Functional Materials 16, No.1 (2009)

Temperature dependence of radiation resistance of scintillation detectors based on lead tungstate crystals

S.F.Burachas, M.S.Ippolitov, V.I.Manko, S.A.Nikulin, A.N.Vasiliev, A.L.Apanasenko[*], *A.N.Vasiliev*[**], *A.V.Uzunian*[**], *G.Tamulaitis*[***]

Russian Research Center "Kurchatov Institute", Moscow, Russia
[*]V.Karazin Kharkiv National University, Kharkiv, Ukraine
[**]Institute for High Energy Physics, Protvino, Russia
[***]Vilnius University, Vilnius, Lithuania

Received November 20, 2008

Effect of gamma irradiation on the radiation resistance of detection blocks based on lead tungstate crystals has been studied in +60 to −25°C temperature range. A decrease in the radiation resistance and in the initial light yield recovery rate has been observed at the crystal temperature decrease. For the qualitative interpretation of the experimental results, the cluster model is used that assumes the presence of tungsten oxide clusters in the regular PWO ($PbWO_4$) matrix. The induced absorption of PWO crystals has been shown to depend on the cluster defect (CD) chemical composition and to be due to its radiation-induced transformation. The temperature dependence of the crystal radiation resistance has been shown to be in correlation with that of the initial CD composition recovery time.

Изучено влияние гамма-облучения на радиационную стойкость блоков детектирования на основе кристаллов вольфрамата свинца в температурном диапазоне от +60 до −25°C. С понижением температуры кристаллов наблюдалось увеличение чувствительности к облучению и более медленное восстановление начального световыхода. Для качественной интерпретации экспериментальных результатов используется кластерная модель, предполагающая наличие кластеров оксидов вольфрама в регулярной матрице PWO ($PbWO_4$). Показано, что наведенное поглощение кристаллов PWO зависит от химического состава кластерных дефектов (КД) и обусловлено его радиационно-индуцированным преобразованием, а температурная зависимость радиационной стойкости кристаллов коррелирует с температурной зависимостью времени восстановления начального состава КД.

The decreasing operating temperature of scintillation detectors produced based on PWO crystals is known to result in increased light yield [1, 2]. However, the radiation resistance of PWO crystals concurrently drops significantly with lowering temperature [3, 4]. These two facts have stimulated us to study the physical origins of radiation resistance of the scintillation detectors based on lead tungstate crystals. The experimental results on PWO have usually been interpreted within the framework of the point defect model. This model, however, does not explain satisfactorily the large volume of experimental data accumulated up to now [5]. An alternative interpretation based on so-called cluster defect model is more suitable for explanation of the experimental results obtained for annealed and irradiated PWO crystals [6–8]. In this paper, we present the results on simultaneous optical transmission and light

Table 1. Characteristics of the first batch of PWO crystals (RM stands for raw material; 1R for the first recrystallization; 2R for double recrystallization)

Crystal	Raw material and number of growth cycles	Doping element and concentration, ppm	Annealing, °C/h	Transmittance, %	Light yield, phe/MeV	I_{+20}/I_{-20}, %	Δ,% $I_{-20}-I_{+20}$	I_{+20}/I_{-20}, %	Δ, % $I_{-20}-I_{+20}$
				360/420 nm		Irradiation rate 2 rad/h		Irradiation rate 20 rad/h	
Size: 22×22×180 mm^3; production: (a) "North Crystals" Apatity; (b) "Technical Chemical Plant" Bogoroditsk									
b389	2R/N/A	N/A	N/A	31.0/70.5	10.3	5/18	13	11/36	25
b404	1R/N/A	N/A	N/A	22.9/66.8	8.9	8/27	19	16/52	36
a1412	RM/5	Y/100	600/3	29.4	64.3	9.2	1/17	16	16/54
a1434	2R/4	Y/100	560/2	33.4	65.6	9.0	5/20	15	18/44
a15500	1R/1	Y/90	600/3	39.1	70.2	12.0	2/18	16	10/45
a15517	1R/1	Gd/80	600/3	42.4	71.3	10.5	1/16	15	8/43
a15851	1R/1	Gd/80	580/2	41.1/71.3	11.0	5/21	16	15/51	36
a15608	2R/1	Gd/80	600/3	37.2/69.0	10.9	2/13	11	9/30	21
a16618	1R/1	La/38	560/2	50.6/71.9	11.2	5/23	18	20/50	30
a16628	1R/1	La,Y/22/20	560/2	46.9/71.3	12.3	6/26	20	26/60	34

