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Cerium-doped $RE^{3+}AlO_3$ perovskite scintillators: Spectroscopy and radiation induced defects

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Abstract

Spectroscopic and scintillation properties of $RE^{3+}AlO_3$:Ce pure and mixed perovskite crystals are presented for $RE^{3+}=Y^{3+}$, Gd^{3+} and Lu^{3+}. Qualitative interpretation of γ-ray induced centres in the crystals (up to 3000 Gy dose) have shown that different types of impurities, such as O^- hole centres and F^+ electron colour centres, arise in these crystals and can change the RE^{3+} ion valency or even change the ion valency unexpectedly.

Keywords: Ce-doping; Defect centres; Perovskite crystals; Scintillators

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1. Introduction

Modern applications of scintillators in the medical imaging of the human body such as PET scanning, various γ-cameras or in computed X-ray tomography [1–3] require improved or new scintillating materials. These materials (mainly crystals) should be characterized by (i) high density (ρ~6–9 g cm^{-3}), (ii) high light yield (l.y.≥l.y. of BGO≈9000 photons MeV^{-1}) and (iii) fast response (scintillation lifetimes in the range 10–30 ns). It appears that, of the various scintillating materials, the most promising exhibit Ce^{3+}-doped or Ce^{3+}-concentrated crystals [3–8].

Ce^{3+}-doped RE^{3+} orthoaluminates (or perovskites) are newly studied crystal scintillators that can fulfil the above characteristics of scintillators for medical imaging applications. They are characterized by (i) high density (ρ ranges from 5.36 g cm^{-3} for $YAlO_3$:Ce to 8.34 g cm^{-3} for $LuAlO_3$:Ce), (ii) their light yields exceed that of BGO [4–6] and (iii) fast Ce^{3+} decays allow fast timing. The most used $RE^{3+}AlO_3$:Ce crystal is $YAlO_3$:Ce [2,4,9]; other crystals, such as $GdAlO_3$:Ce [8] and $LuAlO_3$:Ce [6,7,9–11], have not yet been grown in similarly good size and quality. In addition, pure $RE^{3+}AlO_3$:Ce crystals and also mixed crystals have been studied, such as, for example, $Lu_xGd_{1-x}AlO_3$:Ce [12].

In this paper we present the spectroscopic properties of Ce^{3+} ions in $RE^{3+}AlO_3$:Ce crystals, both pure and mixed ($RE^{3+}=Y^{3+}$, Gd^{3+} and Lu^{3+}), and report their scintillation properties. For the first time, the radiation induced centres in these crystals have been studied systematically (up to irradiation doses of 3000 Gy).

2. Experimental

We used various spectroscopic and scintillation experimental techniques together with other methods (e.g., electron microanalysis) for the investigation of Ce^{3+}-doped $RE^{3+}AlO_3$ crystals grown by the Czochralski method[1]. A description of the measured samples (their composition, Ce concentration, etc.) is given in Table 1.

Spectroscopic studies (emission, excitation spectra and fluorescence decays) were measured by spectrofluorometer Edinburgh Instruments Model 199S in the spectral range 200–800 nm and time scales 10^{-9}–10^{-3} s in the case of decay kinetics. Absorption and transmission spectra were recorded by an absorption spectrophotometer Zeiss

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[1] The crystals were grown by Preciosa Crytur Ltd., Turnov, Czech Republic (Palackeho 175, 51119 Turnov).

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Table 1
Description of the $RE^{3+}AP:Ce$ crystal samples

Parameter	Crystal		
Chemical formula	$Lu_xGd_{1-x}AlO_3:Ce$	$YAlO_3:Ce$	$Lu_xY_{1-x}AlO_3:Ce$
x	0.91		~0.3
Abbreviation	LuGAP:Ce	YAP:Ce	LuYAP:Ce
n(Ce) (at%)	~0.16	~0.1	~0.08
Dimensions of sample (mm)	7.2×4.4×1.4	8.95×5.95×5.2	8.7×10×7.8

SPECORD M40 in the range 200–900 nm. Scintillation studies (mainly scintillation decays) were carried out under γ-ray 511 keV excitation of a ^{22}Na radiation source[2]. The excitation and emission spectra were corrected for the spectral dependence of the excitation energy and the spectral dependence of the sensitivity of detection. Convolution of the considered analytical function with the instrumental response to the excitation pulse was used in the decay curves fitting procedure.

