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Optical absorption and thermoluminescence of Tb^{3+}-doped phosphate scintillating glasses

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Abstract

We present a study of the optical properties of Tb^{3+}-doped $NaPO_3$–$GdPO_4$-based glasses by means of optical absorption measurements performed at room temperature both before and after x-ray irradiation. A numerical decomposition of the absorption spectra is performed, and the possible nature of the defects responsible for the observed absorption bands is discussed; namely, it is proposed that both intrinsic defects and Tb^{4+} ions are responsible for the optical absorption pattern. Moreover, the thermal stability of the radiation-induced absorption bands has also been studied in the temperature range 20–280 °C, and the results are compared with a parallel investigation of trap levels in the glasses, measured by means of wavelength-resolved thermally stimulated luminescence. From the observed phenomenology, it can be proposed that the recovery of optical absorption bands is governed by the de-trapping of charge carriers from defect trap states. The de-trapping should be followed by recombination at activators and/or at defect sites, and at radiation-induced centres responsible for absorption bands, which in this way return to their pre-irradiation configuration.

1. Introduction

In the search for new scintillating materials, glass matrices are potentially attractive systems due to their ability to host luminescent activators in elevated concentrations, their good mechanical properties and easy shaping, and the possibility of pulling optical fibres of them useful in the manufacturing of bidimensional detectors. In recent years there has been a continuous effort to develop appropriately doped glass materials for use as scintillators in the detection of x-rays, gamma-rays, or neutrons. For applications in high-energy physics, high-density

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materials such as fluoride glasses [1] are required; however, classical silicate-based matrices for detecting x-rays or neutrons [2, 3] have been studied, and are now also commercially available. Due to their amorphous matrices and to the presence of defects in high concentration, a typical problem with glass scintillators is a low efficiency of scintillation conversion and a low radiation resistance. Recently, a new way of increasing the efficiency of Ce^{3+}-and Tb^{3+}-doped phosphate scintillation glasses has been presented, which is based on the introduction of Gd^{3+} in elevated concentrations giving rise to a nearly resonant energy migration within a Gd^{3+} sublattice in the glass matrix followed by single-step energy transfer towards Ce^{3+} or Tb^{3+} emission centres [4, 5]. On these phosphate glasses, systematic studies of radiation damage under ^{60}Co irradiation have been performed [6], while radiation-induced absorption bands related to rare-earth ions with modified valence (Tb^{4+}, Ce^{4+}, Eu^{2+}) in similar matrices were recently determined [7]. It was also found that intense laser irradiation at 308 nm (direct excitation of $^6P_{5/2-7/2}$ levels of the Gd^{3+} ions) results in instabilities of the emission intensity and in the appearance of laser-induced absorption bands [8]. Such phenomena indicate the presence of an unwanted energy exchange between the guiding Gd sublattice and point defects of the glass matrix, which lowers the overall scintillation efficiency of such glass materials.

So, a systematic study of radiation-induced point defects and their thermal stability appears to be useful, for both the basic comprehension of the complex interaction between rare-earth ions and defects, and the optimization of the glass matrix with respect to unwanted energy losses during the scintillation conversion. In this work, an investigation on point defects induced by x-ray irradiation of Tb^{3+}-doped $NaPO_3$–$GdPO_4$-based glasses is proposed.

Parallel optical absorption and thermally stimulated luminescence (TSL) measurements are presented, and the results allow a discussion on the possible nature of radiation-induced defects and on their stability.

2. Experimental conditions

The glasses were prepared using $NaPO_3$, $GdPO_4$, and $TbPO_4$ of 99.9% purity as starting materials (for preparation details, see [4, 5]). In the following, the samples are labelled as $Na_xGd_yTb_z$, where x, y, z denote the molar percentages of the corresponding starting materials in the melt. The samples studied here are the following: $Na_{97}Gd_0Tb_3$, $Na_{75}Gd_{25}Tb_0$, $Na_{77}Gd_{20}Tb_3$. Polished plates of 1 mm thickness were used for both optical absorption and TSL measurements.

Optical absorption spectra were measured at room temperature (RT) by a Varian Cary 50 spectrophotometer. Spectra were detected both for as-received glasses and after x-ray irradiation using a Machlett OEG 50 x-ray tube operated at 30 kV.