yield (LY) measurements of PWO crystals subjected to gamma irradiation. The temperature was varied in the range between −25°C and +60°C. The radiation resistance of scintillating elements produced from crystals grown from different raw materials, with different doping and annealed in different conditions. It is shown that the experimental results can be qualitatively explained within the framework of the cluster model.

Parameters of the first batch including 10 crystals are presented in Table 1. The crystals of that batch were studied at IHEP, Protvino (Russia). The crystals were examined using a setup providing simultaneous measurements of PWO crystal scintillation response under gamma irradiation in temperature range from −25°C to +20°C. The crystals were irradiated at the dose rates of 2 and 20 rad/h. The detailed description of the IHEP experimental setup can be found in [3]. The samples from the second batch consisting of 6 crystals were irradiated in temperature range from +20°C to +60°C at the dose rate of 15 krad/h. The measurements were performed using the GUT-200M irradiation setup at the RRC "Kurchatov Institute". The total dose of 3 krad was accumulated. Light transmission at 420 nm wavelength was measured for each crystal prior to and 3 min after irradiation. The experimental results and the initial parame-

Table 2. Characteristics of the second batch of PWO crystals

Crystal	Raw material	Number growth	Doping element and concentration, ppm	Transmission, 420 nm, %	T = 20°C Decrease of transmission at 420 nm, %	T = 60°C Decrease of transmission at 420 nm, %
Size: 30×30×230 mm^3 production: "North Crystals" Apatity						
64	2R	6	Y/90	71.3	12.3	6.1
67	1R	2	Y/90	70.0	12.9	5.0
68	1R	3	Y/90	72.1	13.3	5.5
70	1R	5	Y/90	70.0	16.2	7.2
80	1R	4	Y/100	69.1	12.5	5.4
81	1R	5	Y/100	71.3	13.7	7.0

