

Hole capture in PbWO₄:Mo,La(Y) scintillator crystalsV. V. Laguta,¹ M. Buryi,¹ M. Nikl,¹ J. Rosa,¹ and S. Zazubovich²¹*Institute of Physics AS CR, Cukrovarnicka 10, 162 53 Prague, Czech Republic*²*Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia*

(Received 8 December 2010; revised manuscript received 11 February 2011; published 31 March 2011)

The processes of hole localization in PbWO₄:Mo,La(Y) single crystals were investigated by electron spin resonance. It was found that the holes created by uv irradiation are trapped at the regular oxygen ions in the vicinity of perturbing defects such as lead vacancies, impurity ions (La,Y), and other lattice imperfections. This leads to a variety of O⁻ centers which differ in both the thermal stability (from about 160 K up to 240 K) and spectroscopic parameters. The thermal release of such trapped holes and their subsequent recombination with electrons stored at different traps, including (MoO₄)³⁻ complexes, are accompanied by the appearance of the thermally stimulated luminescence peaks located at around 190 K and in the 225–250 K range.

DOI: [10.1103/PhysRevB.83.094123](https://doi.org/10.1103/PhysRevB.83.094123)

PACS number(s): 61.72.-y, 71.38.Ht, 61.82.Ms, 76.30.Mi

PbWO₄ (PWO) is a high-density scintillator with fast intrinsic luminescence applied in the new generation of high-energy physics detectors. For example, the crystal is used as a scintillator in the CMS and ALICE detectors at the Large Hadron Collider in CERN.^{1,2} However, the low light yield of this crystal remains a serious drawback which disables its use in other applications. Recently, some progress in the increase of the light yield was achieved by double doping with Mo and La or Y.^{3,4} Such doping provides a light yield increase by a factor of 2–3 without deterioration of other scintillation characteristics. In PWO, the intrinsic luminescence is of excitonic nature and a charge transfer transition at the (WO₄)²⁻ oxyanion complex gives rise to emission in the blue spectral region.⁵ Self-trapped excitons thermally disintegrate already at around 150 K. Therefore, any shallow trap states in the PWO lattice taking part in carrier capture processes become very important. They modify the migration characteristics of free charge carriers through retrapping. Consequently, the speed of their delayed radiative recombination is altered.

The use of thermally stimulated luminescence (TSL) and electron spin resonance (ESR) experiments proved efficient to gain insight into the nature of traps and details of the energy storage in the PWO lattice. Specifically, electron-type traps have been well investigated in this crystal (see, e.g., the review⁶). However, the problem of the origin of the radiative recombination centers in TSL processes, i.e., the counterpart hole traps, is not yet resolved and no such hole traps were evidenced within the ESR studies. Hole stabilization by another defect seems necessary due to the low probability of hole self-trapping in the PbWO₄ lattice.⁷ The possible nonparamagnetic character of the hole states suggests that a couple of trapped holes could be stabilized around a lead vacancy to restore the local charge balance.⁸ An indirect indication of the existence of hole defects has been observed in Mo, La-doped and some other PbWO₄ crystals.^{9,10} A possible coupling between the La³⁺ impurity and Pb vacancy was proposed from electrical measurements.¹¹ However, no direct observation of hole defects in PbWO₄ crystals has been reported yet.

In this paper, we provide direct evidence of the existence of intrinsic (related to regular lattice ions) hole centers in PWO doped with Mo and La(Y) from the study of their ESR spectra.

It was found that the holes created by uv irradiation are trapped at the lattice oxygen ions near the lead ion vacancy (V_{Pb}) and impurity ions forming a variety of O⁻ centers with the thermal stability ranging between about 160 and 240 K.

Crystals with concentrations of 40–1200 ppm of Mo and 80–120 ppm of La or Y were grown by the Czochralski method from high-purity (99.999%) raw materials. The ESR measurements were performed at 9.22–9.25 GHz in the temperature range 10–290 K using an Oxford Instrument ESR9 cryostat. A mercury high-pressure arc lamp with broad (300–370 nm, centered at 330 nm) and narrow (313 nm) bandpass filters was used for the optical irradiation of the samples. For the TSL study, the crystal was selectively irradiated at 140–250 K in the 4.7–3.5 eV energy range with a deuterium lamp through a monochromator. The TSL glow curves were measured with a heating rate of 0.2 K/s⁻¹.

