Photoinduced $(WO_4)^{3-}$-La^{3+} center in $PbWO_4$: Electron spin resonance and thermally stimulated luminescence study

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The localization of electrons at W^{6+} sites perturbed by lanthanum in $PbWO_4$ is studied by electron spin resonance (ESR) and thermally stimulated luminescence (TSL) measurements. The $(WO_4)^{3-}$-La^{3+} centers are created at the W^{6+} sites close to La^{3+} in two different ways: (i) direct trapping of electrons from the conduction band under ultraviolet or x-ray irradiation at $T=60$ K; (ii) retrapping of electrons freed from unperturbed $(WO_4)^{3-}$ centers after irradiation at $T<40$ K followed by heating up to T around 60 K. Electron transfer from La^{3+}-perturbed to unperturbed W^{6+} sites stimulated by red light illumination is also observed. The proposed mechanism of electron localization at one of four equivalent tungstate ions close to La^{3+} is based on the pseudo-Jahn-Teller effect, which gives rise to a rhombic distortion of $(WO_4)^{3-}$ complex. At $T \approx 95$–98 K the $(WO_4)^{3-}$-La^{3+} centers are thermally ionized giving rise to a TSL glow peak due to the recombination of detrapped electrons with localized holes. The emission spectrum of the TSL features one band peaking at 2.8 eV. The temperature dependence of both TSL and ESR intensity is analyzed in the frame of a general order recombination model. The thermal ionization energy of $(WO_4)^{3-}$-La^{3+} centers has been calculated to be approximately 0.27 eV.

I. INTRODUCTION

Lead tungstate–$PbWO_4$ (PWO) single crystals became a subject of intense studies some years ago, when this material was selected due to its favorable scintillation characteristics for coming applications in electromagnetic calorimeter detectors in high energy physics.[1,2] Apart from detailed reports dealing with its luminescence and scintillation characteristics (for a recent review see Ref. 3), the nature and role of various defect states in the processes of energy transfer and storage became a subject of debate. At room temperature, the trapping states can be usually divided into two groups: deep centers, in which the lifetime of captured carriers is at least several minutes, and shallow ones, which can localise charge carriers for a few (milli) microseconds or even less. While the former group of traps is responsible for the formation of quasistable color centres, i.e., so-called radiation damage (induced absorption) phenomena in PWO,[4,5] the latter trapping states essentially slow down the diffusion rate of free charge carriers in valence/conduction bands and are reflected in the appearance of slow decay components[6,7] both in photoluminescence and scintillation PWO decays. The doping of PWO by selected large and stable A^{3+} trivalent ions, namely, La^{3+} (Refs. 8–10), Gd^{3+} (Ref. 11), Lu^{3+} and Y^{3+} (Refs. 12–14) was found as an efficient tool for suppressing the deep and some of the shallow trapping centers. It resulted in several times higher radiation hardness and speed of scintillation response in such A^{3+}-doped crystals. This, essentially phenomenological finding, even if of crucial importance for the mentioned applications, did not answer the fundamental questions about the nature of trapping states in the PWO matrix. Several hypotheses were put forth, based on the existence of Pb^{3+} and O^- hole centers, and of F and F^+ electron centers.[15] Alternatively, more complex bi-hole or bi-oxygen vacancy centers were proposed by other authors,[16] and even the existence of Pb^{4+} centers was hypothesized.[17] However, none of these hypotheses was confirmed, e.g., by electron spin resonance (ESR). A systematic study of the processes of charge carrier localization in PWO was initiated by an ESR study, which revealed an electron autolocalized at a regular tungstate site [polaronic $(WO_4)^{3-}$ center] produced by ultraviolet (UV) light irradiation below 40 K.[18,19] Soon after, the perfect correlation between this ESR study and wavelength-resolved thermoluminescence (TSL) measurements[20] enabled one to make a detailed scheme of the microscopical mechanism of electron and hole capture and recombination processes around 50 K: electrons thermally detrapped from $(WO_4)^{3-}$ centers recombine radiatively

with holes localized nearby, and the excitonlike emission in the blue spectral region is detected in TSL.

This paper presents a correlated ESR and TSL study of undoped and La-doped PWO samples in the temperature region 60–100 K which reveals the existence of a La^{3+}-stabilized $(WO_4)^{3-}$ center, as well as its role in the observed TSL features.

