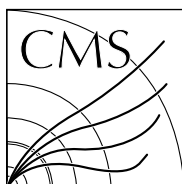


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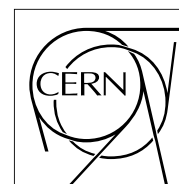
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IMPROVEMENT OF SEVERAL PROPERTIES OF LEAD TUNGSTATE CRYSTALS WITH DIFFERENT DOPING IONS

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Abstract

A very good radiation resistance of Lead Tungstate crystals is mandatory for their use in the high precision electromagnetic calorimeter of the CMS experiment at LHC. Since the beginning of 1996 we have organised systematic investigations of the parameters influencing the radiation hardness of this crystal. Two classes of parameters have been particularly studied, the first one related to the control of the stoichiometry and structure associated defects, the second one connected with the suppression and the charge compensation of existing defects with different kinds of doping ions. This paper reports about the second part of this study and complements a first paper where the role of the stoichiometry was already discussed. Results of tests are given on a significant statistical sample of full size crystals (23cm) which show a considerable improvement in the optical properties and the radiation resistance of appropriately doped crystals.

1-Introduction

The very high event rate at the Large Hadron Collider at CERN (LHC) will create unprecedented radiation levels in all parts of the detectors. In particular the operation of high precision calorimeters, like the Lead Tungstate electromagnetic calorimeter of the CMS experiment [1], will require a very high stability of the optical properties of the crystals (PWO) to achieve the required energy resolution of 0.5% at high energy. The total accumulated γ dose during 10 years of operation is expected to reach 400Krad in the barrel and 5Mrad in the most exposed part of the endcaps with dose rates ranging from 10rad/hour up to 150rad/hour depending on the region of the calorimeter and the luminosity of the collider [2]. The energy spectrum of the γ produced mainly from the decay of π^0 from minimum biased events is rather low (below 1GeV) and most of the dose will be deposited in the region of shower maximum of these γ which is situated typically between 3 and 10cm from the entrance face of the crystals. In addition to the electromagnetic radiation crystals will be exposed to a neutron fluence of 10^{12} to 10^{13} n/cm²/s [2].

We have already established [3] and recently confirmed on a large statistics in other papers [4,5] that the main effect of the radiation on PWO crystals is the production of colour centres. The scintillation mechanism and intrinsic efficiency are not modified by irradiation, at least in the range of dose and dose rate considered here. Colour centres absorb a fraction of the scintillation light on its way from the point of emission to the photodetector glued on the back of the crystal. The shape of the crystal (small cross section of about 2x2cm² for a length of 23cm), the high refractive index of PWO (2.3 at 500nm) [6] and the small size of the avalanche photodiode (APD) for the light readout (5x5mm²) increase the average path length for the light rays up to 3 to 4 times the length of the crystal if it has a good transparency. The acceptable density of colour centres has to be therefore reduced to a very small level if one wants the amount of light collected by the APD to not be reduced by more than a few percents under irradiation, a level which is considered to be acceptable for the monitoring system of the calorimeter [7].

Since the beginning of 1996 a systematic investigation of the influence of the parameters related to the formation and compensation of colour centres has been undertaken. The role of stoichiometry and related structural defects was studied and is reported in other papers [4,8]. In order to decrease the number of primary defects or to compensate their induced charge unbalance, different doping conditions were tested on full size crystals of tapered geometry (20.5x20.5, 23.8x23.8, 230mm) and a few 15cm long rectangular crystals. This work was made in close collaboration with two crystal producers, the Bogoroditsk Technochemical Plant (BTCP) in Russia and CRYTUR in the Czech Republic who produced by the Czochralski method a large quantity of crystals grown in different conditions for this study. The crystals were then irradiated on several set-ups at different accumulated dose and dose rates and optical transmission and light yield were

monitored during and after irradiation. Thermoluminescence spectra were also recorded on a large number of these samples and systematic impurity analysis was performed using glow discharge mass spectroscopy (GDMS) and induced coupled plasma technique (ICP). A summary of the results of all these measurements is discussed here and a model of colour centre in PWO is discussed which was guiding us for the choice of the different conditions to be tested.

