

---

# CMS Conference Report

---

2 October 2001

## Non-stoichiometry Defects and Radiation Hardness of Lead Tungstate Crystals $PbWO_4$

E.G. Devitsin, V.A. Kozlov, S.Y. Potashov, A.R. Terkulov

*Lebedev Physical Institute of the Russian Academy of Sciences, Moscow, Russia*

V.A. Nefedov, E.V. Polyansky, B.I. Zadneprovski

*All-Russian Research Institute of Synthesis of Mineral Raw Materials, Alexandrov (Vladimir Region), Russia*

P. Kjellberg

*LUND University, Sweden*

### Abstract

It has been stated many times that the formation of radiation infringements in  $PbWO_4$  is to big extent stipulated by non-stoichiometry defects of the crystals, arising in the process of their growth and annealing. To refine the idea of characteristics of non-stoichiometry defects and their effect on the radiation hardness of  $PbWO_4$  the current study is aimed at the melt composition infringements during its evaporation and at optical transmission of crystals obtained in these conditions after their irradiation ( $^{137}Cs$  source). In the optical transmission measurements along with traditional techniques a method "in situ" was used, which provided the measurements in fixed points of the spectrum (380, 470 and 535 nm) directly in the process of the irradiation.

X-ray phase and fluorescence analysis of condensation products of vapours over  $PbWO_4$  melt has found  $PbWO_4$  phase in their content as well as compounds rich in lead,  $PbO$ ,  $Pb_2WO_5$ , with overall ratio  $Pb/W = 3.2$ . Correspondingly the lack of lead and variations in the content of oxygen are pointed out as the major growth defects of non-stoichiometry of  $PbWO_4$  crystals. The oxygen variations are determined by the partial oxygen pressure in the atmosphere of growth or annealing of the crystals.

The obtained results were compared with known conceptions of  $PbWO_4$  crystal colour centres. The possibilities of the formation of these centres accounting for the discovered loss of lead and oxygen exchange between the external medium and the crystal were considered.

Presented at the VI-th International Conference on Inorganic Scintillators and their Use in Scientific and Industrial Applications (*SCINT2001*), Chamonix, France, September 16-21, 2001

# 1 Introduction

The solution of the problem of  $PbWO_4$  (PWO) crystal radiation hardness improvement remains to be one of the most important conditions for application of this scintillator in the range of well-known high energy projects. One of the most significant consequences of crystal degradation during irradiation is the decrease of optical transmission. To explain the mechanism of these effects a range of models have been suggested for absorption and colour centres in initial PWO crystals as well as the crystals irradiated and annealed in different atmospheres [1]- [3]. The majority of these models are based on investigation of optical spectra and, as was correctly mentioned in [3], "all these explanations and proposals are preliminary and based on indirect arguments, because there is no direct evidence for the existence of any of the centres proposed". However, there is a well-grounded assumption that the absorption centre formation, including radiation centres, is significantly dependent on the presence of non-stoichiometry defects and of related to them point defects in the crystals. A big set of experimental data available by now convincingly testifies to a conclusion, that the formation of such PWO structure defects is decisively determined by technological conditions of the crystal production. The most important of these conditions, as formulated in [4], are: thermochemical stability of the melt, the evolution of the stoichiometric composition of the melt and the crystals during their growth, composition and pressure of the gaseous medium during growth and annealing of the crystals. The necessity to account for these factors is evident during the analysis of defect genesis and of absorption centres in PWO crystals and, as a consequence, of the mechanism of their radiation hardness.

Taking this into account, the current work considers possible defects of PWO crystal stoichiometry, their vacancy positional disorder and associated defect formation depending on the evaporation of components from initial melt and of the atmosphere of crystal growing and annealing. The products of melt evaporation during the growth of PWO crystals as well as of evaporations during their annealing have been investigated. The effect of crystal annealing in air and argon on their radiation hardness after gamma-irradiation was studied. The nature of optical transmission variation of PWO crystals immediately in the process of their irradiation were determined using measuring technique 'in situ'. Experimental data was compared with the analysis results of defect formation in crystals.

## 2 Experiment

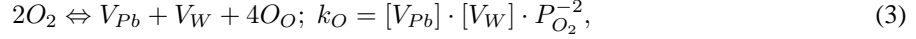
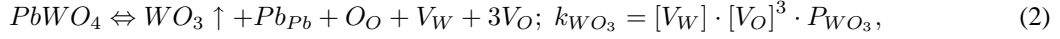
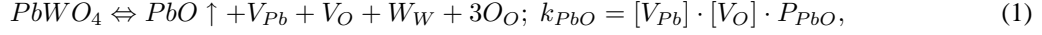
The experimental part of the work was based on PWO crystal samples grown using Chokhralsky method in Bogoroditsk Techno-Chemical plant and in VNIISIMS. The techniques of their growth are described in [5] and [6] correspondingly. The main difference of the techniques was in different composition of the gaseous atmosphere. The Bogoroditsk crystals were grown in the atmosphere of nitrogen containing  $10^{-3}$  volume % of oxygen; the VNIISIMS crystals - in the air of atmospheric pressure. During the crystal growing in VNIISIMS the nature of melt composition defects was determined with the help of analysis of evaporation product condensation on the crystal support elements. Very small quantities of sediment, deposited on platinum or corundum backing were used to analyse evaporations during crystal annealing. The methods of phase X-ray diffraction and quantitative X-ray fluorescence analysis were used for this purpose.