Prior to any irradiation, only traces of Gd³⁺ impurity¹² were detected in PWO:Mo,La(Y) crystals. Independently of the accidental impurities in the crystals, the irradiation in the temperature interval 155–165 K along with the presence of (MoO₄)³⁻ (Ref. 9) induces a paramagnetic defect with the ESR spectra shown in Fig. 1. When the irradiated crystals are heated up to a temperature of about 185 K, these spectra disappear and other spectra appear. Under gradual heating of the Mo,La-doped crystal from 165 to 240 K, at least six types of such spectra can be distinguished (Fig. 1, left panel). In the crystal doped with Mo,Y, only two types of photoinduced centers are visible (Fig. 1, right panel). It will be shown below that all the created spectra are associated with a hole trapped by an oxygen ion, i.e., O⁻ centers are created. We denote them as O_I up to O_{VI}. It should be noted that the O⁻ spectra can be measured by the conventional ESR technique starting from 30–40 K up to the temperatures of their thermal destruction. At lower temperatures, due to the relatively long spin-lattice relaxation time, the O⁻ ESR spectra strongly decrease in intensity until they completely disappear. In addition, the concentration of the hole centers depends on both the irradiation temperature and the photon energy. Depending on the thermal stability, the O⁻ centers can be effectively created under irradiation in the 150–240 K temperature range. In particular, the concentration of O_I centers almost exponentially decreases with decreasing irradiation temperature at $T < 160$ K.

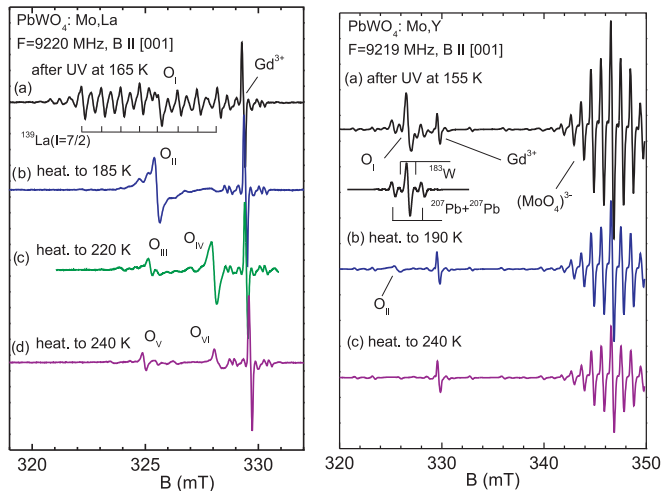


FIG. 1. (Color online) ESR spectra of various O^- centers created in PWO:Mo,La (left panel) and in PWO:Mo,Y (right panel) by uv irradiation at 155–165 K followed by heating up to a given temperature. The spectra are measured at 60 K. This figure also illustrates the transformation of one O^- center into another. The simulated hf structure is presented for the O_I center in a Mo,Y-doped crystal.

The spectrum of the first center in PWO:Mo,La shows a pronounced hyperfine (hf) structure which with $\mathbf{B} \parallel \mathbf{c}$ consists of eight equidistant major lines accompanied by other less intense satellite lines [Fig. 1(a)]. This hf structure is clearly produced by the interaction of a paramagnetic particle with the ^{139}La nucleus which has the nuclear spin 7/2 and natural abundance 100%. The spectra of the other centers also show hf structure in their resonance lines. However, the hf lines are much less intense than the central lines. The detailed analysis of these hf structures suggests that a paramagnetic particle interacts with both ^{183}W ($I = 1/2$, 14.4%) and ^{207}Pb ($I = 1/2$, 22.6%) nuclei. The simulated hf structure for O_I center in PWO:Mo,Y is shown as an example in Fig. 1(a), right panel. For this center, all the hf lines are clearly visible. The strongest splitting is produced by two nearly equivalent ^{207}Pb nuclei, while the smaller splitting is produced by a single ^{183}W nucleus.

