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Shallow traps in $PbWO_4$ studied by wavelength-resolved thermally stimulated luminescence

M. Martini, F. Meinardi, G. Spinolo, and A. Vedda*
Istituto Nazionale per la Fisica della Materia and Dipartimento di Scienza dei Materiali dell'Universita' di Milano, Via Cozzi 53, I-20125 Milano, Italy

M. Nikl
Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Prague, Czech Republic

Y. Usuki
Furukawa Co. Ltd, Kamiyoshima, Iwaki 970-1153, Japan

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The thermally stimulated luminescence (TSL) properties of lead tungstate in the temperature range 10–250 K have been investigated by wavelength-resolved measurements performed on undoped and lanthanum doped crystals after *x* irradiation at 10 K. Glow peaks at around 10 and 20 K have been observed, followed by a strong and composite structure in the 40–70 K region. At higher temperatures TSL emission in the 85–100 K range has also been detected, whose intensity is higher in the lanthanum doped crystal with respect to the undoped one. Additionally, the undoped crystal displays a composite glow peak in the 180–200 K region. The emission spectrum of the TSL varies both as a function of temperature and doping: a band centered at 2.85 eV is found in the undoped sample below 70 K; a similar emission is found in the case of the lanthanum doped crystal, with the exception of a limited temperature interval around 60 K where another band at lower energy ($E=2.63$ eV) is found. In the 200 K region, the emission is centered at 2.5 eV. These results are discussed in comparison with literature photoluminescence and scintillation data. A detailed investigation of the composite TSL structure in the 40–70 K range has been performed through several partial heating treatments: three distinct TSL peaks have been found at 50, 55, and 67 K, characterized by trap depths of 48, 65, and 104 meV, respectively. The comparison with recent literature electron paramagnetic resonance studies allows us to propose that the TSL peak at 50 K is related to the thermal disintegration of $(WO_4)^{3-}$ electron centers followed by radiative recombination. Spatial correlation between traps and luminescent centers is suggested, leading to localized recombination not involving the conduction band. [S0163-1829(99)07431-7]

I. INTRODUCTION

In recent years, the use of lead tungstate ($PbWO_4$) as a scintillator material was proposed:[1,2] in fact, although it is characterized by a low light yield (lower than 150 photons/MeV), its high density and fast radio-luminescent (scintillation) response make this intrinsic scintillator particularly interesting for applications in high energy physics experiments.

The photoluminescence properties of the material were already investigated in the past.[3–6] In view of the mentioned application, much effort was recently devoted to the optimisation of the scintillation properties and several new studies of photoluminescence and decay kinetics,[7–13] as well as of optical absorption[2,9,14,15] appeared. These studies were accompanied by a continuous improvement of the quality of the crystals grown by the Czochralski method,[16] and included also the effect of the doping with selected aliovalent ions.[9,13]

In spite of the optimization of the material, the nature of the centres responsible for the photo and radioluminescence emissions is still matter of debate. Different proposals have been put forth: the blue emission centered at 2.8 eV has been ascribed to a transition within a regular WO_4 group,[3] while WO_3 centers have been proposed as responsible for an emission centred at around 2.5 eV;[5] this latter emission appears to be composite, and recently possible relations both with a lead deficient phase ($Pb_7W_8O_{(32-x)}$) and with local lattice distortions towards the wolframite structure have been proposed;[17,18] emission in this region appears also to be related to the MoO_4 group, i.e., to the Mo impurity.[19] Moreover, a recently observed emission at 2.1 eV, excited at 3.5 eV, was ascribed to O^- and Pb^{3+} centers respectively, by different investigators.[9,15]

No contributions to the investigation of the nature of hole centers came up to now from electron paramagnetic resonance (EPR) studies. In fact, no hole centers signals were detected in this material, at variance with another tungstate as $CaWO_4$ in which Pb^{3+} and a hole localized at regular tungsten groups were found;[20–22] this latter hole center was observed in $BaWO_4$ as well.[23]

According to their thermal depth, trap levels in the forbidden gap can seriously affect the scintillation properties. Significant information on such trap states can be reached by thermally stimulated luminescence (TSL) and thermally stimulated conductivity (TSC) measurements; if the intensity of the TSL signal allows to perform wavelength resolved measurements, information on the emission site is also obtainable. In agreement with previous studies,[24] recent investigations confirmed the existence of several peaks in a wide temperature range.[13,25–33] Thermally stimulated conductivity