To investigate the effect of PWO crystal annealing on its radiation hardness after small doses of gamma-irradiation the samples with dimensions of  $12 \times 12 \times 24 \text{ mm}^3$  were prepared. They were annealed under the temperature of  $800^\circ\text{C}$  in air during 24 hours and in argon during 48 hours. Transmission spectra of PWO samples annealed in different atmosphere were investigated (measured) on a spectrophotometer in the wavelength range of 330-700 nm. Online measurements of the radiation damage of PWO crystals were performed on a special set-up (see figure 1) located at DESY [7].

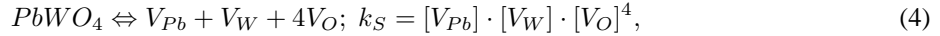
A radioactive source  $^{137}\text{Cs}$  (150 GBq, 4 Ci) was used for these studies. The PWO samples were positioned at 5 cm away from the source, the dose rate was about 2.6 Gy/hour. The set-up was equipped with three light emission diodes (LED), produced by Nichia Chemical Industries, Ltd., Japan with the following maximum emission wavelengths: 380nm (UV), 470nm (blue) and 535nm (green). The LED light travels through the centre of a sample and is detected by a photomultiplier Hamamatsu R928 in the spectral range 165-900 nm. A PMT signal is digitised by an ADC, connected to a PC, which controls the set-up. Changes in the LED or in the PMT performance are corrected by a reference channel. The measurements were performed 'online' during irradiation and self-annealing at the rate of one measurement per minute.

### 3 Non-stoichiometry and proper point defects of $PbWO_4$

During the growth of PWO crystals out of a  $PbO \cdot WO_3$  binary system melt in air atmosphere the breaking of stoichiometry of the melt takes place as a result of irregular evaporation of oxides and interaction with atmospheric oxygen. The evaporation losses of  $PbO$  exceed that of  $WO_3$  which follows from comparison of saturated vapor pressure of the oxides under growth temperatures of PWO  $1125 \div 1200^\circ\text{C}$ :  $P_{PbO} = (1.9 \div 3.3) \cdot 10^3$  Pa,  $P_{WO_3} = 1.2 \div 5.1$  Pa [8]. A crystal, growing out of such a melt, is non-stoichiometric and in general case contains vacancies of three types - lead ( $V_{Pb}$ ), tungstate ( $V_W$ ) and oxygen ( $V_O$ ). The variation in oxygen content takes place also during the annealing of PWO [9] [10]. Using the method of "quasi-chemical reactions" [11], the formation of the mentioned vacancies can be expressed by the following equations:



where:  $k_i$  - constants of reaction equilibrium,  $[V_i]$  - vacancy concentrations,  $P_{O_2}$  - oxygen pressure. The values of  $k_i$ ,  $P_{PbO}$ ,  $P_{WO_3}$  depend only on the temperature. The internal positional disorder in the crystal according to Schottky is described by equation:



where:  $k_S$  - is Schottky constant. Accounting for (1) and (2) it is evident, that

$$k_S = (k_{PbO}/P_{PbO}) \cdot (k_{WO_3}/P_{WO_3}) = k_{S_1} \cdot k_{S_2}. \quad (5)$$

Then the solution of the system of equations (1,2,3) makes it possible to obtain dependencies of vacancy concentrations on oxygen pressure in the atmosphere of growth in the form:

$$[V_{Pb}] = k_S^{-1/4} \cdot k_{S_1} \cdot k_O^{1/4} \cdot P_{O_2}^{1/2}; [V_W] = k_S^{-3/4} \cdot k_{S_2} \cdot k_O^{3/4} \cdot P_{O_2}^{3/2}; [V_O] = k_S^{1/4} \cdot k_O^{-1/4} \cdot P_{O_2}^{-1/2}. \quad (6)$$

The approximate estimates of the relation of the constants according to thermodynamical data yield  $k_S > k_O > k_{S_1} > k_{S_2}$ . Diagrams of vacancy concentration dependence on oxygen pressure  $P_{O_2}$ , plotted using these relations are presented in figure 2 in coordinates  $\ln[V_i] \sim \ln P_{O_2}$ .

