TUNNELLING PROCESSES-DRIVEN RADIATIVE RECOMBINATION IN COMPLEX OXIDE SCINTILLATORS

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Abstract. Photo- and thermo-luminescence techniques are applied to several kinds of single crystal complex oxide scintillators to reveal tunnelling-driven radiative recombination processes. The tunnelling mechanism provides the physical ground to interpret the observed luminescence and scintillation characteristics which could not be explained by classical radiative recombination schemes.

1. Introduction

Scintillator materials should efficiently and quickly transform high-energy photons or accelerated particles into UV/visible photons [1]. A critical stage of the scintillation mechanism is the transport of free electrons and holes in the conduction and valence bands, respectively. The presence of traps in the forbidden gap can result in electron/hole temporary localization causing a considerable delay in their radiative recombination at the emission centers [2]. Consequently, slow components appear in the scintillation decay, that deteriorate the temporal performance and the overall figure-of-merit of a scintillator.

To evaluate the charge transport delay, it is usual to consider the thermally stimulated detrapping of electrons (or holes) into the conduction (or valence) band. In such a case the decay time \( \tau \) can be considered to be proportional to a factor \( \exp \left[ E_T/kT \right] \), with \( E_T \) being the trap depth and \( kT \) the thermal energy at a given temperature \( T \) (usually room temperature (RT)). However, in the case of close proximity between electrons in traps and holes at the recombination site, the radiative recombination of charge carriers may occur also via a tunnelling process without their previous delocalization in the conduction or valence bands. The tunnelling probability decays exponentially with the electron-hole distance in a single pair. Due to spatial averaging over many pairs with various distances in a macroscopic volume, the radiative decay via tunnelling mechanism manifests a \( t^\rho \) time.
dependence, with $p=1-1.5$ [3]. The tunnelling process can also be thermally assisted, at temperatures sufficiently high to populate excited states of the trap [4].

In this paper we present some examples of tunnelling-driven radiative recombination processes in well-known complex oxide crystalline scintillators such as Ce-doped aluminum garnets ($A_3\text{Al}_5\text{O}_{12}$, $A=\text{Y, Lu}$), perovskites ($\text{YAlO}_3$), orthosilicates ($\text{(Lu-Y)}_2\text{SiO}_5$), and PbWO$_4$. The tunnelling mechanism can satisfactorily account for the shape of the photoluminescence and scintillation time decays when shallow traps are present in the material; this approach can substitute the usually considered analysis of such decays by a sum of exponential functions, where the slower components would lack any physical interpretation. In thermally stimulated luminescence (TSL) measurements, thermally assisted tunnelling can justify the presence of a unique trap depth corresponding to various glow curve peaks in a wide temperature range. Moreover, the presence of tunnelling processes proves the spatial correlation of traps and recombination centers and poses a question if such correlation can be understood exclusively as a matter of statistics or if it reveals defect aggregation.

2. Experimental

Wavelength-resolved TSL measurements were performed in the 10-310 K range using a CTI closed-cycle refrigerator after x-ray irradiation at 10 K (with a Philips 2274 x-ray tube operated at 20 kV), with a home made apparatus allowing the detection of the TSL signal both as a function of temperature and wavelength in the 200-1100 nm interval. A heating rate of 0.1 K/s was adopted. Phosphorescence decays were measured by the same set-up after x-ray irradiation at fixed temperature in the 10-30 K interval.

Radioluminescence (RL) spectra and scintillation decays were measured at room temperature (RT) under X-ray tube and $^{22}\text{Na}$ radioisotope excitation (511 keV photons), respectively; in the latter case a modified spectrofluorometer (199S Edinburgh Instrument) was used.

Photoluminescence (PL) decays were measured after excitation by excimer laser (308 nm, XeCl line, 5 ns pulse width (FWHM), 5 mJ per pulse, 10 Hz repetition rate). The decays were detected by a fast photomultiplier (Hamamatsu R1398) in the current regime coupled with a digital scope (Tektronix TDS 680B). At each temperature several decays were recorded with different scales both in amplitude and time. By a software procedure these partial decays were „patched up“ to obtain an overall decay curve, covering a broad range in both time and dynamical scales.

