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LAPP-EXP-2006-03.

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Presented by Dr. G. Drobychev at the Workshop
"Les journées CMS France", Strasbourg, Mont Saint Odile, 29-31 March, 2006.

Abstract

Shallow traps influence the radiation damage behaviour of lead tungstate scintillation crystals when exposed to continuous low dose rate radiation. Radiation initiates diffusion of Oxygen vacancies in the crystal giving rise to their aggregation if their density is high enough, which creates deeper traps than single vacancies. The situation may occur in high luminosity experiments where scintillation crystals are exposed for long periods of time to irradiation. The experimental results presented in this paper illustrate the importance of optimizing the crystals by reducing the concentration of the shallow traps and not only of the deep traps.

Keywords: High energy physics, electromagnetic calorimetry, lead tungstate single crystal, scintillation, electron and hole centres, radiation damage, light yield, light collection.
PACS: **61.72.Ss, 61.80.Az, 29.40.Mc**

1. Introduction

The long term stability of the scintillation material parameters in a radiation environment is one crucial feature of precise electromagnetic calorimetry for experiments at high luminosity accelerators. Lead tungstate PWO scintillator seems to be a very promising material for this application. Low level radiation damage of currently produced scintillation crystal's optical transmission has been confirmed [1]. Moreover, the scintillation mechanism is not damaged in PWO crystal grown in optimized conditions at doses and dose rates expected at new high luminosity machines such as LHC at CERN. This has been obtained through a long and systematic development [1, 2] aiming at reducing the concentration of deep electron and hole traps in the crystal, which are at the origin of metastable color centers. The main source of deep centers in PWO crystals are Oxygen related Frenkel defects. However, lead tungstate synthetic crystals even grown from purified raw material, contain also shallow electron centers associated to Oxygen vacancies. Their influence was found to be negligible to contribute to the optical transmission radiation damage in lead tungstate [2]. This assumption is based on the fact that shallow capturing centers create shallow electron centers which release electrons in the conduction band in a very short time at room temperature and therefore do not contribute to the quasi- stationary induced absorption. However shallow traps create short life-time color centers contributing to transient

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induced absorption bands decreasing the amount of light seen by the photo-detector in a short time scale [3]. This occurs at relatively high irradiation dose rate in inorganic scintillators when a reasonable fraction of the shallow traps becomes populated. However steady state crystal irradiation creates conditions for the diffusion of the neutral shallow electronic centers significantly increasing the probability of their coupling in pairs and more complex defects. Pairs have deeper capture levels as compared to single vacancies and can create metastable color centers increasing the optical absorption in the visible spectral region under ionizing radiation. In this paper we show experimental evidence of this pair creation effect under continuous irradiation of lead tungstate scintillation crystals and we devise about its influence on the scintillation detector properties. This effect appears to be related to the conversion of single Oxygen vacancies Vo in di-vacancies (WO_3-WO_3). It leads to the absence of induced absorption dynamic saturation at moderate dose rates and to a slow and continuous decrease of the amount of light detected by photo detectors.

2. Oxygen vacancy based defects in the lead tungstate crystal

Whatever the lead tungstate crystal growth technique from stoichiometric raw materials, a dominant leakage of lead from the melt takes place during the process, leading to the creation of cation vacancies V_c on the lead site in the host. These cation vacancies V_c are compensated by Oxygen vacancies Vo and other defects including not controlled impurities. Both types of vacancies are significantly suppressed in the crystal by additional doping with trivalent ions with stable valence state as described in [1]. For undoped crystals grown from purified raw materials the Oxygen vacancies are the main source of charge balance of cation vacancies. The main parameters of the electron centers related to single vacancies and their aggregates, have been measured by thermo-stimulated luminescence (TSL) and are listed in Table 1 [1, 3], where S is the frequency factor, γ the order of the kinetic, E_T the thermal activation energy of the trap and τ the relaxation time of the trap at room temperature . The 70 meV trap is related to Oxygen vacancies in regular scheelite tetrahedra and the 230 and 270 meV traps are related to superstructure distorted Oxygen tetrahedra. The group of peaks around 200 K has been attributed to di-vacancy centres localized in the same polyhedron in the regular and super-structures [1]. Finally, the 580 meV centre is formed by di-vacancies from different neighbouring polyhedra. The relaxation time τ of di-vacancies is less than one hour (of the order of a few minutes) and in agreement with radiation induced absorption recovery data [4].

