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Deep traps can reduce memory effects of shallower ones in scintillators†

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X-ray induced luminescence sensitization results have been obtained on three commercially relevant scintillators, namely CsI:Tl, YAG:Ce and LSO:Ce. The obtained curves have been used to validate a model based on the competition among trapping and recombination of free charge carriers. The model was able to accurately describe the complex phenomenology of the detected sensitization curves. We also used the model to predict the role of a high temperature and concentration trap in shaping the sensitization curves. Based on these modelling results we also proposed a novel, and rather counterintuitive, strategy to deal with the sensitization phenomenon based on the deliberate introduction of deep traps able to significantly reduce the bright burn effect.

1 Introduction

Scintillating materials are able to efficiently absorb ionizing radiation and to emit photons in the visible or ultraviolet range which can be easily detected by standard photodetectors. They are widely used for radiation detection in many applications such as medical X-ray and nuclear imaging, homeland security, and high energy calorimetry.[1] The scintillation process is a complex phenomenon which encompasses the conversion of high energy radiation into a multitude of low energy free electrons and holes, their transfer to the luminescence centres and the final radiative recombination of the excited centres.[2] The transfer stage, in particular, involves the migration of the free carriers over distances of the order of few tens to hundreds of nanometres,[3,4] rendering this stage particularly susceptible to the presence of lattice imperfections acting as traps for carriers. Indeed, point defects can trap carriers slowing down, if not stopping altogether, their diffusion and transfer to the luminescence centres; carrier self-trapping, as well, is involved in such phenomena.[5] The resulting competition between carrier trapping and transfer affects scintillator performances giving rise to slow tails in the scintillation time decay and to a decreased efficiency. The role of defects in scintillation is widely established, and several strategies have been devised in order to reduce their concentration or to limit their influence.[6–8]

The same competition scheme between carrier trapping and recombination on luminescence centres in scintillators is also the cause of a different phenomenon consisting in an increase in scintillation efficiency (often called "hysteresis", "sensitization" or "bright burn") with accumulated dose. Combined with afterglow these phenomena are usually called "memory effects". This sensitization has been ascribed to a progressive trap filling, substantially increasing the probability for free carriers to end on recombination centres. Such effect has been observed in several matrices,[9–14] and it is particularly critical in X-ray imaging and dosimetry even at a few percent levels, since it leads to the formation of ghost images or to dose misevaluations.[15,16] Also scintillator light yield appears to be affected by such phenomenon.[12,17] Despite the relevant role in many detection or imaging devices and its relatively common presence in various materials, it has been studied in rather little details,[9] mainly because of the critical dependence on material reproducibility in terms of traps which are related to uncontrolled defects in standard scintillators.

In this respect, we have recently proposed a model material (YPO_4:Ce,Nd) in which the main electron trap is represented by Nd ions, whose content can be easily selected during synthesis.[18] The results have clearly shown that the bright burn relevance and shape are strongly dependent on trap thermal stability and concentration, as well as measurement temperature. On the basis of these experimental results we have also proposed a rate equation system describing the competition among trap filling and recombination, which is able to quite accurately describe the observed phenomenology.

In this paper, we are going to test the validity of the proposed

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model on more complex systems, namely CsI:Tl, Lu_2SiO_5:Ce, and $Y_3Al_5O_{12}$:Ce which are commercially relevant crystalline scintillators. The model will be used to gather more information about the role of very high temperature traps in determining the RL sensitization process. An alternative approach to deal with this phenomenon is also proposed, and it will be shown that additional deep traps may have a beneficial effect on the hysteresis.

2 Experimental

CsI:Tl sample has been obtained by the Czochralski method with a Tl concentration of 0.1 mol %, its dimensions are 5x7x1 mm^3. Lu_2SiO_5:Ce (LSO:Ce) sample has been cut from a hexagonal-shaped pixel, with dimensions of about 2x2x1 mm^3, the Ce concentration is not known. In the case of $Y_3Al_5O_{12}$:Ce,Lu (YAG:Ce,Lu), it is a triangular plate, with thickness of about 0.9 mm and 5 mm sides, Ce and Lu actual concentration is 0.54 and 1.85 at%, respectively.

