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journal homepage: www.elsevier.com/locate/cplettTrapping states and excited state ionization of the Ce^{3+} activator in the SrHfO_3 hostE. Mihóková^{a,*}, V. Jarý^a, M. Fasoli^b, A. Lauria^{b,1}, F. Moretti^{b,2}, M. Nikl^a, A. Vedda^b^a Institute of Physics, AS CR v.v.i., Cukrovarnická 10, 16253 Prague, Czech Republic^b Dip. di Scienza dei Materiali, Università di Milano-Bicocca, via Cozzi 53, 20125 Milano, Italy

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ABSTRACT

We study trapping states of Ce^{3+} -doped SrHfO_3 by thermally stimulated luminescence in a wide temperature range (10–730 K). We determine characteristic parameters of the traps by the initial rise technique. We also determine the energy of thermal ionization of the excited state of Ce^{3+} in SrHfO_3 host by purely optical method based on the study of UV illumination-induced thermoluminescence. The method provides a value of the thermal ionization energy of about 0.25 eV.

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1. Introduction

Ce^{3+} -doped SrHfO_3 (SHO) has attracted recent interest as a scintillating material due to its high density (7.56 g/cm³) and high effective atomic number. Because of its high melting point ($T_m > 2400^\circ\text{C}$) the material is not available as a single crystal and therefore is currently being investigated in the form of nanocrystals [1,2] or ceramics obtained from crystalline powders prepared by solid-state synthesis [3]. Alternative techniques for the preparation of Ce-doped SHO powders are the sol–gel route [4,5] or acetate–citrate combustion [6,7].

Fast photoluminescence (PL) and scintillation response of $\text{SHO}:\text{Ce}^{3+}$ are ensured by the allowed $5d_1 \rightarrow 4f$ transition of the Ce^{3+} ion. The PL and scintillation room temperature (RT) decay times previously reported were 36 and 42 ns, respectively [2,3]. More recent studies [6] performed in powder samples prepared by two different preparation techniques found PL decay time values of about 15 ns. Not only is this value significantly different from that reported in [2], but it is also the shortest decay time observed for a Ce^{3+} activator in any known scintillating host. The surprisingly short RT decay time indicates the possibility of temperature quenching or ionization of the luminescent center, undesired phenomena degrading scintillator performance. A recent study [8] devoted to this issue indeed confirmed thermal ionization of the excited state of the Ce^{3+} center in the SHO host. The evidence is provided by several observations: (i) shortening of the prompt nanosecond PL decay time with increasing temperature, (ii) observation of delayed recombination decay at the Ce^{3+} center

after its UV excitation, and (iii) detection of the thermally stimulated luminescence (TSL) signal after UV excitation at RT.

The energy of thermal ionization of the excited state of a luminescent center in a host is an important characteristic affecting the figure of merit of a scintillating material. It is usually experimentally determined by photoconductivity measurements. The conventional photoconductivity technique is applicable only to materials in the form of crystals. For materials in powder form one has to look for ‘contactless’ alternatives. The microwave resonator technique for the study of photoconductivity in rare-earth-doped dielectric crystals [9] was for the first time used for powder samples in [10]. Another possibility is given by the recently described optical experimental method involving the study of temperature dependence of the TSL signal obtained after UV illumination [11].

In this Letter we study trapping states of $\text{SHO}:\text{Ce}^{3+}$ in a wide temperature range (10–730 K). We determine characteristics of the traps by the initial rise technique. We also study the thermal ionization of the Ce^{3+} excited state in the SHO host in a greater detail. We aim to determine the ionization energy of the luminescence center by an approach introduced in [11]. It is based on the study of the temperature dependence of the TSL glow curve observed after UV excitation of the Ce^{3+} center.

2. Experimental details

Ce^{3+} doped SHO samples were prepared by acetate and citrate combustion. The preparation technique is described elsewhere [6,7]. Dopant concentration was 0.1 mol%. The final sintering temperature was 1150 °C.

