The Compact Muon Solenoid Experiment

CMS Note

Mailing address: CMS CERN, CH-1211 GENEVA 23, Switzerland

July 20, 1998

On the origin of the transmission damage in lead tungstate crystals under irradiation

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Abstract

The origin of the transmission damage in PWO crystals is discussed. It is shown that both electron and hole centers created on the basis of structural defects in PbWO_4 crystals contributed to the induced absorption of the crystals. The different aspects of the suppression of the recharge processes in PWO scintillation crystals are also discussed.

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1 Introduction

The design and construction of new experiments to be installed in accelerator facilities with high luminosity similar to the Large Hadron Collider at CERN require detector elements able to keep their stability under long-term exposure to ionizing radiation. This is particularly relevant for the scintillation materials used in precise electromagnetic calorimeters. The lead tungstate PbWO_4 (PWO) scintillator is used to make Electromagnetic CALorimeter (ECAL) of the CMS experiment at CERN [1]. It is also the most attractive candidate for the photon detectors of the ALICE and COMPASS experiments [2–4]. At present, most of the PbWO_4 (PWO) scintillator properties satisfy the CMS ECAL requirements. Impressive progress in the reproducibility of these parameters has been achieved at the production thanks to the optimization of the crystal growth conditions and the use of specified raw materials. The current level of the laboratory production technology of PWO scintillation elements allows bright, rather fast, optically clear, scintillation elements to be produced with acceptable radiation hardness [5]. A model describing the origin of the scintillation, the interaction and the modification of different point structure defect charge states in PWO crystals has been used for the development and the stabilization of the scintillator-production laboratory technology. Some of its aspects related to the scintillation mechanism, the specification of the raw materials and the slow components and afterglow in PWO crystals have been already published [6–8]. In this paper we used this model to describe the radiation-induced effects in PWO crystals. As determined previously, the radiating centers are not affected by irradiation [9]. We discuss here the mechanisms leading to a modification under irradiation of the crystal optical absorption in scintillation spectral region. These results will assist the specialists involved in PWO production in the tuning and uniformization of the technology and to reach the crystal quality needed for applications in precise calorimeters.

2 Raw materials and samples

Radiation damage in lead tungstate crystals is caused by heterovalent impurities and defects of the matrix host itself. The most dangerous impurities influence have been described in [8]. An excessive amount of impurities, for instance in the crystals grown from 4N or worse raw-material quality, does not allow the contribution of impurities to be distinguished from that of structural point defects in charge compensation processes. The impurities mask the spectroscopic properties of the defects, giving ambiguous information about their contribution in the recharge mechanisms. Just after the cleaning of the raw material from specified impurities and its application for the crystal growth, the structural point defects dominate in the recharge process in the crystal and cause a crystal absorption change in an irradiation environment. An indirect estimate of the order of magnitude of the structural point defect's concentration in the PWO crystals may be done from the data of irradiation-induced absorption are taken from [9]. Usually, a lead tungstate crystal grown from specified raw material with melt stoichiometric tuning shows, after γ -irradiation, induced absorption bands with typical absorption coefficient maxima in the 2–3 m^{-1} range. Then assuming the oscillator strength of appropriate transitions is of the order of 0.01, the concentration of centers induced by irradiation is about $1 \times 10^{16} \text{ cm}^{-3}$ or about some tens of ppm. Thus the study of the defects requires the use of a well-specified raw material. However this does not mean that a super-cleaned raw material has to be used for the crystal growth of scintillation elements. Only some ions concentration as described in Refs. [8, 9] need to have such a 6N purity limitation. The others, which are separated in groups with the same valence state and localized at the site of lead or tungsten ions in the matrix host, have a limited total amount which does not exceed the requirements of 5N qualification. The recent results of the crystals obtained from such raw materials have demonstrated a real improvement of PWO radiation hardness [10].