Thermally stimulated luminescence measurements (TSL) have been performed from 90 up to 700 K by using a liquid nitrogen cooled heating stage (Linkam HFS600), after irradiation at 85 K with a Philips X-ray tube with W anode set at 30 kV. The emitted light was collected by an optical fibre (Thorlabs BF20HSMA2), and detected in photon counting mode by an EMI 9789QB photomultiplier. The variable heating rate method has been used in order to evaluated the trap energies and frequency factors. LSO:Ce and YAG:Ce,Lu glow curves have been corrected for the experimental radio-luminescence (RL) intensity temperature dependence.

RL sensitization measurements have been performed at 290 K for LSO:Ce and YAG:Ce,Lu, and at 283 K for CsI:Tl by exciting the samples with the same excitation source used for TSL measurements but operated at 40 kV (dose rate $\simeq$ 1 mGy/s). The emitted light has been detected with the TSL detection chain but working in current mode. Both for TSL and RL measurements no filter have been used to select the emitted light. A single sensitization measurement was performed on CsI:Tl, while for YAG:Ce,Lu and LSO:Ce a more complex scheme was used (fig. 1) in order to take into account the presence of several high temperature trapping states, not present in CsI:Tl, and possibly to have a better understanding of the role of the various trap groups in the sensitization results. The scheme is composed by a series of 300 s long irradiations, with the first one followed by a phosphorescence measurement. The other irradiations, on the other hand, are followed by a sample heating up to different temperatures (T_{pc}), which allow a partial cleaning of the occupied traps:[19] the T_{pc} have been selected from the TSL glow curves. The time elapsed between two irradiation was set to 400 s for YAG and 360 s for LSO, reflecting the time to complete a full TSL measurement up to 700 and 650 K for YAG and LSO, respectively.

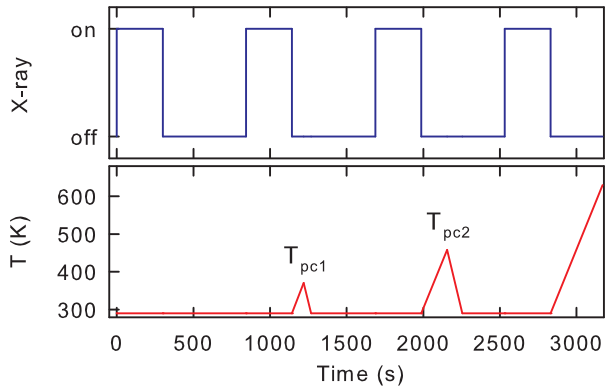

Fig. 1 Scheme of the irradiation and heating profiles used for YAG:Ce,Lu and LSO:Ce samples

3 Results and discussion

3.1 Sample TSL characterization

The TSL glow curves of the studied samples are reported in fig. 2. The obtained curves are characterized by the presence of several glow peaks which span over the entire temperature range, highlighting the presence of several defects acting as traps for delocalized carriers. The presence of other trapping states outside the temperature interval accessible with the used set-up is highly probable, particularly so for CsI:Tl whose glow curve usually presents two other major peaks in the 10-90 K region.[20,21] All the glow curves are substantially in agreement with those reported in the literature for the three materials.[22–27] Beside the total number of traps, the three sample glow curves have different barycentres, with the major peaks located at temperatures higher than room temperature in the case of LSO:Ce, between 100-300 K for YAG:Ce,Lu and below 150 K in the case of CsI:Tl.

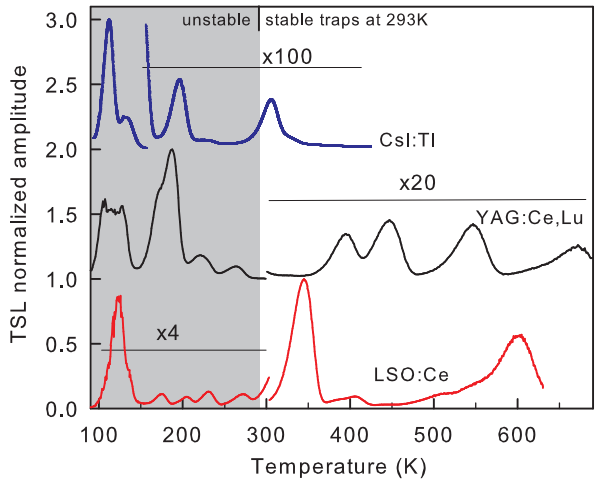

Fig. 2 Normalized TSL glow curves obtained after irradiation at 85 K of the three investigated samples. The heating rate of the presented curve is 0.1 K/s for LSO:Ce and YAG:Ce,Lu, and 0.5 K/s for CsI:Tl. The curves have been shifted along the ordinate axis for clarity