3. Experimental results

3.1. Spectroscopic and scintillation properties of $Re^{3+}AlO_3:Ce$ crystals

We observed broad and almost structureless Ce^{3+} emission and excitation bands in the near UV spectral range for all Ce^{3+}-doped $RE^{3+}AP$ crystals studied at RT, both pure and mixed (see Fig. 1). We did not observe significant changes in Ce^{3+} emission peaks for all studied crystals, λ_{em}(peaks)≈360–370 nm at RT. At low temperature, Ce^{3+} ground state splitting is observed in the emission spectra [7,9].

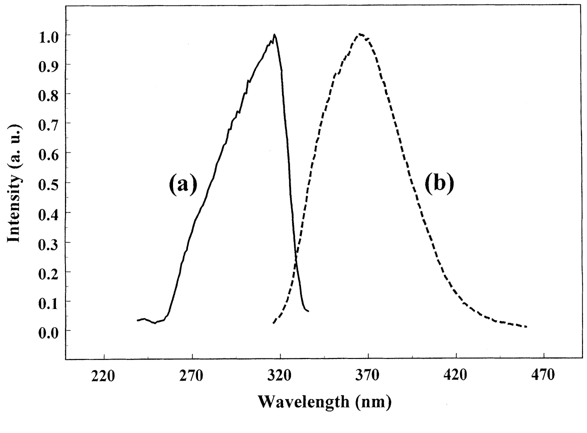

Fig. 1. Excitation (a) and emission (b) spectra of a LuGAP:Ce crystal (for parameters, see Table 1) at RT for $\lambda_{em}=380$ nm (a) and $\lambda_{ex}=300$ nm (b).

Ce^{3+} fluorescence and scintillation decays of $RE^{3+}AP$ pure or mixed crystals are presented in Figs. 2 and 3. Ce^{3+} fluorescence decays are, in general, a bit faster than the scintillation decays, where slow decay components also appear. The fluorescence and scintillation decay curves were approximated by convolution of the instrumental response (see Section 2) with a linear combination of up to three exponentials:

$$I(t)=A_1\,e^{-t/\tau_1}+A_2\,e^{-t/\tau_2}+A_3\,e^{-t/\tau_3} \tag{1}$$

where $I(t)$ is the measured fluorescence or scintillation intensity, and τ_i and A_i (for $i=1$, 2 and 3) are the lifetimes