Five zones can be distinguished on the diagram, where the correlation of vacancy concentrations is significantly different. Presenting the deviation of PWO stoichiometry as a disbalance in the complex cation and disbalance between the complex cation and oxygen content, i.e.  $(Pb_{1-x}W)O_{4-y}$ , one can separate five main types of non-stoichiometry of lead tungstate depending on the oxygen pressure (see Table 1). Comparing this model of position disorder of PWO to experimental data, we will point out the following. According to [12] for the crystals of Bogoroditsk Techno-Chemical plant the following composition was established:  $Pb_7W_8O_{32-y}$ , where  $y=2,8$ , i.e.  $Pb_{1-0.125}WO_{4-y}$ ,  $y=0.35$ . The crystals were grown in the atmosphere with low content of oxygen  $P_{O_2} \simeq 1 \div 10^3$  Pa [5]. This corresponds to zone 2. The influence of higher oxygen pressures on the composition of complex cation characterizes the study of vapor condensation products over the melt during the growth of PWO and evaporations during crystal annealing. During the crystal growth in the air under pressure  $P_{O_2} = 2.1 \cdot 10^4$  Pa in the composition of condensate such phases rich in lead as  $PbO$ ,  $Pb_2WO_5$  and in small quantities  $\alpha$ -PWO were discovered. The ratio of  $Pb[\text{mass.}\%]/W[\text{mass.}\%]$  in the condensate made up 3.56. During the annealing of these crystals under  $950^\circ\text{C}$  in pure oxygen and pressure higher than atmospheric ( $P_{O_2} = 1.22 \cdot 10^5$  Pa) the evaporations contained  $WO_3$ ,  $WO_{2.90}$ ,  $PbO$  with  $Pb[\text{mass.}\%]/W[\text{mass.}\%] = 0.34$ . As a result, the crystals grown in air had the lack of lead, i.e.  $[V_{Pb}] > [V_W]$ . Their annealing under higher  $P_{O_2}$  created the lack of tungstate, i.e.  $[V_W] > [V_{Pb}]$ . Similar character of dominant cation vacancy shift follows from the diagram in the transition from mean oxygen pressures (zone 4) to high pressure (zone 5).

When considering the formation of charge defects which depend on  $P_{O_2}$ , we assume that, at high temperatures, the effective charges of the vacancies are inverse to formal physical charges of the corresponding ions, and the probability of combining defects of opposite charges is low [11]. The formation of an oxygen vacancy ( $V_O^{\bullet\bullet}$ ) is accompanied by the appearance of two free carriers with the negative charge ( $e$ ), and formation of lead ( $V_{Pb}''$ ) and tungstate ( $W_W^{6'}$ ) vacancies, i.e., by the appearance of two and six holes ( $h$ ), respectively. The allowance for the relations between the vacancy concentration and the character of the non-stoichiometry in the diagram zones  $\ln[V_i] \sim \ln P_{O_2}$  makes it possible to indicate the dominant types of charged defects for each zone together with

approximate condition of the crystal electroneutrality (Table 1). Hence, it follows that for the low oxygen pressure zone and for the zone with elevated pressures  $P_{O_2}$ , electrons and holes, respectively, are dominant free carriers. This is consistent with the experimentally detected passage from the  $n$ -type to the  $p$ -type conductivity of  $PbWO_4$  [13] when elevating the oxygen pressure. This passage takes place near the equilibrium point  $[V_O] \simeq [V_{Pb}]$ .

The interaction of defects, which is negligible at high temperatures, is enhanced with crystal cooling. As a result, the concentrations of simple defects at room temperature are low, and associates become the main forms of defect [11]. Taking into account the difference in dominant simple defects in  $PbWO_4$  crystals, grown at different  $P_{O_2}$  (Table 1), we can indicate the most probable adequate forms of associates. Evidently, at low  $P_{O_2}$ , simple associates, i.e., oxygen vacancies that captured one or two electrons become dominant:  $V_O^{\bullet\bullet} + e \Leftrightarrow V_O^\bullet$  and  $V_O^{\bullet\bullet} + 2e \Leftrightarrow V_O^\times$ . Along with, the deficiency of oxygen in the "gas-crystal" system makes possible the partial reduction of tungstate ( $W^{6+} \rightarrow W^{5+}$ ) by the reaction  $W_W^\times + e \Leftrightarrow W_W'$ . The localisation of additional electron transfers the complex anion  $(WO_4)^{2-}$  into the  $(WO_4)^{3-}$  state. The concentration of  $W_W'$  is presumably low due to competing capture of electrons by traps on oxygen vacancies.

With the increase of oxygen pressure the concentration of  $[V_O^{\bullet\bullet}]$  and  $[V_{Pb}^{\prime\prime}]$  vacancies becomes comparable (zone 2), and then  $[V_{Pb}^{\prime\prime}]$  predominate (zones 3 and 5). The analysis of possible associative interactions involving this structure defects and dominant free carriers shows, that in zone 2 the formation of neutral associates is quite real. Besides, two partially ionised vacancies of oxygen can localise on one as well as on two neighbouring  $WO_4$ -tetrahedrons. In zones 3 and 4 as a result of localisation of holes in the nearest surrounding of the lead vacancy the formation of associates  $(V_{Pb}^{\prime\prime}2O_O^\bullet)^\times$ ,  $(V_{Pb}^{\prime\prime}2Pb_{Pb}^\bullet)^\times$  and  $(V_{Pb}^{\prime\prime}O_O^\bullet Pb_{Pb}^\bullet)^\times$  is mostly possible. The formation of any of the mentioned associates is adequately described by a chain of quasi-chemical reactions. For zone 5, according to the electroneutrality condition, the prevailing interaction between tungstate vacancies and holes:  $V_W^{6'} + z \cdot h \Leftrightarrow V_W^{(6-z)'}$  is predictable. Such reaction in  $PbMoO_4$  crystals was observed judging by the increase of molybdenum diffusion [14]. The tungstate prevalence in discharge during  $PbWO_4$  annealing at high  $P_{O_2}$ , is evidently, also the consequence of interaction between  $V_W^{6'}$  and holes.