II. SAMPLES AND EXPERIMENTAL DETAILS

Crystals of undoped and La-doped PWO were grown by Furukawa Ltd (Y.U.) from 5N purity raw material using the Czochralski method in air and the third crystallization method. The lanthanum doping level was 80 and 460 at. ppm in the melt. Due to the high value of the segregation coefficient of La in PWO ($k=2.4$–2.5) and close-to-seed position of the samples cut from the parent boule, the true concentration of La in the samples is expected to be about two times higher with respect to that in the melt. Samples for ESR measurements, $2.4\times2.6\times8$ mm^3, were cut along the (001) and (100) planes. For TSL measurements, samples of 1 mm thickness and approximately 1 cm^2 area were cut and polished. The ESR measurements were performed at 9.21 GHz in the standard 3 cm wavelength range of the ESR spectrometer ERS230 (ZWG Berlin). An Oxford Instruments ESR–9 cryosystem allowed the measurements at temperatures of 4–300 K. The applied magnetic field was rotated in the (001) and (100) planes of the PWO crystal structure. A mercury high pressure arc lamp was used for optical irradiation of the samples. Alternatively, an x-ray tube Siemens Dermopan, Cu anode operated at 50 kV, 20 mA was used for irradiation as well. Wavelength-resolved TSL measurements were performed following x-ray irradiation (Philips 2274 x-ray tube operated at 20 KV) at 10 and 60 K. The TSL apparatus consists of a 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 used was about 5 nm. The system operates between 10 and 320 K, amd a heating rate of 0.1 $K\,s^{-1}$ was used.

III. EXPERIMENTAL RESULTS

A. ESR spectra

After UV irradiation of PWO:La crystals at low temperatures ($T<40$ K) an intense ESR spectrum belonging to the intrinsic $(WO_4)^{3-}$ center usually arises[18,19] [Fig. 1(a)]. Heating the sample up to 50–60 K completely destroys $(WO_4)^{3-}$ centers, while a new ESR center appears [Fig. 1(b)]. Alternatively, this new center can be produced by direct irradiation at $T=60$ K. The same effect can be obtained under x-ray irradiation. It will be shown below that this new ESR center can be ascribed to a paramagnetic $(WO_4)^{3-}$-La^{3+} complex. There are four magnetically nonequivalent $(WO_4)^{3-}$-La^{3+} centers which differ in their g-tensor axes orientations and exhibit a strong g-factor anisotropy in the (ab) crystal plane. If, in a following step, the crystal is cooled down again to $T<40$ K and irradiated by red light (671 nm) at that temperature, $(WO_4)^{3-}$-La^{3+} centers completely disappear and the polaronic $(WO_4)^{3-}$ centers arise again [Fig. 1(c)].