In order to identify the origin of the observed spectra, we measured their angular dependencies at two crystallographic planes: (001) and (100). The results are shown in Fig. 2 for the O_I center in PWO:Mo,Y and O_{II} center in PWO:Mo,La. The latter center has practically the same spectroscopic parameters in both crystals. For an arbitrary orientation of the magnetic field, the spectra of all the centers consist of four central lines which pairwise coincide when the magnetic field is rotated in the ab plane. For $\mathbf{B} \parallel \mathbf{c}$, all the four lines merge into one. These facts indicate that each of the paramagnetic centers occupies four magnetically inequivalent positions in the lattice. These lattice positions can be related to oxygen sites only, as follows from the structure of the WO_4 tetrahedron which contains four oxygen ions at sites with C_1 symmetry (see, e.g., O^- centers in CaWO_4).¹³ Together with positive g factor shifts, all these facts indicate that the paramagnetic substance is a hole trapped at the lattice oxygen ion.

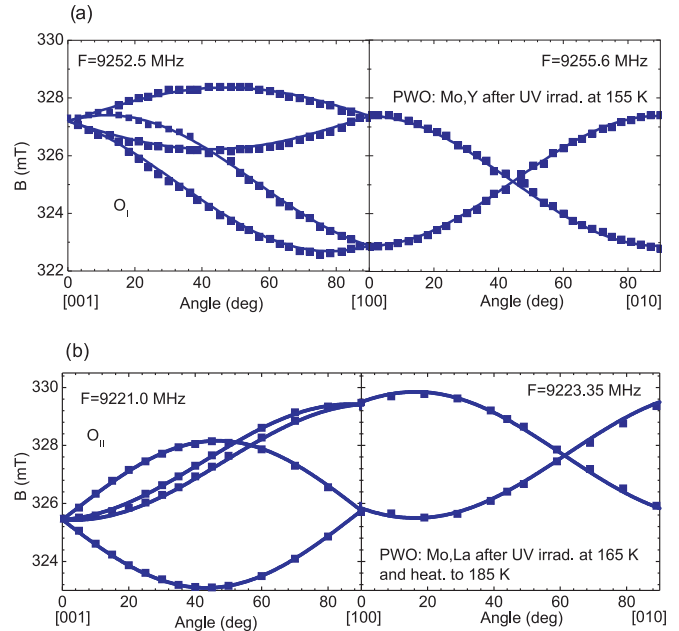


FIG. 2. (Color online) Angular dependences of resonance fields for (a) O_I center in PWO:Mo,Y and (b) O_{II} center in PWO:Mo,La. The measured and calculated resonance fields are shown by symbols and solid lines, respectively.

The resonance fields of $1/2 \leftrightarrow 1/2$ electron transitions were described by a spin Hamiltonian with spin 1/2, and the g factors and principal-axis directions for two of the centers are presented in Table I. The parameters of other centers will be presented elsewhere. One can see that the g tensor components are typical for O^- trapped hole centers¹⁴ and their values are close to those reported for isostructural CaWO_4 crystals.¹³ One can, therefore, conclude that, similarly to the trapped holes in CaWO_4 , the electron deficiency is created at oxygen orbitals of π type. In Table I, we also include the hyperfine constants. Electron-nuclear interactions are nearly isotropic and are in the range between 1.3 mT for ^{183}W and 2.8 mT for ^{207}Pb nuclei. The last column in Table I contains the temperature of the thermal stability.