As a whole, the performed consideration shows that depending on oxygen pressure crystal composition as well as type of dominant simple and associate defects are regularly changing. The comparison of the analysis results with the models of the centres proposed for  $PbWO_4$ , makes it possible to indicate types of characteristic defects on which the occurrence of definite centres is probable (Table 2), and thus associate opportunity of the centre occurrence with crystal growing and annealing conditions. This is important for the analysis of  $PbWO_4$  behaviour under irradiation since the formation of radiation damage centres should be expected, above all, on the initial crystal defects.

## 4 Discussion of results

Results of the transmission measurements of standard (initial) PWO samples and the samples, additionally annealed in the atmosphere of air and argon are presented in figure 3. Dependence of radiation induced absorption coefficient ( $\mu$ ) on the time of irradiation by  $^{137}Cs$  using the dose of 2.6 Gy/hour for these samples is shown in figures 4-6. As seen in figure 4 the irradiation of the initial PWO sample causes sharp increase of  $\mu$  in its beginning as well as fast recovery after its end (two cycles of irradiation and one cycle of recovery are shown). Figure 5 shows  $\mu$  for the time of irradiation of about 170 hours for another standard PWO sample (without additional annealing). A saturation of the absorption coefficient is observed after about 80 hours of irradiation. For standard PWO crystals, grown in the atmosphere with lowered pressure of oxygen such behaviour of  $\mu$  can be explained in the following way. During irradiation of a standard PWO crystal the creation of electron-hole pairs (free charge carriers) as well as a separate localisation of both electrons and holes on traps, such as lattice distortions, vacancies and impurity ions, take place. For this reason in the beginning of irradiation a rapid increase of the colour centre number, associated with the vacancies already existing before the irradiation takes place. The following electron and hole centres are created:  $F$ ,  $F^+$ ,  $Pb^{3+}$ ,  $O^-$ . The slowing down of the colour centre production is connected with filling of the vacancies. Similar behaviour of  $\mu$  is shown by PWO samples additionally annealed in air.

However, for PWO samples, additionally annealed in argon atmosphere, the behaviour of the absorption coefficient noticeably differs. It is seen (figure 6) that there is no sharp starting jump and after the gamma-source is switched off there is no rapid recovery. To explain such phenomenon let us consider processes happening in the crystal during an additional annealing in argon. Oxygen leaves the crystal and an increased concentration of oxygen vacancies and of free carriers (electrons) is produced. Along with it goes an intensive production of absorption centres at the expense of localisation of present in surplus negative carriers on the vacancies. The general deterioration of absorption is determined by a cumulative effect from various absorption bands of different centres, which is seen

from the transmission curve of the argon annealed PWO sample, going 10% lower than the standard sample curve. During irradiation of such crystals the initial jump in the absorption is missing, since all the available centres in the crystal have already been filled. The speed of new absorption centre formation grows slowly mainly due to the production of new crystal structure defects - in the first place on the defects of the oxygen sublattice, the most probable of which are Frenkel defects [2].

## 5 Conclusion

In the current work we have made an attempt to minimise the susceptibility of PWO crystals to radiation damage of low dose by searching for optimal conditions during the crystal annealing. Radiation damage at low doses is not by itself a big problem, because the crystal degradation saturates at low doses with no further deterioration up to very high level. However as soon as irradiation is stopped a quite fast crystal recovery takes place. Unfortunately the exposure of the crystals to radiation is not continuous at high energy colliders, but has a cyclic nature, defined by accelerator operation. For this reason, the energy response (energy calibration) of a lead tungstate calorimeter will fluctuate correspondingly with periods, ranging from hours to days, giving strict requirements to a system, monitoring the calorimeter calibration. The PWO crystals, additionally annealed in argon atmosphere show much smoother behaviour in the beginning and the end of irradiation, so that the requirements to the monitoring could be significantly loosened.