2- Motivations for doping PWO crystals

We have found a good correlation between the PWO radiation sensitivity and the shape of the optical transmission edge around 360nm, which allowed us to classify the crystals in 3 types: uniform radiation hard with a sharp cut-off in the transmission spectrum, uniform non radiation hard with an absorption band at around 360nm overlapping the short wavelength edge, non uniform with increasing band at 360nm and correlated increasing radiation sensitivity along the crystal [4,9]. However, even for the best type, an induced absorption coefficient around the peak of light emission of typically 1m^{-1} for the first 500 rads with a saturation of 2m^{-1} at higher doses results in a loss of collected light of 15 to 20% which is incompatible with the goal of a high precision calorimeter. It must be noticed that this effect is even more important for very transparent crystals, in which the contents of impurities in the raw material has been lowered at the level of 1ppm or less for most of the elements. More generally we have established that as long as some heterovalent impurities are removed from the raw oxides the origin of radiation damage is not related to the purity of the raw material but to structural defects produced during the growth process. These defects result from the leakage of Lead ($V_c(\text{Pb})$) and Oxygen (V_o) and introduce local charge unbalance which easily traps electrons or holes and act as temporary colour centres under irradiation.

The radiation damage can be considered as a three step process consisting in:

- creation of hot electrons and holes from the interaction of high energy photons with the lattice
- free carrier separation during thermalization and diffusion process
- localisation of electrons and holes near some lattice defects where coulombic compensation is needed for local charge balance.

Evaporation of Lead during the different phases of the growth of long crystals is compensated either by anion vacancies (V_o) and F^+ centres (one electron trapped in an Oxygen vacancy), or by a hole trapped by a single Oxygen (O^- defect) or a molecular Oxygen with two anti-parallel spin electrons: $(O-Vc-O)^2-$. The two later defects can be easily recharged by free carrier during irradiation and are the main sources of colour centres in PWO crystals [4].

There are three ways to suppress or compensate these defects:

The first one consists in organising them in a superstructure where long range charge compensation is provided by the lattice itself.

The second one is to prevent the trapping of holes on Oxygen near a Lead vacancy by forcing Oxygen leakage. This is achieved by doping with a pentavalent ion on the Tungsten site, a method which some of us have already proposed two years ago [3].

The third one is to compensate cation vacancies by substituting stable trivalent ions to Lead ions in the nearest co-ordination sphere around the defect. Different ions have been tried like Y^{3+} , La^{3+} , Lu^{3+} , Al^{3+} .

This paper gives results about the last two points. The first approach is described in another paper [4].

Facility number	Facility	Type of measurement
1	JINR Microtron e^- 25MeV lateral 300Rad, 15and 50Rad/mn	Transmission several λ
2	Minsk ^{60}Co 100Krad, 30Krad/h on top of ingots	Transmission all λ LY with small ^{60}Co source Scintillation kinetics
3	Geneva Hospital ^{60}Co transversal 50Krad, 18Krad/h	Longitudinal+Transverse Transmission all λ LY with small ^{60}Co source
4	Geneva Hospital ^{60}Co transversal 100 to 500 Rad, 360rad/h	Transmission all λ LY a few points with small ^{60}Co source
5	CERN/TIS ^{60}Co front 900Rad, 15Rad/h	LY by HPMT current Transmission all λ
6	CERN/X5 ^{137}Cs lateral and front 200Rad, 15Rad/h	Transmission several λ LY a few points with small ^{60}Co source LY with beam (soon)
7	Saclay ^{60}Co lateral, masks 300Rad, 15 and 58Rad/h	Transmission several λ
8	ENEA ^{60}Co lateral 0.1 to 50Krad, 760Rad/h	Transmission all λ LY a few points with small ^{60}Co source

Table 1 Irradiation facilities and type of measurement (100rad=1Gy)

3-Testing conditions

A total of 102 long crystals (15 to 23cm) have been produced using the Czochralski method by the Bogoroditsk Technochemical Plant in Tula, Russia, and CRYTUR in Turnov, Czech Republic.

56 for the Stoichiometry scan [4,8]

20 doped with Niobium

- 17 doped with Lanthanum
- 5 doped with Lutetium
- 3 doped with Yttrium
- 1 doped with Aluminium

Crystals were irradiated in the conditions described in Table 1 and conclusions were drawn after systematic cross-checks of the results from at least three different facilities for the same crystals.