Wavelength resolved thermally stimulated luminescence (TSL) measurements in the 10–310 K temperature range were performed with a heating rate of 0.1 K/s after irradiation at 10 K. The detection system featured a CCD detector (Jobin-Yvon Spectrum One 3000) coupled to a monochromator (Jobin-Yvon Triax 180) with 100 grooves/mm grating operating in the range 200–1100 nm.

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TSL glow curves above RT were measured after irradiation at RT from 293 up to 730 K using a linear heating rate of 1 K/s. The emitted light was detected in photon counting mode by a photomultiplier (EMI 9635QB). X-ray irradiation was realized with Philips 2274 and Machlett OEG50 tubes operating at 20 and 30 kV for irradiations at 10 K and RT, respectively. UV illumination at 310 nm was performed by exploiting the beam of a Perkin Elmer Lambda 950 spectrometer. The temperature of the sample during UV illumination was controlled by a Peltier cell (20.9W 2.2 APE-127-08-15).

Photoluminescence (PL) measurements were performed by a custom made 5000M Horiba Jobin Yvon spectrofluorometer. Excitation by the deuterium steady-state lamp was used for the emission spectra measurements. An Oxford Instruments liquid nitrogen bath optical cryostat allowed temperature regulation from about 150 to 500 K.

Steady-state PL excitation spectra in the UV–VUV region were measured at the Superlumi station in DESY using the detector in the standard ‘integral’ as well as ‘fast component’ and ‘slow component’ regimes with ‘all times’, ‘0–5 ns’ and ‘150–190 ns’ time gates, respectively (time-0 refers to the excitation pulse arrival).

3. Results and discussion

3.1. Study of the trapping states by TSL

The TSL glow curve of SHO:Ce³⁺ after irradiation at 10 K (Figure 1) features well resolved TSL peaks at about 80, 100, 205, 230, 255 and 290 K. No shifts of the temperature positions of the peak maxima were observed by varying the irradiation dose by about two orders of magnitude. Therefore it may be concluded that these peaks follow first order recombination kinetics [12]. The contour plot displayed in Figure 2 shows the presence of a prominent emission due to Ce³⁺ ion at around 400 nm [6,13] accompanied by a weak defect emission at higher wavelength.

To evaluate the depths of the traps associated with the observed TSL peaks we used the *initial rise* technique (including partial cleaning of the glow curve) [12]. For each TSL peak we performed from two to three partial cleanings of the curve and corresponding initial rise evaluations. The amplitude of initial part of the glow peak can be approximated by an exponential function:

$$\text{Amp}(T) = b + we^{\frac{E}{kT}}, \quad (1)$$

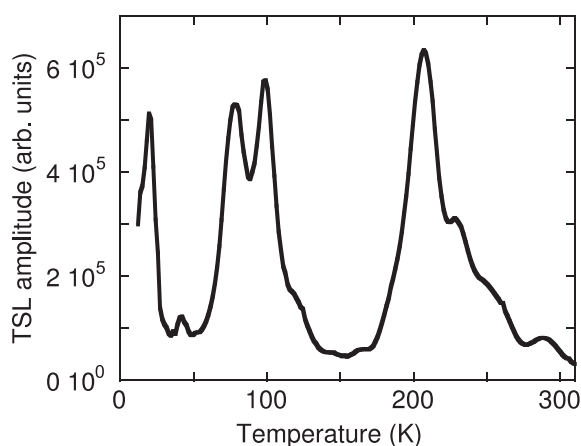


Figure 1. TSL glow curve of SHO:Ce³⁺ plotted as a function of temperature after X-ray irradiation at 10 K. The signal was obtained after integration of the wavelength resolved measurement in the 300–700 nm range.

