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The influence of additional doping on the spectroscopic and scintillation parameters of PbWO_4 crystals

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The structural peculiarities and the influence of additional doping of PbWO_4 crystals with Nb, Bi, Yb, and Mg ions have been investigated. It is shown that even a small presence of specific impurities leads to an important redistribution of the point structure defects, the radiating centres, and their properties in the crystals. The data have been used for further optimization of PbWO_4 scintillator development for CMS ECAL.

1. Introduction

Recently, lead tungstate crystals, PbWO_4 (PWO), a fast and dense scintillator, have found an application in the electromagnetic calorimetry [1–6] of experiments to be carried out in the new Large Hadron Collider (LHC). These crystals have been under investigation for several decades, but their properties are still debated in the literature [7–9]. Significant progress with respect to the improvement of the scintillation properties has been achieved, but at least two problems have arisen which remain to be solved.

1. An additional coloration of PbWO_4 crystals still exists mainly due to the presence of the absorption band around $\lambda_{\text{max}} = 420$ nm. This band intensity varies from crystal to crystal and strongly depends on the crystal growth conditions and on the purity of the raw materials. Its intensity is decreased by the purification of the raw materials, additional recrystallization, or vacuum annealing. This band, overlapping the spectrum of the luminescence, has a typical absorption coefficient at the maximum of about $k = 0.05 \text{ cm}^{-1}$ and leads to a relatively light yield reduction of a factor of two for scintillation elements with a length of 200 mm or more. This band must therefore be suppressed when mass producing long size scintillators.
2. The scintillation properties of PbWO_4 crystals mainly come from radiating centres based on regular (WO_4^{2-}) centres, and irregular (WO_3+F) centres [4–10]. Their contribution to scintillation efficiency and scintillation kinetics strongly depends on the presence of other point structure defects and on the energy transfer processes between them in the crystals. These energy transfer processes may create the quenching of the luminescence centres or, on the contrary, create the conditions of afterglow and slow components appearance in scintillations. The point structure defects that are involved in these processes can be due to the presence of additional impurities or host matrix defects.

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Both of these problems have the same origin, i.e. a local change in the structural properties of the host matrix. This motivated us to investigate the influence of additional doping with ions which, with an *a priori* estimation, could affect (worsen or improve) the PWO scintillation properties.

2. Samples and experimental methods

The crystals investigated were grown using the Czochralski technique from platinum crucibles in an atmosphere similar to that of air with some lead deficiency in the melt. Details of the crystal growth are given elsewhere [4]. Doping with Nb, Yb, Mg, or Bi was introduced in the form of oxide in the melt. Crystals with different doping were grown in separate crucibles but all had the same amount of Nb in addition. The samples investigated in the present work were prepared from the top part of the ingots that were annealed in air. Other parts of the ingots were used for preparing the scintillation elements used in beam tests at CERN. Equipment for spectroscopic and scintillation parameter measurements are described elsewhere [10].

Detailed investigation of the crystal structure has been carried out using the experimental facilities at the University of Technology of Annecy-le-Vieux. For suitable X-ray analysis, single crystals were extracted using mechanical means. The quality of the selected crystals was checked with a precession camera, then 4340 reflections were scanned with a CAD-4 automatic four-circle diffractometer.

3. PbWO₄ crystal structure

PbWO₄ crystals occur in nature as tetragonal stolzite [11] scheelite-type, and monoclinic raspite [12]. A high pressure form has also been prepared using high temperature [13]. Previously, in analogy with PbMoO₄, the structure of PbWO₄ was claimed to be a pure scheelite structure. The scheelite-type PbMoO₄ is characterized by a square lattice of identical columns of Pb and Mo atoms parallel to the Z axis, each column being made by a regular stacking of Pb and Mo atoms. The X-ray precession photographs of PbWO₄ small crystals of 100 × 100 × 100 μm³ approximate size, showed a structure with a tetragonal symmetry but with a unit cell parameter $a = 7.719 \text{ \AA}$, which is $\sqrt{2}$ times larger than the a parameter of the scheelite structure. Refinement of single crystal X-ray diffracted intensities has revealed a new lattice structure [13] with one crystallographic site for W atoms, three different sites for Pb, and two sites for oxygen atoms in the space group P4/n nc. Moreover, the Pb(1) and O(2) sites were not fully occupied. Thus the crystal chemical formula was Pb₇W₈O_(32-x) with $x = 3.2$. The structural data and relationship of this new lattice structure with the scheelite type has been reported [11] and the structure parameters are given in Table 1.