## References

- [1] M. Nikl, K. Nitsch, S. Baccaro, A. Cecilla, M. Montecchi, B. Borgia, I. Dafinei, M. Diemoz, M. Martini, E. Risetta, G. Spinoto, A. Vedda, M. Kobayashi, M. Ishii, Y. Usuki, O. Jarolimek, and P. Reiche, *J. Appl. Phys.*, **82** (1997) vol.11, p.5758.
- [2] A. Annenkov, E. Auffray, M. Korzik, P. Lecoq, and J.-P. Peigneux, *On the origin of the transmission damage in lead tungstate crystals under irradiation*, **CMS Note 1998/041**.
- [3] M. Nikl, *Phys.Stat.Sol.(A)* **178** (2000) 595.
- [4] S. Burachas, V. Bondar, Yu. Borodenko, K. Katrunov, V. Martinov, L. Nagornaya, V. Ryzhikov, G. Tamulaitis, H. Gutbrod, and V. Manko, *J. Cryst. Growth*, **198/199** (1999) 881.
- [5] A. Annenkov, M. Korzik, V.Kostylev, V.Ligun. *Method of production of lead tungstate scintillating crystal*. Patent of the Russian Federation **2132417 C1** (1999).
- [6] M.Belov, et al., *Characteristics of scintillating PbWO<sub>4</sub> crystals produced at different growing conditions*. Preprint **29** of the P.N.Lebedev Physical Inst., Moscow 1995.
- [7] N. Gendner (Hamburg Univ.), DESY-THESIS-2000-024, Jul 2000.
- [8] E.K. Kazenas and D.M.Chizhikov. *Pressure and vapor content over oxides of chemical elements*. Moscow, Nauka, 1976. (in Russian).
- [9] B.I. Zadneprovski, V.A. Nefedov, I.S. Bykov, and A.A. Smirnov, *Inorg. Mater.*, **35** (1999) 295. (in Russian).
- [10] M. Ishii, N. Senguttuvan, K. Tanji, T. Kittaka, Y. Usuki, M. Kobayashi, and M. Nikl, *Proc. 5th Intern. Conf. Inorg. Scint. and Their Applic. SCINT'99*, Moscow State Univer., 2000, 402.
- [11] F.A. Krger, *The chemistry of imperfect crystals*. Amsterdam, Nort-Holland publ. comp., 1964.
- [12] J.-M. Moreau, Ph. Galez, J.-P. Peigneux, and M.V. Korzik, *J. Alloys and Compounds*, **283** (1999) 104.
- [13] W. van Loo, *J. Sol. State Chemistry*, **14** (1975) 359.
- [14] B. Han, X.Q. Feng, G. Hu, P. Wang, and Z. Yin, *J. Appl. Phys.* **84** (1998) 2831.
- [15] M. Bhm, F. Henecker, A. Hofstaetter, M. Luh, B.K. Meyer, A.Scharmman, V. Metag, R. Novotny, O.V. Kondratiev, and M.V. Korzik, *Proc. Intern. Workshop on Tungstate Crystals*, Rome, Oct. 12-14, 1998, Univer. La Sapienza, p.141.
- [16] M. Nikl, K. Nitsch, J. Hybler, J. Chval, and P. Reiche, *Phys. Stat. Sol. (b)*, **196** K7 (1996).

Table 1: Possible types of non-stoichiometry and simple charged defects in  $PbWO_4$  crystal.

Region	Vacancy concentration correlation	Type of non-stoichiometry	Condition of electroneutrality according to to main charged defects
1	$[V_O] \gg [V_{Pb}] \gg [V_W]$	$(Pb_{1-x}W)O_{4-y}, y \gg x$	$2[V_O^{\bullet\bullet}] = n$
2	$[V_O] \gg [V_{Pb}] \gg [V_W]$	$(Pb_{1-x}W)O_{4-y}, y > x$	$2[V_O^{\bullet\bullet}] = 2[V_{Pb}^{\prime\prime}] + n$
3	$[V_{Pb}] > [V_O] > [V_W]$	$(Pb_{1-x}W)O_{4-y}, x > y$	$2[V_{Pb}^{\prime\prime}] = 2[V_O^{\bullet\bullet}] + p$
4	$[V_{Pb}] > [V_W] > [V_O]$	$(Pb_{1-x}W)_{1-y}O_4, y > x$	$2[V_{Pb}^{\prime\prime}] + 6[V_W^{6'}] = p$
5	$[V_W] \gg [V_{Pb}] \gg [V_O]$	$(PbW_{1-x})_{1-y}O_4, y \gg x$	$6[V_W^{6'}] = p$

Table 2: Possible types of associated defects of  $PbWO_4$  and corresponding models of centers.