To study the radiation damage mechanism in lead tungstate crystals, more than 100 doped and undoped crystal samples grown from specified raw materials have been investigated. Crystal growth conditions are described elsewhere [11]. All crystals were grown in conditions with minimization of the deviation of the melt content from stoichiometric ratio. The majority of the crystals were doped by lanthanum or niobium at the level of 100 ppm and obtained in similar crystal growth conditions. The top parts of the ingots were used for detailed spectroscopic investigation and some of them were tested with GDMS analysis [12] to see the correspondence between the raw-material specification and the impurities contamination in the crystals. Full-size scintillating elements of 23 cm length produced from the remaining parts of the ingots were used for detailed tests in irradiation and beam facilities. The measurement technique is described elsewhere [9]. To identify electron and hole centers, optical spectroscopy data, Thermo-Stimulated Luminescence (TSL), Thermo-Stimulated Current (TSC) and EPR spectroscopy data described in [13–17] have also been taken into account.

3 Lead tungstate structural peculiarity

Lead tungstate crystals occur in nature as tetragonal stolzite [18], sheelite type and monoclinic raspite [19]. A high-pressure form has also been prepared under high temperature [18]. The PbWO_4 crystal has been determined by X-ray diffraction as sheelite-type crystal of tetragonal symmetry with space group of $I4_1/a$ [§] and parameters of unit cell $a = b = 5.456(2)$, $c = 12.020(2)$ Å°. With PbO deficiency in the melt, crystallization occurred with a new atomic arrangement determined by X-ray diffraction, which has tetragonal symmetry with space group $P4/nnc$, $a = b = 7.719(2)$, $c = 12.018(2)$ Å° [20]. The unit-cell parameter was related to the sheelite type by a factor of $2^{1/2}$. Oxygen and lead sites not fully occupied gave a formula $\text{Pb}_7\text{W}_8\text{O}_{(32-x)}$ with $x = 3.2$. The stacking of Pb and W atoms are different in these two phases. However recent neutron diffraction studies of PWO powdered samples [21] allow the model with separate columns of Pb and W atoms to be rejected, but are in agreement only with a regular and alternate stacking of Pb and W atoms on each column along the c axis, as in pure PbWO_4 . This new model, which has the final compound composition $\text{Pb}_{7.5}\text{W}_8\text{O}_{32}$, is found to be in agreement with both X-ray and neutron diffraction measurements. Such a composition also has $a = b = 7.719(2)$, $c = 12.018(2)$ Å° unit-cell parameters and its space group is $P\bar{4}$. There are four unequivalent positions of Pb in such a structure. The occupancy factor of Pb(4) is 0.5. It was determined that all superstructure reflections are produced by vacancy in Pb(4) site.

4 Radiating centers, hole and electron centers in PWO

An understanding of the origin of rechargeable defects in PWO crystal comes through the study of its radiating centers. In addition to detailed investigation of lead tungstate crystal spectroscopic properties started in the seventies [13–15, 22–24], a new and systematic study has been made with samples grown by different producers [8, 25–30] over the last five years which has led to a better understanding of the origin of the luminescence in PWO crystals. The luminescence appears to be due to charge transfer transitions in anionic molecular complexes WO_4^{2-} and WO_3 . In the frame of molecular orbital approximation by means of an extended Huckel method [6, 31, 32], anionic complexes have the highest occupied molecular orbital t_1 which is formed by oxygen orbitals $2p(\pi)$ and is separated from the first excited $2e$ state made up mainly from metal d orbitals. Because the WO_4^{2-} complex has a T_d point crystalline field symmetry, final configuration of the energy terms is found to be, 3T_1 , 3T_2 and 1T_1 , 1T_2 with 1A_1 ground state. Both $^1A_1 \rightarrow ^1T_1$, 1T_2 and $^1A_1 \rightarrow ^3T_1$, 3T_2 transitions, causing the radiating transition from triplet levels 3T_1 , $^3T_2 \rightarrow ^1A_1$ [28]^{§§} at the lowest transition has energy $23\,800\text{ cm}^{-1}$ are clearly detected in the blue luminescence excitation ($30\,800\text{ cm}^{-1}$).

