



INFLUENCE OF Mo IMPURITY ON THE SPECTROSCOPIC AND SCINTILLATION
PROPERTIES OF PbWO₄ CRYSTALS *

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Abstract

The influence of molybdenum doping on the spectroscopic and scintillation properties of lead tungstate crystals has been investigated. From the results the slow scintillation component as well as the afterglow are found to be due to the Mo impurity. In addition the blue luminescence from excited (WO₄)²⁻-complex seems to be increasingly suppressed as the doping concentration goes on. Possible mechanisms for the effects have been discussed.

1. Introduction

The spectroscopic properties of the lead tungstate single crystal PbWO₄ (PWO) were studied in detail in the 1970s [1-5]. Interest in a systematic investigation of PWO has recently increased because of its development as a scintillator for high-energy physics applications [6]. PbWO₄ is one of the prospective scintillating materials to be used in the new generation of particle physics experiments such as CMS at the new Large Hadron Collider (LHC) and at other facilities. It can provide the detection of the particles (γ , e^-) with a satisfactory energy resolution

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better than $1.5/\sqrt{E} \oplus 0.5$ starting from 50 MeV with Photo Multiplier Tube readout [7] and allows a time resolution better than 130 ps [8]. Mass-production technology for PWO is still not quite ready since the crystals produced show great sensitivity to the variations in crystal growth conditions and raw material purity. The influence of the most dangerous impurities on the scintillation properties of the PbWO_4 crystals is discussed in Ref. [9], however, the role of some of them especially the impurities which replace host-creating atoms is still a question of debate [10]. The molybdenum ion is one of the most interesting. Firstly, molybdenum creates a single crystal of PbMoO_4 (PMO) with a structure identical to PbWO_4 but without suitable scintillator properties. Secondly, the molybdenum ion is chemically very close to the tungsten ion and is rather hard to separate at the raw material production level. Finally, molybdenum impurity creates in the PbWO_4 crystals specific defects [5] which have an influence on the scintillation yield and have to be clarified. The imminent arrival of PWO scintillator mass-production motivated us to perform a detailed investigation of the influence of Mo impurity on the PWO scintillation properties. We combined relevant data obtained by some of us 20 years ago with new data obtained recently from the same samples. The results of the study are described in this paper.

2. Experimental Results

Single crystals of $(\text{PbWO}_4)_{1-x}(\text{MoO}_4)_x$ (P(Mo-W)O) were grown using the Czochralskii method described in Ref. [2]. The value of x was changed in the range from 10^{-3} to 0.25. Luminescence and luminescence kinetics by photo and gamma-ray excitation, as well as thermally stimulated luminescence (TSL), and the scintillation yield of samples with dimensions of a few cubic millimeters have been tested. The equipment and techniques used for spectroscopic and scintillation parameter measurements are described elsewhere [5], [11].

Radioluminescence spectra of the samples under excitation by a ^{57}Co source (122 keV) with $x = 0.001$ and 0.05 are shown on Fig. 1. At low impurity concentration the spectrum peaks at 490 nm, however, with an increase in its Mo concentration maximum is shifted to 520 nm. The integral radioluminescence intensity is lowered when there is an increase of the molybdenum concentration as shown on Fig. 2. The trend and spectral composition of radioluminescence band

is changed as well. The relative contribution of the luminescence with wavelength shorter than 400 nm in the total intensity decreases with the doping concentration increase. At the same time the short wavelength cut-off in the absorption spectra is changed in the investigated crystals as described in Ref. [2]. Such a change can be characterized by the 'relative cut-off' R which is defined as