The Pb^{1+}-V_0 centre is stable until 175 K and has been detected by EPR method. As for other V_0 based centres it is strongly suppressed by additional doping of La^{3+} or Y^{3+}.

Through the relaxation time of the electronic centres at room temperature it is possible to determine their influence on the crystal radiation damage behaviour. Centres based on single anion vacancies have relatively short relaxation constants and contribute only to the transient radiation induced absorption up to rather high dose rates. On the contrary, $(WO_3^-WO_3)^{2-}$ centres have a relatively long relaxation time and their contribution to radiation induced absorption is observable. They cause a wide induced absorption band in the red-NIR spectral region with a maximum around 670-700 nm [2] which partially overlaps the scintillation band.

At room temperature there is a spontaneous transfer of Oxygen ions to empty sites, which leads to a migration of the vacancies [5,6]. Some of the vacancies are recombining with Oxygen at the crystal surface and macro-defects, but for the majority of them there is a spontaneous aggregation during this migration. This process results in the creation of di-; tri- four- vacancy clusters. The spontaneous process of aggregation is rather slow because uncharged vacancies have a positive uncompensated charge and have a tendency to repel each other. However the process of aggregation may be significantly accelerated if (i) part of the vacancies are neutralized, and (ii) a gradient of vacancy concentration is created in the crystal. Under irradiation free conduction band electrons are captured by Oxygen vacancies which are then transformed to neutral electronic center. The dose profile in the crystal as well as the non-homogeneous distribution of vacancies during the crystal growth create a gradient of concentration of neutral and charged vacancies. Under continuous irradiation for a time significantly higher than the relaxation time of the deepest electron defect some of the defect can capture two electrons and become attracted by genuine vacancies, leading to the creation of di-vacancies sharing the two electrons. This process progressively increase the concentration of deep electron centers in the crystal with longer relaxation time constants. This results in a slow decrease of the crystal transmission (and therefore of the light yield) at the point where dynamic saturation (equilibrium between damage and recovery) would normally appear. This damage slope is determined by the time constant of the creation of di-vacancies.

3. The model

Let's consider a model where ionizing radiation produces n_e electrons in the crystal conduction band with a rate V per ($s \times m^3$). The crystal contains vacancies with a concentration n for uncharged, n^* for charged and Y for di- vacancies. Let's define Ω as the rate of two electron being captured by a shallow vacancy, b as the total (radiative and non-radiative) recombination rate of the conduction band electrons which is close to $1/\tau_{sc}$ for lead tungstate (10^8 s^{-1}), Ω_1 as

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the rate of electron relaxation from the shallow centers based on a single vacancy, D as the single vacancy diffusion parameter, r_0 as the capture radius of an uncharged vacancy by a charged vacancy, ω_{TA} as the thermo initiated relaxation rate of di-vacancy centers. To simplify the model we suppose here that the diffusion coefficients are the same for charged and uncharged vacancies.

The kinetics equations describing the system are therefore:

$$\frac{dn_e}{dt} = -n_e \cdot \Omega - n_e \cdot b + V + n^* \cdot \Omega_1$$

$$\frac{dn}{dt} = -n_e \Omega + n^* \Omega_1 - 4\pi r_0 D n n^* \cdot (1 - \frac{r_0}{\sqrt{4\pi D t}})$$

$$\frac{dn^*}{dt} = n_e \cdot \Omega - n^* \Omega_1 - 4\pi r_0 D n n^* \cdot (1 - \frac{r_0}{\sqrt{4\pi D t}})$$

$$\frac{dY}{dt} = 4\pi r_0 D n n^* \cdot (1 - \frac{r_0}{\sqrt{4\pi D t}}) - Y\omega_{TA}$$

For numerical calculations we used the following parameters. It is reasonable to set the diffusion radius r_0 to 10^{-9} m, which is the typical size of the unit cell. There are no reliable methods to determine the V_o concentration in lead tungstate crystal. Even EPR gives an indirect estimation through the measurement of Pb^+- V_o centers. The actual concentration may be even larger, because not all the anion vacancies create such centers. Nevertheless, our study has shown that both types of vacancies, cation and anion, are well suppressed in lead tungstate by trivalent doping by La or Y with concentration of about 10^{24} m^{-3} [1]. This value can be considered as a reasonable estimate of the V_o initial concentration n_0. We choose V to be equal to 10^{17} particles/($s*m^3$) which corresponds to a dose rate 100 rad per hour for the lead tungstate material.