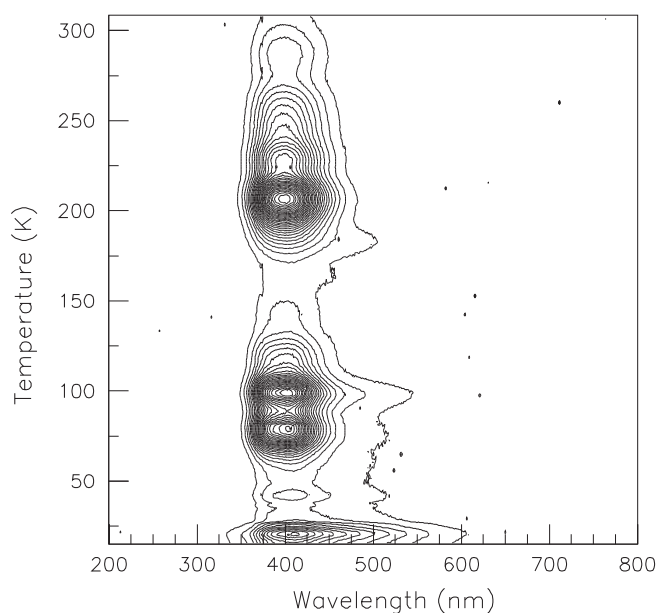


Figure 2. Wavelength resolved TSL measurements performed on SHO:Ce³⁺ after X-ray irradiation at 10 K.

where b is a constant, E is the trap depth, w is a pre-exponential factor, k is the Boltzmann's constant and T is the absolute temperature. The frequency factors associated with traps whose TSL peaks follow the first order recombination kinetics can be calculated from the formula relating the frequency factor s , the heating rate β and the temperature maximum of the TSL peak T_m :

$$\beta E/kT_m^2 = s \times e^{-\frac{E}{kT_m}} \quad (2)$$

The lifetime of the trap τ at the temperature T can be calculated as:

$$\tau = s \times e^{\frac{E}{kT}} \quad (3)$$

The average value of the trap depths, frequency factors corresponding to the first order recombination kinetics and RT lifetimes are listed in Table 1. Considering an error of about 1 K in the determination of the position of the TSL peak maximum, only the order of magnitude of the frequency factor can be estimated.

The TSL glow curve of SHO:Ce³⁺ after irradiation at RT (see the inset of Figure 3) features the TSL peaks at about 320, 413, 473 and 583 K. It should be pointed out that due to variation in the heating rate (1 K above RT versus 0.1 K below RT) the TSL peaks at 320 K (the inset of Figure 3) and 290 K (Figure 1) most probably corre-

Table 1
Trap parameters obtained by initial rise technique and consideration of the first order recombination kinetics.

T_m (K)	E (eV)	s (s ⁻¹)	τ (s) at RT
<i>Irr. at 10 K</i>			
78	0.12 ± 0.01	~10 ⁶	~10 ⁻⁶
100	0.19 ± 0.01	~10 ⁸	~10 ⁻⁵
205	0.48 ± 0.01	~10 ¹⁰	~10 ⁻²
230	0.46 ± 0.01	~10 ⁸	~1
255	0.60 ± 0.01	~10 ¹⁰	~1
290	0.76 ± 0.01	~10 ¹¹	~10 ²
<i>Irr. at RT</i>			
320	0.9 ± 0.1	~10 ¹³	~10 ²
413	0.97 ± 0.01	~10 ¹⁰	~10 ⁶
473	1.15 ± 0.04	~10 ¹¹	~10 ⁹
583	1.60 ± 0.04	~10 ¹²	~10 ¹⁵