Region	Associated defects	Type of defect concentration dependence on oxygen pressure	Corresponding centres	Centre activity	Reference
1-2	$[V_O^{\bullet}]$	$\sim P_{O_2}^{-1/3}$	$F^+$	absorption $\lambda_{max} \simeq 694$ nm	[1], [3]
	$[V_O^{\times}]$	$\sim P_{O_2}^{-1/2}$	$F$	absorption $\lambda_{max} \simeq 521$ nm	[1], [3]
	$W_W^{\prime}$	$\sim P_{O_2}^{-1/6}$	$(WO_4)^{3-}$	EPR spectra	[15]
2-3	$(V_{Pb}^{\prime\prime} 2O_O^{\bullet})^{\times}$	$\sim P_{O_2}^{-1/2}$	$(WO_2)^{2-}$	absorption $\lambda_{max} \simeq 350$ nm	[10]
			$(WO_3 - WO_3)^{2-}$		
3-4	$(V_{Pb}^{\prime\prime} 2O_O^{\bullet})^{\times}$	$\sim P_{O_2}^{1/2}$	$O^- V_{Pb} O^-$	absorption band 500-750 nm	[2]
	$(V_{Pb}^{\prime\prime} 2Pb_{Pb}^{\bullet})^{\times}$	$\sim P_{O_2}^{1/2}$	$Pb^{3+} - V_{Pb} - Pb^{3+}$	dielectric relaxation measurements	[14]
	$(V_{Pb}^{\prime\prime} O_O^{\bullet} Pb_{Pb}^{\bullet})^{\times}$	$\sim P_{O_2}^{1/2}$	$O^-$ or $Pb^{3+} - O^- - V_{Pb}$	absorption $\lambda_{max} \simeq 420-430$ nm	[9], [16]
5	$(V_W^{(6-z)'}, 0 \leq z \leq 6$	$\sim P_{O_2}^{m/2}, 1 \leq m \leq 3$	-	-	-

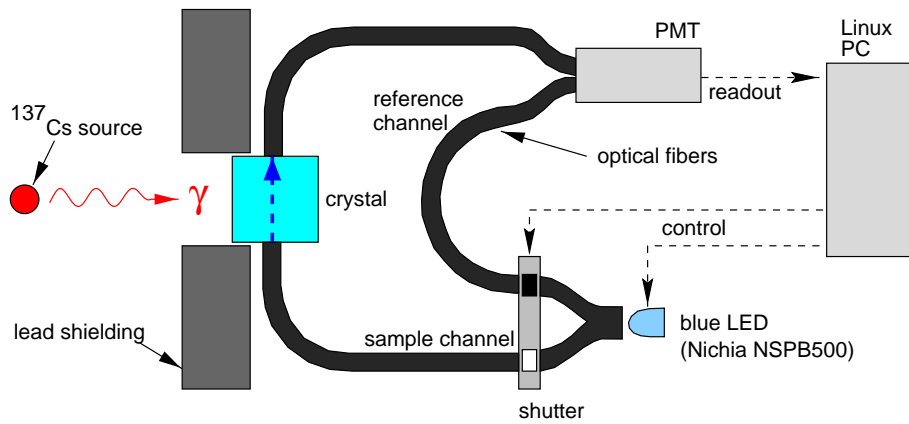


Figure 1: Layout of experimental setup measuring crystal transmission during irradiation.

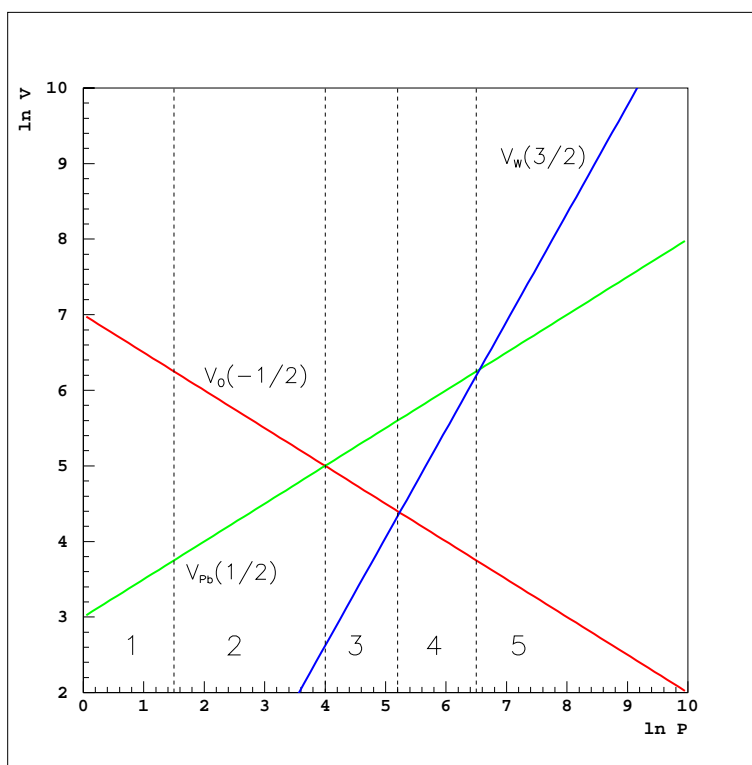


Figure 2: Dependence of vacancy concentration  $[V_i]$  in  $PbWO_4$  crystal on partial oxygen pressure  $P_{O_2}$  in gaseous phase under fixed temperature.