The electron capture time is estimated from the following assumption. The scintillation rise time in lead tungstate is shorter than 100 ps, corresponding to a rather high electron capture rate (10^{10} s^{-1}). The simultaneous capture of two electrons by Oxygen vacancies is less probable because it requires the presence of at least two electrons in the vicinity of the vacancy. Nevertheless this rate has to be larger than the shallow trap release rate at room temperature which is of the order of 10^6 s^{-1} [1]. On the other hand it is limited on the high value side by the scintillation kinetics ($2*10^{-8}$s), as no scintillation quenching has been observed even for high electron density. Therefore we estimated Ω to be 10^7 s^{-1}. The estimation of Ω_1=10^5 s^{-1} is obtained from TSL data of the centers in Table 1. The initial conditions have been chosen as $n_e(0)$= n*(0)=0.

4. Samples and experimental studies

The effect of Oxygen vacancies condensation has been measured for ^{60}Co front irradiation of 23 cm long PWO crystals in the CMS ECAL crystal laboratory facilities at CERN. For front crystal irradiation the amount of scintillation photons detected by the photo-detector is f=αY, where α- is the light collection efficiency and Y is the light yield. The light collection efficiency is proportional to the crystal optical transmission T. Therefore f/f_0 varies with time as T/T_0. Consequently f/f_0= exp(-Δk*l), where Δk is the induced absorption coefficient and l is the path-length of photons through the irradiated part of the crystal. Full size PWO crystals of the CMS ECAL barrel [7], grown in two different conditions have been investigated. Crystals of the first type (Type I) have been grown from specified raw material with small amount of additional doping to compensate Pb (Vc) and O (Vo) vacancies in the crystal whereas crystals of the second type (Type II) were doped by trivalent ions according to an optimization procedure already discussed in [1]. This has been confirmed by EPR studies of crystals of both types produced at the same time, but for another experiment (PANDA, GSI) [8], from which it appears that Type I crystals have a systematic larger concentration of Pb^+-V_o centres due to a larger concentration of Oxygen vacancies.

Crystals are continuously irradiated with ^{60}Co (1.23 MeV) in the front geometry as described in [9] at a dose rate of 0.15 Gy/h. The crystal light output variation caused by the optical transmission radiation damage in the front part of the crystal has been evaluated through the measurement of the current of the PMT coupled to the rear face of the crystal. The bench is thermo-stabilized with an accuracy of 0.1°C. This method of irradiation is currently used for a fast control of the crystal radiation hardness. The correlation between the light collection loss measured by this method, the crystal light yield and the optical transmission losses measured in the different geometry and irradiation environment is well understood [10]. In the present study we irradiated crystals for 10^5 min and a correction of the data for the irradiation source decay has been applied. More than 10 crystals of each type have been tested, all satisfying the CMS specification. Results shown here are significant examples.

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All measured crystals show a similar shape of the radiation induced absorption spectrum indicating the presence of the same types of deep capturing defects and corresponding color centers [2] in the crystals. However, Type I crystals have a systematic higher induced absorption in the red-infrared region as a result of a higher concentration of di-vacancies in as grown crystals. Fig1. shows the radiation induced absorption spectra of one crystal of each type as an example.

Fig 2(a, b, c) shows the variation of the light collection of full size barrel type lead tungstate crystals under those irradiation conditions.

A continuous decrease of the light output in the second and third crystals is clearly visible as a result of a much larger concentration of initial single vacancies, leading to an increased probability of aggregation.

Fig.3 shows simulation data. For comparison we selected the experimental data points, which are marked by dots in Fig.2c. Considering that the first stage of the radiation damage kinetics is due to the creation of the color centers associated to Frenkel defects we have added a two time constant exponential decay to our model to take also into account this "standard" radiation damage mechanism. The agreement between the simulation model and the data of Type I crystal is very good for $n_0=10^{24}$ cm^{-3} and $D=10^{-10}$ cm^2 s^{-1}. If on the other hand a proper charge compensation of Oxygen vacancies is achieved by an appropriate doping, in order to reduce the concentration of active Oxygen vacancies to about $10^{22}cm^{-3}$ (as it is the case for Type II crystals) the slow light yield decrease almost disappears.