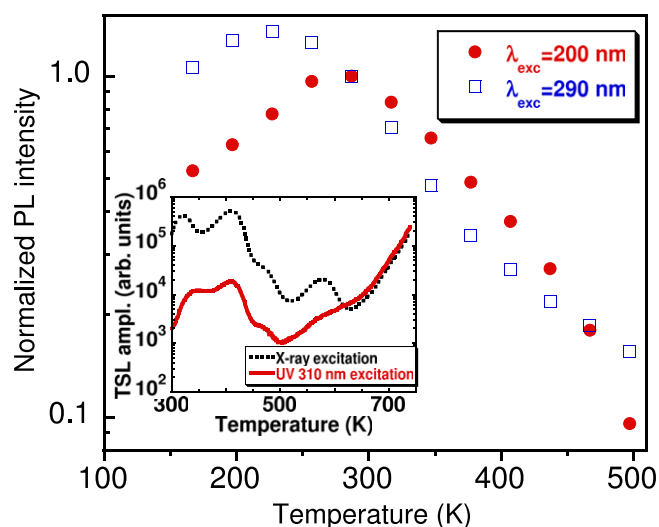


Figure 3. Temperature dependence of the normalized (at RT) PL intensity of $\text{SrHfO}_3:\text{Ce}^{3+}$. The PL emission spectra excited at 200 nm (solid circles) and 290 nm (empty squares) were integrated in the range 350–540 nm of the 5d–4f Ce^{3+} emission. In the inset are reported TSL glow curves of $\text{SrHfO}_3:\text{Ce}^{3+}$ after X-ray irradiation as well as UV illumination (310 nm, 35 min) at RT. The high temperature monotonic increase of the signal corresponds to black body emission.

spond to the same trap. Variation of the irradiation dose by about two orders of magnitude confirmed that TSL peaks above RT also follow the first order recombination kinetics. Corresponding TSL spectra [8] similarly to those below RT confirmed the predominant presence of the Ce^{3+} recombination center emitting around 400 nm. To evaluate the characteristic parameters of the traps associated with TSL peaks an analogous procedure described above was applied. For quantitative analysis, however, the TSL glow curves above RT had to be corrected for the temperature quenching of the Ce^{3+} recombination center, as was done, for example, in [14]. The details on the correction procedure are given below. Corresponding trap depths, frequency factors and RT lifetimes are listed in Table 1.

3.2. Correction for the temperature quenching of the Ce^{3+} emission center

The correction curve for Ce^{3+} emission quenching can be obtained from the temperature dependence of the steady-state PL intensity. In Figure 3 we present the PL intensity of the Ce^{3+} emission band measured under excitation in both the host lattice (200 nm) and the Ce^{3+} absorption band (290 nm). We find the data obtained for the excitation at 200 nm more suitable for determination of the correction since they are less affected by possible distortions due to following reasons.

First and most important, there is a larger energy separation between excitation and emission light, i.e., less of a problem with light scattering. The data obtained for the 290 nm excitation (cf. Figure 3) show a less steep decrease above 400 K due to the contribution of the scattered excitation light which distorts the true shape of the curve. This problem does not occur in emission spectra for the host lattice 200 nm excitation.

Second, the temperature change has a weaker effect on the absorption profile. Unlike the case of an optically thick bulk crystal, the outgoing PL light in powder is collected only from several outer grain layers of the sample due to scattering losses on powder grains. As a result, the portion of the incident light contributing to the measured PL amplitude critically depends on the amplitude of absorbance. It is extremely difficult to experimentally quantify the scattering losses. On the other hand, the temperature change