TSL measurements were performed after x-ray irradiation (by the above-mentioned x-ray tube) from RT up to 280 °C, using a heating rate of 1 °C s^{-1}. The TSL emitted light was detected in photon-counting mode by means of an EMI 9635 QB photomultiplier tube. The emission spectrum of the TSL was also investigated by spectrally resolved measurements where the light intensity was measured as a function of both temperature and wavelength. In such a case, the detector was a double-stage microchannel plate followed by a diode array. The detection range was 200–800 nm and the spectral resolution was 5 nm.

3. Results and discussion

3.1. X-ray-induced optical absorption bands

The effect of x-ray irradiation on the optical absorption spectra of glasses was investigated first: the results are displayed in figures 1–3, where comparisons between the optical absorption

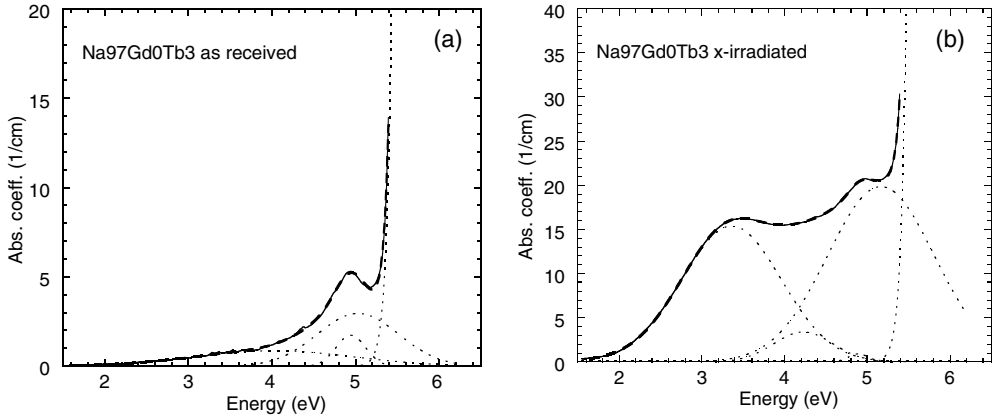

Figure 1. RT optical absorption spectra of (a) as-received and (b) x-ray-irradiated $Na_{97}Gd_0Tb_3$ glass. Continuous curve: experimental data; long-dashed curve: numerical fit; short-dashed curve: spectral components.

Table 1. Peak energies and full widths at half maximum (FWHM) of the Gaussian components obtained by the numerical fitting of the optical absorption spectra of as-received and x-irradiated glasses. The measurements were performed at RT. The error on all the parameters is lower than 0.1 eV.

		E(FWHM) (eV)							
$Na_{97}Gd_0Tb_3$	Unirradiated				4.0(1.3)		4.9(0.2)	5.0(0.7)	
	X-irradiated			3.4(0.8)		4.2(0.5)	4.9(0.2)	5.1(0.8)	
$Na_{75}Gd_{25}Tb_0$	Unirradiated						4.9(0.5)		5.8(0.3)
	X-irradiated	2.3(0.2)	2.9(0.5)				4.9(0.6)		5.9(0.3)
$Na_{77}Gd_{20}Tb_3$	Unirradiated						4.9(0.2)	5.0(0.7)	
	X-irradiated			3.3(0.7)		4.3(0.7)	4.9(0.2)	5.1(1.0)	