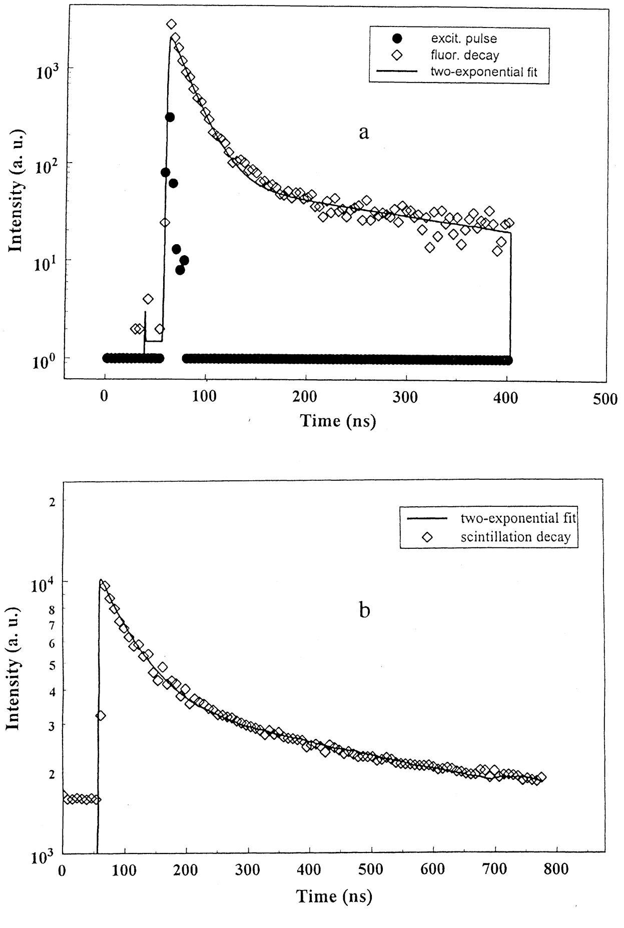

Fig. 2. Fluorescence (curve a – $\lambda_{ex}=300$ nm, $\lambda_{em}=360$ nm) and scintillation (curve b – ^{22}Na 511 keV γ-ray excitation; λ_{em}~whole emission band) decays of a LuGAP:Ce crystal at RT. Fitting parameters are given in Table 2.

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[2] These studies were carried out at the PPE Division, CERN, Geneve, in the framework of a CCC collaboration and a CERN RD18 R&D project for the study of new fast and radiation hard scintillators for calorimetry at LHC.

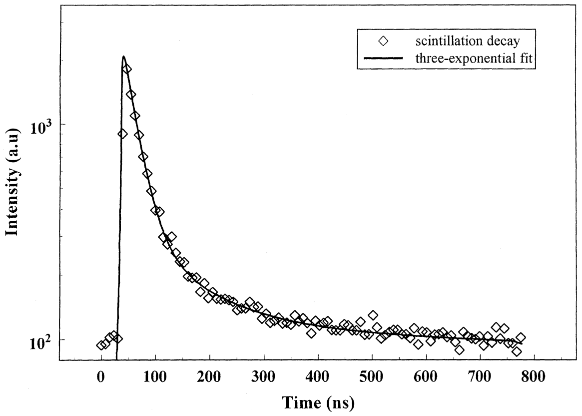

Fig. 3. Scintillation decay of a LuYAP:Ce crystal at RT under ^{22}Na 511 keV γ-ray excitation for λ_{em}~whole emission band. Fitting parameters are given in Table 2.

or the preexponential factors. The Ce^{3+} scintillation decays are particularly complicated due to the transfer mechanisms of excitation energy from e–h pairs to Ce^{3+} ions or the release of electrons or holes from traps [1,3,7]. The results of the evaluations of the decay curves according to Eq. (1) are summarised in Table 2. For LuGAP:Ce crystals particularly, "intense" slow Ce^{3+} decay components appear. Less intense slow decay components were also observed for good quality YAP:Ce crystals (see Table 2 and Fig. 5).

3.2. Radiation induced centres in Re^{3+}AP:Ce crystals

RE^{3+}AP:Ce crystals were irradiated with γ-radiation from a ^{60}Co active source up to radiation doses of 3000 Gy. After irradiation of the RE^{3+}AP:Ce crystals we did not observe any substantial changes in the Ce^{3+} emission and excitation spectra (see Fig. 4) or their decays. As a measure of change in crystals as a result of γ-ray irradiation, the radiation induced coefficient α_{ir} is used, which is given by

Table 2
Fluorescence (τ_f) and scintillation (τ_{sc}) lifetimes and the preexponential constants ($A_f^{(i)}$ and $A_{sc}^{(i)}$) of the individual decay curve components (according to Eq. (1)) for LuGAP:Ce, YAP:Ce and LuYAP:Ce crystals at room temperature

Parameter	Crystal		
	LuGAP:Ce	YAP:Ce	LuYAP:Ce
$\tau_f^{(1)}$ (ns)	17	17	16.8
$A_f^{(1)}$	1510	2600	15000
$\tau_f^{(2)}$ (ns)	263		
$A_f^{(2)}$	180		
$\tau_{sc}^{(1)}$ (ns)	57	22.3	22.9
$A_{sc}^{(1)}$	6246	2500	2000
$\tau_{sc}^{(2)}$ (ns)	960	75	112
$A_{sc}^{(2)}$	3557	160	118
$\tau_{sc}^{(3)}$ (ns)		3600	2980
$A_{sc}^{(3)}$		72	92