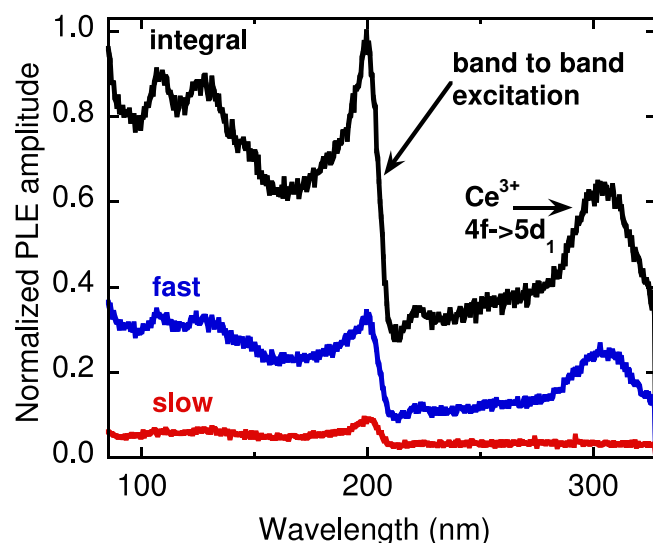


Figure 4. Normalized PL excitation spectra of $\text{SrHfO}_3:\text{Ce}^{3+}$ at RT with $\lambda_{\text{em}} = 380$ nm. The curves indicated in the figure correspond to measurements performed in various detector regimes: integral, fast component and slow component (cf. Section 2).

of absorbance amplitude can be significant, also due to effects like temperature exchange of absorption strengths for 4f–5d₁ and 4f–5d₂ transitions of Ce^{3+} as shown in Ce^{3+} -doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) crystal [15]. The change in absorbance of 4f–5d₁ transition of Ce^{3+} in YAG:Ce between 300 and 500 K becomes more than 25% [16]. A much smaller effect of absorbance amplitude is expected under excitation at the absorption edge of the host when the excitation light is fully absorbed within only a thin layer (several μm) of the powder. On the other hand, in this case the distortion of the temperature dependence of the PL intensity could occur due to the energy losses in the process of transfer between the host and the Ce^{3+} center. Nevertheless, PLE spectra of $\text{SHO}:\text{Ce}^{3+}$ measured in the VUV region [13] showed rather efficient energy transfer between the SHO host and the Ce^{3+} ion. PLE spectra at RT (see Figure 4) show in great detail that the transfer of excitation from the host to the Ce^{3+} luminescence ion is not only efficient but also fast. This is because the contribution of the slow component (time gate 150–190 ns) to the PLE peak at 200 nm is substantially weaker compared to that of the fast component (time gate 0–5 ns), at least from RT above.

The PL intensity under the 200 nm excitation features a monotonic decrease from RT down to low temperatures (cf. Figure 3). The observation might be due to decreasing efficiency of the energy transfer between the host and the Ce^{3+} center with decreasing temperature. This is feasible considering that the Ce^{3+} excitation is competing with the excitation of the self-trapped exciton or some other state [13] that is quenched (thermally disintegrated) with increasing temperature. Consequently, for the purpose of defining the correction curve (due to the intracenter Ce^{3+} temperature quenching) the PL intensity from RT down to low temperatures was considered constant.

3.3. Study of ionization of the Ce^{3+} excited state by TSL

Detection of the TSL signal in the material after the PL excitation of the luminescence center indicates that the carriers were thermally promoted into the conduction or valence bands. In the case of the Ce^{3+} luminescence center in the SHO host the PL excitation would involve a direct 4f → 5d₁ transition of Ce^{3+} located around 300 nm. Electrons migrate in the conduction band and can be trapped by point defects. When they are released and finally deliv-

ered to the luminescence center, their radiative recombination produces the TSL light. The TSL intensity after the PL excitation of the luminescence center will be proportional to the fraction of carriers N_I that thermally ionizes and enters the conduction band:

$$N_I(T) = w e^{-\frac{E_{\text{ion}}}{kT}}, \quad (4)$$

where T is the excitation temperature, w is a pre-exponential factor, E_{ion} is the thermal ionization energy (the energy separation between the excited state of the luminescent center and the bottom of the conduction band) and k is Boltzmann's constant. Eq. (4) is a reasonable approximation when retrapping to Ce^{3+} is either not significant or temperature independent, and one does not consider possible intrinsic temperature dependence of E_{ion} . When this holds, from the study of the temperature dependence of the TSL intensity excited by the UV light one can, in principle, estimate the ionization energy E_{ion} .