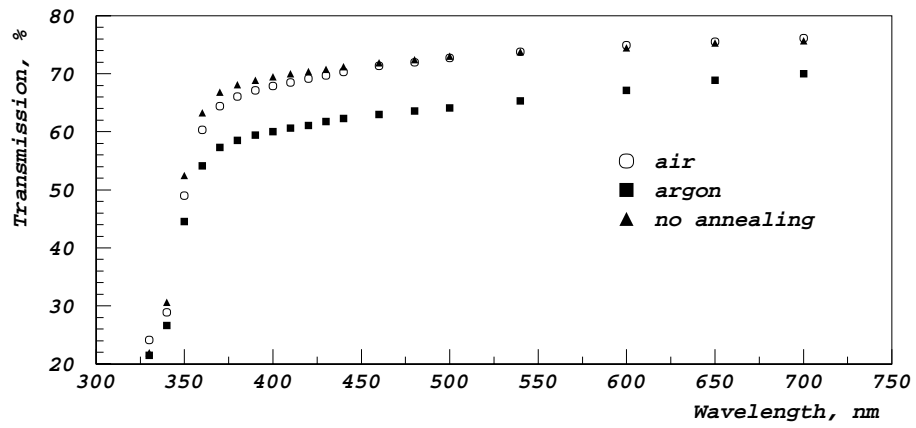


Figure 3: **Transmission spectra of additionally annealed PWO samples.**

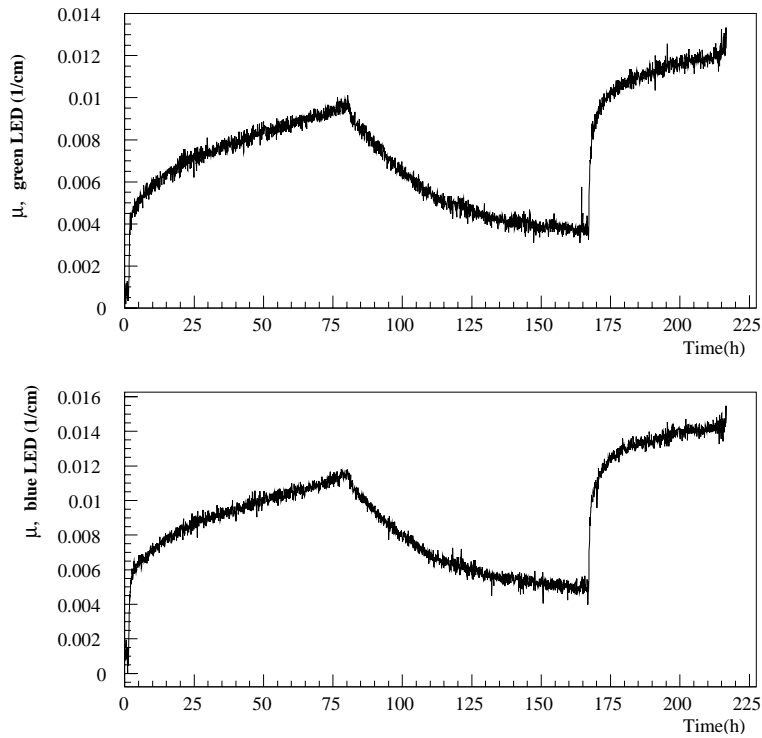


Figure 4: **Radiation induced absorption coefficient of a standard PWO(La) sample (short time irradiation).**



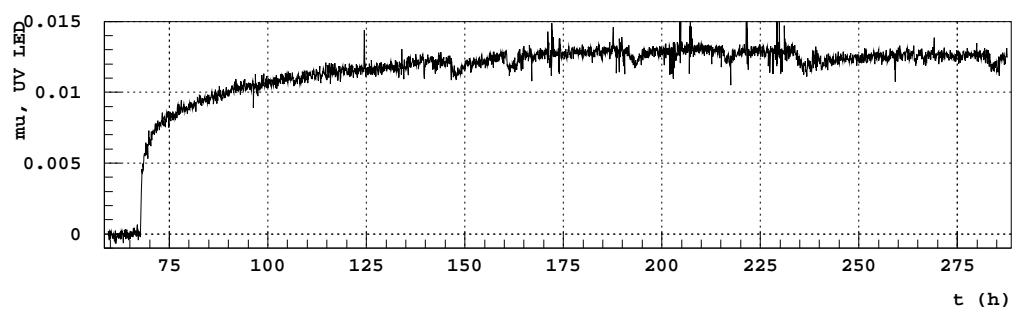
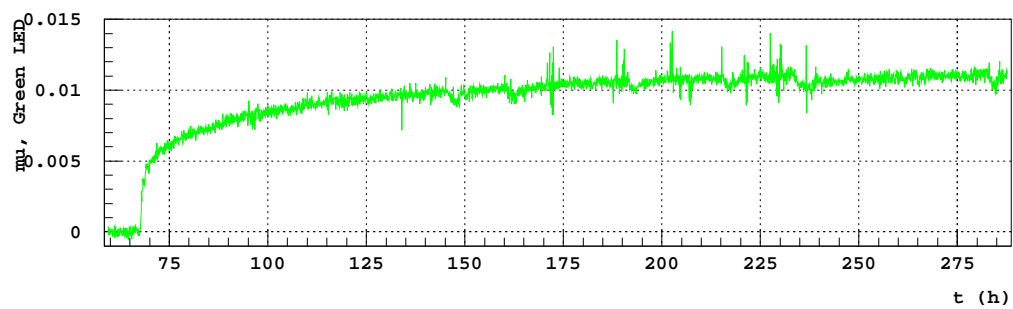
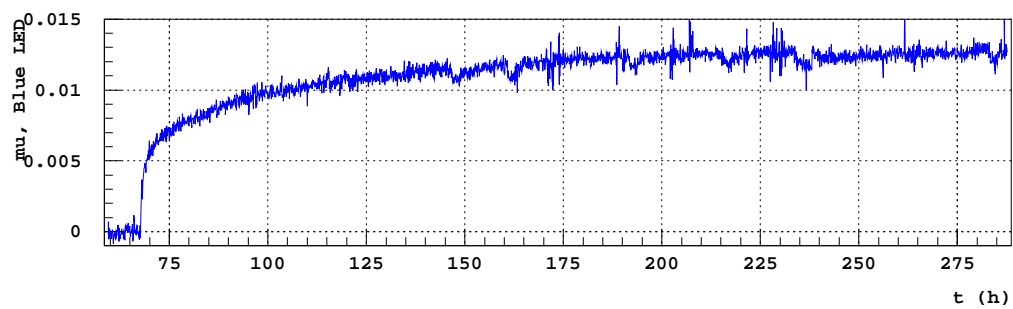