When anion vacancy appears in a WO_4^{2-} anionic complex the local symmetry of the new WO_3 complex is reduced to C_{3v} . An additional low-symmetry component of the crystalline field splits triplet levels in (A+E) components, giving some shift of the excited energy terms. Transitions similar to the above ones are detected through the excited spectra of green ($20\,400\text{ cm}^{-1}$) luminescence at room temperature [28] through the excitation band with a lowest energy of $32\,800\text{ cm}^{-1}$. However electron-phonon interaction is strongly changed at the transition from regular to irregular anionic complex. It causes a large increase of the Stokes shift of the luminescence in irregular groups, giving shift of the luminescent band maximum in the green range.

There is another luminescent center in PWO crystals associated with the red ($15\,400\text{ cm}^{-1}$) luminescence. In Refs. [25, 26] we associated this luminescence with a center which appeared because of incorporation of the Pb^{3+} center in PWO crystals. Trivalent lead ion is stabilized in PWO crystals by a Frenkel defect (oxygen ion shifted to inter-site position with simultaneous creation of V_o) [8]. A Frenkel defect also lowers the local symmetry of such WO_3 tungsten complex toward a C_3 , or even lower, establishing the shift and the splitting of the original excited energy terms. Such distorted tungsten anionic complex is responsible for the red luminescence in PWO crystals. Its first excitation band according to [28] is wide band with a maximum around $28\,600\text{ cm}^{-1}$ (350 nm). The charge transfer mechanism of this luminescence is in good agreement with the results of [33] where room-temperature photoconductivity of nominally pure PWO crystals was measured at excitation near 350 nm. The energy-level scheme of radiating centers in PWO crystals is shown in Fig. 1. It indicates that due to charge transfer origin all optical transitions may be the source of the vacancies populated by electrons and holes.

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^{§§} For unfamiliar with notation see for instance optical spectroscopy of inorganic Solid B. Henderson G.F. Imbusch Clarendon Press Oxford 1989

Figure 1: Energy-level diagram of the optical transitions in PWO crystals. The splitting of the first excited states in WO_3 groups is shown.

PbWO_4 is exceptional with respect to the other tungstate crystals and analogies with other crystals of the tungstate family for spectroscopy and defect identification are not adequate.

Firstly, the whole set of TSL bands in PWO crystals can be created as well by X-ray as by UV (340 nm) excitation.

Secondly, the characteristic of intrinsic $(\text{WO}_4)_2^{3-}$ hole defect for the MWO_4 tungstate family ($\text{M} = \text{metal}$) was never observed in PWO crystal.

Thirdly, the characteristic set of sharp peaks in the range 110–130 K of TSL spectra is not assigned to thermal decay of the centers detected by means of EPR.

Fourthly, intrinsic defects with paramagnetic ground states are not detected in PWO crystals at a temperature higher than that of liquid nitrogen. This indicates that centers like separate F^+ (anion vacancy $\text{V}_\text{o} + \text{e}$) or O^- most probably are not stable in such crystals even at low temperature.