The thermal stability of O^- centers was studied by the method of pulsed heating. After irradiation at the selected temperature T_{irr} , the sample was heated at a rate of 1–2 K/s up to a certain temperature T_{an} , held at that temperature for 3 min and then quickly cooled (with a rate of 4 K/s) to a fixed temperature where the ESR intensity was measured. Except for the irradiation, which was done only once at the first step, this procedure was repeated for different temperatures T_{an} . The 3 min interval turned out to be the best compromise to ensure good thermalization of the sample and sufficient reproducibility of the measured ESR intensities. Measurements at low temperatures were necessary in order to avoid the influence of the spin-lattice relaxation on the spectral linewidth and signal intensity. The signal amplitudes obtained in such a way are depicted in Fig. 3. One can see that as a result of the heating, the spectrum of the O_I center vanishes gradually and another spectrum appears. With continued heating, the new spectrum also vanishes and other spectra appear; i.e., the hole centers are gradually transforming one into the other. Obviously, this

TABLE I. Spectral characteristics of the hole traps in the PbWO_4 crystals obtained from the ESR data. The principal axis directions of g tensors are given by polar (θ) and azimuthal (φ) angles relative to the a, b, c crystal axes and presented for one of four equivalent centers. The error margin of the polar and azimuthal angles is approximately 2° .

| Center | g tensor | Principal axes | | hf interaction ^a | Temperature of thermal stability; see Fig. 3 |
|--------------------------|----------------------|----------------|-----------|-----------------------------|--|
| | | θ | φ | | |
| O_I^{Y} | g_1 2.0142(5) | 46 | 351 | A^{W} 1.5 mT | ~ 160 K |
| | g_2 2.0274(5) | 78 | 93 | A^{Pb} 2.8 mT | |
| | g_3 2.0503(5) | 47 | 194 | | |
| O_I^{La} | $g_{[001]}$ 2.027(3) | Not determined | | A^{La} 0.9 mT | ~ 160 K |
| | $g_{[100]}$ 2.010(3) | Not determined | | | |
| O_{II} | g_1 1.9973(5) | 100 | 22 | A_{W}^1 1.3 mT | ~ 190 K |
| | g_2 2.0094(5) | 134 | 122 | A_{W}^2 0.7 mT | |
| | g_3 2.0400(5) | 45 | 102 | | |

^ahf splitting is measured along c axis.

transformation of O^- centers may be caused by their thermal ionization when part of the liberated holes can be re-captured at deeper traps. One can also see from Fig. 3 that the thermal destruction of O^- centers is accompanied by a corresponding decrease in the concentration of electron $(\text{MoO}_4)^{3-}$ centers and appearance of TSL glow peaks (at 187 and 227 K in PWO:Mo,La and at 192 and 238 K in PWO:Mo,Y). In the TSL spectrum, Mo-related ~ 2.4 eV emission is observed. It proves that the liberated holes recombine with the electrons localized at $(\text{MoO}_4)^{3-}$ centers which remain stable up to yet higher temperatures. The creation spectra of the TSL peaks indicate that O^- centers are most effectively created under irradiation in the 4.1–4.2 eV energy range where

the photothermally stimulated disintegration of the localized excitons takes place.¹⁵ In the general case, however, the hole-related TSL peaks can overlap with the electron-type TSL peaks located in the same temperature range.^{6,10,15}

Models of the hole centers result from the analysis of g tensors and hf structure. The g factors indicate that the hole is mainly localized at one of the oxygen ions perturbed by a lattice defect. Determination of the origin of this defect is usually a difficult problem even for ESR. However, as the hf structure of the first center in PWO:Mo,La is clearly dominated by the contribution from the ^{139}La isotope, the oxygen ion with a trapped hole has to be perturbed by the La^{3+} ion which substitutes for Pb^{2+} . The excess of positive charge from the