Table 1 Structural parameters of lead tungstate

Atom	Site	X	Y	Z	Occupancy	B*eq
Pb(1)	2a	1/4	1/4	1/4	0.5(1)	2.1(2)
Pb(2)	2b	1/4	1/4	3/4	1.0	0.7(1)
Pb(3)	4c	1/4	3/4	3/4	1.0	0.9(1)
W	8f	0	0	0	1.0	0.3(1)
O(1)	16k	0.037(5)	0.181(5)	0.086(4)	1.0	0.3(1)
O(2)	16k	0.653(5)	0.095(5)	0.096(4)	0.80(5)	2.0(3)

4. Impurities and point structure defects in PbWO₄ crystals

Structural data show the existence of lead and oxygen deficiency. The lead deficiency in the Pb(1) positions is compensated by the oxygen deficiency in the O(2) sites that coordinate Pb(1) ions in the second coordinating sphere. Therefore, in agreement with Ref. [4], the irregular WO₃ groups connected with the oxygen vacancies V_O, or the F centres (V_O + 2e⁻) based on them, exist in crystals. On the other hand, the lack of Pb ions leads to the creation of O⁻ hole centres which are located near the W tetrahedra. Additional hole centres near W arise in crystals grown in an atmosphere whose composition is similar to that of air, due to oxidization of Pb³⁺ ions. Thus, two types of host matrix defects (hole centres and F centres) dominate in undoped crystals.

An additional doping of the crystals causes a significant redistribution of the host matrix defects enabling us to understand the origin and possible effects of different defects on crystal scintillation properties. Let us consider the possible influence of ions with different valence located at the Pb and W ions sites in the host. Single valent ions at the lead site will lead to the creation of O⁻ hole centres near the W tetrahedra. Ions with variable valence 2⁺ ↔ 3⁺ at the lead site will provide the same effect as the Pb ions and will create hole centres. Ions with a smaller valence at the W site such as 5⁺ will, on the contrary, prevent the creation of the hole centres near the tetrahedra. Other ions that can create tungsten compounds with the same valence as Pb or W can lead to the appearance of local crystal structure changes.

The previous considerations have motivated the investigation of the influence of Bi, Yb, Mg, and Nb doping on the scintillation properties of PWO crystals and have guided our choice of activators. With our crystal growth conditions, Bi ions are in eightfold oxygen coordination, and mainly in a trivalent state. The Yb ions, having a variable valence, will be stabilized in valence state two or three — but predominantly the trivalent state — and Mg ions will be in the 2⁺ state only.

Nb ions will be located in oxygen tetrahedra in the 5⁺ state, or compensate a W ions deficiency, or simply replace one. Additional correlation between the spectroscopic properties and the presence of other elements with variable valence was also detected.

5. Spectroscopy of PbWO₄ doped crystals

Figure 1 shows the transmission (a), luminescence and its excitation (b), and scintillation kinetics (c) spectra of the crystals doped with Bi. An increase of the absorption band peaking at 420 nm is detected. At the same time, spectra of the radioluminescence as well as the scintillation kinetics have the same shape as described in Ref. [4]. With the additional optimized procedure of vacuum annealing at 1000°C, the yellow coloration of the Bi doped crystals can be significantly decreased. The luminescence excitation and luminescence emission spectra of undoped and annealed Bi doped crystals are shown in Fig. 2. The full spectrum maximum of the luminescence excited by γ-rays is shifted in the blue region by about 30 nm compared to the unannealed crystal. It is an indication that the contribution of the green luminescence band decreases in the total spectrum of scintillations [10]. A similar effect of absorption increase is observed with Yb activation of the crystals. Data of PWO:Yb are displayed in Fig. 3. When the Yb content increases in the crystals, the intensity of the absorption band peaking at ~ λ 420 nm increases, and red luminescence excitation spectra are detected. The excitation luminescence spectra of Yb doped crystals are very close to those of Bi doped crystals annealed in vacuum. The scintillation's light yield in this crystal is suppressed significantly as indicated in the scintillation kinetics. The Mg activation does not change the typical transmission, luminescence, and luminescence excitation spectra of the PWO crystals, but reduces the light yield of the scintillations.