The point structure defects created in pure sheelite (PbWO_4) and sheelite-like type ($\text{Pb}_{7.5}\text{W}_8\text{O}_{32}$) crystals are different. The PbWO_4 crystal has casually distributed vacancies caused by Pb or O leakage during crystal growth; the sheelite-like type crystal in addition contains regular cation vacancies in one of the lead positions. The dependence of the vacancy concentration on the structure of the crystal is shown schematically in Fig. 2. During PWO crystal growth by the Czochralski method from stoichiometric raw material, a leakage of lead from the melt takes place leading to the creation of casually distributed cation vacancies V_c in the lead site of the PbWO_4 crystal. Such vacancy is charge compensated by oxygen vacancy V_o , which is also casually distributed in the matrix. With transition of the crystal matrix to the sheelite-like type, the amount of V_c decreases with the decrease of the PbWO_4 fraction in solid solution. However regular cation vacancies V_c^* for the $\text{Pb}_{7.5}\text{W}_8\text{O}_{32}$ matrix arise. They are compensated for by shifts of the oxygen atoms in the host. Usually during growth of PWO crystals the two-phase solid solution mentioned above occurred; however the fraction of each phase in the crystal strongly depends on the crystal growth conditions. The V_c , V_c^* vacancies are the main holes traps in PWO crystals at irradiation. The centers $\text{O}^-\text{V}_\text{c}\text{c}^*\text{O}^-$ are the only possibility to have hole centers with a singlet and not a paramagnetic ground state. In oxide crystals, di-hole defects near cation vacancy have been well investigated, usually showing wide absorption bands in the red region [34].

Most of the investigated centers in PWO are proven to be electron centers created under irradiation or light excitation. Such centers affect the scintillation properties of PWO crystals and strongly influence the distribution of the emitted light among scintillation and afterglow as well as the recovery of the crystal transmission after irradiation.

Figure 2: Defects in PWO crystals with crystal structure.

A typical electron center in a PWO crystal is $(\text{MoO}_4)^{3-}$, which is formed in irradiated crystals. It is related to the MoO_4^{2-} anion complex impurity which is a stable electron trap center. Although raw material is cleaned especially from molybdenum before crystal growth, the molybdenum ion is very close chemically to the tungsten ion and is rather hard to separate at the raw material production level. Molybdenum impurity is usually present in PWO at the level of few ppm. The properties of the $(\text{MoO}_4)^{3-}$ center and its influence on PWO scintillation parameters are described in Refs. [6, 7, 14]. This center decays relatively fast at room temperature and does not contribute to radiation-damage effects in PWO crystals but to slow component.

Summarizing PWO TSL data one can conclude that three groups of characteristic TSL peaks, and consequently electron centers, are present in the spectra. They are respectively in the 110–125, 170–205 and 330–400 K range [17]. The Fig. 3-1 shows also typical TSL spectra below room temperature for La and Nb doped crystal that we have obtained. A luminescence band emitted through thermo-activation of the centers associated with bands 110–125 and 170–205 K is peaked at $20\,400\text{ cm}^{-1}$ (490 nm). However TSL emission through activation of 330 and 400 K bands is centred near $16\,800\text{ cm}^{-1}$ (600 nm) [29]. It indicates that traps associated with the high-temperature bands are released because of interaction with green ($20\,400\text{ cm}^{-1}$) and red ($15\,400\text{ cm}^{-1}$) luminescence radiating centers. However the red luminescence radiating centers dominate in this process. The individual trap parameters such as the thermo-activation energy E , the frequency factor S , and the trap release time τ have been calculated by the total glow method [35]. Their values, as well as the calculated energy depths E_d and $(E_g - E_d)$ where E_g is energy gap of PWO ($30\,800\text{ cm}^{-1}$), are given in Table 1. Values of E_d were calculated taking into account zero-phonon transition energies of appropriate luminescence bands. Following this calculation at least two electron centers, with $E_d = 1.7$ ($13\,680\text{ cm}^{-1}$) and 1.85 eV ($14\,800\text{ cm}^{-1}$), give an absorption band after irradiation in the region of $13\,000\text{--}14\,000\text{ cm}^{-1}$. We have precisely detected such a band but only in the transmission spectrum of a long (23 cm) just grown or irradiated undoped crystal. As expected, after irradiation with a ^{60}Co source this band grows, giving a wide long-wave wing to the characteristic absorption band induced by irradiation with a maximum of $16\,200\text{ cm}^{-1}$. Initial and after-irradiation transmission spectra of the crystal are shown in Fig. 3-2. Also determination of the long-wave wing by electron centers is in agreement with the optical bleaching of irradiated PWO crystals described in [36].