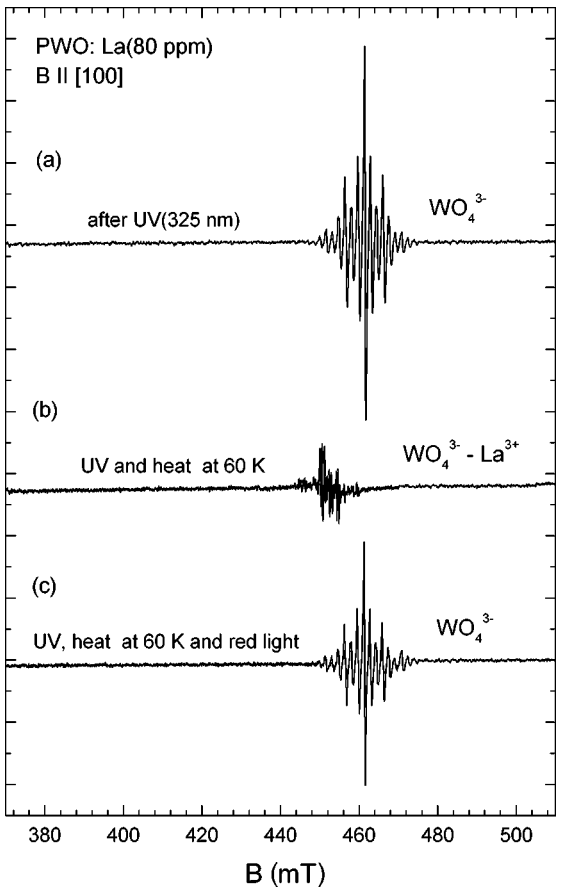

FIG. 1. ESR spectra of light-induced centers in $PbWO_4$: (a) after irradiation at 40 K [$(WO_4)^{3-}$ center]; (b) after irradiation at 40 K and subsequent heating up to 60 K [$(WO_4)^{3-}$-La^{3+} center]; (c) after irradiation at 40 K, subsequent heating up to 60 K, cooling back to 40 K and illumination by red light (671 nm) [$(WO_4)^{3-}$ center].

Angular dependencies of resonance magnetic fields were described by a spin Hamiltonian of rhombic symmetry taking into account only $1/2\rightarrow-1/2$ electron-spin transition, because ^{139}La ($I=7/2$) superhyperfine (s.h.f.) lines are strongly masked by the superhyperfine pattern arising from the interaction of the paramagnetic electron with neighboring ^{207}Pb nuclei. The spectroscopic data of $(WO_4)^{3-}$-La^{3+} centers are presented in Table I. As can be seen from Table I, the principal X and Y axes of the centers coincide with the $\langle110\rangle$ crystal axes and the Z axis is deviated from the c crystal axis by 3°.

Our assignment of the observed spectrum to the $(WO_4)^{3-}$ paramagnetic center pertubed by lanthanum is based on the following arguments.

TABLE I. ESR parameters of $(WO_4)^{3-}$-La^{3+} centers in PWO.

Center	g factor	Thermal stability
$(WO_4)^{3-}$	$g_{[001]}=1.733(1)$	50 K ($E_a=50$ meV)
	$g_{[100]}=1.476(1)$	
$(WO_4)^{3-}$-La^{3+}	$g_{[001]\pm3^0}=1.770(1)$	95 K ($E_a=270$ meV)
	$g_{[1\bar{1}0]}=1.542(1)$	
	$g_{[110]}=1.471(1)$	

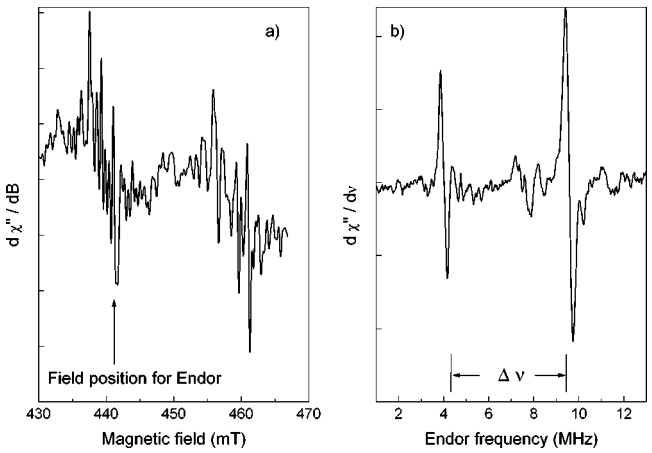

FIG. 2. (a) ESR spectrum of $(WO_4)^{3-}$-La^{3+} center at $B\|[110]$; $\nu=9.5$ GHz, $T=20$ K. (b) ENDOR resonances measured on the ESR line at $B=442$ mT; $T=10$ K.

(i) The values of g_{zz} and $1/2(g_{xx}+g_{yy})$ are close to those found for the $(WO_4)^{3-}$ center (see Table I for comparison).

(ii) The anisotropy of the g tensor suggests that one of four lead ion sites in the (ab) plane is the place of a disturbing defect. Taking into account that the spectrum was observed only in the crystals doped by La and that due to its ionic radius La^{3+} substitutes for Pb^{2+} cations, we can expect, namely, La^{3+} as the most probable candidate for such a defect.

(iii) Direct electron-nuclear-double-resonance (ENDOR) measurements performed on this center unambiguously prove that manifold of superhyperfine lines is due to the interaction with ^{139}La, since the frequency separation $\Delta\nu=5.32$ MHz between the ENDOR doublet exactly corresponds to the difference in nuclear Zeeman splitting for this nucleus at the external magnetic field used (Fig. 2).