Both LSO:Ce,Lu and YAG:Ce glow curves above room temperature (RT) are composed by at least four components, while CsI:Tl appears to have a much simpler defect structure, which gives rise to the two rather closely spaced glow peaks evidenced in fig. 2.

3.2 Mathematical model description and simulation details

The mathematical model that will be used in the subsequent section is an extension of the one previously presented and used in the case of YPO_4:Ce,Nd.[18] The differences are related to the necessity of considering more than one trap: this results in the addition of new differential equations governing the trapping/detrapping probability for each of the considered trap, as well as in the addition of several terms in the equation related to the electron population in the conduction band. As in the case of the previously proposed model, only centres able to trap one kind of free charge carrier are considered. Non radiative recombination between trapped carriers and the counterpart is not taken into account. The resulting set of equations is:

$$\frac{\mathrm{d}n_c}{\mathrm{d}t} = f(1-\alpha) - \sum_{j=1}^{K} n_c\left(N_j - n_j\right)A_{ej} + \sum_{j=1}^{K} n_j s_j \exp\left(-\frac{E_j}{k_B T}\right) - n_c A_r m \quad (1)$$

$$\vdots$$

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = n_c\left(N_j - n_j\right)A_{ej} - n_j s_j \exp\left(-\frac{E_j}{k_B T}\right) \quad (2)$$

$$\vdots$$

$$\frac{\mathrm{d}m_v}{\mathrm{d}t} = f(1-\alpha) - m_v(M-m)A_h \quad (3)$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = m_v(M-m)A_h - n_c A_r m \quad (4)$$

$$n_c + \sum_{j=1}^{K} n_j = m_v + m \quad (5)$$

where eqns. (1) and (2) represent the time evolution of the electron concentration in the conduction band and on the j^{th} trap, respectively, and K is the number of considered traps. The terms in these equations are: the creation rate (f) for free electrons and hole pairs in the delocalized bands and the direct recombination coefficient (α); the electron trapping ($n_c\left(N_j - n_j\right)A_{ej}$) and detrapping ($s_j \exp\left(-E_j/k_B T\right)$) rates for each of the traps, where T is the absolute temperature, k_B the Boltzmann constant, E_j and s_j the trap energy and frequency factor, respectively; $n_c A_r m$ is the recombination rate. The hole occupancy in the valence band and on the recombination centre is represented by eqns. (3) and (4) and they contain the rate of hole capture on the recombination centre itself ($m_v(M-m)A_h$). Equation (5) guarantees the charge neutrality during the simulations. The instantaneous RL intensity can be calculated by

$$I_{RL} \propto \alpha f + n_c A_r m. \quad (6)$$

A more in-depth description of the parent model, including its experimental validation, has been presented in ref. 18.

The RL sensitization simulations have been calculated solving numerically eqns. (1)–(4) with MATLAB using the available data for recombination centre concentration (M), energy (E) and frequency factor (s) of the traps. These latter have been calculated from the TSL results by using the heating rate method. The pair creation rate has been estimated from the measured dose rate in air by considering the sample density and energy gap (E_g), with e-h pair creation threshold of $3E_g$. Trap concentrations and the transition coefficients (the A parameters in the above equations) are unknown: we supposed a larger recombination centre concentration than the defect one, and that the recombination centres themselves act as very efficient traps for delocalized carriers; for these reasons the values of the transition coefficient have been set considering $A_r \gg A_e$ (with A_h playing practically no role for sufficiently large values, see ref. 18), and all the A_e as identical. The use of the latter simplification implies that the trap filling rates and the relative intensity of the glow peaks are related exclusively to each trap concentration. The relative concentration among traps has been evaluated from the glow curve peak intensity. The simulations have been performed by keeping constant the ratio among the considered trap content and changing the overall concentration in order to obtain the best possible reconstruction of the experimental results. The arbitrariness of the used parameter choice is however irrelevant, since what actually matters is the ratio among the recombination and the trapping rates and not their absolute values. Anyway, the chosen A values are coherent with those evaluated in ref. 5 for CsI:Tl and the cross sections for carrier trapping reported for silicon defects.[28]