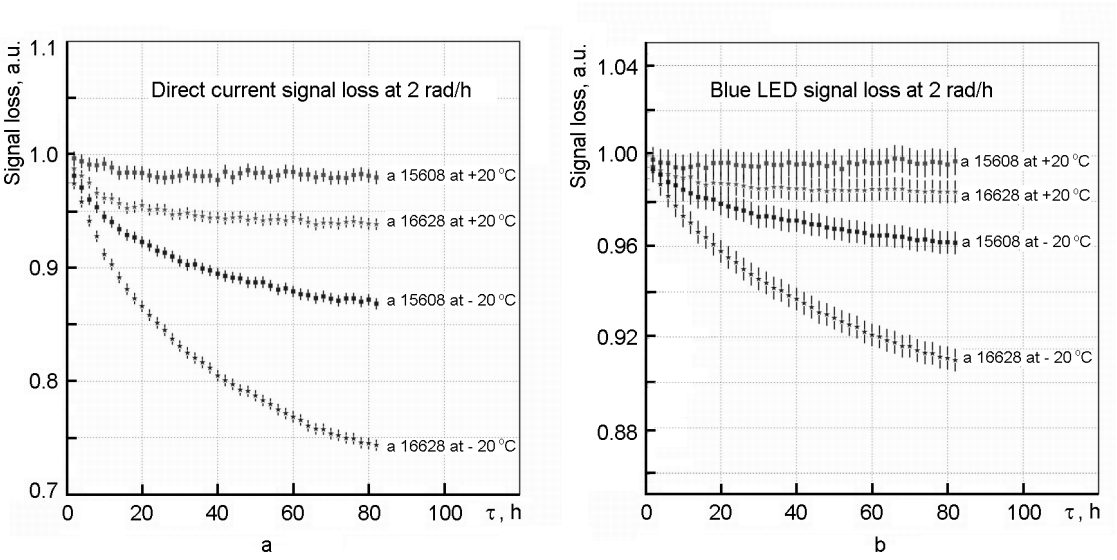

Fig. 1. Time evolution of the scintillation signal relative value (the left) and transmittivity of blue light emission diode (the right) for different crystals at temperatures +20°C and −20°C under gamma irradiation at dose rate 2 rad/h.

ters of the crystals of the second batch are presented in Table 2.

The post-irradiation time dependences of the light yield and optical transmission at 450 nm at −20°C and +20°C for two typical crystals are presented in Fig. 1. The measurements were carried out at the dose rate of 2 rad/h. The light yield and optical transmission decrease in a correlated way, in accordance with the commonly accepted assumption that the light yield decrease is mainly defined by the light absorption increase in the emission region. A trend to saturation can be seen in the simultaneous drop of the light yield and optical transmission. For crystal samples with similar light yield at room temperature, the slope of decay curves and saturation level are vary strongly from one sample to another (i.e. depending on raw material, doping, annealing conditions, etc.).

It is seen from Figs. 1, 2 that the temperature lowering slows down the light yield saturation. The light yield and especially its saturation level depends heavily on the irradiation dose. The absolute value to which the light yield asymptotically approaches under continuous irradiation (so called quasi-plateau) shows no linear dependence on the dose rate. For example, the light yield saturation levels in crystal No. 404 are 0.69 and 0.43 at the dose rate of 2 and 20 rad/min, respectively (see Fig. 2). On the other hand, the light yield decrease after the same irradiation dose is different in otherwise the same samples but annealed

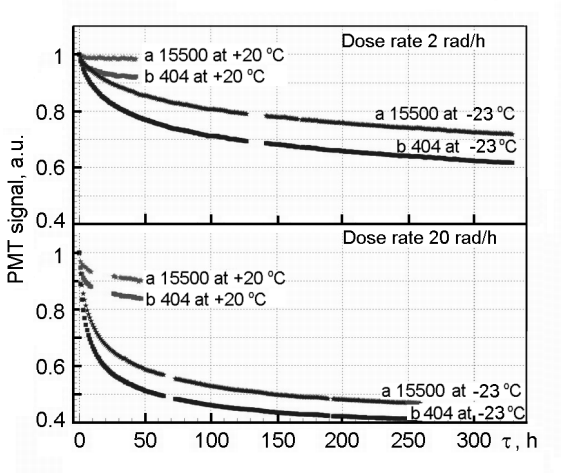

Fig. 2. Time evolution of the scintillation signal relative values for different crystals at +20°C and −20°C under gamma irradiation at dose rate 2 rad/h (upper part) and 20 rad/h (lower part).

under different conditions (see crystals Nos. 15517 and 15851 in Table 1).

The relative LY drop at the dose rate of 2 and 20 rad/h is presented in Table 1 for different PWO samples in the temperature range from −20°C to +20°C. The light yield behavior after 80 h irradiation at the dose rate of 20 rad/h is presented in Fig. 3. For samples grown from different raw materials, with different doping and annealing conditions, the light yield decrease is close to linear in the temperature range from −20°C to +20°C.