spectra before (a) and after x-ray irradiation (b) are shown for $Na_{97}Gd_0Tb_3$, $Na_{75}Gd_{25}Tb_0$, and $Na_{77}Gd_{20}Tb_3$ samples, respectively. A numerical fit of all the spectra in terms of Gaussian components was also performed, and the parameters of the bands are reported in table 1. In the spectra of all the as-received glasses, an absorption band peaking at approximately 5 eV can be seen; in fact, the precision of the fit could be significantly improved if a composite structure of this band was assumed in the cases of $Na_{97}Gd_0Tb_3$ and $Na_{77}Gd_{20}Tb_3$ glasses, as reported in table 1. Moreover, the $Na_{75}Gd_{25}Tb_0$ glass features a weak and very broad absorption peaking at 4 eV, while a band at 5.8 eV is detected only for $Na_{75}Gd_{25}Tb_0$. At energies higher than 5.2 eV, a very strong increase of the absorption is evidenced in Tb-doped glasses, which could be satisfactorily fitted by an exponential function. In Tb-free glass, the increase of the absorption is less steep, and it was better approximated by a Gaussian component peaking at approximately 7–8 eV; however the experimental limit of the measurement prevents us from determining accurately its position and halfwidth, and for this reason it has not been included in table 1. Upon x-ray irradiation, the intensity of the 5 eV band (for $Na_{97}Gd_0Tb_3$ and $Na_{77}Gd_{20}Tb_3$, particularly the higher-energy component of the composite structure) is significantly increased, while a slight increase is observed for the highest energy band at 5.8–5.9 eV in $Na_{75}Gd_{25}Tb_0$. Marked differences in the absorption pattern are observed at energies below 4.5 eV: Tb-doped samples display a rather intense band at 3.3–3.4 eV, together with a weaker band at 4.2–4.3 eV; in contrast, Tb-free glass does not display such features,

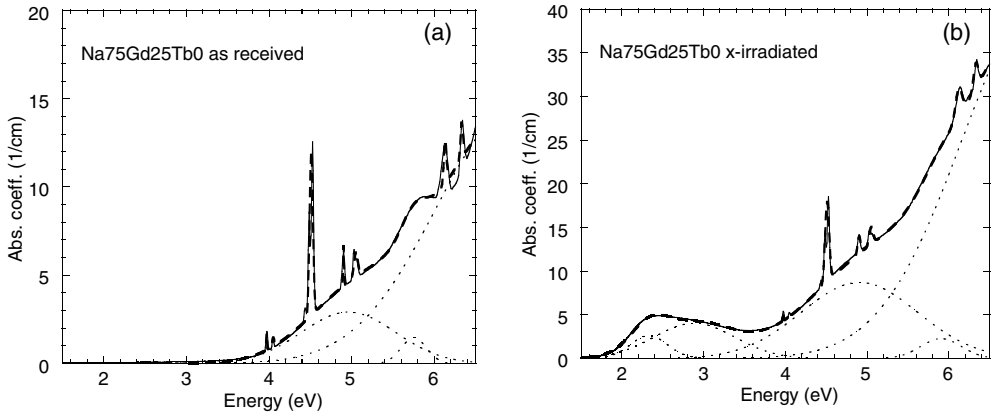

Figure 2. RT optical absorption spectra of (a) as-received and (b) x-ray-irradiated $Na_{75}Gd_{25}Tb_0$ glass. Continuous curve: experimental data; long-dashed curve: numerical fit; short-dashed curve: spectral components.

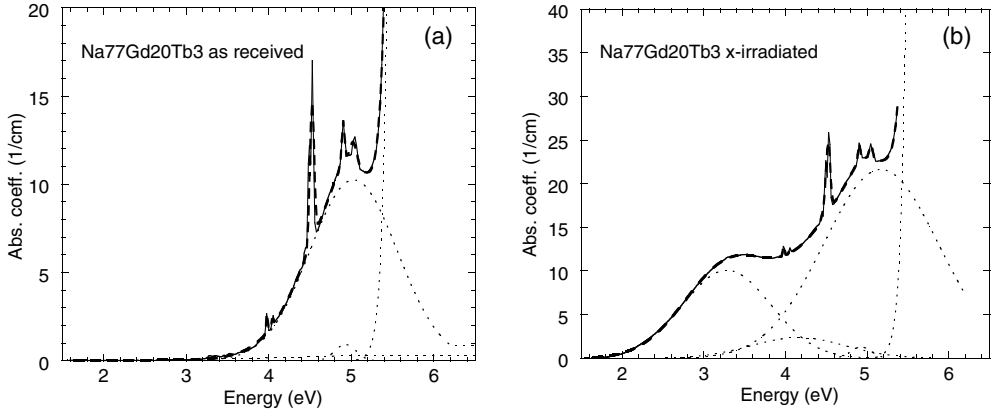

Figure 3. RT optical absorption spectra of (a) as-received and (b) x-ray-irradiated $Na_{77}Gd_{20}Tb_3$ glass. Continuous curve: experimental data; long-dashed curve: numerical fit; short-dashed curve: spectral components.

while two bands at 2.3 and 2.9 eV are observed instead. Finally, in all the spectra of Gd-containing glasses, the Gd^{3+} lines relating to transitions to ^6P (∼4 eV), ^6I (∼4.6 eV), and ^6D (∼4.9–5.0 eV) multiplets within its 4f shell are also detected. For the sake of brevity these were not included in the table.