4- Experimental results

4.1- Improvement of optical transmission

Measurements have been done on crystals produced from both companies using different sources of raw materials. In both cases a significant improvement is seen on all doped crystals in the region of absorption edge (Fig. 1 and 2), as was already noticed on small samples [10]. Whatever the doping, Niobium, Yttrium and Lanthanum, a strong suppression of the 360nm absorption band is observed, confirming a significant suppression (Nb) or compensation (Y, La) of rechargeable defects. The absorption edge extension is reduced from 60nm to about 20nm for BTCP crystals and from about 100nm to 30nm for CRYTUR crystals. A much more efficient transmission for scintillating light between 400 and 550nm is therefore ensured for doped crystals than for undoped ones (see longitudinal transmission through 23cm, solid curve). This results in an improved light collection of about 40% and nearly 100% for crystals produced by BTCP and CRYTUR respectively. The difference between two sets of crystals is related to the quality of the raw material. A good compensation can only be achieved if there are not competing process generated by uncontrolled impurities or defects. A small absorption band is still visible in some cases at 420nm which shows that the fine tuning of the doping conditions is still needed. On the other hand the optical transmission measured transversally (through 2cm, curve with different marks) shows that the doping was controlled very well during the growth and resulted in very uniform crystals. GDMS and ICP analysis were systematically performed in the melt before and after growth and at both extremities of the crystals (Table 2). These measurements allowed us to determine the segregation coefficients of the doping ions and to tune the doping conditions.

CRYTUR (ICP)	Lanthanum doped	Lutetium doped
in the melt before growth	324 ppm	200 ppm
at the beginning	888 ppm	61 ppm
at the end	100 ppm	92 ppm
in the melt after growth	65 ppm	288 ppm

BTCP (GDMS)	Lanthanum doped	Niobium doped
in the melt before growth	50 ppm	110 ppm
at the beginning	110 ppm	26 ppm
at the end	85 ppm	28 ppm
in the melt after growth	41 ppm	120 ppm

Table 2. GDMS and ICP analytical results for some crystals

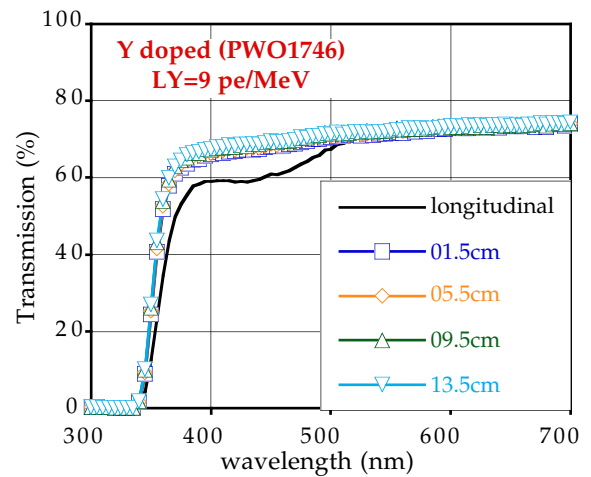
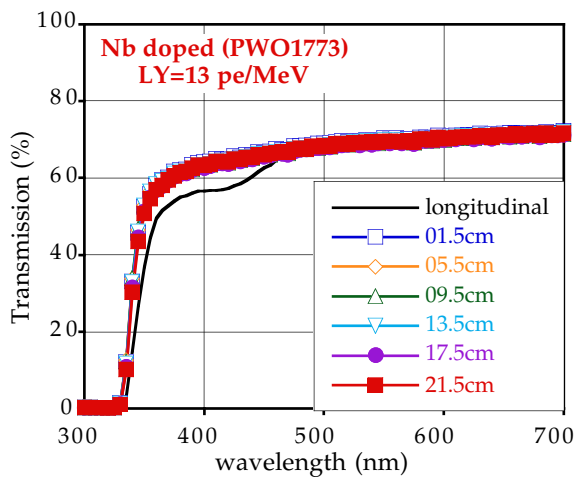
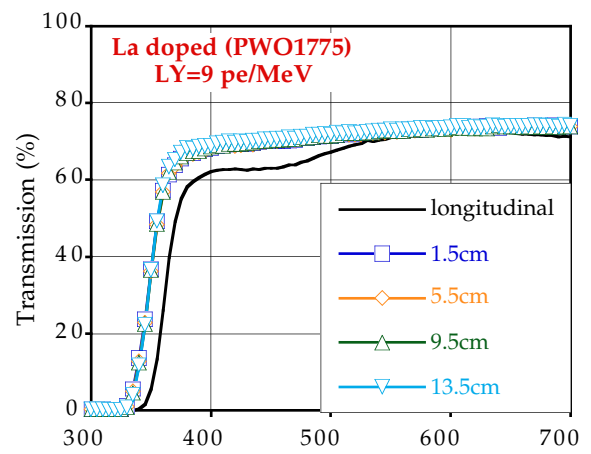
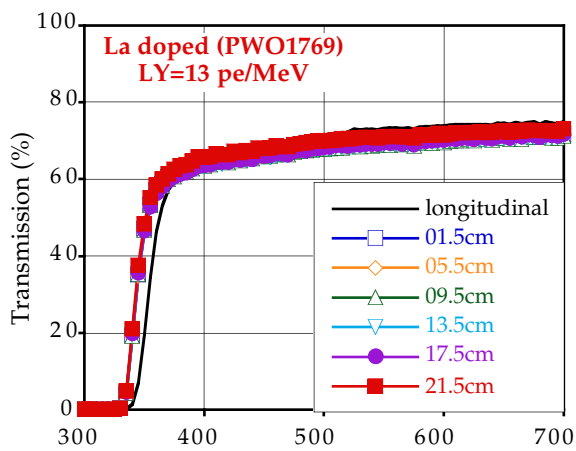
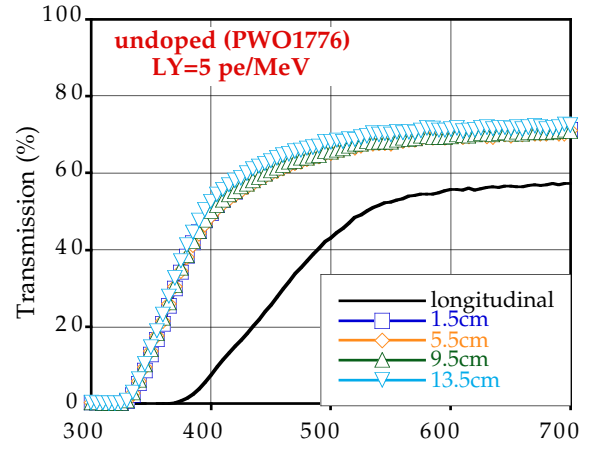
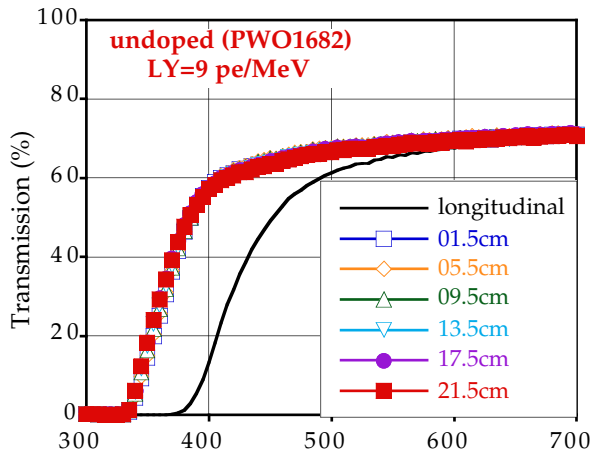