Obviously, the model developed shows a dependence of the aggregation phenomena to both the concentration of the vacancies and their ability to diffuse in the crystal. The largest uncertainty is for the diffusion parameter D. However its value can be estimated on the basis of simple arguments. It is reasonable to assume that D depends on the mass of the diffusing particles. We can therefore estimate the range of realistic D values for a diffusing neutral vacancy in the PWO structure. The lightest neutral species in the crystal is an exciton (coupled e- and hole), which has a typical diffusion parameter of the order of 10^{-4}-10^{-6} cm^2 s^{-1} in perfect oxide crystalline media. For Oxygen vacancies not only their mass (about 10^4 larger than for electron) but also the intersite potential barrier strongly limits the diffusion parameter to values several orders of magnitude smaller, in the range 10^{-8}-10^{-10} cm^2 s^{-1}. We have checked the sensitivity of the model to the diffusion parameter D for different values of the single Oxygen vacancy concentration n_0 (Fig.4). It appears that even for relatively high values of $n_0=10^{24}$ cm^{-3} the di-vacancy creation process becomes negligible for $D\leq10^{-11}$ cm^2 s^{-1}. If on the other hand D is larger than 10^{-10} cm^2 s^{-1} the optical transmission falls too sharply, which does not corresponds to the experimental data. Considering that the vacancies concentration varies from $n_0=10^{24}$ m^{-3} (Type I crystals) to $n_0=10^{22}$ m^{-3} (Type II crystals) we can concluded that the best fit between the model and the experimental data is observed for $D= 10^{-10}$ cm^2 s^{-1}. This study confirms that Oxygen vacancies, although at the origin of shallow electron centers when their concentration is small enough, can lead to much deeper traps by aggregation at higher density. Therefore they must be suppressed by additional refining of the raw material or compensated as much as possible in PWO crystals to be used in a radiation environment. Additional doping of the crystals during crystal growth is the most effective way to further reduce the number of uncompensated vacancies at the required level of 10^{22} m^{-3}.

5. Conclusion

It is shown in this paper that high concentration of Oxygen vacancies in lead tungstate crystals leads to the following effects:

- An aggregation of the Oxygen vacancies under ionizing radiation occurs in the crystal giving rise the creation of more stable di-vacancies.
- The increase of the di-vacancy concentration in the crystal under ionizing radiation leads to the suppression of the induced absorption dynamic saturation at moderate dose rates, and to a continuous decrease of the light yield at a rate which is defined by the time constant of the di-vacancies creation.
- The creation of the di-vacancies is an irreversible process at room temperature. The percentage of non-recoverable damage will therefore increase with accumulated dose in such crystals. The process will stop when the density of damaging single vacancies will become small enough to stop the aggregation process.

Acknowledgments

The authors wish to express their gratitude to the French Ministery of National Education, which invited one of authors to Savoie University in the framework of the "invitations biennales".

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Table 1. Parameters of the electronic centres of undoped lead tungstate crystals

Electronic center	T_{max} (K)	E_T (eV)	S	γ	τ (s)
$(WO_3)^{2-}$	47	0.07	2.00E+06	1.2	8.30E-06
$(WO_3)^{2-}$	105	0.23	6.70E+09	2.2	2.20E-06
$(WO_3)^{2-}$	114	0.27	9.00E+10	2.2	7.30E-07
$(WO_2)^{2-}$	172	0.4	2.00E+10	1.1	3.10E-04
$(WO_2)^{2-}$	190	0.5	9.00E+11	1.4	5.00E-04
$(WO_2)^{2-}$	226	0.49	2.00E+09	1.0	9.00E-02
$(WO_3^-WO_3)^{2-}$	330	0.58	1.1E+07	1.0	480