It should be mentioned that the s.h.f. pattern in $(WO_4)^{3-}$-La^{3+} center is much more complex in comparison with a simple $(WO_4)^{3-}$ center. Substituting one of the neighboring Pb^{2+} ions for La^{3+} makes superhyperfine splittings from ^{207}Pb nuclei nonequidistant. As a result a great number of overlapping superhyperfine lines makes any detailed analysis of this s.h.f. interaction impossible.

The proposed local model for $(WO_4)^{3-}$-La^{3+} center is schematically shown in Fig. 3. In general, due to the tetragonal symmetry of PWO, the electron should be localized with equal probability at each of four tungstate ions closest to La^{3+} to conserve a tetragonal symmetry of the center as before trapping the electron. The observed s.h.f. structure as well as g-factor symmetry clearly indicate that the electron is localized only at one of four tungstate ions. This means that after being trapped, the electron lowers its local energy level and a potential barrier appears, which prevents its moving towards the other three W^{6+} ions. Such an energy decrease can be considered due to pseudo-Jahn-Teller effect, which gives rise to a rhombic distortion of $(WO_4)^{3-}$ complex as well as a displacement of related W^{5+} ion in the direction opposite to La^{3+} (see Ref. 21). In fact, a deviation of the Z axis of the center from the c crystal axis by 3° supports this assumption. A simple geometric calculation shows, that a deviation of the principal Z axis can lead to the displacement of W^{5+} from their central position of about 0.0052 nm.

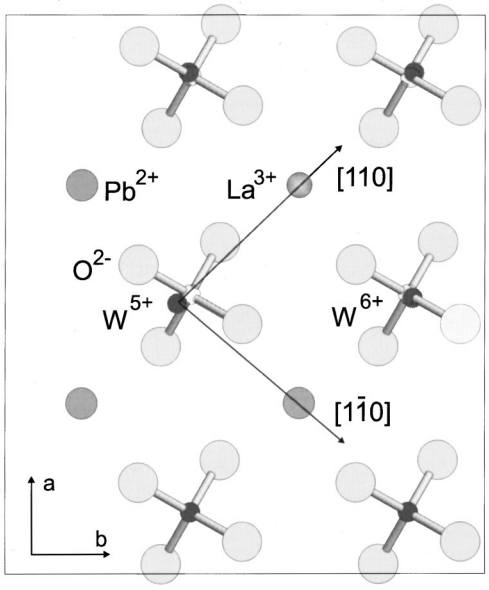

FIG. 3. Model of $(WO_4)^{3-}$-La^{3+} center in $PbWO_4$. Projection of one layer of $(WO_4)^{2-}$ tetrahedra on the (001) plane is shown.

B. Thermally stimulated luminescence

In order to further investigate carrier trapping in lead tungstate, TSL measurements were also performed. As it will be shown below, a TSL structure characteristic for the La-doped samples has been put in evidence, and the existence of a correlation between the ESR and TSL characteristics has been found. The contour plots of the TSL measurements obtained after irradiation at 10 K of both undoped and La-doped crystals are shown in Figs. 4(a) and 4(b), respectively. Common TSL structures are observed at 20–30 K and at around 50 K, with emission peaking in the blue spectral region. As already mentioned in Sec. I, this latter structure was recently studied in detail and related to the $(WO_4)^{3-}$ ESR active defect.[20] Moreover, the La-doped sample displays another intense structure at around 100 K: as already pointed out in Ref. 20, a peak in the same temperature region was only barely detectable in the undoped sample. This structure is characterized by an emission similar to that observed at lower temperatures. In Fig. 5 the TSL glow curve is reported after x-ray irradiation at 60 K, and obtained by integration of the wavelength-resolved measurement in the investigated spectral range. The glow curve exhibits two peaks at 75 and 96 K. In the following, the analysis of the trap depths corresponding to these peaks (particularly the 96 K principal structure) is presented by two different methods: (i) the so-called ''initial rise'' method and (ii) the numerical fit based on general order kinetics. The analyses were performed after several subsequent heatings of the sample up to selected temperatures between 70 and 99 K (partial cleaning) in order to separate the individual glow peaks. The inset of Fig. 5 displays the analysis by the initial rise method performed on the glow curves obtained after partial cleaning at 70 K [curve (a)] and at 94 K [curve (b)]: The corresponding trap depths were determined to be 0.15 and 0.25 eV for the 75 and 96 K peaks, respectively. The numerical fit of the main 96 K peak was then attempted. Some experimental evidences suggested the presence of a complex recombination process, possibly due to charge carriers retrapping. In fact, a slight shift of the temperature maximum of the peak was noticed by increasing the partial cleaning temperature (T_{max} is shifted to 102 K by