We have already noted [14] that Nb activation of the PWO leads to a slight increase of the transmission in the near UV region (λ ~ 350 nm) as the Nb content increases in the crystals (Fig. 4). It indicates that the presence of Nb ions suppresses the absorption band with the

maximum at 350 nm, but does not act on the band with the maximum at 420 nm. The transmission luminescence and luminescence excitation spectra of Nb doped crystals are shown in Fig. 5. They differ from the spectra of undoped crystals mainly by the absence of red luminescence and its excitation bands in the spectra, and by the appearance of a new green luminescence band slightly shifted in the yellow region compared to those of the (WO₃+F) centres. Although the 420 nm absorption band is still present in the Nb doped crystals, they do in fact exhibit a better transmission and a lighter coloration. Furthermore, Nb doped crystals show a better radiation hardness. The radiation-induced absorption band with a maximum at 620 nm in undoped crystals does not appear in Nb doped crystals [15]. We therefore conclude that the decrease of radiation damage in PWO:Nb crystals is related to the suppression of colour centres absorbing in the 350 nm band. The above-mentioned effects were found for an Nb content of about a few tens of ppm. By increasing the Nb content to a few thousand ppm, an additional suppression of the green luminescence radiating centres is observed. The band maximum of γ -rays excited luminescence is shifted to the blue region and the light yield is three to four times less than the light yield of undoped crystals. With Nb doping, the green luminescence in PWO crystals is at least a superposition of three bands. The luminescence kinetics of these combined bands under photo excitation depends on the Nb content in the crystals. Table 2 shows the data of the luminescence ($\lambda_{lum} = 520$ nm, $\lambda_{exc} = 313$ and 337 nm) kinetics as a function of the Nb content. The (WO₃+F) centre's luminescence is mainly triggered by 313 nm excitation, but the band connected with Nb doping appears in the kinetics when 337 nm excitation is applied. With an Nb presence of 1000 ppm or more a component with a decay of up to one hundred nanoseconds appears. This component, having a contribution in the total kinetics of about 10–15%, becomes slower and slower when the Nb content increases. For an Nb content of a few tens of ppm the kinetics is close to that of undoped crystals.

The scintillations measured with Philips XP1911 or Philips XP 2262 photomultipliers from Nb doped crystals with an Nb content of some tens of ppm did not exhibit a slow component [6]. In comparison with undoped crystals where the main contribution to scintillation kinetics is due to components with $\tau_{1.2} \approx 3.20$ ns (more then 85% of the total light) the components with $\tau_{1.2} \approx 2.5, 14$ ns dominate the Nb doped crystals.

Table 2 Parameters of green luminescence kinetics of undoped and Nb doped crystals under photo excitation

Nb content (ppm)	λ_{exc} (nm)	Decay time τ_1 (ns)	Decay time τ_2 (ns)	Decay time τ_3 (ns)
Undoped	313	1.8	16.5	—
	337	4.3	17.3	—
~ 30 ppm	313	2	18	—
	337	3.5	24	—
~ 1000 ppm	313	1.1	4.5	47.6
	337	0.5	6.2	70.3
~ 5000 ppm	313	1.3	7.0	43
	337	0.8	6.7	88.3
~ 10000 ppm	313	1.1	5.3	54.5
	337	1.2	11.5	104

6. Discussion

We have already mentioned the specific defects induced in PWO crystals with oxygen deficiency [9]. It was noted that these scintillations appear in PWO crystals due to the contribution of regular WO₄²⁻ and irregular (WO₃+F) centres which give, respectively, fast

blue and slower green luminescence bands. It has also been shown [10] that the green luminescence consists of two bands with close maxima which is in good agreement with two possible anion vacancies or F centres based on them in the O(2) position only. It was found that Pb^{2+} ions play an important role in the scintillation production [4, 16].