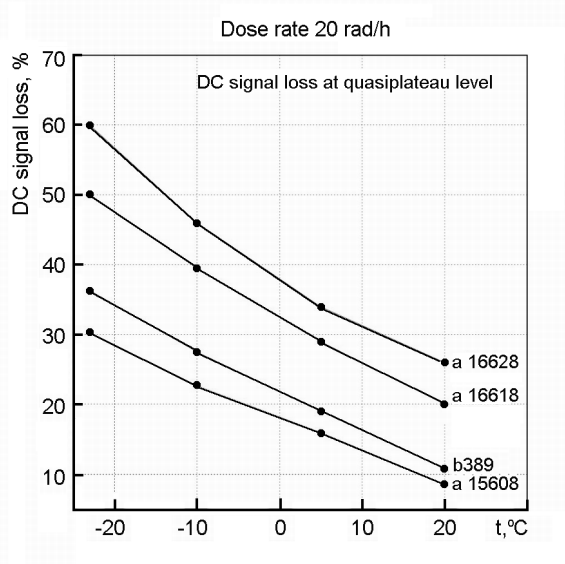

Fig. 3. Relative decrease of scintillation signal as a function of temperature for crystals after gamma-ray irradiation at dose rate 20 rad/h during 80 h. (After each irradiation cycle at temperatures +20°C, +5°C, −10°C and −23°C, crystals were exposed to the day light at temperature +40°C until full recovery of initial state).

For all samples under study, the temperature decrease from +20°C to −20°C results in essentially the same LY increase approximately by a factor of 3 with respect to LY at room temperature. This factor value shows no significant dependence on growth conditions. As seen in Table 2, the temperature increase from 20°C to 60°C results in an increase of the transparency stability under irradiation by a factor of about 2.3.

The crystal light yield shows no significant recovery at −25°C during tens of hours. At the same time, temperature elevation up to +20°C ensures the light yield recovery in approximately 100 h.

All the experimental results can be described in the framework of the cluster defect model. According to this model [6–9], the light yield of PWO is influenced by light absorption in clusters of tungsten oxides. Those clusters are always presented in the regular PWO lattice. Formation of the variable valence cluster defects is due to stoichiometry break during crystal growth and is inherent in all oxide crystals [9]. Since tungsten can form oxides with valence +4, +5 and +6, the cluster composition depends on the oxygen content and is defined by the concentration of tungsten ions in different valence states. The cluster composition can be described by a compact formula WO_{3-x} or presented in more detail as

$$WO_{3-x} = (1 - 2a - b)WO_3 + a W_2O_5 + b WO_2, \quad (1)$$

where $x = a + b$. Here, a and b characterize the relative content of W^{5+} and W^{4+} in a cluster, respectively. The coefficients are related to the oxygen deficit in the cluster in comparison with pure tungsten oxide WO_3 which contains tungsten ions only in the W^{6+} valence state. The absorption spectrum of the clusters and, consequently, the crystal color depend on the cluster composition, i.e. they can be related with the coefficients a and b. This relationship for certain typical compositions of cluster compound WO_{3-x} is illustrated in Table 3, where the color of tungsten oxide is indicated together with the corresponding values of a and b [10]. According to [6, 9], the colorless crystals fabricated for CERN projects CMS and ALICE had an optimal x value of ~0.11 at $a \approx 0.11$, $b = 0$.

The composition of WO_{3-x} clusters in PWO crystals depends on growth conditions. It can also be changed by heat treatment. Annealing in an oxygen-enriched atmosphere increases the number of oxygen ions in a cluster (x becomes smaller). Such an-

Table 3. Color of tungsten oxides with different ratio of W_2O_5 and WO_2 content described by coefficients a and b in equation (1), and regions of maximum of optical absorption

	a				
b	0	~0.11	0.115	0.16	1
0	WO_3 yellow (410–450) nm	~$WO_{2.89}$ colorless	$WO_{2.885}$ Bluish (580–595) nm		$WO_{2.5}$ Blue (580–595) nm
0.12				$WO_{2.72}$ Violet (500–560) nm	
1	WO_2, dark brown (450–600) nm				

nealing results in reduction of radiation-induced optical absorption and in shortening of the time necessary for the initial transparence recovery. Meanwhile, annealing in reducing environment has an opposite result (see Fig. 3 in [6]). The concentration of cluster defects in the crystal depends on raw material and, hence, on the crystal stoichiometry. Value ΔI in Table 1 reflects this concentration. The lower is this value, the higher is the radiation resistance (see Table 1, crystal No.15608).