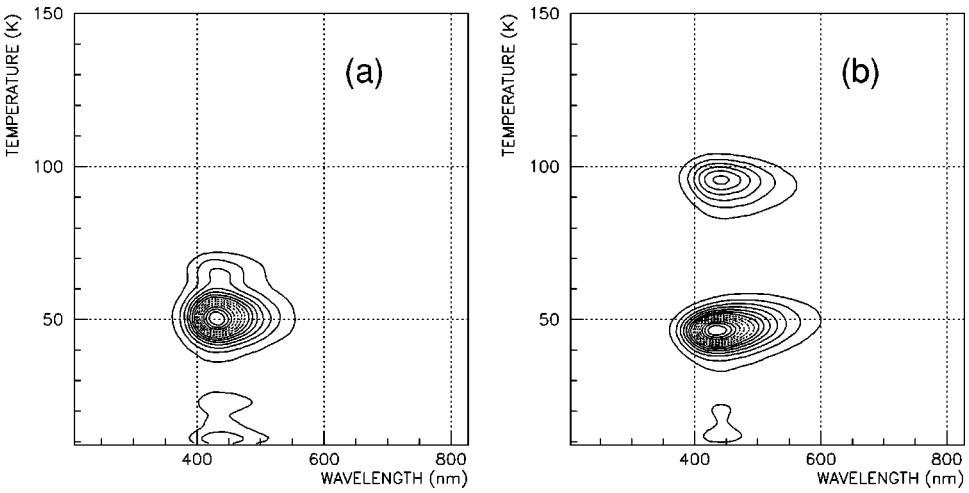

FIG. 4. TSL contour plots following x-ray irradiation at 10 K of (a) undoped PWO; (b) La^{3+}-doped PWO.

a partial cleaning at 99 K); moreover, a recombination process of higher order is also suggested by the symmetrical shape of the glow peak. For these reasons, a fit of the TSL intensity $I(T)$ considering general order recombination kinetics was performed, based on the following empirical equation:[22]

$$I(T)=s''n_0\exp(-E/kT)\Big/\left\{1+[(b-1)s''/\beta]\times\int_{T_0}^{T}\exp(-E/kT)dT\right\}^{b/(b-1)}, \quad (1)$$

where n_0 is the number of initially populated traps, E is the thermal depth, b is the order of the kinetics, β is the heating rate; s'' is defined as $sn_0^{(b-1)}/RN$, where s is the frequency factor, R is the ratio between the transition coefficients of trapping and recombination for electrons in the conduction band, and N is the concentration of available electron traps. The results are depicted in Fig. 6: the fit was performed simultaneously for three glow curves obtained after partial cleaning at 90, 94, and 99 K, and by considering the trap depth, the order of kinetics b, and the s/RN value as common parameters. The simultaneous fit of these three glow curves allowed us to consider directly the dependence of $T_{\max}$ from the initial trap population, as expected in a general order recombination process.[23] On the other hand, possible slight variations of the kinetics order due to the different trap filling in the considered glow curves were here neglected. The results gave $E=0.27$ eV and $b=1.6$; a very good fit is obtained for curves (b) and (c), while the lower quality of the fit of curve (a) could be due to a residual presence of the 75 K structure in the low T side of the peak. It is worth remarking that a good agreement is found between the values of trap depth evaluated by this method and by the initial rise method. We point out that the existence of two closely lying peaks could also in principle account for the observed shift of $T_{\max}$ with partial cleaning temperature, and this possibility was not *a priori* excluded. However, the existence of a composite structure of the 96 K peak was never proved in our measurements, neither by changing the partial cleaning temperature, nor by varying the irradiation dose.