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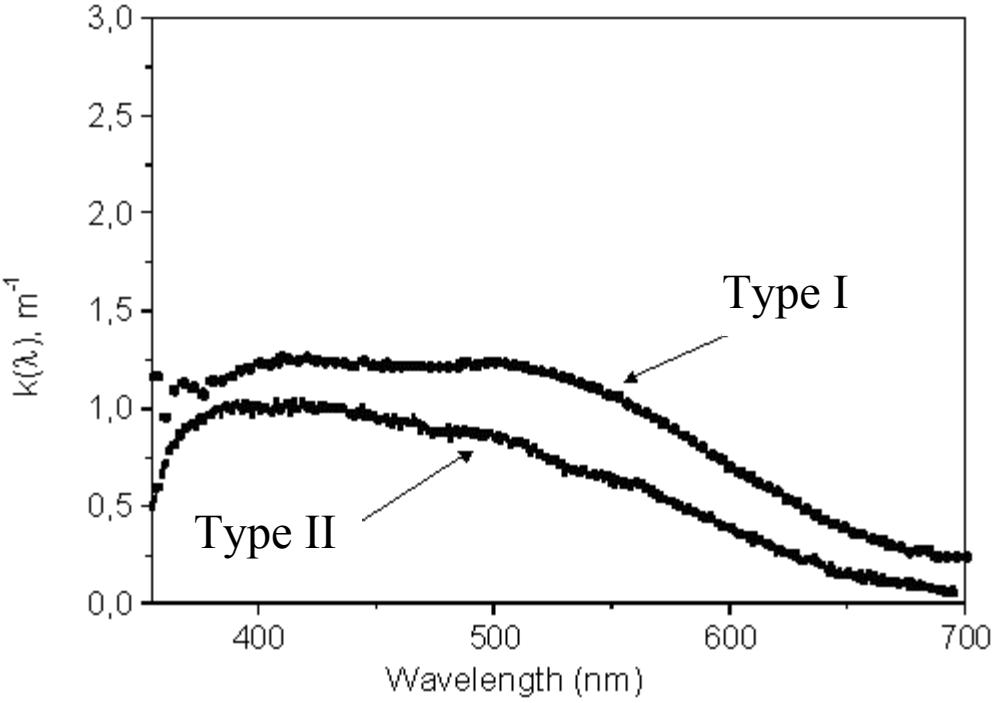

Fig. 1. Radiation induced absorption spectra of the measured crystals.

