quenching most likely happens by nonradiative energy transfer to Ce^{3+} ions, it is too weak to be of importance for Ce^{3+} excitation.

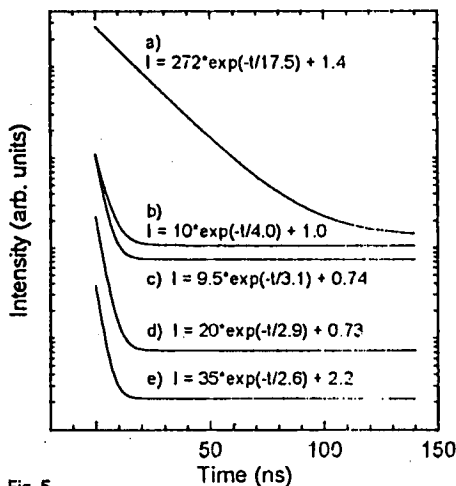


Fig. 5

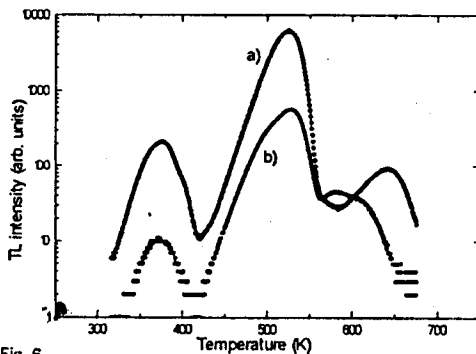


Fig. 6

Fig. 5. Luminescence pulse shapes of Ce^{3+} (a) and 280 nm (b-e) emission under optical excitation: a — 292 nm, RT, 0.11 mole% Ce doped LuAP, b — 161 nm, 13 K, undoped sample, c — 161 nm, RT, undoped sample, d — 161 nm, RT, 0.035 mole% Ce doped LuAP, and e — 161 nm, RT, 0.11 mole% Ce doped LuAP.

Fig. 6. Glow-curves of LuAP following γ irradiation: a — 0.11 mole% Ce doped, b — undoped.

In Fig. 6 glow-curves of Ce-doped a and undoped b LuAP are presented. At a heating rate of 6 K/s, following γ -ray irradiation, both glow-curves have three peaks, two common at about 380 and 530 K, and third at 640 K (a) or 580 K (b). The thermoluminescence (TL) signal is however much weaker for the undoped sample, which suggests a correlation between presence of Ce and the

number of traps. The series of experiments employing an X-ray tube and a Hg lamp as irradiators was also performed. Regardless of the irradiation source similar glow peaks were observed. Yet, after the Hg lamp irradiation, the TL signal was much weaker. Using filters the 250 nm Hg line was recognized as responsible for sample excitation. While energy of absorbed photons is too low to stimulate band-to-band transitions, it is sufficient to release electrons from deeper traps. These electrons can then be retrapped into shallower traps. The shapes of TL emission spectra presented in Fig. 7 resemble those of X-ray excited luminescences, except that the relation of intensities is different. The TL signal of undoped sample (b) consists of

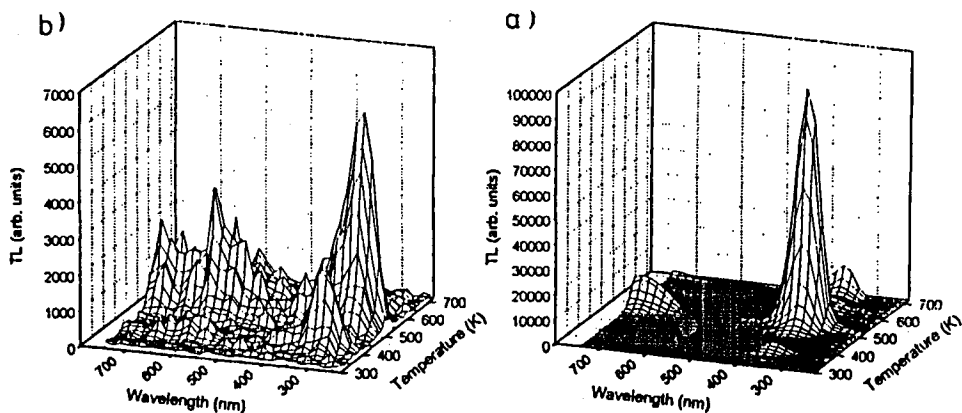


Fig. 7. TL emission spectra of LuAP following X-ray irradiation: (a) 0.11 mole% Ce doped, (b) undoped.

a very weak host emission while the spectrum of doped one (a) is dominated by a strong emission of Ce^{3+} ions. Assuming that the simple classic model of TL [11] is true for LuAP, one can assert that Ce^{3+} ions effectively trap holes during the irradiation stage and then, gaining a positive potential, easily attract conduction band electrons. A more detailed description of TL processes in LuAP, including estimations of trap depths and frequency factors, will be published elsewhere.

4. Conclusions

Although there was no entirely Ce-free sample available, the LuAP lattice emission has been identified. The excitonic 280 nm band was recognized as a main component of this emission. The comparison of decay times of 280 nm luminescence at various Ce doping levels demonstrated only slight quenching of host emission, definitely not sufficient to account for nonradiative energy transfer as a significant source of cerium excitation. Despite of obvious signs of reabsorption of host emission by Ce^{3+} ions, no vital consequences of that were found in scintillation pulse shapes. Excitation spectra indicate competition for free charge carriers between Ce and host emissions, Ce^{3+} being a winner of that contest.

Theoretical speculations presented in [10] lead to the conclusion that Ce^{3+} ions in wide band gap materials will act as hole traps much more likely than as

electron traps. It was confirmed by thermoluminescence spectra which showed that Ce^{3+} ion is a very efficient hole trap and works perfectly as radiative recombination center. All the above observations, together with an astonishing Ce capability to collect excitation deposited in the crystal lattice by γ photons in the form of hot band charge carriers, let us conclude that scintillation of Ce:LuAP is accomplished by consecutive trapping first band holes and then electrons by Ce^{3+} ions.

Acknowledgments

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