The nature of the absorption bands detected here can be now briefly discussed, taking into account the possible roles of both point defects in the glass matrix, and transitions related to the Tb dopant. In fact, a striking feature of the Tb-doped glass considered here is the presence, after irradiation, of an intense band peaking at 3.4 eV which is completely absent for Tb-free samples. A band at exactly the same energy was assigned to a transition within the Tb^{4+} ion in several phosphate-based glasses [7]. So, it is reasonable to suggest that in our samples also, ionizing irradiation gives rise to Tb^{4+} centres featuring the same absorption. On the other hand, Tb-free samples clearly display bands at 2.3 and 2.9 eV, which may be partially masked by the Tb^{4+} transition in Tb-doped glass. As regards the origin of these

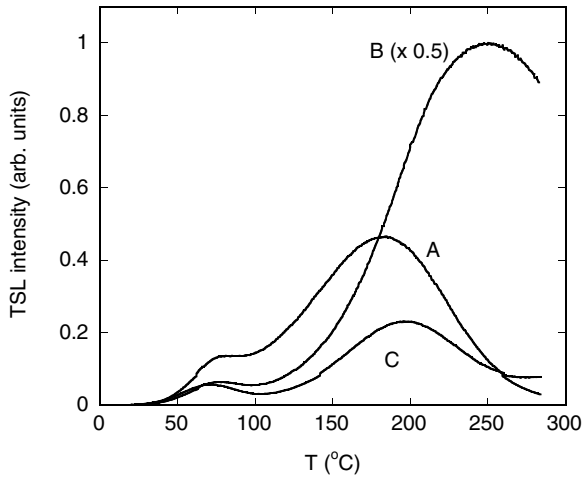

Figure 4. TSL glow curves of (A) $Na_{97}Gd_0Tb_3$, (B) $Na_{75}Gd_{25}Tb_0$, and (C) $Na_{77}Gd_{20}Tb_3$ samples after x-irradiation at RT. Heating rate: 1 °C s^{-1}.

bands, and of the others detected above 4 eV for all samples, precise assignments cannot be given at present; however, it can be mentioned that several absorption bands in the 2.5–3 eV and in the 4–5 eV regions were detected for gamma-irradiated P-doped silicate glasses, and assigned to different variants of phosphorus-related centres by a parallel investigation of the thermal stability of absorption bands and of EPR-active centres [9, 10]. In analogy to such studies, a relation between the 2.3, 2.9, 4.2, and 5 eV (and possibly also the 5.8 eV) bands detected here and point defects of the glass matrix itself can be proposed. It is worth noting that the 2.3, 2.9, and 4.2 eV bands are created by ionizing irradiation; in contrast, according to our fits, the structures at higher energies are already present for as-received samples, and are just enhanced by irradiation. In this respect we cannot exclude the possibility that the true absorption pattern in the 5 eV region is even more complex, including bands of different origin, both existing before irradiation and radiation induced, so close in energy that they can hardly be distinguished by the fit. Finally, the significant increase of the absorption towards high energies indicates the existence of additional bands, whose presence should be investigated by absorption measurements extended to the VUV region.

3.2. Thermally stimulated luminescence

The effect of x-irradiation on point defects was also investigated by means of TSL from RT up to 280 °C; higher temperatures could not be investigated due to the low glass transition temperature of the samples (approximately 330 °C) [11]. The glow curves are displayed in figure 4: broad TSL structures are apparent, probably related to distributions of trap levels as can be expected in glass matrices [12]. The glow curves of samples $Na_{97}Gd_0Tb_3$ and $Na_{77}Gd_{20}Tb_3$ have similar shapes with two peaks at about 70 and 190–200 °C, while for the $Na_{75}Gd_{25}Tb_0$ glass the latter peak is markedly shifted to higher temperatures (250 °C). The emission spectra of the TSL are reported in figure 5. Tb^{3+} emission is evident in Tb-doped samples; in contrast, for the Tb-free glass, two emission bands possibly of defect-related origin are observed at approximately 320 and 590 nm, the former superimposed on the Gd^{3+} line at around 310 nm. For $Na_{77}Gd_{20}Tb_3$, besides Tb^{3+} lines, also a weak Gd^{3+} emission line is observed. So, TSL measurements show that a composite and composition-dependent