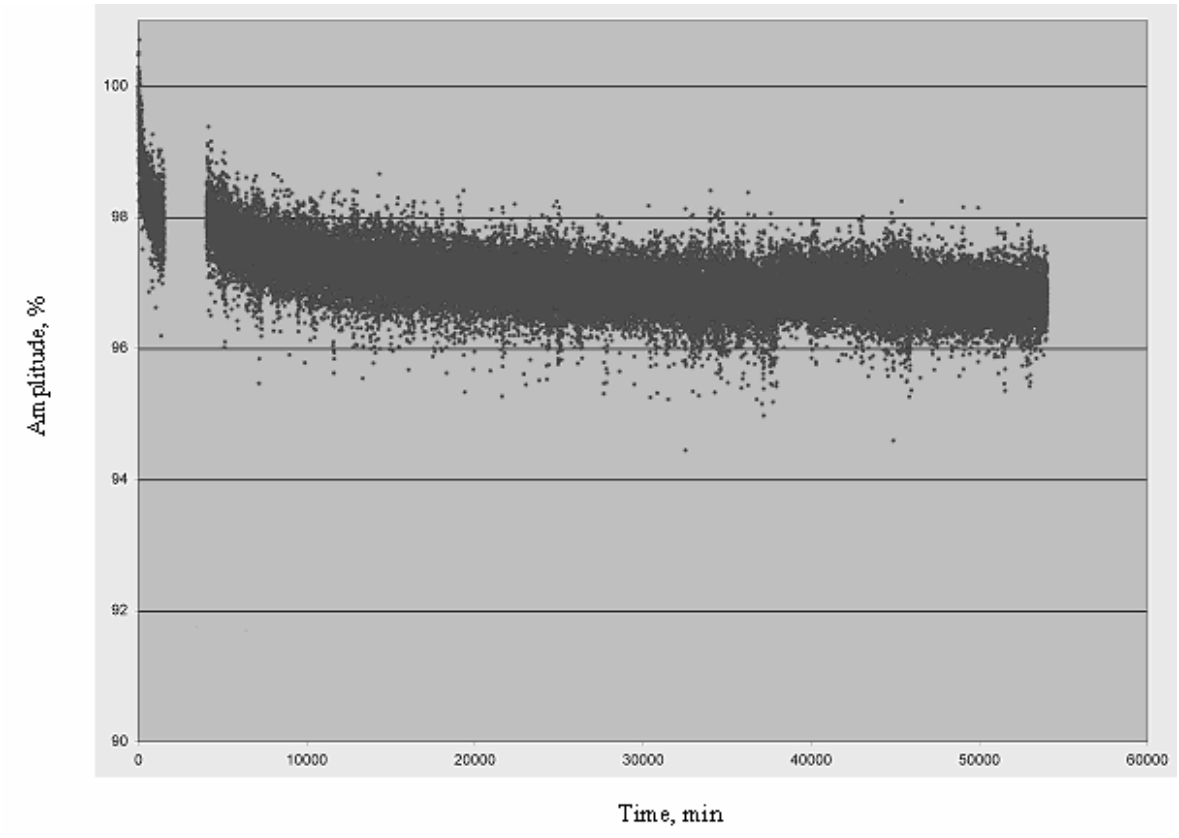

Fig. 2 a. Light output decrease of a 23 cm long PWO (Type II) under 0.15 Gy/h ^{60}Co front irradiation. A small recovery takes place during a 2 days irradiation break.

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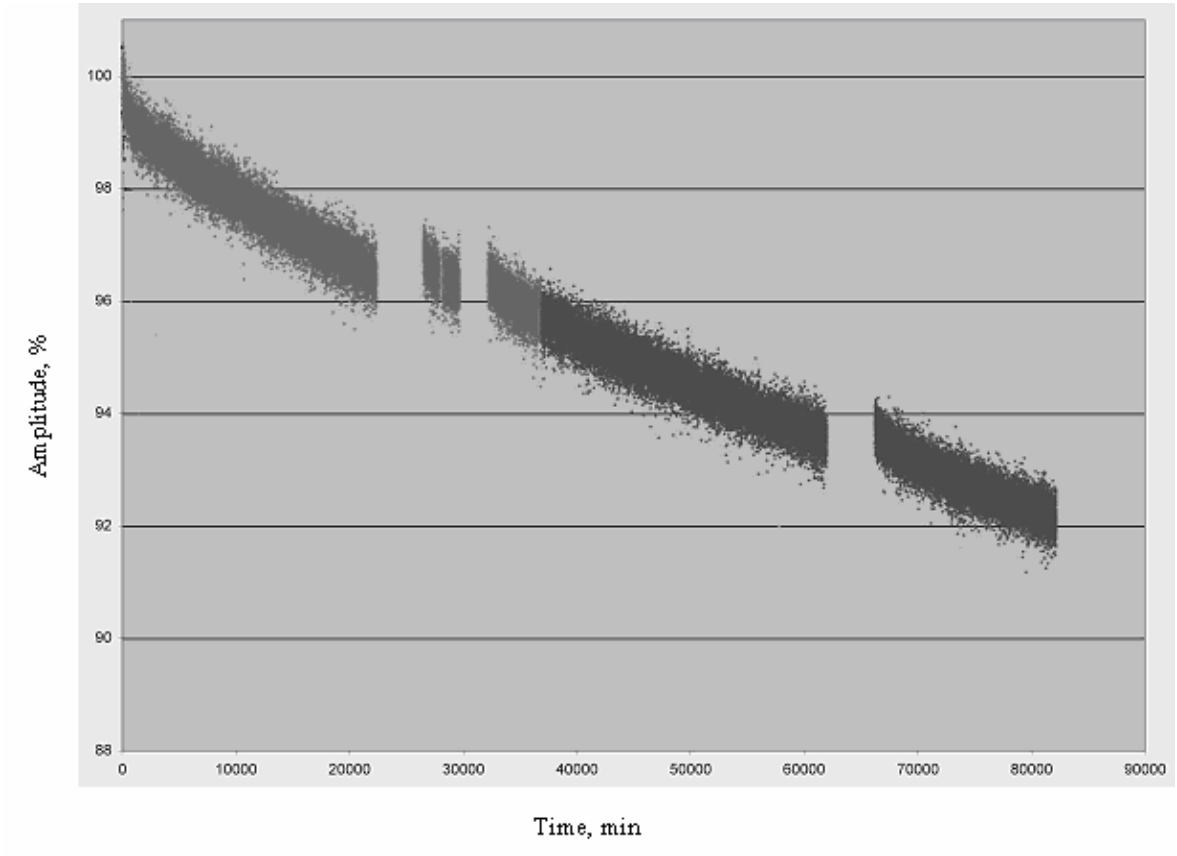

Fig. 2 b. Light output decrease of a 23 cm long PWO (Type I) under 0.15 Gy/h ^{60}Co front irradiation