3.3 Experimental and simulated RL sensitization results

The experimental and the simulated radio-luminescence sensitization curves are reported for all the three samples in fig. 3. For all the samples the RL intensity is characterized by a sudden and practically vertical jump (due to direct recombination processes) from the background level followed by a further much slower and smaller increase as a function of the irradiation time: this latter part is the actual X-ray–induced sensitization, and the only one which will be discussed. In the case of CsI:Tl, the RL intensity curve is characterized by a relatively fast increase followed by stabilization of the intensity after 20–30 s with an overall increase of about 5%. In the case of the two oxides, the initial irradiation (curve a) caused a substantially monotonic increase in the RL signal of a few percent with no clear sign of a tendency toward saturation. As mentioned in the experimental section, in the case of the two oxides a series of irradiations, separated one to the other by either phosphorescence or sample heating at different temperatures, has been performed. The scope of such a scheme was to try to figure out the role of the TSL trap groups in shaping the bright burn curves. The results are quite complex and deserve some explanations.

For both LSO:Ce and YAG:Ce,Lu the RL intensity at the beginning of the second irradiation - curve b in fig. 3 - (performed after phosphorescence) is practically coincident with that at the end of the first irradiation - curve a - this implies that the traps unstable at the measurement temperature (290 K) have very little or no role in the sensitization results, likely because of their low concentration, particularly in the case of LSO, and low charge carriers population during irradiation. Indeed, it is reasonable to state that unstable traps will arrive in short times to an equilibrium be-

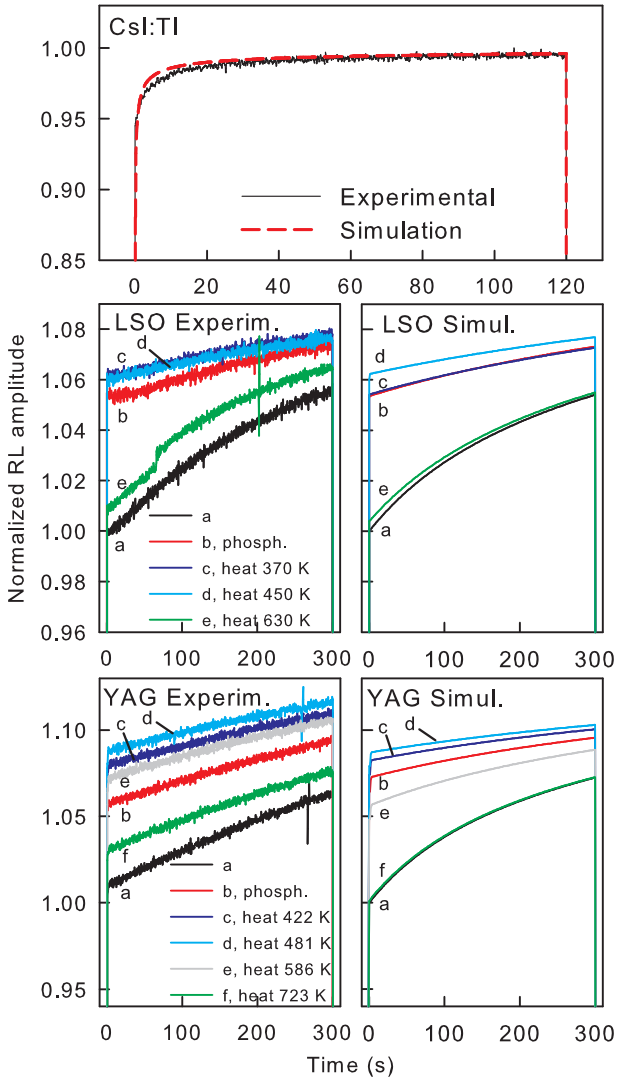

Fig. 3 Experimental and simulated bright burn curves of CsI:Tl, LSO:Ce. and YAG:Ce,Lu. The measurements have been performed at 290 K in the case of LSO:Ce and YAG:Ce,Lu samples, and at 283 K for CsI:Tl one. The curves have been normalized to the maximum of the RL signal in the case of CsI:Tl, and to the first non-zero point of the first measurement in the case of the two oxides.

tween their filling and their temperature induced emptying; this equilibrium is evidently affected by the trap thermal depth and concentration: the shallower the traps, the lower is going to be their carrier population during irradiation; an analogous argument is valid for the role of the trap concentration.