Fig. 1 Transversal and longitudinal transmission for BTCP crystals

Fig. 2 Transversal and longitudinal optical transmission for CRYTUR crystals

4.2- Improvement of radiation hardness (high dose and high dose rate)

In order to control the concentration of uncompensated defects crystals were then irradiated with a high accumulated dose and high dose rate in order to reach full saturation of damage centres (facilities 3 and 8 in table 1). The changes in the sample transmission due to the irradiation were evaluated using the radiation induced absorption coefficient μ defined as:

$$\mu(\lambda) = (1/L) \ln (T_0(\lambda)/T(\lambda)) \quad (1)$$

where $T(\lambda)$ stands for the transmission after the irradiation, $T_0(\lambda)$ for the initial transmission, L is the length of the PbWO_4 sample, 23cm or 15cm in our case.

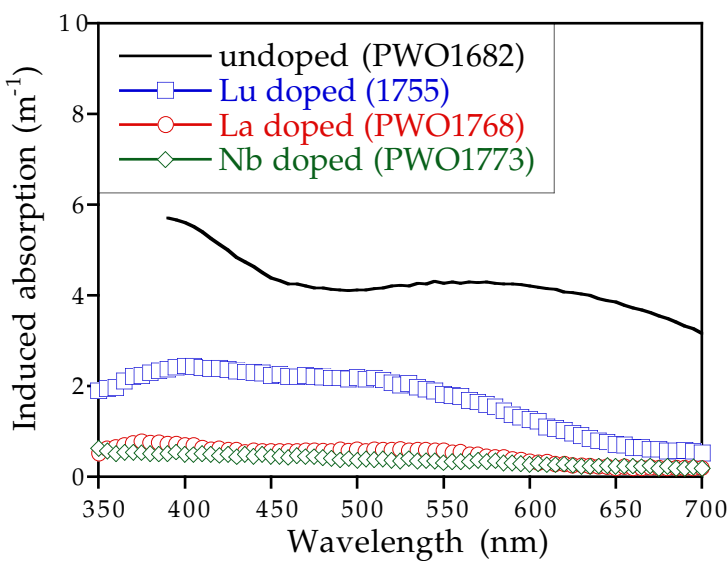


Fig. 3 Induced absorption coefficient in 23 cm long BTCP crystals after 500Gy ^{60}Co