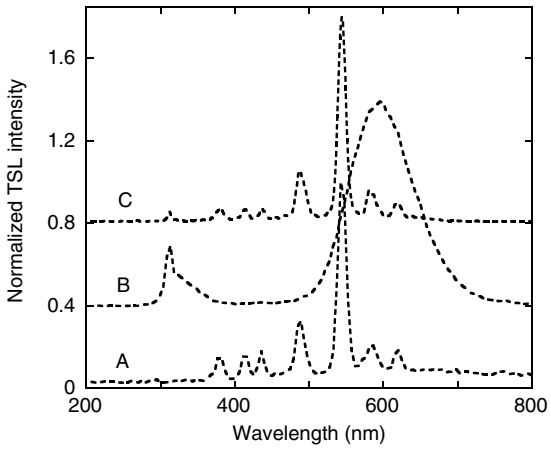

Figure 5. TSL emission spectra of (A) $Na_{97}Gd_0Tb_3$, (B) $Na_{75}Gd_{25}Tb_0$, and (C) $Na_{77}Gd_{20}Tb_3$ samples. The spectra were obtained by integration of wavelength-resolved TSL measurements in the 20–280 °C interval.

distribution of trap levels exists in the samples considered, and that the radiative recombination of freed carriers occurs at luminescent activators or at defect sites according to the doping of the glasses. It is worth mentioning that a correlation between defect-related optical absorption bands and emission bands at 320 and 590 nm observed in TSL can be suggested, and should be verified by photoluminescence excitation–emission studies.

3.3. Thermal stability of the optical absorption bands: role of thermally freed carriers

The thermal stability of radiation-induced optical absorption bands is worth investigating, for both the basic comprehension of defect dynamics and the evaluation of all aspects of radiation hardness, in view of possible applications. In this work, it was investigated by means of several irradiation and heating cycles, and parallel sets of TSL measurements were also performed. Specifically, each glass was irradiated at RT, and the absorption spectrum was measured; then, it was heated at a linear heating rate of 1 °C s^{-1} up to a selected temperature; immediately after reaching the required temperature it was cooled down to RT. The optical absorption was measured again, and this was followed by a TSL measurement up to 280 °C; several cycles of this kind were repeated for increasing partial cleaning temperatures at intervals of 50 up to 280 °C, and a numerical fit of all the spectra was performed so that the intensity of each band could be finally plotted versus the partial cleaning temperature. The spectra are displayed in figure 6 in the case of the $Na_{97}Gd_0Tb_3$ sample: a strong reduction of the absorption coefficient is noted for the whole energy range, and after heating to 280 °C (curve G) the spectrum is reduced almost back to the level observed prior to irradiation (curve A). The TSL of the same $Na_{97}Gd_0Tb_3$ sample, monitored after each heating cycle (figure 7), shows a progressive reduction of the signal, accompanied by a shift of the maximum temperature of the main peak; such behaviour is in accordance with the progressive de-trapping of carriers from a continuous or quasi-continuous trap distribution [13]. In figure 8, the intensities of the principal optical absorption bands of $Na_{97}Gd_0Tb_3$ are plotted as a function of partial cleaning temperature; in this graph, the dependence of the 4.9 eV band was not reported due its very low intensity after irradiation with respect to the 5.1 eV one. In the same figure, the intensity of the residual TSL integral after the partial cleaning steps is also displayed, and the similarity