Single crystals with typical dimensions $\varnothing 20 \times 50$ mm of Ce-doped (0.1-0.5 mol%) in the crystal) $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) and $\text{YAlO}_3$ (YAP) were grown by the Czochralski technique from 5N $\text{Y}_2\text{O}_3$, 4N $\text{Al}_2\text{O}_3$ and 5N $\text{Lu}_2\text{O}_3$ raw powders in a molybdenum crucible under reducing atmosphere and by $\mu$-PD technique ($\varnothing 3 \times 20$ mm, YAP:Ce). 0.5% Ce-doped (Lu-$\text{Y})_2\text{SiO}_5$ orthosilicate and PbWO$_4$ single crystals were grown by Czochralski technique from iridium and platinum crucibles respectively, using 4N raw powders. Plates of about $7 \times 7 \times 1$ mm$^3$ and cubes of about 1 cm$^3$ were cut and polished for TSL, RL, PL and scintillation decay experiments, respectively.

3. Experimental results and discussion

3.1. Ce-doped aluminum garnets

In Fig. 1 the TSL glow curve of YAG:Ce after x-irradiation at 10 K is shown. The rich TSL pattern below RT has been already shown and discussed in the literature [5,6], but the smooth and structureless signal below approximately 80 K was not discussed. In fact, it is qualitatively indetical to that of LuAG:Ce, which has been ascribed to an athermal electron tunnelling from an electron trap towards an adjacent hole localized at Ce$^{3+}$ ion [7]. A further evidence of such a mechanism in LuAG:Ce was obtained by measuring the phosphorescence decay at constant temperature which at long times approaches a $\sim t^{-1}$ regime. The same measurement was performed within 10-30 K on YAG:Ce and the same decay characteristics were obtained (Fig. 2). Hence, also in YAG:Ce such a tunnelling-driven radiative recombination mechanism can explain the TSL glow curve pattern below 80 K. In LuAG:Ce a combination of an exponential and an inverse power law ($t^{-1}$) function was
successfully used to fit the scintillation decay at RT and was interpreted in the way that the tunnelling recombination is responsible for the observed slow sub-microsecond decay components [7]. In YAG:Ce, however, the smaller amplitude of slower decay components, prevents any similar reliable fit [6].

Fig. 1: TSL glow curve of YAG:Ce0.2% after x-irradiation at 10 K. In the inset are reported the TSL spectra observed in the temperature regions marked in the legend.

Fig. 2: Phosphorescence decay of YAG:Ce after x-irradiation at 30 K (full circles). The red continuous line is a fit to the data according to the formula: $y=a(x+b)^c$ with $a=1\times10^9$, $b=44$, $c=-1$. 
Fig. 3: TSL glow curves of YAP:Ce after x-irradiation at 10 K. The inset shows the TSL spectra of both samples in the temperature interval of athermal tunnelling.

3.2. Ce-doped aluminum perovskites

In Fig. 3 the TSL glow curves and their emission spectra are shown for YAP:Ce samples with different content of Cerium. Similarly to aluminum garnets, a temperature region governed by athermal tunnelling can be noticed below approximately 80 K, already evidenced also by phosphorescence decays [8]. It is worth to note that the relative intensity of the tunnelling process increases with Ce concentration: such an effect was observed also in LuAG:Ce [7]. In Fig. 4 the spectrally unresolved scintillation decay of YAP:Ce0.5mol% sample is displayed. We attempted to fit this decay by the same formula as in the case of LuAG:Ce, but the exponent in the power law component is far off ($p = 3.9$) the range predicted in [3] where $p$ is expected to be approximately between 0.95 and 1.5. In contrast to Ce-doped garnets in YAP:Ce there can be a competition for the hole capture between Ce ions and lattice perturbed oxygen sites [9]. As a result, a mix of different recombination processes can easily occur in the scintillation decay curve and obscure the presence of tunneling recombination. Moreover, the very strong dependence of the TSL glow curve pattern on the rare earth ion dopant [10] requires further investigation to understand the scintillation mechanism in YAP host in greater detail.
3.3. Ce-doped orthosilicates

In the case of LSO:Ce, it was soon recognized that it presents a fairly strong afterglow at RT [11] persisting for several minutes up to hours. Fundamental studies, aimed at the comprehension of the microscopic physical mechanism governing afterglow were thus carried out in order to find possible technological solutions to suppress it. The activation energy of the process was found to be approximately 1 eV [11]; it is in accordance with the calculated trap depth of a TSL peak at 375 K (using a heating rate of 6 K/s) so that afterglow appears to be due to RT carrier detrapping from the trap responsible for this peak followed by radiative recombination at Ce\(^{3+}\) luminescent centers.