(TSC) signals related to TSL peaks above 150 K were also detected.[29] Moreover, it was found that trap levels occurring in the 150–250 K range and characterized by decay times at room temperature in the μs-ms time scales, strongly affect the scintillation process by giving rise to slow decay components at room temperature.[26] A limited number of wavelength resolved TSL measurements appeared up to now: in previous investigations performed on undoped samples, emission centers at 2.5 eV, 2.7, and 2.95 eV were detected in peaks below room temperature, while above room temperature a dominant emission at 2.0 eV was found.[27,29] Additional efforts are needed in this direction, so to reach a detailed description of the TSL processes in the material inclusive of the understanding of the influence of dopant ions on the recombination centres.

Glow peaks observed above 150 K appear to be related to point defects induced by the occurrence of Pb^{2+} deficiency in crystals grown by the Czochralsky technique, as demonstrated by the crucial role played by trivalent dopants (La^{3+}, Gd^{3+}) in lowering their intensity.[13,32,33] The proposal of a relation of the traps with oxygen vacancies has been put forth, but once again no electron centers directly related to those defects were found by EPR studies up to now. On the other hand, it was demonstrated that among extrinsic defects, $(MoO_4)^{3-}$ paramagnetic centers are associated to TSL traps evidenced in the 200 K region.[24] The recent finding of another paramagnetic electron center observed at liquid helium temperatures after UV light exposure, namely an electron localized in a regular tungsten group $(WO_4)^{3-}$, is of particular interest.[34] Its thermal stability, limited to about 50–60 K, allowed to suggest a possible correlation with the TSL peaks observed in the 40–70 K region.[30] The thermal ionization energy of this center was calculated and turned out to be about 50 meV.[34]

In this paper we present a detailed picture of the TSL properties of lead tungstate at low temperatures. By wavelength resolved measurements, the TSL emission spectra have been obtained on undoped and lanthanum doped crystals and the results are discussed in comparison with photoluminescence and scintillation data. Moreover, through the analysis of the TSL glow curves the thermal energies of the peaks observed in the 40–70 K region have been obtained: the correlation between the trap responsible for a peak at 50 K and the $(WO_4)^{3-}$ electron center is clearly demonstrated.

II. EXPERIMENTAL CONDITIONS

Crystals of undoped and La^{3+}-doped $PbWO_4$ crystals were grown by Furukava Ltd (Iwaki, Japan) from 5N purity raw material. The samples used in this investigation were cut from the same parent crystals used in Ref. 34. The lanthanum doping level was 80 ppm in the melt. TSL measurements in the 10–250 K range were performed following 10 K x-ray irradiation (by a Philips 2274 x-ray tube operated at 20 KV). The TSL apparatus was a high sensitivity spectrometer measuring the TSL intensity both as a function of temperature and wavelength: 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 about 5 nm. It operates between 10 and 320 K. A 0.1 $K\cdot s^{-1}$ heating rate has been adopted.

III. RESULTS AND DISCUSSION

A. Spectrally resolved TSL glow curves of undoped and La^{3+}-doped crystals

The 3D TSL glow curves relative to undoped and lanthanum doped crystals following irradiation at 10 K are displayed in Figs. 1 and 2, respectively, together with the contour plots of the measurements. In the case of the undoped crystal, several glow peaks appear at different temperatures. Peaks at around 10 and 20 K are detected, whose low intensity is possibly due to their closeness to the irradiation temperature. These are followed by a composite structure in the 40–70 K region [Fig. 1(a)]; a qualitatively similar behavior up to 70 K is observed in the case of the lanthanum doped sample measured in the same conditions, while at higher temperatures an additional peak at 95 K is also observed [Fig. 1(b)]. In order to put in evidence the existence of higher temperature peaks, TSL measurements were also performed following irradiation at 10 K in different experimental conditions, namely by a higher dose and higher sensitivity of the detection system: Fig. 2 displays the results obtained on the undoped crystal after a partial heating up to 70 K, which was necessary to avoid the very strong signal of low temperature peaks. In this case, a composite structure at 70–85 K is detected showing a contribution to the emission at longer wavelengths, as well as one peak at 190 K. Further very weak peaks at around 100 K (as in the lanthanum doped case) and at 220 K are observed too, which are visible in the 3D spectrum. No TSL peaks at temperatures above 100 K were detected in the lanthanum doped crystal, in accordance with previous results already obtained by wavelength unresolved measurements[13] and explained by the ability of the trivalent dopant to reduce the concentration of defects responsible for glow peaks in the 150–300 K range; a much higher intensity of the peaks in the 100 K region in the case of the La-doped samples was already noticed as well.[13]