In our further discussion, we shall proceed from the assumption that the initially pure PWO crystal is colorless, while its coloration is caused by the increase in W^{5+} and W^{4+} ion concentrations in the cluster composition. It follows from [8] that the formation of additional tungsten ions may be due to irradiation or reducing annealing. Negative O^- ions can be formed only under irradiation. Annealing simply results in a changed oxygen content in the cluster defect while it remains in the bivalent condition. The presence of O^- in the irradiated crystal makes the process reversible. Thus, the initial cluster composition in the irradiated crystals is restored after the irradiation is over. Meanwhile, the cluster composition after a thermal annealing remains stable.

Let us discuss in more detail what happens after gamma irradiation of a crystal (in non-equilibrium state). Clusters with high content of W^{4+} ions are dark in color (see Table 3) and are not typical of PWO crystals intended for high energy physics applications. W^{4+} ions are formed under very high irradiation dose (1 Mrad and more). Such doses considerably exceed those expected in ALICE and CMS experiments at CERN [11]. Therefore, from here on, the coefficient b is assumed to be zero.

Due to irradiation, some oxygen ions in cluster defects lose electrons which are captured by tungsten ions. These tungsten ions take a state of lower valence, while some oxygen ions are repelled out of the cluster. Consequently, in contrast to the initial defect clusters before irradiation, charged clusters with W ions in lower charge states and ions O^- with one electron (effectively positively charged O^- ions) are formed in the cluster defects. At the same time, coloration of the initially colorless PWO crystal occurs due to increased amount of W^{5+} in the clusters. The formation of the charged clusters can be supposed to be stimulated by Coulomb interaction which defines direction of returning O^- ions back to their "mother" clusters.

The nonlinear decrease of the light yield and optical transmission at constant temperature (see Figs. 1, 2) can be explained as follows. At the initial irradiation stage, the radiation-induced transition of W^{6+} ions into W^{5+} influences most strongly the composition of the cluster defects. Accumulation of W^{5+} ions increases probability of their transition back to W^{6+} state (thermal reduction). This process slows down the irradiation-induced changes in the cluster defect composition and, hence, slows down the light yield decrease. Saturation occurs when the rates of the radiation transition and thermal reduction of W^{6+} ions become equal to one another. The cluster composition formed during irradiation up to saturation conditions becomes furthermore unchanged. The light yield of the crystal does not fall further. Taking into account expression (1) and assuming $b = 0$, the change in composition of the cluster defect can be expressed as

$$WO_{3-x} \rightarrow [WO_{3-x-\Delta x}]^- \leftrightarrow [(\Delta a)O^-]^+,$$

where

$$WO_{3-x-\Delta x} = \quad (2)$$
$$= [1 - 2(a + \Delta a)]WO_3 + (a + \Delta a)W_2O_5.$$

Here Δa and Δx are irradiation-induced changes of the corresponding coefficients. The expression (2) defines the final result of cluster composition after irradiation. It defines the level of induced absorption at quasi-plateau. In accordance with the new cluster defect composition, the optical absorption spectrum of the cluster defect will change. The spectrum of optical absorption of the whole crystal will also change. The remaining oxygen ions do not influence the crystal color [8]. A study of the dynamic of change in cluster defect composition during irradiation can be found in [12].

After the irradiation is over, only the W^{6+} thermal recovery is present resulting in decreasing density of charged complexes. This process ends when initial electrically neutral clusters WO_{3-x} without presence of O^- ions are recovered.

It is seen from the experimental data that the rate of radiation-induced transition from W^{6+} to W^{5+} depends on irradiation dose while the rate of temperature-induced recovery from W^{5+} to W^{6+} depends on the crystal temperature. It is obvious (see (2)

that the quasi-plateau level increases with increasing Δa and depends on the crystal temperature.

The influence of raw material and annealing conditions on radiation stability was already discussed in this paper. The criterion of the optimal doping concentration is discussed in [6, 7]. The lower is the dopant concentration, the lower is the concentration of cluster defects in the crystal. In this case, the crystal LY increases, according to [13].