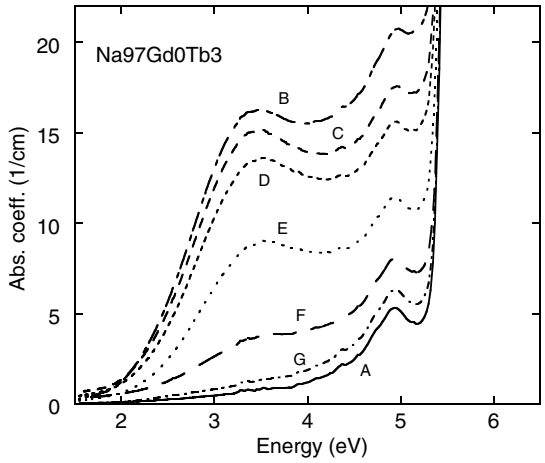

Figure 6. RT optical absorption spectra of $Na_{97}Gd_0Tb_3$. (A) as received; (B) after x-ray irradiation; (C) after heating to 100 °C; (D) after heating at 150 °C; (E) after heating to 200 °C; (F) after heating to 250 °C; (G) after heating to 280 °C.

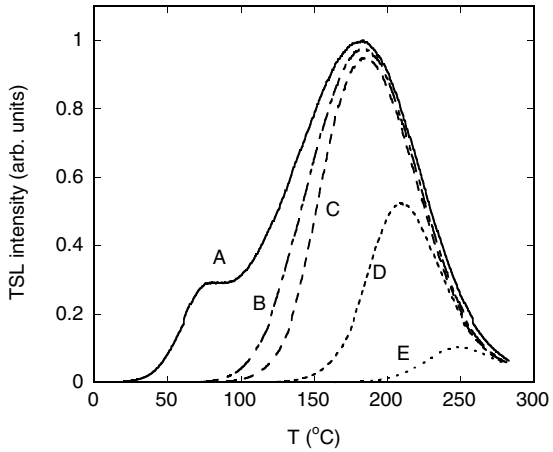

Figure 7. TSL glow curves of $Na_{97}Gd_0Tb_3$ after x-ray irradiation at RT. (A) as irradiated; (B) after heating to 100 °C; (C) after heating to 150 °C; (D) after heating to 200 °C; (E) after heating to 250 °C.

between the temperature dependences of both optical absorption and TSL integrals is clearly evident. From the observed phenomenology, it can be proposed that the disappearance of optical absorption bands is governed by the de-trapping of charge carriers from defect trap states. The de-trapping should be followed by recombination at activators and/or at defect sites (as displayed by the TSL emission spectra), and at radiation-induced centres responsible for absorption bands, which in this way return to their pre-irradiation configuration. Such a proposal can be readily exemplified by the case of Tb^{4+} ions (giving rise to the 3.4 eV band) which, by electron capture, return radiatively to their 3+ charge state, and can be extended to other intrinsic defect configurations which capture electrons or holes during irradiation. A very similar phenomenology was observed in the case of $Na_{77}Gd_{20}Tb_3$ glass, while a slightly stronger stability of radiation-induced absorption was noticed in the case of $Na_{75}Gd_{25}Tb_0$ glass.

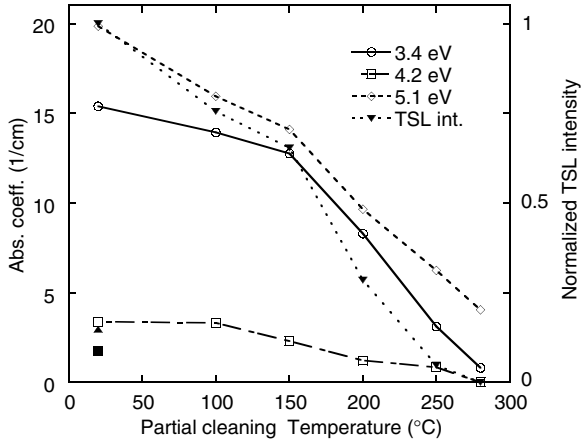

Figure 8. Intensities of the radiation-induced optical absorption bands at 3.4, 4.2, and 5.1 eV of $Na_{97}Gd_0Tb_3$ versus partial cleaning temperature (left ordinate scale). The full triangle and full square are the absorption coefficients of the 5.0 and 4.9 eV bands respectively, prior to irradiation. The normalized TSL integral versus partial cleaning temperature is also reported (right ordinate scale).