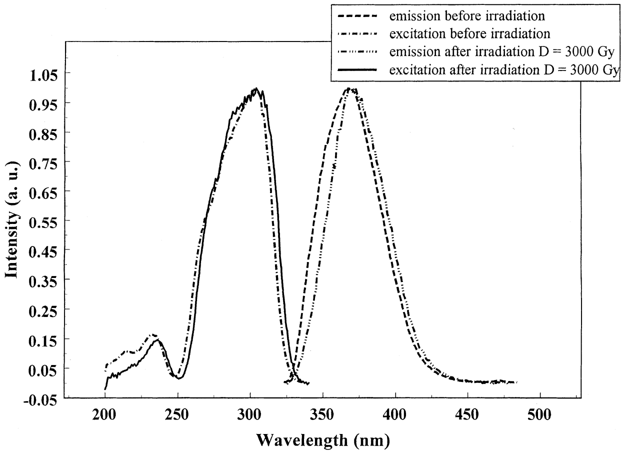

Fig. 4. Emission and excitation spectra of a LuYAP:Ce crystal at RT before and after irradiation (λ_{em} = 360 nm, λ_{ex} = 300 nm).

$$\alpha_{ir} = \left(\frac{1}{d}\right)\log\left\{\frac{T_1^b(\lambda)}{T_1^a(\lambda)}\right\} \tag{2}$$

where d is the sample thickness, and $T_1^b(\lambda)$ and $T_1^a(\lambda)$ are sample transmissions before and after irradiation, respectively. Radiation induced bands (coefficient α_{ir}) up to 3000 Gy dose are given in Fig. 5 for a YLuAP:Ce crystal. The additional radiation induced absorption bands were decomposed into three individual Gaussian curves peaking at λ_1~380, λ_2~425 and λ_3~560 nm with half-widths ranging from 0.28 to 1.5 eV.

We also studied the stability of radiation induced centres and their absorption bands. It was possible to remove almost all of the radiation induced absorption centres (with the exception of the LuYAP:Ce crystal) by optical bleaching or temperature treatment. RE^{3+}AP:Ce crystals were also annealed in various atmospheres. Almost no changes were observed for reducing atmospheres (hydrogen or vacuum), but a sharp increase in absorption in the UV

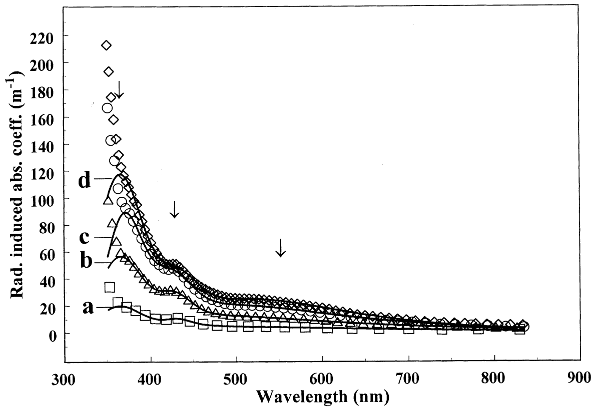

Fig. 5. Additional radiation induced absorption coefficients of a LuYAP:Ce crystal at RT for different irradiation doses: (a) 100 Gy, (b) 300 Gy, (c) 1000 Gy and (d) 3000 Gy). Arrows indicate the peaks of the individual decomposed Gaussian bands.

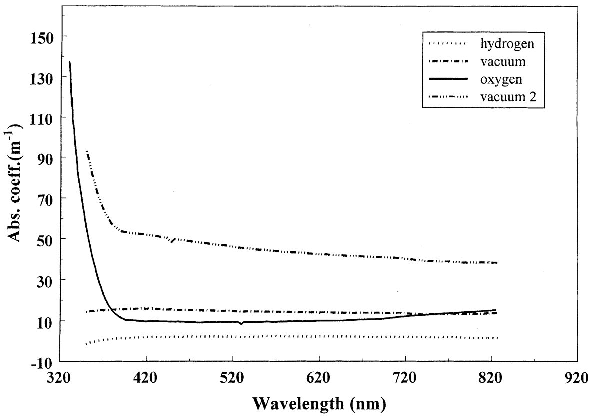

Fig. 6. Absorption coefficient of a YAP:Ce crystal sample at RT after annealing in various atmospheres: hydrogen – 4 h at 1180°C; vacuum – 4 h at 1240°C; oxygen – 10–12 h at 1500°C; and vacuum – 2–5 h at 1240°C. The latter was carried out after the previous treatments.

arises when annealing in an oxidizing atmosphere (see Fig. 6).