At −25°C, there is essentially no recovery of light yield. The long recovery time at low temperatures can be explained by a strong temperature dependence of the transition from W^{5+} to W^{6+}. In our model, this transition corresponds to returning of oxygen ions back to cluster defect across a potential barrier. Probably, the temperature dependence of this transition is intensified by phonons of a certain energy or is influenced by electric field or other additional effects.

Thus, the light yield increase in PWO crystals by lowering the crystal temperature is independent on growth technology. The light yield decrease during irradiation at constant temperature is related to the radiation-induced transformation of the cluster defect composition. This process causes an additional light absorption in the crystal. Decrease of radiation resistance of crystals with temperature decrease is due to increase in time necessary for recovery of the cluster defect composition. The recovery time also depends on the crystal production technology.The higher is the temperature of PWO crystal, the less pronounced is the radiation dependence of the main crystal characteristics.

Acknowledgments. We would like to thank the IHEP management and the IHEP Radiation Department for support in performing a part of the study on radiation resistance.

References

1. D.Aleksandov, S.Burachas, M.Ippolitov et al., *Nucl. Inst. Meth. Phys. Res.*, **A550**, 169 (2005).
2. R.W.Novotny, *IEEE Trans. Nucl. Sci.*, **51**, 3076 (2004).
3. P.Semenov, A.Uzunian, A.Davidenko et al., *Nucl. Inst. Meth. Phys. Res.*, **A582**, 575 (2007).
4. R.Novotny, S.Burachas, W.Doring et al., *IEEE Trans. Nucl. Sci.*, **55**, 1283 (2008).
5. M.Nikl, *Phys. Stat. Sol. (a)*, **178**, 595 (2000).
6. S.Burachas, S.Beloglovski, I.Makov et al., *Nucl. Inst. Meth. Phys. Res. A*, **505**, 656 (2003).
7. S.Burachas, S.Beloglovsky, Yu.Saveliev et al., *Functional Materials*, **12**, 287 (2005).
8. S.Burachas, Yu.Saveliev, M.Ippolitov et al., *J. Cryst. Growth*, **293**, 62 (2006).
9. S.Burachas, A.Vasiliev, M.Ippolitov et al., *Kristallografiya*, **52**, 1124 (2007).
10. Gmelin Handbuch der Anorganische Chemie, System No.54, Wolfram B2, Springer Verlag, Berlin (1997).
11. R.Y.Zhu et al., *Nucl. Instr. Meth. Phys. Res. A*, **413**, 297 (1998).
12. S.Burachas, M.Ippolitov, V.Manko et al., *Rad. Meas,* (to be published).
13. R.W.Novotny, W.M.Doring, F.Hjelen et al., in: Proc. IEEE Nuclear Science Symp., Puerto Rico, 2005 Conf. Rec., N12-4.

Температурна залежність радіаційної стійкості блоків детектування на основі кристалів вольфрамату свинцю

С.Ф.Бурачас, А.А.Васильєв, М.С.Іпполітов, В.І.Манько, С.А.Нікулін, А.Л.Апанасенко, А.Н.Васильєв, А.В.Узунян, Г.Тамулайтіс

Досліджено вплив гамма-опромінення на радіаційну стійкість блоків детектування на основі кристалів вольфрамату свинцю у температурному діапазоні від +60 до −25°С. Зі зниженням температури кристалів спостерігалося збільшення чутливості до опромінення та уповільнення відновлення початкового світловиходу. Для якісної інтерпретації експериментальних результатів використовується кластерна модель, яка припускає наявність кластерів оксидів вольфраму у регулярній матриці PWO ($PbWO_4$). Показано, що наведене поглинання кристалів PWO залежить від хімічного складу кластерних дефектів (КД) та обумовлено його радіаційно індукованим перетворенням, а температурна залежність радіаційної стійкості кристалів корелює з температурною залежністю часу відновлення початкового складу КД.