$$R = \frac{BG_{PMO} - BG_{P(Mo-W)O}}{BG_{PMO} - BG_{PWO}} \quad (1)$$

where BG are the measured short wavelength cut-off or **B**and **G**ap of the PWO (325 nm, 30800 cm⁻¹), PMO (385 nm, 26000 cm⁻¹) [12] and P(Mo-W)O crystals respectively. The R value is rather well correlated with the relative intensity of the blue part of the radioluminescence band. This correlation is shown for the luminescence intensity at 400 nm in Fig. 3. Photo-Luminescence (PL) and Photo-Luminescence Excitation (PLE) spectra of doped and undoped crystals are found to be different and are presented in Figs. 4(a)–4(d). Undoped crystals show three luminescence bands with maxima 420 nm, 490 nm and 650 nm at room temperature. The lowest excitation bands of blue, green, and red luminescence bands are 325 nm (30800 cm⁻¹), 305 nm (32800 cm⁻¹) and 350 nm (28600 cm⁻¹) respectively. Just one green luminescence band is detected in Mo-doped crystals. At the smallest Mo concentration its maximum is close to 490 nm, however, similar to radioluminescence (Fig. 1) it is shifted to 520 nm as the Mo concentration increases. The excitation spectra of the green luminescence consist of an unresolved broad band with its maximum following the cut-off of the absorption spectra as shown in Fig. 5. It indicates that with Mo concentration increase those Mo correlated centers responsible for the green luminescence become dominating in the crystals. A second excitation band for the green luminescence with a maximum at 366 nm (27300 cm⁻¹) shows up as a shoulder just at the highest Mo impurity concentration. The absence in doped crystals of the blue luminescence band in the spectra by photo-excitation is due to the effect of a strong edge absorption caused by Mo doping.

All doped crystals have comparably fast luminescence kinetics by photo-excitation at room temperature, however they differ from kinetics of scintillations. This is shown for the luminescence (a, c) and the scintillation kinetics (b, d) of doped samples with $x = 0.001$ (a, b) resp. $x = 0.05$ (c, d) in Fig. 6. One should note that Mo doping led to the suppression of the fast

decaying components in scintillation. Figure 7 gives the changes of the scintillation kinetics parameters with the Mo concentration increase.

TSL spectra have been measured in the region 5–300 K. Samples activation was done by X-irradiation at liquid helium and nitrogen temperature, respectively. In Mo doped samples the spectral composition of the glow emission reveals only the green luminescence. TSL spectra on samples with an increase in impurity concentration show the same tendency as described in Ref. [4]. At the smallest Mo concentrations three groups of peaks with maxima near 50, 110 and 230 K are detected. With increasing activator concentration the intensity of some TSL peaks belonging to the high temperature group is found to be diminished drastically. The detailed analysis of the TSL data will be described in another report, here these data are used only to determine the trap parameters and their influence on scintillation. The individual trap parameters such as activation energy E , the frequency factor S and the trap's realize time (life time of temporarily trapped carriers) have been calculated by the total glow method [13]. Parameters of the bands measured are presented in the Table 1.

3. Discussion

Let us consider the role of the Mo impurity in the energy transfer processes and defect creation in PbWO_4 doped crystals. A Mo^{6+} ion replaces isomorphously a W^{6+} ion in the host and like the tungsten ion creates a molecular anionic complex MoO_4^{2-} . These tetrahedral species with T_d site symmetry which are commonly assumed to be the luminescence centers in tungsten and molybdenum scheelites are described in the frame of molecular orbital approximation by means of an extended Hückel method [14], [15]. As a result the highest occupied molecular orbital t_1 is formed by oxygen orbitals $2p(\pi)$ and is separated from the first excited $2e$ state made up from metal d - and oxygen $2p$ -wave-function by an energy of about 5 to 6 eV as seen in Fig. 8 (a). The electronic transition with lowest energy from the 1A_1 ground state corresponds to the excitation of an electron from the t_1 orbital to the $2e$ orbital. The final configuration resulting from the decomposition of the direct product representation $t_1 \otimes 2e$ is found to be 3T_1 , 3T_2 and 1T_1 , 1T_2 , respectively [16] and is shown in Fig. 8 (b). For T_d symmetry the only electric dipole allowed transition is ${}^1A_1 - {}^1T_2$. However, from studying luminescence kinetics the results of which show