These measurements show that the emission wavelength of the TSL varies both as a function of temperature and doping: specifically, in the undoped sample the emission is centred in the blue region (430 nm) below 70 K, while it is rapidly shifted to the green (500 nm) at higher temperatures from 80 K upwards; in the La^{3+}-doped crystal, a dominant blue emission is observed, but a tail extending to longer wavelengths is detected at around 60 K. The detailed characteristics of the emissions are better depicted in Fig. 3 displaying emission spectra taken at selected temperatures: a band centered at 2.85 eV, with 0.60 eV full halfwidth at half maximum (FWHM), is responsible for the emission of the undoped sample below 70 K; at higher temperature the emission is centered at 2.5 eV ($\mathrm{FWHM}=0.60\,\mathrm{eV}$). An emission at around 2.8 eV is found in the case of the doped sample ($\mathrm{FWHM}=0.65\,\mathrm{eV}$), with the exception of a limited temperature interval around 60 K where another band at lower energy ($E=2.63\,\mathrm{eV}$, $\mathrm{FWHM}=0.74\,\mathrm{eV}$) is found.

In undoped samples, both the blue and green emitting centres are well known to exist from photoluminescence measurements: as already mentioned, they were ascribed to the transitions within WO_4 and WO_3 groups respectively;[3,5]