Among the electron centers, the most obvious non-paramagnetic center is $F(V_0 + 2e^-)$, which is a candidate to be the characteristic defect in the PWO. Thus we attribute the first group of the peaks (110–125 K) in TSL to that F center. Such an approach is in good agreement with the Thermo Stimulated Current (TSC) measurement [30] where just a weak TSC peak is observed in the temperature range 110–125 K. Another non-paramagnetic electron center is $(V_0V_0)^{2-}$ di-vacancy. Here there are two possibilities for creation of di-vacancy. One is due to two oxygen vacancies of the same polyhedron and the other can be created by vacancies from the different

neighbouring polyhedra. The last kind of di-vacancy may be very stable in tungsten crystals [37]. This center is probably responsible for the glow peaks at 330 K. The next group (170–205 K) of TSL peaks is also caused by the di-vacancy but localized in the same polyhedron. The probability of the di-vacancy creation in the crystal is proportional to N^2 , where N is normalized concentration of the V_o defects, and is considerably smaller than that of simple localization of the F center. This is confirmed by the fact that the intensity of the low- temperature group of glow peaks is greater than that of two others. The V_o vacancy created by Frenkel defect also can trap electrons giving center like $(WO_3)^{2-}$. Such center appears at irradiation, it is stable at room temperature and shows absorption spectra close to the WO_3 center near Frenkel defect. We associated to this center the highest detected TSL band at 400 K.

Table 1: Parameters of the glow peaks measured in PWO crystals in the range above 80 K

T, K	E_a , eV	E_d , eV	$E_g - E_d$, eV	t, s - trap release time
110	0.24	0.76	3.09	2.9×10^{-6}
125	0.3	0.8	3.05	6×10^{-6}
170	0.38	0.9	2.85	3.8×10^{-4}
205	0.44	1	2.85	3.5×10^{-2}
330	0.58	1.71	2.14	480
400	0.7	1.85	2	10 000

Figure 3-1: Typical TSL spectra below room temperature for La doped crystal (a), and Nb doped crystal (b).

Figure 3-2: Longitudinal optical transmission of 23-cm-long undoped PWO crystal before (a) and after (b) irradiation (^{60}Co source, accumulated dose 1 krad), $T = 300\text{ K}$.

5. PWO doping and point structure defect compensation

The complete suppression of the point structure defects in PWO full-size elements just by means of stoichiometric tuning is not possible. Therefore an additional means to compensate for or destroy the point structure defects is required. Among annealing, doping and additional coloration, doping is found to be technologically more convenient to reach the minimal level of the damaged defect concentration in the crystals. The doping of PWO crystals by specified impurities like La, Lu, Y, Nb improves significantly the radiation hardness of the scintillation elements [9, 38]. Moreover an impressive suppression of absorption induced by irradiation in full-size scintillation elements was observed at the level of doping of some tens of ppm. Let us discuss the compensation process in detail. For instance in the case of doping by Nb, Fig. 4(a,b) shows a change of the induced absorption by irradiation for the two characteristic bands in PWO (620 and 390 nm) versus the Nb concentration in the crystal. A similar tendency is seen with Nb concentration increase, which shows a fast suppression of both the rechargeable defects. Fig. 4(c) shows a comparison of the relative change of the induced absorption at 620 nm in Nb-doped crystals — defined as $(k_{\text{Nbmin}} - k_{\text{Nb}})/k_{\text{Nbmin}}$, where k_{Nbmin} and k_{Nb} are induced absorption coefficients at minimal and any Nb concentration respectively — and the curve of the defect compensation probability at different Nb concentrations.

We defined defect compensation probability as the probability for the doping ion to be within a sphere of radius R around the defect. In this range of Nb concentration the best fit between probability curve and experimental data is achieved at $R = 90\text{--}100\text{ Å}$ (fig. 4(c)). At such a large distance, direct interaction between defect and doping ion seems to be negligible. Moreover, impurity influences both defects simultaneously. In other words it indicates clearly that the compensation of the defects is due to spatial charge compensation which as a result decreases the concentration of vacancies.