Concerning the measurements performed after having heated up the samples at different temperatures T_{pc} (curves c to e for LSO:Ce, and c to f for YAG:Ce,Lu), for moderate heating (370 K and 480 K for LSO:Ce and YAG:Ce,Lu, respectively), the RL intensity at the beginning of the various irradiations is increasing, with a slight reduction in the overall increase in the RL signal. For higher T_{pc}, the initial RL intensity decreases remarkably as the temperature is increased, accompanied by a more evident increase over time of the RL intensity itself. These results are due to two contrasting phenomena: the presence of partially filled high T traps is the cause of a higher radiative recombination probability which is, at the same time, counterbalanced by the growing amount of emptied traps as T_{pc} is increased. These two phenomena result in the complex dependence of the RL intensity at the beginning of each irradiation as a function of T_{pc} clearly visible in fig. 3. The difference in the intensity at the end of a measurement and at the beginning of the successive is dependent on the total amount of charges being released by the heat treatment. It is also worth of mentioning that the measured sensitization curves after the full TSL for both LSO:Ce and YAG:Ce,Lu (measures e and f, respectively) appear to be different from those obtained during the first irradiation. This was unexpected, since the complete emptying of the traps should have brought the samples to their initial configuration and hence to very similar sensitization curves. This discrepancy is likely caused by a non-complete emptying of the trap at 600 and 680 K for LSO:Ce and YAG:Ce,Lu, respectively, or by the presence of other traps at even higher temperatures.

The simulations have been performed by considering the lowest possible number of trapping states able to give the closest reconstruction of the experimental results: in the case of CsI:Tl, two trapping states were eventually considered, while 3 and 4 were necessary in order to describe the complex experimental curves of LSO:Ce and YAG:Ce,Lu, respectively. In the case of the two oxides where several RL measurements have been performed, the calculated curves were obtained by simulating the entire measurement scheme. The parameter values used in obtaining these reconstruction are reported in the ESI.[†]

The simulation results, reported as well in fig. 3, are quite satisfactory. In fact for all the samples the reconstructed curves are close to the experimental ones, and also the general trends are well described. However, discrepancies can be noticed: the initial portion, for instance, of the bright burn of CsI:Tl is slightly overestimated and, in the case of LSO:Ce and YAG:Ce,Lu, the RL intensity dependence upon T_{pc} is not always in good agreement with the experimental results. The addition of more trapping states in the simulations did not remarkably improve the reconstruction quality, particularly so in the case of the unstable ones, substantially confirming the small/negligible role of these traps in the bright burn results, as discussed few lines above. The observed discrepancies between the experimental and simulation results could be due to the still relatively simplified picture the model portrays. In fact, the current model considers only traps for one kind of the free charge carriers (i.e. electrons for LSO:Ce and YAG:Ce,Lu) and a possible role of the other kind in the determination of the bright burn cannot be dismissed. Moreover, the temperature dependence of sample luminescence efficiency, particularly for LSO:Ce[22] and CsI:Tl,[25] could also have a role since it renders the estimation of high temperature traps relevance more problematic, adding a further source of uncertainty for the simulations. A possible other origin of errors could be related to the presence of non-radiative recombination pathways during TSL, leading to a lower amount of detected light and to an underestimation of the trap relative intensity. Finally as previously discussed, the presence of very high temperature traps, which could not be emptied with the used set-up, might as well be another source of the discrepancies.

Despite the various simplifications and the missing data concerning the trap concentration and their transition coefficients, the model describes rather accurately the observed complex phenomenology of the bright burn measurements. The model, then, can be used to predict behaviours and to give the opportunity to look for the appropriate trap parameters to tune the memory effect characteristics.