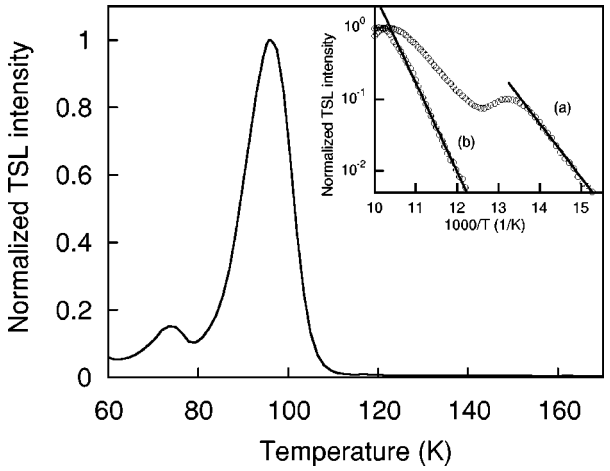

FIG. 5. TSL glow curve of La-doped PWO following x-ray irradiation at 60 K. The inset shows the Arrhenius plots of the TSL curves obtained after partial cleaning at (a) 70 K; (b) 94 K. The solid lines are exponential fits based on the initial rise method.

C. Thermal stability of $(WO_4)^{3-}$-La^{3+} center and correlation with TSL

The thermal stability of $(WO_4)^{3-}$-La^{3+} centers is apparently higher with respect to the intrinsic $(WO_4)^{3-}$ ones. Un-

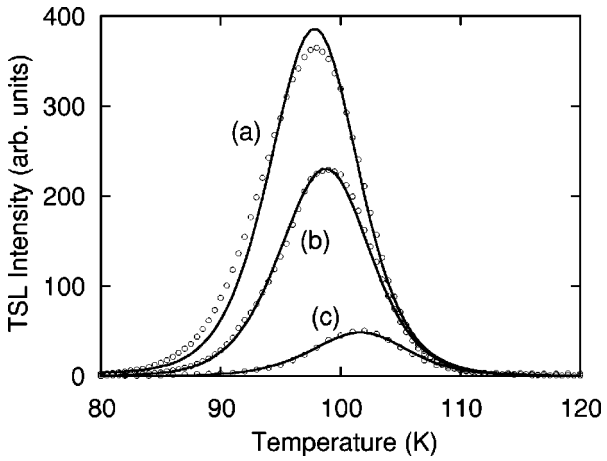

FIG. 6. TSL glow curves of La-doped PWO after different partial cleaning temperatures. (a) 90 K; (b) 94 K; (c) 99 K. Solid lines are numerical fits, based on general order recombination model.

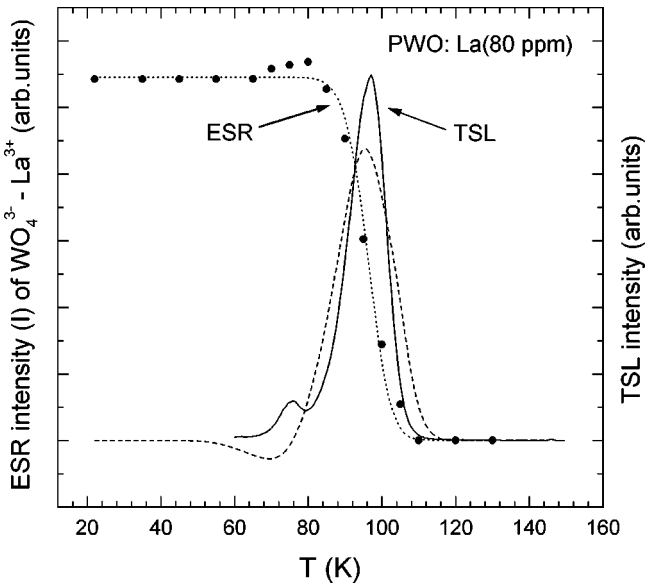

FIG. 7. Comparison between the TSL intensity and the thermal stability of $(WO_4)^{3-}$-La^{3+} centers. Filled circles and solid line are ESR and TSL intensity, respectively; dotted line is calculated ESR intensity. The first derivative of the ESR signal is represented by a dashed line.