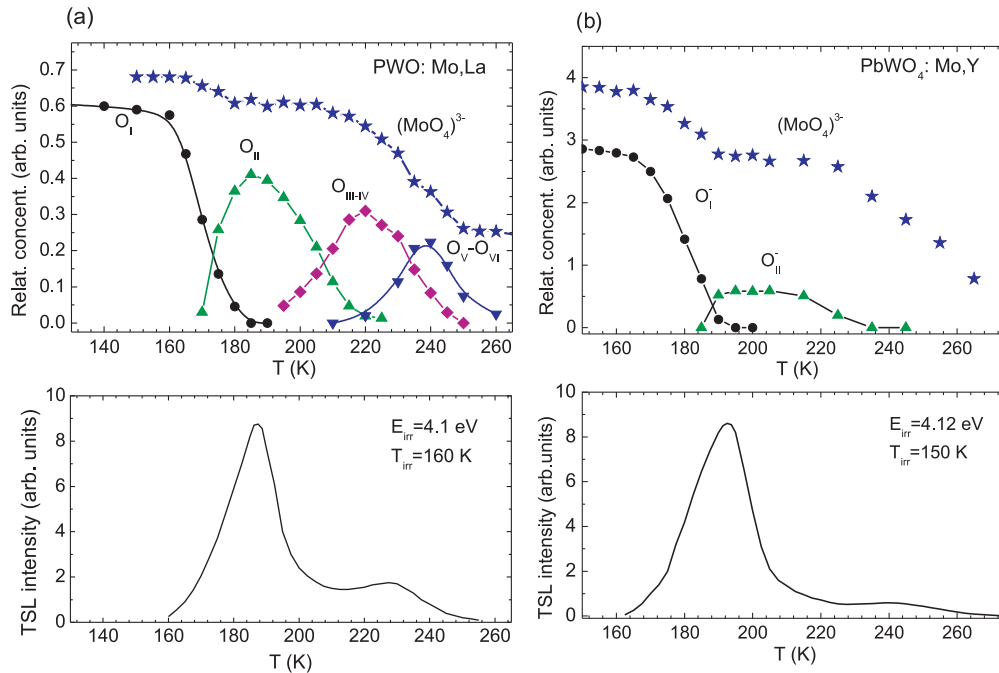


FIG. 3. (Color online) Dependence of O^- and $(\text{MoO}_4)^{3-}$ ESR intensities on the temperature of pulsed annealing measured at 90 K in PWO:Mo,La (a) and PWO:Mo,Y (b) showing transformation of one hole center into another (the upper graphs, see also Fig. 1). TSL glow curves measured for the same crystals are presented in the lower graphs. Note that due to different crystal heating conditions used in the ESR and TSL measurements, each TSL peak is shifted (about 15 K) toward higher temperatures with respect to the temperatures where the ESR signal intensity from the corresponding center decays.

La^{3+} ion in this center can be compensated by a lead vacancy. One can also suppose that some of the La^{3+} ions substitute at the tetrahedral sites, i.e., for W^{6+} . In this case, holes can also be localized in the vicinity of La^{3+} ions. However, at a low doping level, the probability of such substitution is very low due to the much larger ionic radius of La^{3+} as compared to W^{6+} , about 0.9 and 0.42 Å, respectively. Recent theoretical calculations¹⁶ have shown that the formation energy of the point defect La_W is so high that such a defect can hardly exist in the crystal. These calculations also suggest that, in slightly La-doped PWO, the main compensating mechanism is $[2\text{La}_{\text{pb}}^+ + \text{V}_{\text{pb}}^{2-}]$. Our experimental results partly support these theoretical predictions. The ESR data suggest that in PWO:Mo,La, the compensating mechanism should be in the form of $[\text{La}_{\text{pb}}^+ + \text{V}_{\text{pb}}^{2-}] + \text{O}^-$ defects, i.e., the lead vacancy is attended by only one La ion. This situation is physically more realistic.

One can suppose that a similar compensation mechanism — $[\text{Y}_{\text{pb}}^+ + \text{V}_{\text{pb}}^{2-}] + \text{O}^-$ — exists in PWO:Mo,Y and is also responsible for the O_I^Y center, even though the ^{89}Y hf structure was not resolved here. The reason is the small value of the ^{89}Y nuclear magnetic moment (three times smaller than that of ^{139}La). Therefore, the expected ^{89}Y hf splitting is only about 0.3 mT, i.e., smaller than the linewidth. On the other hand, for this spectrum, the superhyperfine structure was well resolved [Fig. 1(a), right panel]. It shows that the unpaired spin interacts with two nearly equivalent ^{207}Pb nuclei and with a single ^{183}W nucleus. In the PWO lattice, each O ion is surrounded by one neighboring W ion ($d_{W-O} = 1.796$ Å) and by two more distant Pb ions ($d_{\text{Pb}-O} = 2.58$ and 2.64 Å). It is worth noting that the ^{207}Pb hf interaction is stronger due to the larger magnetic moment of ^{207}Pb and large covalency contribution. This is similar to the polaronic $(\text{WO}_4)^{3-}$ center, where ligand- ^{207}Pb hf splitting is even larger than the splitting from the ^{183}W nucleus itself. From the comparison of the spectroscopic data for the O_I center in both types of crystals, one can conclude that O^- ion is perturbed by the Y(La) impurity and V_{pb} is located at a more distant second coordination sphere. This center can, therefore, be considered a small-hole-polaron state localized near $\text{Y}_{\text{pb}}-\text{V}_{\text{pb}}$ and $\text{La}_{\text{pb}}-\text{V}_{\text{pb}}$ pairs.