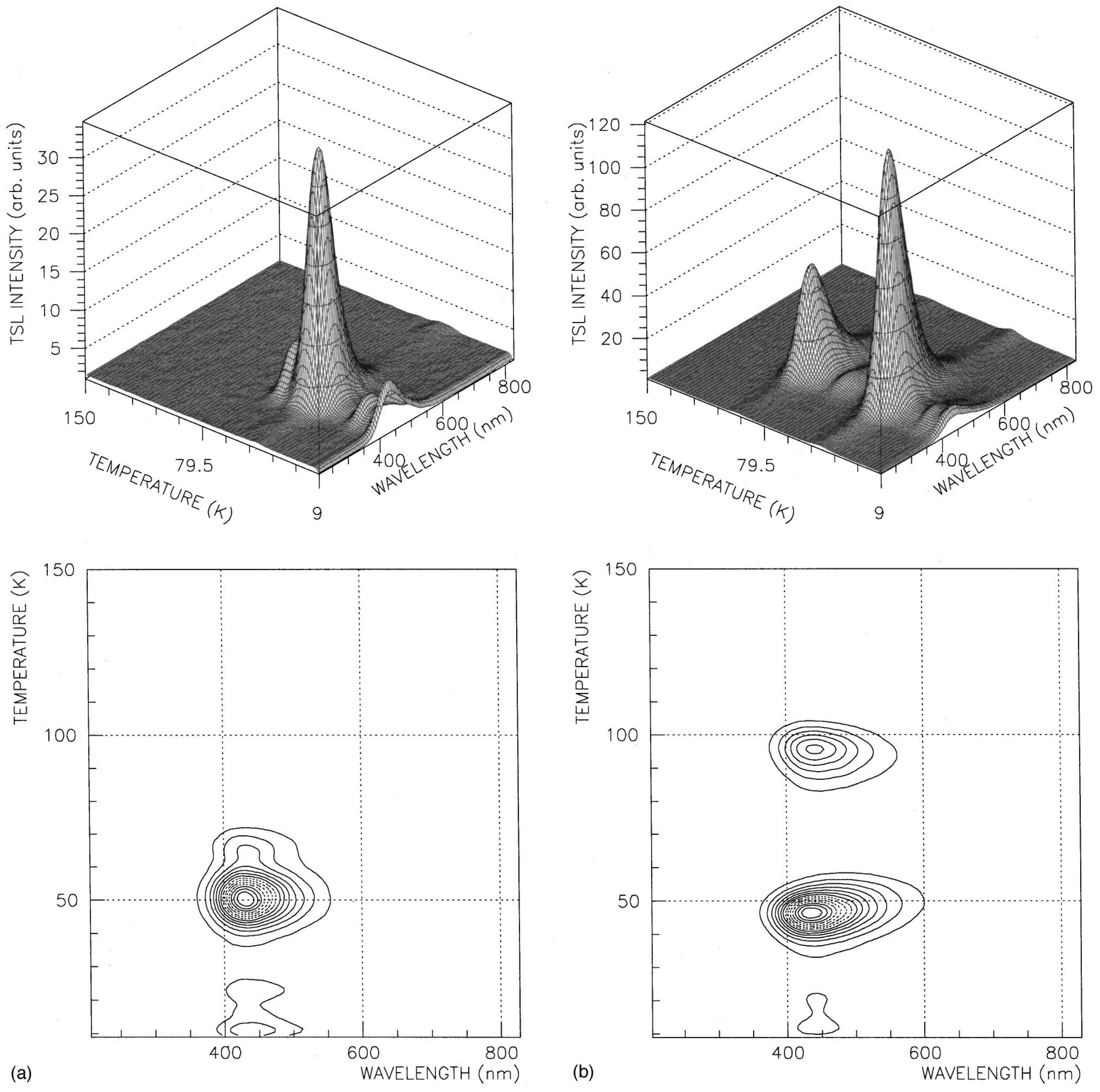

FIG. 1. (a) 3D TSL measurement and contour plot of the TSL in the 10–150 K range, following x-ray irradiation at 10 K of undoped (a) and La^{3+} doped (b) $PbWO_4$. Data are slightly smoothed by a bidimensional fast-Fourier transform algorithm.

moreover, contributions in the 500 nm region due to a lead deficient phase or to distortions towards the wolframite structures were proposed.[17,18] It is worth remarking that preliminary TSC measurements failed to detect any current signal in this temperature region, supporting the proposal of a spatial correlation between traps and luminescent sites leading to localized recombination not involving the conduction band. At higher temperatures, a dominant green emission is noticed. This can be explained by the thermal quenching of the blue emission, related to the thermal ionization of the excited level: the ionized electrons then reach the excited level of the green center, therefore increasing the green emission. This mechanism explains the energy transfer process from the blue to the green component operating above 160 K.[11] No green component is observed in the TSL of the La^{3+}-doped crystal, in accordance with scintillation results.[13] So, the spectrum is mostly centred in the blue spectral region up to 100 K. A different behavior is observed only in a very limited temperature region at around 60 K, where the emission is shifted at 2.6 eV; the band shape allows us to exclude a superposition of both 2.8 and 2.5 eV emissions, so that this band should be looked at as an additional feature of the emission pattern. A transition within a $(WO_4)^{2+}$ group slightly perturbed by the presence of a nearby trivalent lanthanum ion could possibly be suggested. The presence of this emission just in this limited temperature interval could be explained by a very strong spatial correlation between the trap and the emitting center.