an unexpected slow decay, the observed blue luminescence (420 nm, 23800 cm⁻¹) of tungstate complexes is supposed to be due to a transition involving a triplet state $^3T_1, ^3T_2-^1A_1$. The molecular orbital state 2e in (MoO₄)²⁻-complexes is usually found to be at lower energies than in the (WO₄)²⁻-complex [14], [15]. As a consequence the energy shift gives rise to the assumption that the green emission band in CaWO₄ (535 nm, 18700 cm⁻¹) originates from the analogous transition $^3T_1, ^3T_2-^1A_1$ in a regular (MoO₄)²⁻ tetrahedron. An additional optically detected magnetic resonance (ODMR) study on MoO₄²⁻-complexes directly proved this [17]. Such (MoO₄)²⁻-complexes are competitors at localization of excited matrix states and consequently reduce the importance of tungstate complexes in the scintillation.

From photoluminescence excitation measurements the lowest excitation energy of the molybdenum complex in PbMoO₄ is found to be 366 nm (27300 cm⁻¹), so the energy of the $^3T_2, ^3T_1$ levels in such complex is around 27300 cm⁻¹. Consequently in the Mo-doped crystals this transition overlaps the short wavelength wing of the WO₄²⁻ luminescence giving its quenching caused by multipole Coulomb interaction. Even if the oscillator strength of the transition into the excited state should be small the probability for the quenching process is enhanced by the contribution of electron-phonon interaction [3]. In this way with the impurity concentration increase an additional source of decrease of the WO₄²⁻ luminescence yield appears.

These two phenomena are the origin of the scintillation yield decrease and of the blue WO₄²⁻ luminescence fraction reduction in the total scintillation pointed out in Figs. 2 and 3.

Another green emission band (500 nm, 20000 cm⁻¹) is possibly caused by an analogous transition within an irregular tungstate complex. The simplest defect model is based on the concept of a WO₃-group resulting from oxygen deficiency. For the luminescence of such irregular tungstate complexes an analogous concept of quenching process based on energy transfer does not work in a reasonable manner. The green emission is shifted to longer wavelengths due to a large Stokes shift and consequently the shape indicates a vanishing overlap with the excitation band of the (MoO₄)²⁻-complex. In addition from studies of PLE the excitation energy is found to be somewhat larger as compared with that of the (MoO₄)²⁻-complex. As a result the probability of energy transfer between the excited irregular tungstate complex and the (MoO₄)²⁻-complex in ground state condition is expected to be negligible. Thus,

the yield decrease of the WO_3 groups' green luminescence in lead tungstate occurs just at the sufficient concentration of the impurity due to the decreasing amount of the irregular group when the W atoms are replaced by the Mo ones in the host matrix.

One important consequence of such quenching processes is a suppression of the fast component in the scintillation kinetics indicated in Fig. 7. The luminescence of MoO_4^{2-} groups in agreement with [3] is rather fast at room temperature, however, scintillations in Mo-doped crystals show a significant contribution of afterglow and slow components. These phenomena are found to be dependent on Mo concentration. At small Mo impurity concentration a significant background is detected in the scintillation. With the Mo concentration increase this background level in the scintillation is decreased but slow components with decay times within a range of some hundreds of nsec- μ sec show up in the scintillation kinetics. This tendency is well correlated with the creation of trap centers as seen from the data of Table 1. Centers which establish glow peaks in the region below 150 K cause just slow components in the scintillations, others with realize time parameters in the msec-sec region contribute to the afterglow. Thus following the tendency of the changes in TSL spectra the afterglow dominates in crystals at small impurity content. On the contrary at high Mo concentration slow components appear in the scintillations due to the shallow centers noted above. EPR measurements [5] have shown that $(\text{MoO}_4)^{3-}$ centers formed in irradiated samples are stable electron traps in PWO and thereby contribute to this unwanted property. Further EPR investigations are under way in order to clarify other defect structures in these materials.

However, Mo doping creates in PWO crystals relatively quickly decaying electron capturing centers. Therefore at room temperature such centers do not contribute to the permanent crystal optical transmission damage due to ionizing irradiation. Even at small impurity concentration when the most deep lying Mo-related traps are present in the crystal, their total contribution to the induced absorption in the visible region at dose rate 100 rad/h estimated within the model described in [18] does not exceed 0.01 m^{-1} .