The appearance of a wide absorption band in the blue region in various crystals based on molybdenum and tungsten with a structure different from the PbWO_4 crystal has already been reported. The absorption band with a maximum of about 420 nm was detected in PbMoO_4 crystals. Its intensity varied with crystal growth conditions and the purity of the raw materials [17]. The same band was found in $\text{Ba Gd}_2(\text{MoO}_4)_3$ crystals doped with Eu that has a variable valence of $2^+ \leftrightarrow 3^+$ like Yb ions [18]. These crystals were grown in an air atmosphere with a deficiency of divalent Ba ions. This wide band has been reported on only for doped crystals, without any explanation of its origin.

The data obtained so far show that two absorption bands vary with additional doping. The 420 nm absorption band is generated mainly by the trivalent ions at the Pb site. At the same time, the absorption band with 350 nm maximum is present in undoped crystals and disappears with Nb activation. We therefore conclude that the origin of this band is due to the presence of cation vacancies. Two defects are responsible for these bands. Both are hole centres, but one is due to the uncompensated charge W link with 3^+ ions located at the Pb site, and the other is due to O^- hole centres near the cation vacancy V_k (Pb) at the Pb site. This interpretation of the 350 nm absorption band is in agreement with the data for Nb activated crystal. The Nb^{5+} ions located at the W^{6+} site, compensate the O^- centres arising near V_k (Pb). This is clearly indicated in the transmission spectra of Nb doped crystals. The red luminescence, that has an excitation band at 350 nm and exists in undoped crystals, is also suppressed with Nb doping [14]. Although we did not activate PWO by 1^+ ions, it was found that Na^{1+} activation of the crystals leads to the appearance of a red luminescence [8]. The creation mechanism of the hole centre with 1^+ ion activation is similar to the creation one caused by a lack of Pb. Another impurity with a valence of 3^+ or 4^+ that can be stabilized at the W site also generates O^- hole centres. The Fe ions, being in crystals grown in the above-mentioned conditions, will replace the W ions with a maximal valence state of 3^+ or 4^+ . Thus they will generate O^- centres with an absorption near 350 nm. This is illustrated by the correlation between the transmission worsening of PWO at the 350 nm wavelength and the presence of iron in the crystals, as shown in Fig. 6.

The influence of Nb ions on the 420 nm band intensity is twofold. As mentioned in Ref. [6] with a lack of oxygen ions, Nb^{5+} ions replace the W^{6+} ones or compensate their deficiency and prevent Pb^{3+} appearance by the creation of F^+ centres. On the other hand, Nb ions that do not lack oxygen lead to the creation of Pb^{3+} centres. These two opposite tendencies lead to the limited influence of Nb doping on the intensity of the 420 nm band. Vacuum annealing will provide a suppression of the hole centres with $\text{Pb}^{3+} \rightarrow \text{Pb}^{2+}$, but it will also lead to the creation of the same centres near already existing $V_k(\text{Pb})$ vacancies. However, these two processes have a different velocity. The first process caused by thermoactivation is faster than the second process caused mainly by thermoactivated diffusion. Thus the contribution of each of them in bleaching or debleaching can be tuned by the optimization of the annealing temperature or by the speed change of the heating/cooling procedure. Even crystals activated with Bi^{3+} ions that were cooled from 1000°C down to 400°C during 1h were bleached considerably. On the other hand, vacuum annealing leads to a decreasing amount of O^- centres with simultaneous bleaching in the region of 350 nm. Unfortunately, with the already existing lack of Pb and oxygen ions in the crystals, with a long time vacuum annealing, a permanent decrease of anion vacancies or of irregular WO_3 centres will occur. When their number decreases a reduction of the scintillation light yield occurs. The influence of Mg activation can be inferred from the results mentioned above. The Mg^{2+} ions replace or compensate the lack of Pb^{2+} ions and finally leads to a decrease in the oxygen vacancies and thus a reduction of the green luminescence radiating centres based on them. These crystals have the same spectroscopy as the undoped crystals and,

at the same time, have luminescence under γ -excitation shifted to the blue wavelength due to the reduction of the green luminescence contribution in the total spectrum.