CsI:Tl, used in both medical and homeland security X-ray imaging, is a really interesting example to simulate since the decay times of the traps responsible for the observed bright burn are relatively short (few tens and few thousand of seconds for the 300 K and the 330 K trap, respectively); this gives rise to a possibly very complex RL sensitization behaviour (from an application point of view) as a function of irradiation history and time elapsed between successive irradiations. In the following paragraphs, the model will be used to simulate the effect of a hypothetical very stable trap on the CsI:Tl RL sensitization and memory effects.

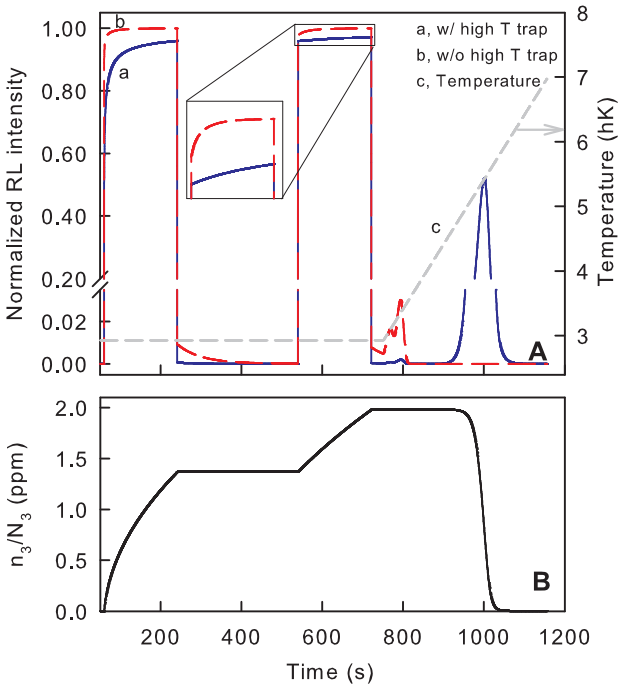

Fig. 4 Simulation of an *irradiation- phosphorescence- irradiation-thermoluminescence* measurement scheme: A) comparison between a two trap model and a three trap one, starting from the results obtained on CsI:Tl presented in Fig. 3. The added third trap has E= 1.74 eV and concentration equal to 10^{19} cm^{-3}. B) Calculated occupation ratio of the third trap as a function of time

Figure 4–A presents simulation results of a sequence of two irradiations followed by a TSL 'measurement' obtained from the above discussed CsI:Tl results and parameters. The two simulations differ as following: in one case only the two stable traps have been considered. In the other case a further deeper hypothetical trapping state, as already mentioned few lines above, has been added in a concentration comparable to that of the recombination centre. All the other parameters have not been modified. As expected, the presence of the third trap changes significantly the charge equilibrium resulting in a more evident bright burn during the first irradiation (60–240 s region, in fig.4–A); considering the second one, though, the situation is the opposite (in the 540–720 s region): the bright burn of the three-trap case is much less evident than that of the two-traps system. The new equilibrium caused by the additional trap tends also to disfavour the filling of shallower ones, resulting in a less evident phosphorescence (region 240–540 s) and a reduced TSL signal related to the low T traps (720–850 s). Moreover, considering that the third trap population can hardly be modified by thermal emptying at RT (see fig. 4–B), the detected reduction in bright burn will be preserved also for successive irradiations. The positive effect of the additional trap after the initial irradiation can be easily understood by considering that the holes related to the electrons stored on the deep trap are localized on recombination centres. The higher amount of trapped holes modifies the equilibrium between electron trapping and recombination favouring the latter process. This finally results in a lower probability of carrier trapping on the unstable traps, and thus to lower TSL and phosphorescence signals. Recent results[22,29] on alkaline earth co-doped LYSO:Ce and LuAG:Ce clearly suggest that chemically stabilized Ce^{4+} ions still participate in the scintillation process by acting as electron traps (becoming temporarily trivalent, thus able to give rise to luminescence) and that they are responsible for a reduction of the detected long scintillation decay tails and phosphorescence. A similar mechanism[30] has also been suggested in order to explain the good radioluminescence properties of Ce-doped sol-gel silica glasses densified in oxidizing atmosphere and containing large quantities of Ce^{4+}.