fortunately their decay cannot be studied directly because of strong ESR line broadening as a result of faster spin-lattice relaxation with increasing temperature. Therefore we used a different approach: first the crystal was irradiated at about 20 K and then heated up to 60 K in order to create $(WO_4)^{3-}$-La^{3+} centers. The ESR spectrum was then recorded under identical conditions at $T=22$ K before and after a 2 min annealing at higher temperatures. The experimental results obtained are shown in Fig. 7 by solid circles. The decay rate of the concentration of the centers as a function of temperature is given by the first derivative of the signal (dashed line). In a crude approximation, the first derivative of the ESR signal can be compared with the TSL intensity (solid line in Fig. 7). It is clearly seen that the peak positions nearly coincide; the small difference of the temperature maxima (approximately 2 K) could be reasonably accounted for by the slightly different heating cycles used, and by the different irradiation conditions. Such coincidence can be considered as a qualitative proof of a correlation between the trap responsible for the TSL peak at 96 K and the $(WO_4)^{3-}$-La^{3+} electron center. This correlation is further supported by a numerical reconstruction of the temperature dependence of the ESR intensity, obtained by using the following equation derived from Eq. (1):

$$(I/I_0)^{(1-b)/b}=1+A\exp(-E/kT)t, \qquad (2)$$

in which $E=0.27$ eV and $b=1.6$, as derived from the TSL analysis, while $A=(b-1)s''$ is left as a free parameter. A good numerical reconstruction of the experimental data was obtained (dotted line in Fig. 7). The correspondence of the TSL glow curve and the $(WO_4)^{3-}$-La^{3+} center concentration temperature dependence becomes evident also from another fact: if the electron trapped at the *W* site has in its close neighborhood (at a distance of 0.386 nm) one trivalent cation, it will be subjected to the attractive force of one additional elementary charge. Taking into account the dielectric constant of PWO (Ref. 24) ($\varepsilon=23.6$) this results in an additional electrostatic energy of 0.16 eV which is in an approximate agreement with the difference of thermal activation energies for the intrinsic and La-perturbed centers.

At $T=75$–80 K, the concentration of $(WO_4)^{3-}$-La^{3+} centers increases by 5–10 %. This could be tentatively explained by considering also the TSL peak at 75 K, whose origin is presently still not determined. In fact, it can be suggested that electrons freed from traps responsible for the 75 K peak move towards La^{3+} sites creating additional $(WO_4)^{3-}$-La^{3+} paramagnetic centers.

Finally, the effect of a thermal treatment on both ESR and TSL was investigated: it was found that annealing of the lanthanum doped sample at 850 °C in oxygen reduces the intensity of the TSL peak at 96 K, while the 50 K peak is left unchanged. At the same time, the number of $(WO_4)^{3-}$-La^{3+} centers becomes much smaller. This corresponding behavior provides further support for the correlation between $(WO_4)^{3-}$-La^{3+} centers and the TSL peak at 96 K.

IV. DISCUSSION

As it was described above, $(WO_4)^{3-}$-La^{3+} centers can be created both by direct irradiation at 60 K or by heating previously irradiated (below 40 K) samples up to $T=60$–80 K, when the polaronic $(WO_4)^{3-}$ centers become thermally ionized. This second procedure demonstrates that not all the electrons detrapped from $(WO_4)^{3-}$ centers recombine with holes giving rise to the TSL peak near 50 K (see Ref. 20). Part of them move towards $(WO_4)^{2-}$ sites pertubed by lanthanum and deeper $(WO_4)^{3-}$-La^{3+} complex centers are created [Fig. 1 (b)]. A subsequent cooling of the crystal at $T<40$ K, followed by irradiation with red light (671 nm) completely converts $(WO_4)^{3-}$-La^{3+} centers into polaronic $(WO_4)^{3-}$ centers again [Fig. 1 (c)]. This suggests that the electrons, detrapped under red light irradiation, move only on a short distance since they are localized immediately at the polaronic $(WO_4)^{3-}$ levels with a higher probability than that of recombination with localized holes. This is in agreement with the absence of photoconductivity below 150 K (see Refs. 19 and 25).

The thermal stability of $(WO_4)^{3-}$-La^{3+} centers is limited to 95–98 K; according to the present study, $(WO_4)^{3-}$-La^{3+} centers can be identified with the traps responsible for the 96 K TSL peak.

We point out that the mechanism for the creation of $(WO_4)^{3-}$-La^{3+} here proposed could be possibly applied also to other rare-earth dopants (Y^{3+},Lu^{3+}), the ESR spectra of which were shortly described in Ref. 19.

Some comments on the hole centers participating in the recombination process might be deserved.