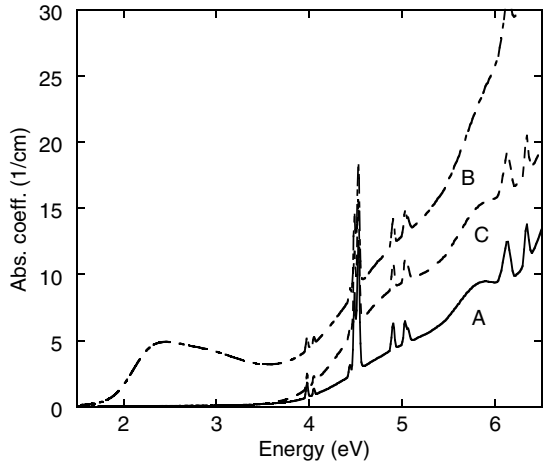

Figure 9. RT optical absorption spectra of $Na_{75}Gd_{25}Tb_0$ glass. (A) as received; (B) after x-ray irradiation; (C) after x-ray irradiation and heating up to 280 °C.

Figure 9 displays the comparison between the spectra before irradiation, after x-ray irradiation, and after subsequent heating up to 280 °C; it is evident that after heating to 280 °C only the lower energy bands are completely recovered, while above 4 eV the effect of irradiation is still clearly present. Finally, in figure 10 we show the intensities of the 2.3 and 2.9 eV bands versus the partial heating temperature. It is interesting to note that the temperature dependences of these two bands (as well as of those reported in figure 8) are qualitatively similar to those observed for P–O-related centres in P-doped silica glass (figures 16 and 17 in [9]). In view of such similarities, one could propose an explanation of the induced absorption phenomena within the 2–3.5 eV energy region in the phosphate glasses studied as being a result of competition for the hole capture between the just-mentioned hole centres derived from the glass matrix

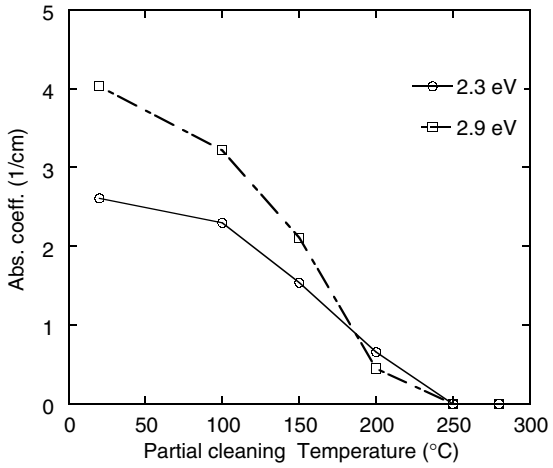

Figure 10. Intensities of the radiation-induced optical absorption bands at 2.3 and 2.9 eV of $Na_{75}Gd_{25}Tb_0$ versus partial cleaning temperature.

and Tb^{3+} ions. A precise evaluation of the partial recovery of the 5 and 5.8 eV bands was prevented by their strong superposition, and also by the contribution of bands peaking in the VUV; however, it is clear from figure 9 that their intensities are still rather strong even after the highest heating. Such a difference in behaviour of the Tb-free sample with respect to the other glasses is in agreement with the markedly higher temperature of the principal TSL peak (figure 4), which indicates a higher stability of trapped carriers. The complete disappearance of radiation-induced bands in the visible region after heating to 280 °C is however a positive feature from the applications point of view, as these could give rise to self-absorption of the light emitted by Tb^{3+} ions.

4. Conclusions

The effect of ionizing irradiation on Tb^{3+}-doped $NaPO_3$–$GdPO_4$-based glasses was investigated by means of optical absorption and TSL measurements. Several radiation-induced absorption bands were evidenced and ascribed to Tb^{4+} ions or to intrinsic defects (mostly P–O-related hole traps) of the glass matrices. Their thermal stability was also studied, and the results were correlated with the thermal de-trapping of charge carriers from defect states evidenced as TSL peaks; thermal treatments at temperatures above 250 °C were found to have a key role in the recovery of optical absorption bands. The results open the way to a better comprehension of the origin of defect states in such glassy matrices, and to the optimization of the materials for applications as scintillators.

Acknowledgments

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