Based on this concept we pursue determination of the ionization energy of the Ce^{3+} center in the SHO host. Then we studied the excitation temperature dependence of UV excited TSL glow curves.

The sample was illuminated at the defined temperature by UV light (310 nm) corresponding to the $\text{Ce}^{3+} 4f \rightarrow 5d_1$ absorption band. After illumination it was cooled (or heated) to RT and the TSL glow curve in the 293–730 K temperature interval was recorded.

TSL glow curves obtained after both X-ray and UV (310 nm) irradiations of the $\text{SHO}:\text{Ce}^{3+}$ sample at RT (the inset of Figure 3) were already presented in [8]. The observed TSL peaks have been associated with electron traps and Ce^{3+} as also mentioned above was identified as the single TSL-active recombination center.

The TSL glow curves obtained for a sequence of illumination temperatures are displayed in Figure 5a,b. Here we present only the temperature region (where the TSL signal is not masked by black body radiation) that was used in a subsequent analysis. One can see that starting from the highest illumination temperature, 347 K, the TSL glow curves become less intense as the illumination temperature progressively decreases. This observation nicely correlates with the expected decreasing probability of the center thermal ionization according to formula (4). Note that from illumination temperature 347 K down to 313 K we only observe one dominant TSL peak at about 410 K. As the illumination temperature decreases, a TSL peak at about 330 K appears. Its intensity increases with decreasing illumination temperature. From 272 K to the lowest illumination temperatures it becomes consistently more intense relative to that of the 410 K peak. The temperature evolution of these two peaks reflects their partial or even full (for the 330 K peak) thermal decay above certain illumination temperatures.

To exclude possible effects of signal saturation we checked that the measured glow curves fall into the linear regime of the TSL signal dependence on the irradiation dose. The results in the inset of Figure 6 demonstrate that up to about six times the TSL intensity presented in Figure 5a,b, the dependence on the dose is indeed linear.

For subsequent attempts to determine the ionization energy of the Ce^{3+} center from the TSL data, those with fully or partially decayed TSL peaks are not directly applicable. For simplicity, we decided to take into consideration only the data obtained in the range of illumination temperatures where the TSL signal is reasonably intense and both TSL peaks are sufficiently stable. Alternatively, all glow curves could have been considered, integrating the signal only in the temperature range unaffected by thermal decay.

The TSL intensity corresponding to a specific illumination temperature was obtained by integration of the TSL glow curve in the range 300–470 K. Arrhenius plot of TSL intensity as a function of