4. Conclusion

The Mo impurity in lead tungstate crystals has a negative influence on its scintillation properties. It decreases the yield of the scintillation, suppressing scintillation of regular tungsten groups.

At higher concentration, Mo impurity causes shallow traps which give rise to slow components in the scintillation.

At low (down to trace) concentration the related traps are much deeper and therefore do not spoil the scintillation process but result in afterglow.

Although Mo impurity in PWO does not cause radiation damage stable at room temperature within the detection limit they therefore should be carefully avoided in scintillator crystals.

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Table 1

Kinetic parameters of thermoluminescence peaks detected in X-irradiated PWO crystals doped with Mo; T_{\max} : peak temperature, E : activation energy, S : pre-exponential factor, τ_t : life time of trapped carriers estimated at 300 K.

T_{\max} (K)	E (eV)	S (10^9s^{-1})	τ_t (s)
56	0.095	0.018	$2 \cdot 10^{-6}$
78	0.13	0.021	$8.2 \cdot 10^{-6}$
92	0.17	0.1	$8 \cdot 10^{-6}$
110	0.24	4.3	$2.9 \cdot 10^{-6}$
125	0.30	18	$6.0 \cdot 10^{-6}$
140	0.33	6.3	$5.5 \cdot 10^{-5}$
170	0.38	6.2	$3.8 \cdot 10^{-4}$
205	0.44	0.7	$3.5 \cdot 10^{-2}$
260	0.51	0.2	1.8

Figure Captions

- Fig. 1 Luminescence spectra of the $P(\text{Mo}_x\text{-W}_{1-x})\text{O}_4$ samples with $x = 0.001$ (a) and 0.05 (b) at excitation by ^{57}Co source, 122 keV, $T = 300$ K.
- Fig. 2 Integral of the radioluminescence spectra of the $P(\text{Mo}_x\text{-W}_{1-x})\text{O}_4$ samples with impurity concentration. ^{57}Co source excitation, 122 keV, $T = 300$ K.
- Fig. 3 Relative cut-off R versus relative intensity of the radioluminescence at 400 nm, $T = 300$ K.
- Fig. 4 Excitation and luminescence spectra of the doped and undoped crystals, $T = 300$ K.
Undoped PWO: a) 1- $\lambda_{\text{reg}} = 500$, b) 2- $\lambda_{\text{exc}} = 302$, 3- $\lambda_{\text{exc}} = 325$, 4- $\lambda_{\text{exc}} = 350$ nm.
 $P(\text{Mo}_x\text{-W}_{1-x})\text{O}$: c) 1- $\lambda_{\text{reg}} = 500$ nm, $x = 0.001$, 2- $\lambda_{\text{reg}} = 500$ nm, $x = 0.05$, 3- $\lambda_{\text{reg}} = 500$ nm, $x = 0.25$, d) 4- $\lambda_{\text{exc}} = 303, 320$ nm, $x = 0.001$ (3), 5- $\lambda_{\text{exc}} = 303, 320$ nm, $x = 0.05$ and 6- $\lambda_{\text{exc}} = 320, 370$ nm, $x = 0.25$.
- Fig. 5 Relative cut-off R versus green luminescence excitation (500 nm) in Mo-doped crystals, $T = 300$ K.
- Fig. 6 Luminescence and scintillation kinetics of the $P(\text{Mo}_x\text{-W}_{1-x})\text{O}$, $x = 0.001$ (a, b), $x = 0.05$ (c, d) respectively, $T = 300$ K.
- Fig. 7 Change of the scintillation kinetics parameters of $P(\text{Mo}_x\text{-W}_{1-x})\text{O}$ samples with Mo concentration, $T = 300$ K.
- Fig. 8 Molecular orbital energy scheme for free tetrahedral $(\text{MO}_4)^{2-}$ complexes (M: W, Mo) as calculated in [15] (a); schematic configuration coordinate model for the lowest electron transition $t_1 \rightarrow 2e$ (b).





