La^{3+} type ions at its localization in the Pb^{2+} site introduce in the crystal extra positive uncompensated charge, and so will compete with the creation of V_o vacancies reducing some fall of anion vacancy and dramatically decreasing the di-vacancy concentrations respectively.

La^{3+} doping also decreases the number of tungsten groups distorted by Frenkel defects in the crystal, giving improvement of the PWO optical transmission in the region 340–450 nm, noted for instance in [39]. For this reason the intensity of the second and third characteristic group of peaks in TSL are suppressed [17].

On the contrary, Nb^{5+} doping ions localized in the W^{6+} site introduce in the crystal extra negative uncompensated charge and do not affect anion vacancy concentration or defects based on it, as discovered from TSL data. Nb

ion in PWO creates a shallow hole center and prevents stabilization of the hole defects on the base of cation vacancy.

Figure 4: Induced absorption in full-size scintillation PWO crystals at 390 (a) and 620 nm (b) with Nb concentration in the crystal, ⁶⁰Co source, 30 krad accumulated dose, T = 300 K; (c) the relative change of the induced absorption at 620 nm in Nb doped crystals defined as $(k_{\text{Nbmin}} - k_{\text{Nbi}})/k_{\text{Nbmin}}$, where k_{Nbmin} and k_{Nbi} are induced absorption coefficients at minimal and any Nb concentration consequently, and defects compensation probability at different Nb concentration).

6. PWO transmission damage at irradiation

Fig. 5(a–c) presents typical curves of the radiation-induced absorption of crystals undoped and doped by Nb and La. Undoped crystals show a complicated spectrum with one clear detected maximum near 620 nm. As was noted above, electron centers contribute in a long-wave wing to this band. The maximum of the band in the shorter-wave range varies from crystal to crystal, having a value in the 350–400 nm range. It appears to be due to crystal-to-crystal variation of the cut-off of the transmission spectrum in the crystal. The Nb doping provides a decrease of the induced damage over a large spectral range, completely suppressing the 620 nm band. The La impurity even better provides a decrease of the induced damage over a full spectral range, suppressing

completely the 620 nm band, although a new band with maximum near 520 nm appears. Also the intensity of this band varies from crystal to crystal. It seems that in undoped crystal, such a band exists in the induced absorption spectrum but is masked in undoped crystals. In La-doped crystals it becomes apparent because of the selective suppression of the centers which cause short-wave and 620-nm induced absorption bands. Thus we concluded that the absorption spectrum induced by irradiation in PWO crystals is formed at least by four bands peaked near 360 or shorter, 520, 620 and 700 nm. The positions of two of these bands are in agreement with the results of the induced absorption spectrum decomposition by Gaussian functions [40]. Following the defects description we assumed that the $O^-V_cO^-$ center is responsible for the 620 nm absorption band induced by irradiation, and that the $O^-V_{c*}O^-$ center causes the 520 nm band. In fact, grown PWO is a solid solution of the two phases described so far and both types of cation vacancies are presented in crystals. The Nb doping ion preventing trapping of the hole centers by both vacancies, provides a gentle sloping-down of the long-wave part of the induced absorption spectrum. The La doping does not affect the $V_{c,c*}$ concentration but promotes a fast recombination of the di-hole centers near cation vacancy. The origin of the short-wave length induced absorption

Figure 5: Radiation-induced absorption spectra in undoped (a), Nb-doped (b), and La-doped (c) long-size PWO crystal, ^{60}Co source, 30 krad accumulated dose, lateral irradiation 25 Krad/h, $T = 300$ K.

band agrees with the above description of the defects in PWO if we assume its appearance is due to the electron capture by V_o in the tungsten group distorted by a Frenkel defect. Such a center in PWO has an energy-level structure similar to other tungsten groups and shows an absorption with a maximum in the 300–400 nm range. Usually in the induced absorption a long-wave wing of this band influenced by crystal absorption cut-off is detected. Such interpretation is in agreement with correlation between initial absorption of crystals in the 375 nm region and in-crystal absorption induced by irradiation [41].