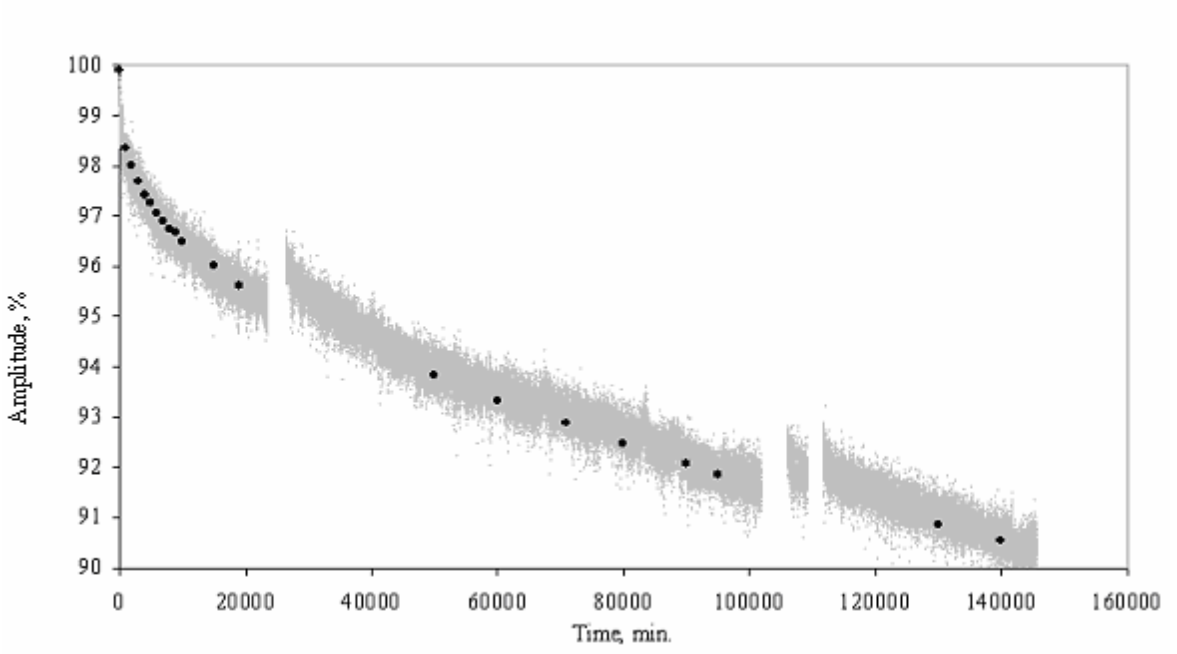

Fig 2 c. Light output decrease of a 23 cm long PWO (Type I) under 0.15 Gy/h ^{60}Co front irradiation. Dots show the data points selected for the simulation (see Fig.3).

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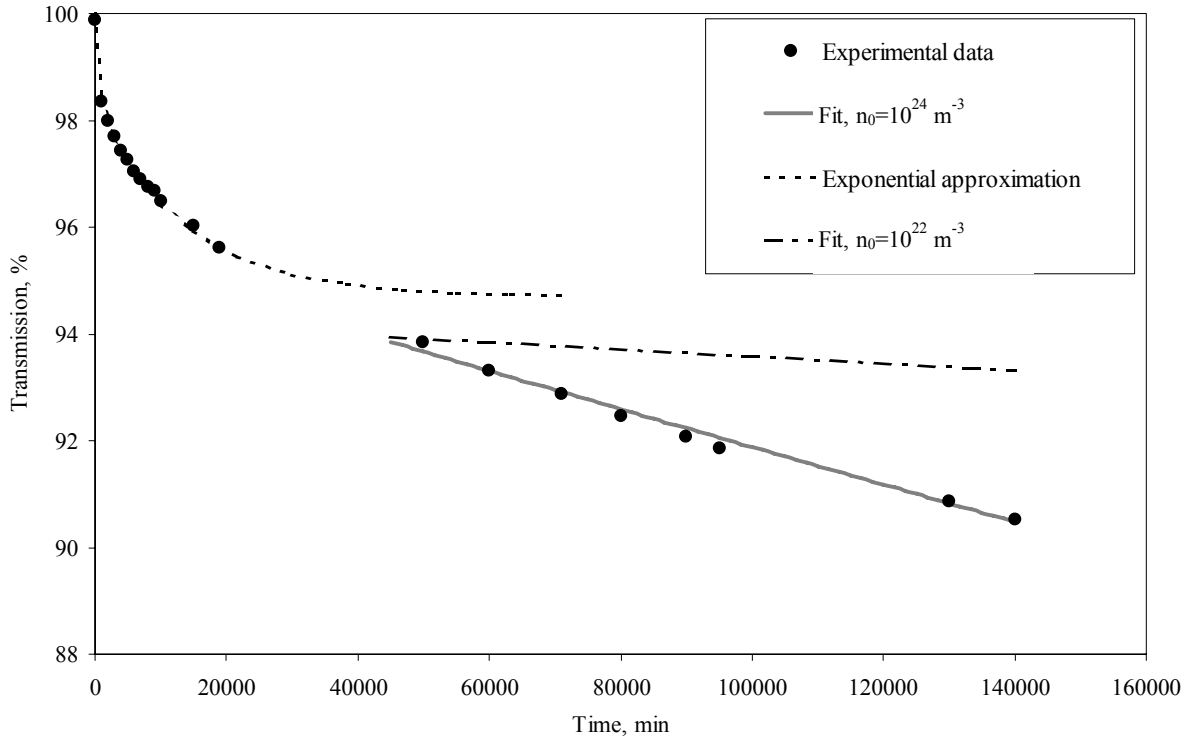