(i) Due to the fact that we did not find any significant difference in the concentration of $(WO_4)^{3-}$-La^{3+} centers (5–20 at. pm) in the 80 and 460 ppm La-doped PWO samples, the number of electronic centers must be limited by the hole ones, so that the origin of the latter may be related to the impurity-based or intrinsic point lattice defects. This conclusion also follows from the fact that under UV irradiation $(WO_4)^{3-}$ concentration starts to grow rather slowly and becomes saturated at a level, which is comparable (within less

than one order of magnitude) to the number of centers created by x-ray irradiation (approximately 50 Gy).

(ii) The hole centers created by irradiation at low temperatures are very probably deeper with respect to the electronic ones because the TSL peaks at 50–100 K are related to the thermal ionization of electronic centers. With respect to this interesting hints have been recently found concerning other tungstate scintillators like $BaWO_4$ and $ZnWO_4$ (see Refs. 26 and 27). For both materials, in contrast to $PbWO_4$ (see Ref. 28), no contribution of cation states to the valence band is expected. Consequently, typical (self-) trapped holes at one of the oxygen ligands are created by x-ray irradiation. Their recombination with trapped electrons gives rise to the TSL peak in the 50–70 K temperature range, too. In contrast to PWO, however, in both Ba and Zn tungstates the holes are the mobile species initiating similar emissions.

(iii) The nature of the recombination partners for the electrons released from both $(WO_4)^{3-}$ and $(WO_4)^{3-}$-La^{3+} traps is still a matter of debate. The TSL emission spectrum of undoped and La^{3+}-doped $PbWO_4$ crystals was discussed in detail in Ref. 20: at 50 K, blue emission peaking at 2.85 and 2.8 eV characterizes the spectrum of undoped and La^{3+}-doped samples, respectively. The latter emission band again dominates the TSL spectrum of La-doped PWO in the 100 K region. On the other hand, green emission (2.5 eV) was observed in the TSL at 100 K of the undoped sample. The blue emission was ascribed to a transition within a regular $(WO_4)^{2-}$ group,[29] while a correlation with (WO_3) defect[30] and the presence of Mo impurity ions[31–33] was proposed for the 2.5 eV band. The slight redshift of the blue emission observed in the La^{3+}-doped sample with respect to the undoped one could suggest an influence of doping on this band. It is worth noting again that very similar TSL spectra around 100 K were observed also for Gd^{3+}-, Lu^{3+}-, and Y^{3+}-doped PWO.[14] On the contrary, rather complex defect- and/or impurity-related emissions in the green-red spectral regions are detected in the cases of Mo, Nb, Eu and in Pb-rich crystals.[14,34,35] Unfortunately, the assignements of all TSL emission bands to specific lattice sites are far from being established, also due to the fact that the nature of hole centers could not be determined until now because no such centers were evidenced by EPR. This might be connected with a strong temperature dependence of the spin-lattice relaxation of the hole centers or, most probably, to the fact that these centres are not paramagnetic. Anyway, hole centers should be neither the simple Pb^{3+} nor O^- defects, as both of them should be observable by EPR. Future studies should take into account the possibility that dopant ions have both (i) an indirect role in modifying the concentration of intrinsic optically active defects and (ii) a direct participation in the structure of additional recombination centres.

V. CONCLUSIONS

In this study, an electron center created by low temperature UV or x-ray irradiation of a lanthanum doped lead tungstate has been investigated by ESR, and ascribed to an electron localized at a tungstate group perturbed by a La^{3+} nearby [$(WO_4)^{3-}$-La^{3+} complex]. Such assignment is supported by the results of ENDOR measurements.

Moreover, this center has been identified with the electron trap responsible for a TSL peak observed at 96 K for the same kind of crystal, and characterized by a thermal depth $E=0.27$ eV. This correlation results from a good correspondence between the numerical analysis of the TSL glow peak and of the thermal dependence of the ESR signal.

The spectral distribution of the TSL features one emission band at 2.8 eV: the recombination process between electrons thermally freed from $(WO_4)^{3-}$-La^{3+} traps and hole centers has been discussed, also in comparison with the data obtained from literature concerning $PbWO_4$ doped by other aliovalent ions, and the low temperature carrier trapping-recombination features in various tungstates.

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