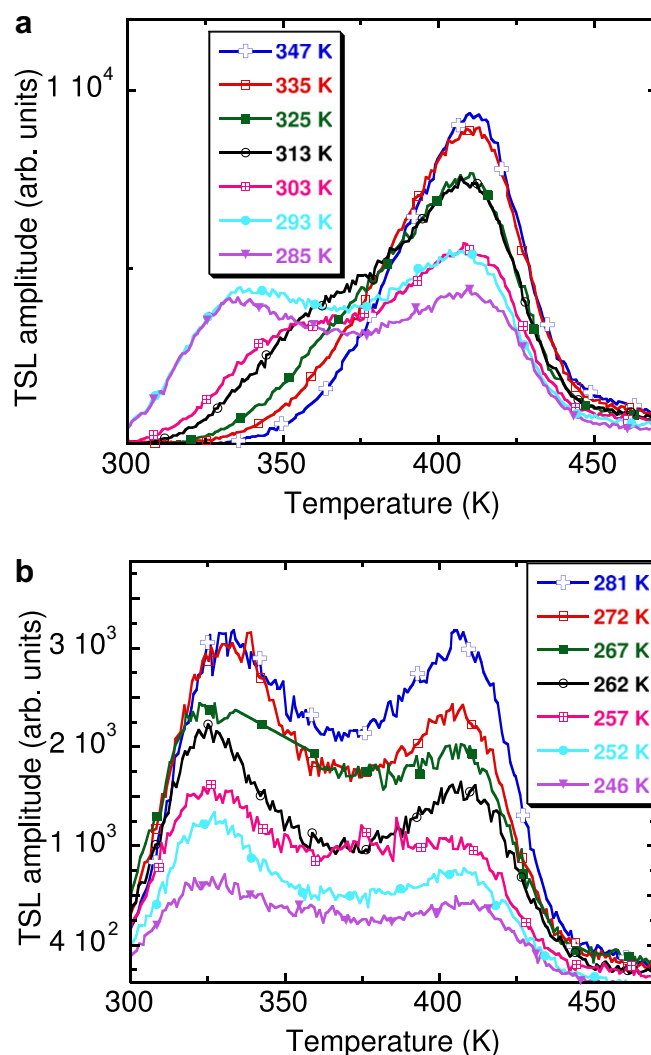


Figure 5. Both (a) and (b) show the influence of temperature variation on the TSL glow curves of $\text{SrHfO}_3:\text{Ce}^{3+}$ after UV illumination at 310 nm for 35 min. The illumination temperature is reported in the legend.

illumination temperature T_{ill} is presented in Figure 6. Due to the reasons discussed above the TSL intensity from intermediate to high T_{ill} (solid squares) does not manifest behavior consistent with formula (4). In contrast, the TSL intensity obtained for T_{ill} in the region from 246 to 293 K (solid circles) manifests a monotonic increase. We fit formula (4) to the data in this region of illumination temperatures. We point out that only relative changes in TSL intensity affect the slope of the line, and thus the value of E_{ion} . These relative changes are, however, unaffected by possible temperature quenching of the Ce^{3+} luminescence center and therefore TSL glow curves need not be corrected for this phenomenon. The value obtained for E_{ion} from the fit is 0.24 ± 0.01 eV. Since we controlled illumination temperature with a precision of about ± 1 K, the final estimated value of ionization energy is 0.24 ± 0.02 eV. We note that the method might also be affected by an extensive shift of the host absorption edge in the temperature interval involved in the fit. We measured excitation spectra of the Ce^{3+} emission band and estimated the shift of absorption edge within 250–310 K to be about 0.02 eV. The value falls within the estimated error of the determined ionization energy.

It is worth pointing out that the value of about 0.25 eV is rather close to the value of barrier quenching, 0.3 eV, obtained from the temperature dependence of PL decay time [8]. As pointed out in

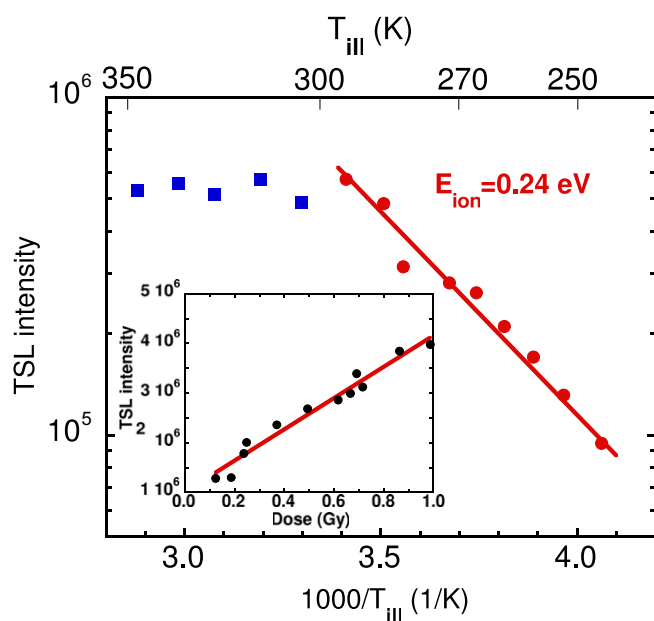


Figure 6. TSL intensity of SHO:Ce³⁺ as a function of illumination temperature. Solid squares and solid circles are obtained by integration of the TSL glow curves in the region 300–470 K. The solid line is the fit of formula (1) in the text to the data represented by the solid circles. In the inset is shown the TSL intensity of SHO:Ce³⁺ as a function of X-ray irradiation dose. The solid circles were obtained by integrating the TSL signal between 300 and 470 K. The solid line is the linear fit to these data.