4. Discussion and conclusions

In this paper we have investigated two important aspects related to the properties of Ce^{3+}-doped $RE^{3+}AP$ perovskite crystals ($RE^{3+}=Y^{3+}$, Gd^{3+} and Lu^{3+}): (i) their spectroscopic and kinetic properties and (ii) radiation induced changes and centres.

Detailed spectroscopic, scintillation and γ-ray irradiation studies of these crystals have shown the following.

(1) For all crystals, Ce^{3+} emission and excitation spectra consist of almost similar broad bands having roughly the same peaks in the near UV range. This is evidence that the local crystal fields of RE^{3+} sites in these crystals (where Ce^{3+} ions are situated) are almost the same. This is the reason why only small differences among Ce^{3+} split energy levels are observed.

(2) Fluorescence and scintillation decays of the main Ce^{3+} centres consist of fast and slow decay components (see Table 2). Generally, Ce^{3+} scintillation lifetimes are slightly longer than the fluorescence lifetimes and the intensities of the individual slow decay components are at least about one order of magnitude weaker than those of the fast (tenths of a nanosecond) components. The only exception is the LuGAP:Ce crystal (Gd content ~9 at%) where the slow decay components appear due to $Gd^{3+}\rightarrow Ce^{3+}$ transfer or even $Ce^{3+}\rightarrow Gd^{3+}$ energy transfer followed by $Gd^{3+}\rightarrow Ce^{3+}$ [9,12].

(3) The spectroscopic properties of Ce^{3+} in $RE^{3+}AP$ perovskite crystals are not influenced very much by γ-ray irradiation up to doses of 3000 Gy, but we plan to carry out a further analysis to elucidate the exact influence of such γ-ray irradiation on the valency of the cerium ions. Because the studied crystals contain small amounts of transition metal impurities [7–9] we can also expect a change in their valency under γ-ray irradiation.

(4) We observed up to three additional radiation induced absorption bands for $RE^{3+}AP$ crystals peaking at 380, 425 and 560 nm, especially for LuYAP:Ce (see Fig. 5). Generally, $RE^{3+}AP$:Ce Czochralski grown crystals contain a small excess of RE^{3+} and Al^{3+} ions and also various colour centres [13]. We compared the induced absorption bands with those arising for crystals due to colour centres or other defects, such as, for example, O^{-} and O^{2-} centres [13–16]. The most probable qualitative interpretation of the induced absorption bands in perovskite crystals is the following: the two additional absorption bands in the range 360–480 nm (peaks at 380 and 425 nm) probably arise due to O^{-} hole centres, while the absorption band peaking at 560 nm is probably due to F^{+} centres of electron origin. γ-Ray irradiation studies have shown that the LuGAP:Ce crystal is radiation harder than other crystals and that the Gd^{3+} ion stabilizes the pure LuAP:Ce crystal even for low Gd^{3+} concentrations (up to several atomic percent).

(5) The behaviour of oxygen in $RE^{3+}AP$:Ce crystals can be seen from Fig. 6. Due to annealing of the crystals in an oxidizing atmosphere an additional broad absorption band arises in the near UV at $\lambda_p \approx 340–350$ nm. Again, this band is probably associated with O^{-} hole centres or their complexes and the hypothesis of a change in the cerium ion valency has to be checked, as well as the presence of other unwanted impurities [15,16].

Clearly, at the present time the attribute of radiation induced centres is only qualitative and other studies (cathodoluminescence, laser excited emission EPR and thermoluminescence) remain to be carried out to improve the model of these centres in crystals.

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