Fig. 3. Comparison of experimental data (dots) and simulation fit with two components: 2-exponential approximation of the damage for the first stage and model of vacancy aggregation for the long time constant tail of the damage process for two different initial concentration of single Oxygen vacancies.

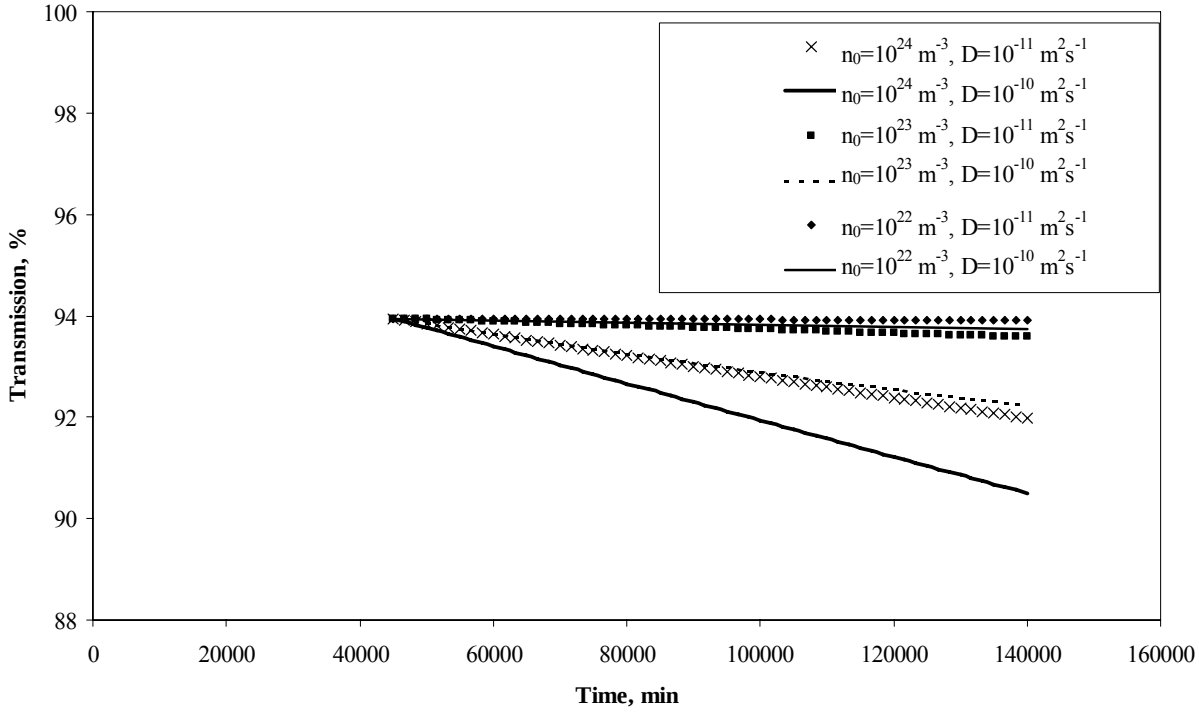

Fig. 4. Change of the linear part of the transmission damage curve versus vacancy diffusion parameter D for different concentrations of the Oxygen vacancies n_0 in the lead tungstate crystal.

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