Actually the 375 K peak is the first one of a series of as many as 6 peaks observed in the glow curve above RT, whose spectral emission coincides with Ce\(^{3+}\) 5d-4f transition [11] (Fig. 5). Annealing experiments in reducing or oxidizing atmosphere led to the suggestion that traps could be related to oxygen vacancies [12] and this hypothesis was further confirmed by finding an F\(^{+}\) center by EPR whose temperature stability is correlated with the TSL glow curve above RT [13].

The TSL glow curve pattern of the samples from different producers and of substantially different intensity does show a striking similarity (Fig. 5). The thermal depth of electron traps was investigated by TSL measurements using the partial cleaning procedure followed by the analysis of glow curves with the initial rise method [14]. LYSO:Ce samples were first irradiated at RT, then heated up to a fixed temperature (T\(_{\text{stop}}\)), cooled to RT again, and further heated up to 400 °C to record the glow curve. In each case, the trap depth could be evaluated by the fit of the initial portion of the glow curve with the relation:

\[
I(T) = n_0 s \exp \left(\frac{-E}{kT}\right)
\]

where \(n_0\) is the initial number of trapped electrons after irradiation, \(s\) is the frequency factor, \(E\) is the trap depth, \(k\) is Boltzmann constant, and \(T\) is the absolute temperature. Fig. 6 reports the trap depth values obtained for partial cleanings performed on LYSO:Ce: in the 40-320 °C extended temperature range; a constant value of \(E = 0.97\ \text{eV} \pm 0.08\ \text{eV}\) was obtained. This value is therefore representative of the thermal depths of the whole series of peaks at 78 °C, 135 °C, 181 °C, and 236 °C. A constant
trap depth was revealed also in the TSL of (Lu-Y)AP:Ce. It was explained by a thermally assisted tunnelling process of electrons from oxygen vacancies to Ce$^{3+}$ ions where holes are localized, at different lattice distances [15]. A similar explanation could also apply in the present case, [16].

![TSL glow curves](image1)

**Fig. 5:** TSL glow curves of two LYSO:Ce0.5% samples from different production laboratories in China (G. Ren, LYSO-1) and USA (B. Chai, LYSO-2), respectively, after irradiation at RT. In the inset the TSL spectra of sample no. 1 in different temperature regions are shown. The signal below 2 eV in the 170-350 °C interval is due to black body radiation.

![Trap depth diagram](image2)

**Fig. 6:** Trap depths of the TSL glow peaks of LYSO:Ce0.5% no. 1 evaluated by the initial rise method.
3.4. PbWO$_4$

PbWO$_4$ single crystal became of interest for scintillation purposes in the early nineties due to its intended applications in high energy physics detectors [17]. Soon it was found that there are intense slow decay components both in the photoluminescence and scintillation decays especially in the extrinsic “green emission component” centered at about 500 nm [18]. In the green emission two different sub-components were resolved [19]. The so called G(I) component was observed mainly in the Mo-doped crystals, while the G(II) is based on the existence of isolated oxygen vacancies (i.e. WO$_3$ groups), persists up to higher temperatures with respect to G(I) and is the dominant source of the mentioned slow decay components at RT [20]. The correlated increase of both the G(II) emission and the overall scintillation efficiency was observed in the crystals grown from non-stoichiometric PbO-poor melt [21]. The radioluminescence spectra measured on samples taken from both the beginning and the end of the PbWO$_4$:Ba (2000 ppm) crystal are displayed in Fig. 7. Ba$^{2+}$ cation has no role in the optical processes due to its stable charge state and no absorption transitions available within the PbWO$_4$ band gap. However, replacing PbO in the melt and having a considerably small segregation coefficient, BaO can induce a gradually increasing PbO-deficiency along the crystal growth axis. At the beginning of the crystal the spectrum shows the dominant blue emission component which originates from self-trapped excitons and is typical for stoichiometric crystals. However, at its end the intense green G(II) emission is observed due to increasing PbO-deficiency in the melt; so, the existence of WO$_3$ groups is enabled by the arising crystal nonstoichiometry. The PL decay measured on the sample from the crystal end shows at 500 nm a very intense slow decay component up to tens of microseconds which has been observed in many PbWO$_4$ crystals [18, 22]. The decay of PWO:Ba at 500 nm is successfully analyzed by the combination of exponential and power law functions: the slow decay part follows a $\sim t^{-0.99}$ course (Fig.8), clearly revealing a tunnelling-driven radiative recombination. At variance, at 400 nm the dominant decay component shows an exponential course with a decay time of a few ns while slower decay components are very weak.