important than for Nb and La. These results are associated with a strong reduction of the thermoluminescence spectrum amplitude and confirm the improvement of radiation hardness already noticed by some of us [10-12] on small samples of $\text{PWO}:\text{La}$.

A study of the dose dependence of the damage has been made on three 15cm long crystals from CRYTUR, undoped, La doped and Lu doped grown from the same initial raw material (facility 8) and on one 23cm long Nb doped crystal produced by BTCP (facilities 3, 4).

In the case of BTCP crystals the improvement with both Niobium and Lanthanum doping is quite spectacular as can be seen on Fig. 3. A reduction of the radiation induced absorption by a factor of 4 has been achieved as compared to undoped crystals in the region of peak emission between 450 and 500nm. This corresponds to an induced attenuation length of more than one meter, about 4 times the length of the crystal, and should lead to a small loss in collected light as will be shown later. There is also a significant improvement with Lu doping, although a factor of 2 less

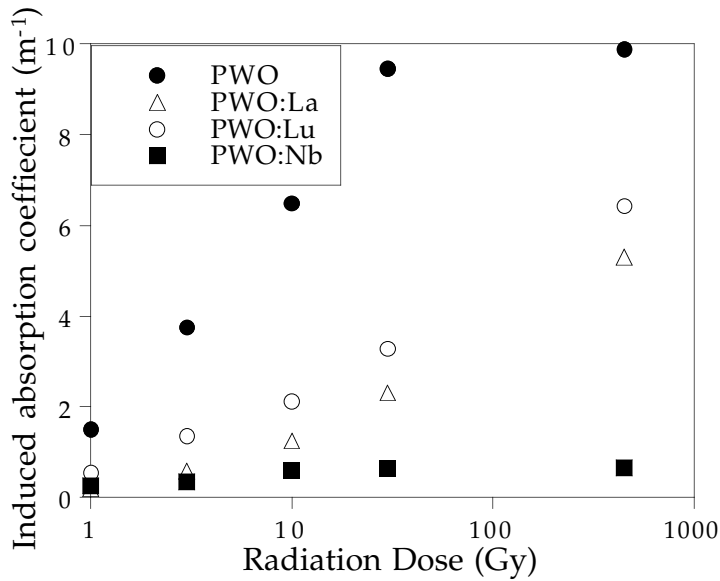


Fig. 4 Induced absorption at 420nm in 15 cm long CRYTUR crystals at different doses

induced absorption higher than for BTCP crystals at the same dose. Nevertheless the damage for all doped crystals is much reduced as compared to undoped crystals.

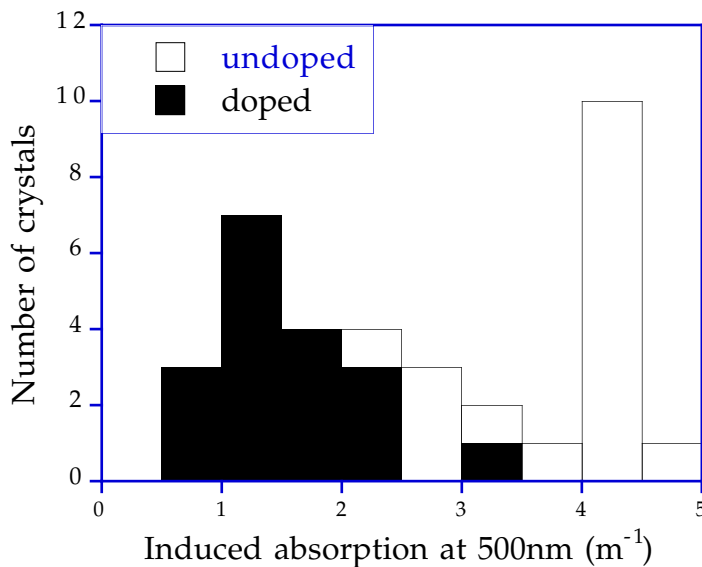


Fig. 5 Distribution of 500nm induced absorption after 500Gy for undoped and doped crystals