[8], the temperature shortening of the PL decay time can have two sources, namely classical thermal quenching and thermal ionization of the luminescence center excited state. Similar temperature dependencies of PL intensity and PL decay time [8] suggested that a classical thermal quenching causes the PL decay time shortening. The current study, resulting in a thermal ionization energy being about 0.25 eV, shows that both processes operate with similar barrier energies.

4. Conclusion

In the present Letter we studied trapping states in SHO:Ce³⁺ by TSL technique in a wide temperature range (10–730 K). We determined the characteristic parameters of traps associated with observed TSL peaks. We also determined the energy of thermal

ionization of the excited state of the Ce³⁺ ion in a SHO host by a purely optical method that yielded a value of the thermal ionization energy of about 0.25 eV.

The method is based on the dependence of the TSL intensity induced by the UV light on the illumination temperature. If the TSL signal is sufficiently strong, one can extract the ionization energy from a simple analysis of such an experiment. An additional advantage of this method is that the analysis does not require the correction of experimental data for the temperature quenching of the TSL-active luminescence center.

The method, first introduced and tested for a Lu₂Si₂O₇:Pr³⁺ crystal [11], has now been applied for a microcrystalline powder of SrHfO₃. Its applicability not only for crystal but also powder materials, while encouraging with respect to the development of methods for studying thermal ionization processes in scintillators, does not eliminate larger issues that might arise in all cases, such as the possible temperature dependence of the ionization energy itself.

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References

- [1] Y.M. Ji et al., *J. Cryst. Growth* 280 (2005) 93.
- [2] H. Retot, A. Bessiere, A. Kahn-Harari, B. Viana, *Opt. Mater.* 30 (2008) 1109.
- [3] E.V. Van Loef et al., *IEEE Trans. Nucl. Sci.* 54 (2007) 741.
- [4] M. Villanueva-Ibanez, C. Le Luyer, S. Parola, O. Marty, J. Mugnier, *J. Sol-Gel Sci. Technol.* 31 (2004) 277.
- [5] M. Villanueva-Ibanez, C. Le Luyer, S. Parola, C. Dujardin, J. Mugnier, *Opt. Mater.* 27 (2005) 1541.
- [6] E. Miháková et al., *IEEE Trans. Nucl. Sci.* 57 (2010) 1245.
- [7] A. Lauria, N. Chiodini, E. Miháková, F. Moretti, A. Nale, M. Nikl, A. Vedda, *Opt. Mater.* 32 (2010) 1356.
- [8] V. Jary, E. Miháková, M. Nikl, P. Boháček, A. Lauria, A. Vedda, *Opt. Mater.* 33 (2010) 149.
- [9] M.F. Joubert, S.A. Kazanski, Y. Guyot, J.C. G?con, C. Pedrini, *Phys. Rev. B* 69 (2004) 165217.
- [10] H. Loudyi, Y. Guyot, J.C. G?con, C. Pedrini, M.F. Joubert, *J. Lumin.* 127 (2007) 171.
- [11] M. Fasoli, A. Vedda, E. Miháková, M. Nikl, *Phys. Rev. B* 85 (2012) 085127.
- [12] S.W.S. Mc Keever, *Thermoluminescence of Solids*, Cambridge University Press, Cambridge, 1985.
- [13] E. Miháková et al., *Phys. Rev. B* 82 (2010) 165115.
- [14] A. Vedda et al., *Phys. Rev. B* 78 (2008) 195123.
- [15] D.J. Robbins, *J. Electrochem. Soc.* 126 (1979) 1550.
- [16] M. Nikl, unpublished results.