7. PWO transmission radiation-damage mechanism

The model of the radiation damage in PWO crystals is schematically shown in Fig. 6. Under ionizing irradiation the population of the different kinds of V_o vacancies through thermalized electron capture or interaction with radiating tungstate groups occurs. Simultaneously the di-hole centers appear because of hole capture by cation vacancies. Such a metastable situation is caused by fast and slow non-radiative relaxation as well as by slow tunnelling. Intermediate states $O^{2-}V_{c,c}^*O^-$, $O^{2-}V_{c,c}^*O^{2-}$, or F^+ centers which appear due to tunnelling, or slow non-radiating relaxation as was previously noted are not stabilized in PWO or have a very fast decay time. Having an energy-level diagram of the radiating centers in PWO crystal and values of the energy depths of the electron centers in PWO, it is easy to understand the creation of electron or hole centers at 340 nm photo-excitation which is detected through TSL peaks or induced absorption [42]. Excitation at 340 nm corresponds in energy scale to the lowest charge transfer transition in PWO crystal. On the other hand, as this transition is the first excited state of the red emitting center, it has an energy which is close to or larger than the energy values ($E_g - E_d$) of the detected electron centers. So light excitation at 340 nm populates the electron centers through tunnelling or non-radiative luminescence quenching. However it is obvious that processes of induced absorption creation such as photo-excitation and ionizing irradiation are different because by photo-excitation just one type of defect is involved in the hole creation.

Figure 6: Scheme of the processes at the damage and recovery of PWO optical transmission.

In conclusion we note that the use of raw materials cleaned from specified impurities, stoichiometric tuning and optimal doping result in a high radiation-resistance uniformity along the crystal. At the Czochralskii crystal growth the top part of the crystals near the seed has a good structural perfection and usually has the lowest concentration of the defects. In highly resistant crystals the difference between transmission damage along all the crystal and only along its top part is less than 30%. Fig. 7 shows the correlation between radiation-induced longitudinal absorption at 500 nm measured with full-size elements (23 cm) and induced absorption (plotted along abscissae scale) measured with samples extracted from the top parts of the crystals.

Figure 7: Correlation between longitudinal induced absorption at 500 nm measured with elements of 23 cm length (^{60}Co source, 30 krad accumulated dose) and induced absorption measured with samples extracted from the top parts of the same crystals (^{60}Co source, 100 krad accumulated dose), $T = 300\text{ K}$.

8. Conclusion

The data obtained led us to the following conclusions.

The irradiation induced reduction of optical transmission in PWO scintillation crystals appears to be due to the creation of di-vacancy $(\text{WO}_3 - \text{WO}_3)^{2-}$, di-hole $\text{O}^-\text{V}_c^*\text{O}^-$, $\text{O}^-\text{V}_c\text{O}^-$ and $(\text{WO}_3)^{2-}$ distorted by Frenkel defect centers. Ionization of $(\text{WO}_3)^{2-}$ distorted by Frenkel defect center and optical transitions in $(\text{WO}_3 - \text{WO}_3)^{2-}$, $\text{O}^-\text{V}_c^*\text{O}^-$, $\text{O}^-\text{V}_c\text{O}^-$ centers causes absorption bands with maxima in the range 500-750 nm. Also $(\text{WO}_3)^{2-}$ distorted by Frenkel defect center causes induced absorption band with a maximum shorter than 400 nm.

The resulting radiation damage can be significantly suppressed in PWO crystals by simultaneous application in the crystal growth technology of specified raw materials, good stoichiometric tuning and optimal doping.

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