Figure 5: Radiation induced absorption coefficient of a standard PWO(La) sample.

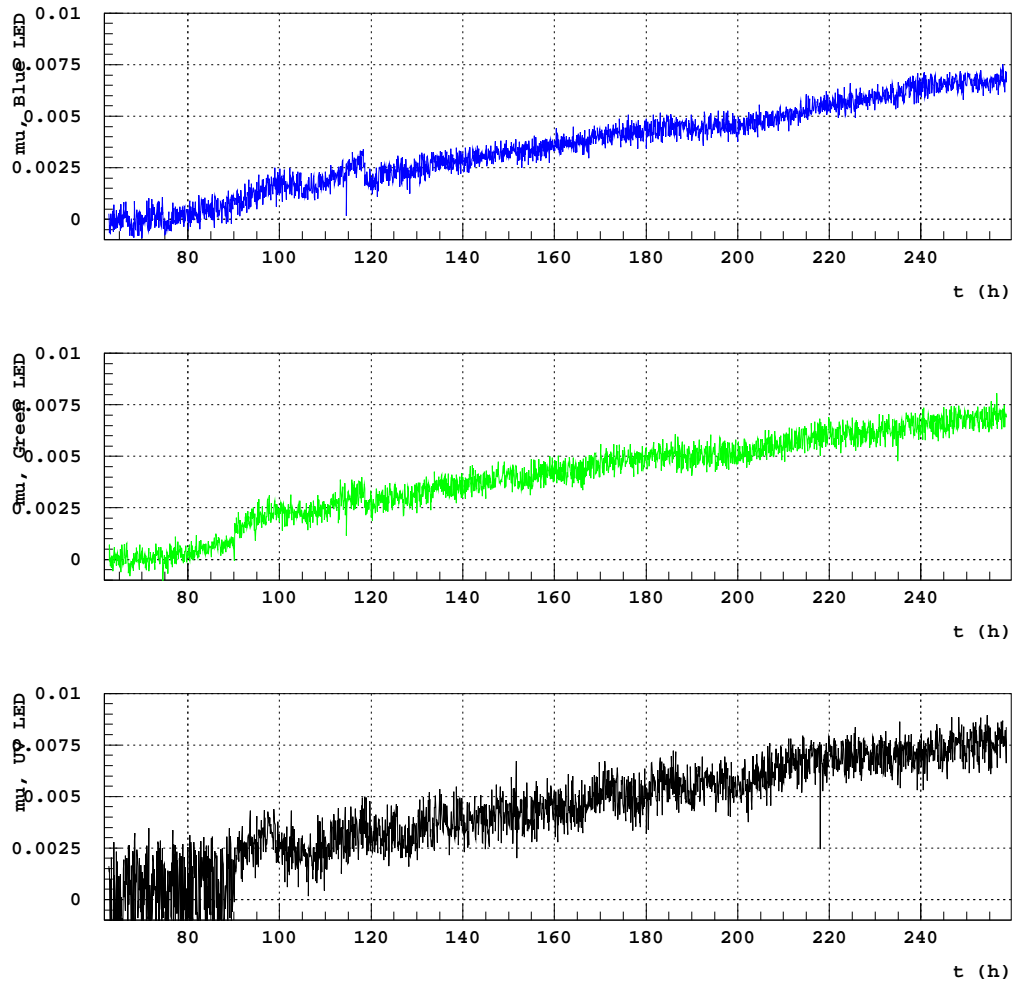


Figure 6: Radiation induced absorption coefficient of PWO(La) sample, additionally annealed in argon.