7. Conclusions

The connection between the structural peculiarities, and the spectroscopic and scintillation properties of PbWO_4 crystals have been investigated. The data obtained have led us to the conclusion that hole centres have a significant negative influence on the scintillation properties of PWO crystals.

Oxygen and lead sites that were not fully occupied gave the formula $\text{Pb}_7\text{W}_8\text{O}_{(32-x)}$ with $x = 3.2(8)$ in crystals grown with some lead deficiency.

The atomic structure of $\text{Pb}_7\text{W}_8\text{O}_{(32-x)}$ is new and differs from the PbMoO_4 one with three different crystallographic sites for Pb atoms and two sites for oxygen atoms, where Pb(1) and O(2) are not fully occupied.

PbWO_4 crystals doped with Bi, Yb, Mg, and Nb were investigated. The different dopings showed that the different absorption bands which were determined are caused by point structure defects.

An absorption band with a maximum of 350 nm originates in O^- centres near Pb cation vacancies. This band is suppressed by Nb doping.

An absorption band with a maximum of 420 nm originates in Pb^{3+} or in the presence of other trivalent ions and can be suppressed by additional vacuum annealing.

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Fig. 1 a) Transmission of Bi-doped crystal (dotted line) compared with the undoped crystals (solid line); b) excitation 1 – $\lambda_{lum} = 420$ nm, 2 – $\lambda_{lum} = 500$ nm, 3 – $\lambda_{lum} = 650$ nm and luminescence: 4 – $\lambda_{exc} = 275$ nm, 5 – $\lambda_{exc} = 325$ nm, 6 – $\lambda_{exc} = 308$ nm, 7 – $\lambda_{exc} = 350$ nm, and c) scintillation kinetics of PWO:Bi crystals. T = 300 K (parameters are given for a $\sum_i C_i e^{-t/\tau_i}$ fit).

Fig. 2 The excitation 1 - $\lambda_{lum} = 420$ nm, 2 - $\lambda_{lum} = 500$ nm, 3 - $\lambda_{lum} = 650$ nm and luminescence: 4 - $\lambda_{exc} = 275$ nm, 5 - $\lambda_{exc} = 325$ nm, 6 - $\lambda_{exc} = 308$ nm, 7 - $\lambda_{exc} = 350$ nm of (a) PWO crystal, and (b) PWO:Bi crystals annealed in vacuum. $T = 300$ K.

Fig. 3 a) Transmission of Yb doped crystal (dotted line) compared with undoped crystals (solid line); b) excitation 1 – $\lambda_{\text{lum}} = 420$ nm, 2 – $\lambda_{\text{lum}} = 500$ nm, 3 – $\lambda_{\text{lum}} = 650$ nm and luminescence: 4 – $\lambda_{\text{exc}} = 275$ nm, 5 – $\lambda_{\text{exc}} = 325$ nm, 6 – $\lambda_{\text{exc}} = 350$ nm, and c) scintillation kinetics of PWO:Yb crystals. $T = 300$ K (parameters are given for a $C \cdot e^{-t/\tau}$ fit).

Fig. 4 Optical transmission of Nb doped samples at 500 and 350 nm with the Nb content increasing in the samples. $T = 300 \text{ K}$.

Fig. 5 a) Transmission of Nb doped crystal (dotted line) compared with transmission of undoped crystals (solid line); b) excitation, (c): 1 – $\lambda_{lum} = 420$ nm, 2 – $\lambda_{lum} = 500$ nm, 3 – $\lambda_{lum} = 600$ nm and luminescence: 4 – $\lambda_{exc} = 275$ nm, 5 – $\lambda_{exc} = 307$ nm, 6 – $\lambda_{exc} = 350$ nm and c) scintillation kinetics of PWO:Nb crystals. $T = 300$ K (parameters are given for a $\sum_i C_i \cdot e^{-t/\tau_i}$ fit) above a constant background level.

Fig. 6 The correlation between the transmission at 350 nm and the Fe content in the crystals.