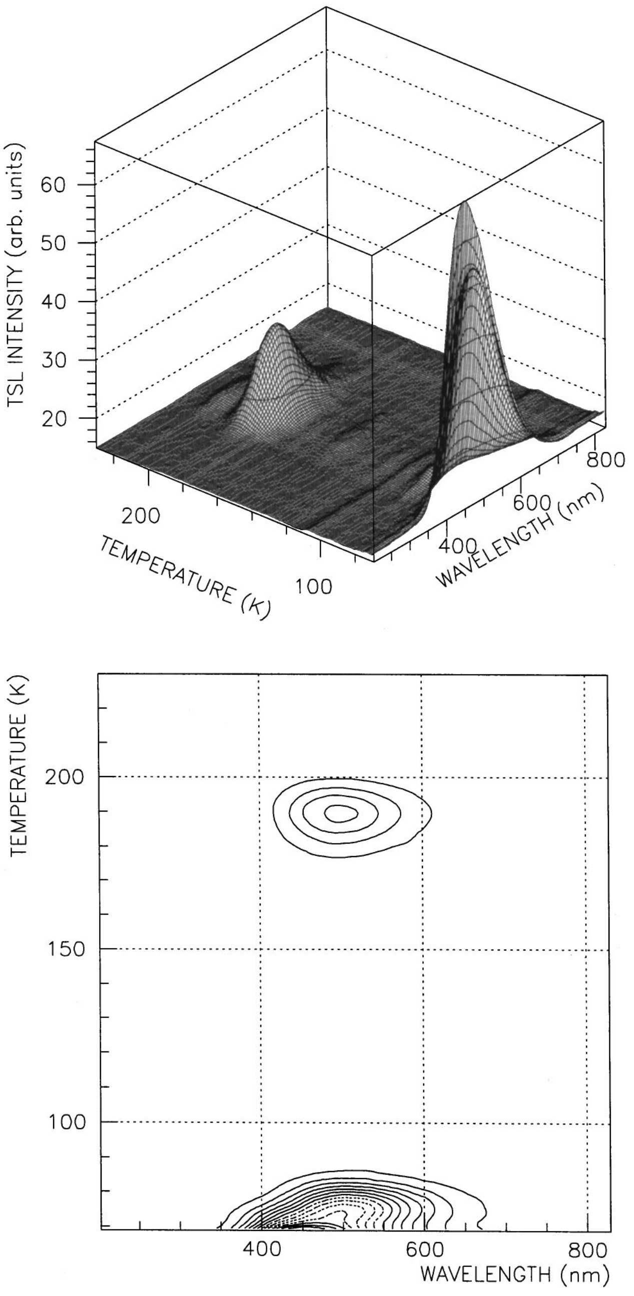

FIG. 2. 3D TSL measurement and contour plot of the TSL in the 70–230 K range, of undoped $PbWO_4$ following x-ray irradiation at 10 K. Data are slightly smoothed by a bidimensional fast-Fourier transform algorithm.

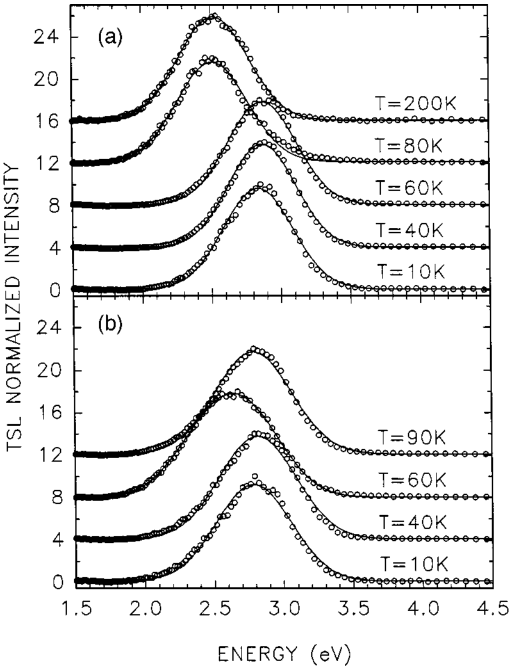

FIG. 3. Emission spectra of the TSL of $PbWO_4$ at selected temperatures. (a) Undoped crystal; (b) La^{3+}-doped crystal.

B. Evaluation of trap depths

As mentioned in the Introduction, the thermal stability of the $WO_4{}^{3-}$ centers suggested them as responsible of TSL traps below 70 K.[30] In order to better investigate this point, a comparison between the thermal depths of the traps in the 40–70 K region and the thermal ionization energy of this center is useful. However, a numerical fit of the observed composite TSL structure should not be reliable, due to the existence of closely lying overlapping peaks and to the lack of knowledge on the type of recombination kinetic. So, in order to separate the different glow peaks, several partial heating of the glow curve at selected temperatures were performed (partial cleaning). The analysis was carried out on the undoped sample: as already shown, the TSL glow curve of the La-doped sample is qualitatively similar in the 40–70 K temperature region: however the strong superposition of the peaks did not allow to separate the glow curve in a satisfactory way so as to reach a clear picture of the individual TSL peaks. The results are shown in Fig. 4 where glow curves integrated in the 390–490 nm wavelength range and obtained after partial cleaning at 38, 55, and 63 K are reported. Two glow peaks are clearly evidenced centred at 50 K and at 67 K, with an additional shoulder at around 55 K. The temperatures of the partial cleaning were chosen in order to assure that the initial portion of each peak was not influenced by the presence of the lower temperature ones. Then, the data of these three glow curves were numerically analyzed by the initial rise method (Fig. 5), which allows to evaluate the trap depth independently from the type of recombination model:[35] the calculated trap depths turned out to be 48, 65,

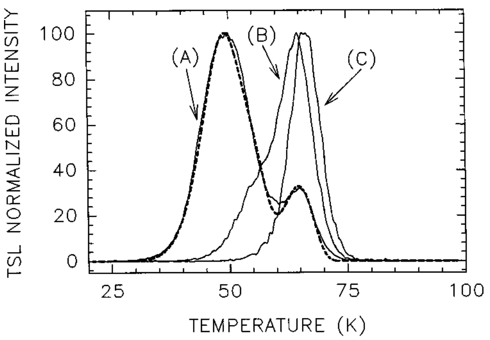

FIG. 4. TSL glow curves of the undoped sample after different partial cleaning, obtained by integrating the signal in the 390–490 nm wavelength range. Curves (A), (B), and (C) refer to partial cleaning at 38, 55, and 63 K, respectively. The dashed line represents the numerical fit of the glow curve after partial cleaning at 38 K.