In the second O_{II} center, the hole mainly interacts with two W isotopes (see Table I) similarly to the V_k center in CaWO_4 , where the electron deficiency is delocalized over two neighboring tetrahedra.¹³ As hf splitting due to Pb nuclei was not resolved for this center, the perturbation might be produced by the neighboring Pb vacancy.

We emphasize that O^- centers were observed only in the doubly (Mo,La and Mo,Y) doped crystals. In our opinion, the presence of the Mo impurity was necessary in order to create a measurable number of traps for electrons and consequently an increased number of trapped holes. La^{3+} and Y^{3+} impurities enable partial charge compensation of lead vacancies in the vicinity of which the single hole can be localized at an

oxygen ion to provide the full charge compensation of the lead vacancy defect.

The reported O^- hole centers, like any other unwanted lattice defects, should decrease the scintillation performance of the crystal. In particular, they can be easily responsible for the slower components in the scintillation decay in (Mo,Y) doubly doped crystals where the dominant emission comes from the $(\text{MoO}_4)^{2-}$ complexes in the green spectral region, i.e., where the Mo concentration is sufficiently high to suppress the intrinsic exciton-related emission component in the blue part of spectra.¹⁷ In such crystals, the generated electrons in the conduction band become promptly localized around Mo ions, while the transport and radiative recombination of the hole counterparts can be delayed due to their trapping at the perturbed oxygen ions. Nevertheless, in the La^{3+} - and Y^{3+} -containing PWO:Mo crystals (where the reported O^- centers are found), both the slow component of the green emission and the TSL intensity are strongly suppressed,^{10,17} which indicates a much smaller content of vacancy-related electron and hole traps in these crystals as compared with other PWO:Mo crystals. Furthermore, the influence of the O^- hole centers on the room temperature radiation damage characteristics will be negligible as such centers are shallow. They have quite a short lifetime at room temperature, in the millisecond range (estimated from the TSL glow peak positions). In fact, it has been shown that the doubly doped (Mo,Y) crystals show much less radiation damage with respect to the Mo-only doped or undoped crystals in a wide Mo concentration range.¹⁸ Thus, the key element in the radiation damage mechanism of PbWO_4 does seem to be the oxygen-vacancy-related electron traps which are efficiently suppressed by trivalent ion doping.¹⁹

In conclusion, a detailed ESR study of PbWO_4 :Mo,La(Y) single crystals shows that the holes created by uv irradiation are trapped at regular oxygen ions near perturbing defects such as lead vacancies, impurity ions (La, Y, Mo), and some other unidentified lattice defects. A variety of O^- centers is formed with a thermal stability of about 160 K up to 240 K. The thermal release of the trapped holes and their subsequent recombination with the electrons stored at $(\text{MoO}_4)^{3-}$ complexes are responsible for some of the TSL peaks located around 190 K and in the 225–250 K range, which, however, overlap with the electron-type TSL peaks located in the same temperature range. Finally, we emphasize that these experimental results are the same for samples of different origin and purity. Therefore, the behavior of the trapped-hole centers described above is an intrinsic property of PbWO_4 :Mo,La(Y) single crystals.

The authors gratefully acknowledge the financial support of the Czech Project No. GA AV IAA100100810, the institutional Research Plan No. AVOZ10100521, and the ESF Project No. 8678.

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