![Radioluminescence spectra](Fig.7: Radioluminescence spectra of Ba-doped (2000 ppm of BaO in melt) PWO at RT. Samples close to the crystal beginning and end are indicated.)
Tunelling-driven radiative recombination in the green part of the spectrum suggests a spatially correlated localization of electron and hole pairs after the excitation. Excitation at 308 nm results in the creation of self-trapped excitons which are thermally disintegrated at RT so that various localized excitons appear [23]. Due to this process, excitons localized around oxygen vacancies or just electrons localized inside oxygen vacancies can arise. Such trapped electrons are localized at least for some milliseconds or even much more [2] and can serve as an anchoring element in the radiative recombination process around WO$_3$ group giving rise to the G(II) emission. The remaining question is how the nearby localization of the hole counterpart occurs in order to enable the tunnelling process: hole pairs can be in principle localized around lead vacancies [24]. Moreover, in partially La$^{3+}$-compensated PbWO$_4$ single O$^-$ holes have been recently evidenced by EPR [2]. The requirement of the vicinity between electrons and holes for tunnelling-driven radiative recombination process can be fulfilled in spatially correlated lead and oxygen vacancy pairs which were indicated by EPR measurements [25].

\[ I(t) = 456\exp(-t/15.6\text{ns}) + 145304(4.8+38t)^{0.99} + 0.075 \]

Fig. 8 PL decays in PWO:Ba (close to crystal end) at RT measured around the maximum of the blue (400 nm) and green (500 nm) emission bands. The former component decay is approximated by two exponential components (4.3 ns (60%) and 17.6 ns (40%) decay times), while the latter is successfully fit by the sum of one exponential and one power law function $I(t)$ reported in the figure. The numerical reconstruction of the decays are reported as black solid lines.

4. Conclusions
We reported several examples of tunnelling-driven radiative recombination processes in complex oxide scintillators. Apparently, this luminescence mechanism is considerably important in explaining the observed emission characteristics. However, our present measurements cannot really support the occurrence of important aggregation processes between traps and recombination sites, due to the difficulty to quantify the contribution of tunnelling recombinations with respect to the contribution of other delocalized processes to the luminescence/scintillation output.

Shallow electron traps adjacent to Ce$^{3+}$ ions in YAG:Ce and LuAG:Ce enable a tunnelling process towards holes localised at Ce$^{3+}$ ion. In YAP:Ce, the tunnelling process might be analogous, but
for its detailed understanding other studies are necessary due to the more complicated charge carrier capture mechanism. The tunnelling process is evidenced by a $\sim t^{-1}$ form of the phosphorescence decay at low temperatures and might be responsible for slower scintillation decay components in the sub-$\mu$s time scale at RT.

In TSL, deep oxygen vacancy-based electron traps adjacent to Ce$^{3+}$ ions in (Lu-Y)AP:Ce and (Lu-Y)SO:Ce give rise to thermally assisted tunnelling-driven radiative recombinations; this can explain the constant trap depth of several TSL peaks above RT, taking into account the occurrence of discrete distances between electron and hole traps defined by the crystal structure. Interestingly, no such a process was found in Ce-doped LuAG [26] possibly due to its more complex crystal structure obscuring the Ce-V$_{O}$ tunnelling path.

In the G(II) green photoluminescence of PbWO$_{4}$ the tunnelling process in radiative recombination is evidenced from $\sim t^{-1}$ decay course at long times at RT. The anchoring role of electrons stored at RT temporarily around oxygen vacancies is probably the crucial element for its existence.

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