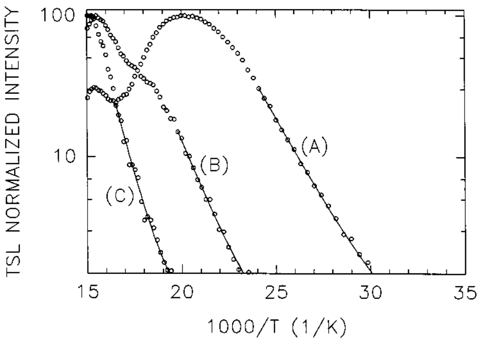

FIG. 5. Arrhenius plot of the TSL curves obtained on the undoped sample after partial cleaning at (A) 38 K, (B) 55 K, and (C) 63 K. The continuous lines are exponential fits performed on the basis of the initial rise method.

and 104 meV for the 50, 55, and 67 K peaks, respectively. The order of kinetics of these peaks was investigated by recording TSL glow curves at different irradiation doses: no shifts of the maximum temperatures of the peaks were noticed by considering approximately three orders of magnitude of dose variation, and this result suggests the presence of first order recombination processes.[35] A numerical fit of the glow curve after partial heating at 38 K was then performed on the assumption of first order kinetics and by fixing the energy values obtained with the initial rise method (dashed line in Fig. 4); from this fit, the frequency factors of the traps were obtained, and turned out to be of the order of 10^3, 10^4, and 10^6 s^{-1} for the 50, 55, and 67 K peaks, respectively. The correspondence between the experimental and theoretical curves is rather good: the deviation observed at around 60 K is probably due to the more difficult independent evaluation of the trap depth of the 55 K shoulder; moreover, the presence of minor structures at the high T side of the 67 K peak could explain the occurrence of higher experimental values in the 70 K region. The low values obtained for the frequency factors are consistent with the picture of spatial correlation between traps and luminescent centres.[35]

The value of the trap depth found for the first dominant TSL peak at 50 K (48 meV) is in very good agreement with that of the thermal ionization energy of the $(\mathrm{WO}_4)^{3-}$ electron center recently investigated by EPR:[34] it is thus possible to propose that the 50 K TSL peak is related to the thermal detrapping of electrons from $(\mathrm{WO}_4)^{3-}$ defects and subsequent radiative recombination at blue emitting centres. The simultaneous presence of additional peaks of lower intensity at around 55 and 67 K could suggest the existence of different variants of $(\mathrm{WO}_4)^{3-}$ centers: however such an hypothesis needs further support from systematic EPR measurements.

Some comments may be finally devoted to the kind of recombination processes involved. Several characteristics appear to be common to the three glow peaks forming the composite TSL structure in the 40–70 K region: these are (i) the presence of first order recombination; (ii) the lack of a TSC counterpart; (iii) the low values of the frequency factors obtained. All these points call for the existence of localized recombination between electrons and closely lying luminescent sites which do not involve the conduction band of the crystal.

IV. CONCLUSIONS

In this paper we have presented a detailed comparison between the TSL properties of undoped and La-doped crystals at low temperatures. This was performed through the investigation of the emission spectra of the TSL and the evaluation of the trap depths of selected glow peaks. The TSL emission features have been discussed and compared with previous results obtained by photoluminescence and scintillation studies. The trap depth related to the dominant TSL peak at 50 K turns out to be in agreement with the thermal ionization energy of the $\mathrm{WO}_4{}^{3-}$ center recently described by EPR: in PbWO$_4$, a clear correspondence between a TSL trap and one intrinsic electron center has been found. It is also possible to state that the recombination process between electrons detrapped from WO_4^{3-} defects and luminescent centers does not involve the conduction band of the crystal.

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*Author to whom correspondence should be addressed. FAX: 39-02-66485400. Electronic address: Anna.Vedda@mater.unimi.it

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