The high T trap presence is, however, also the cause of a reduction of the scintillation yield (clearly visible in the inset of fig. 4–A), but in the current scenario the signal appear to be reduced only by about 4 % with respect to the two-traps case during the second irradiation. The signal loss is anyway going to be reduced as the total dose is increased, and it does not appear to be particularly detrimental from an applicative point of view. It has to be mentioned, however, that the intensity loss is related also to the direct recombination coefficient α present in eqns. 1-4, which has not been modified from one simulation to the other. This coefficient could depend on the overall amount of traps.

The commonly used strategy to reduce the impact of trap on scintillation is to decrease the concentration of defects by improving raw material quality, by optimizing the synthesis, and by post-growth annealing in suitable controlled atmospheres. Co-doping with aliovalent ions is also used. However, the nature of the traps is often unclear and only in relatively few cases it has been possible to unequivocally assign them to specific defects (either intrinsic or extrinsic). The lack of knowledge of the trap nature does not help in considering possible strategies directed to a reduction of their concentration during (and after) the synthesis of materials. Moreover, it has to be considered that some defects (oxygen vacancies, for instance, or antisites in garnets) are in thermodynamic equilibrium during crystal growth, making their incorporation in the matrix fundamentally unavoidable without reconsidering the synthesis method or the whole composition of the material itself. All these factors render the reduction in trap concentration a difficult and laborious way to follow in order to

obtain a less evident bright burn.

The simulation results presented in fig. 4 clearly imply that in the right circumstances the presence of a high temperature and concentration trap can be beneficial, since it can lead to the stabilization of the RL signal and to a simultaneous reduction of the overall change in intensity related to the bright burn, and to a reduction of the detected phosphorescence as well. These suggestions are quite well supported by a recent paper[31] dealing with SiO_2:Yb glasses in bulk and fibre form. In particular, the fibre evidenced a clear modification in the glow curve with a relatively large shift of its maximum toward higher temperatures with respect to that of the bulk. RL measurements performed at increasing times after a long irradiation evidenced a more stable intensity in the case of the fibre with respect to the bulk.

Based on these simulation results, then, we can propose a different approach in order to deal with the bright burn: to make the sample selectively worse from a defect point of view. This could be carried out by co-doping the crystal with suitable ions able to create stable trapping states. This approach has advantages since it is easier to add ions than to strip out the unwanted ones or to reduce the concentration of intrinsic defects. Moreover, the content of these ions could be selected during synthesis and the resulting trap thermal depth could also be chosen. Ideally, these ions should not be optically active, or give rise to absorption bands which overlap with the main scintillation emission. On the practical side, it would be sufficient to 'prime' the scintillator with a sufficiently large irradiation prior of its first use in order to greatly diminish the bright burn.

This approach to deal with the RL sensitization phenomenon might not be a general one, though, and be particularly effective only in those cases where the traps responsible for the bright burn are relatively unstable, as in the case of CsI:Tl above reported. However, considering that the presence of a high concentration trap modifies the charge equilibrium during irradiation, resulting in a lower population of unstable traps, one might consider the use of this strategy also in order to reduce the amount of delayed recombination processes which often occur in scintillators.

4 Conclusions

In this contribution we studied the radioluminescence (RL) efficiency increase of three commercially relevant scintillators (CsI:Tl, YAG:Ce, and LSO:Ce), and used the obtained experimental curves to further test the validity of a model based on competition among trap filling and recombination of free carriers. The model was able to reconstruct the observed sensitization curves quite accurately, despite the complex defect structure of the considered materials. The model was, then, used to predict a possible alternative and novel strategy to tune the X-ray induced sensitization phenomenon. It is based on the deliberate worsening of the material quality, from a defect point of view, by suitable co-dopings able to create very stable traps in high concentration. In fact according to the model results, the presence of this additional trap, coupled with suitably designed pre-irradiations, strongly modifies the charge carrier competition among trapping and recombination on luminescence centres occurring during irradiation, this finally results in a reduction of the sensitization phenomenon magnitude, as well as in a less evident phosphorescence. We believe that this counterintuitive approach represents a further way to obtain scintillators with optimized characteristics.

Finally, the paper further highlights the complexity of the trap role in the scintillation process, and the non-trivial relations among light output, trap characteristics, measurement temperature, and sample irradiation history.

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