The dependence of the radiation induced absorption coefficient at 420 nm on the γ radiation dose absorbed by the four crystals studied in this work is given in Fig. 4. It clearly shows that for both La and Lu doped crystals no saturation was reached at a dose of 300Gy (30Krad) unlike the Nb doped and the undoped crystals for which the damage already saturates at 10 Gy (1Krad) and 20Gy (2Krad) respectively. It must be said that the intrinsic quality of the crystals from CRYTUR was rather poor, due to non optimised raw material, which resulted in

In order to confirm on a statistical basis the improvement due to doping two series of crystals were grown in BTCP using the same conditions of optimisation of the raw material. The first series is made of 17 undoped crystals and the second one is a set of 18 crystals doped with Lutetium, Lanthanum or Niobium (as was shown on Fig. 3, there is practically no difference between Nb and La doping). Fig. 5 shows the distribution of the induced absorption at 500nm after a high irradiation dose of 500Gy

(50Krad) using the facility 3. An average improvement of at least a factor of 2 is clearly seen for doped crystals as compared to undoped ones.

4.3- Improvement of radiation hardness (low dose and low dose rate)

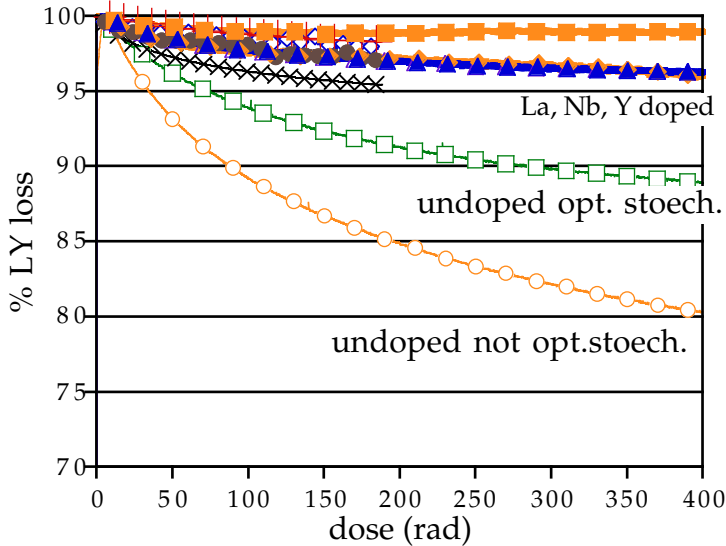


Fig. 6 Low dose rate light yield loss for undoped and doped crystals

cross checks in an electron test beam and with standard light yield measurements. The same trend was observed as for high dose and high dose rate. Doped crystals suffer a light yield loss of typically 5% or less after 400 rads were saturation is nearly reached. Undoped crystals from optimised raw material are a factor 2 worse with a light yield loss of about 10% in the same conditions. Undoped crystals grown with non optimised raw material are another factor 2 worse with a light yield loss of about 20%. Fig. 6 shows normalised light yield as a function of dose for a few crystals representative of each category.

4.4- Damage recovery

We already discussed in a previous paper [14] the kinetics of the radiation damage process. The observed damage results from an equilibrium between the creation of colour centres and their destruction due to room temperature annealing. Some recovery helps to reduce the damage at saturation. But it has to be either very fast (less than a few minutes) or very slow (more than 1hour) as compared to the rate of damage creation, in order to not induce a too strong and too fast dependence of the crystal response to small variations of the dose rate in the conditions of operation of the calorimeter.

The next step was to reproduce irradiation conditions as similar as possible to what is expected at LHC for the CMS calorimeter. The front face of the crystals was exposed to Cobalt radiation at a dose rate of about 15 rad/h up to integrated doses of a few hundred rads using the facility 5. This should damage the front part of the crystal in a rather similar way to the γ produced from the decay of π^0 from minimum biased events (see introduction). The light yield loss was then monitored from the current in a HPMT tube [13] with several

A study was made of the decrease of absorption coefficient at 420nm after a high dose (facility 8) on 3 CRYTUR crystals, undoped, La and Lu doped and on one Nb doped crystal from BTCP. Recovery within the first few days after irradiation was found very large in the case of La doped sample, medium for the undoped and Nb doped crystals and below the measuring error limit in the case of the Lu doped sample, when the samples were strictly kept in the dark.

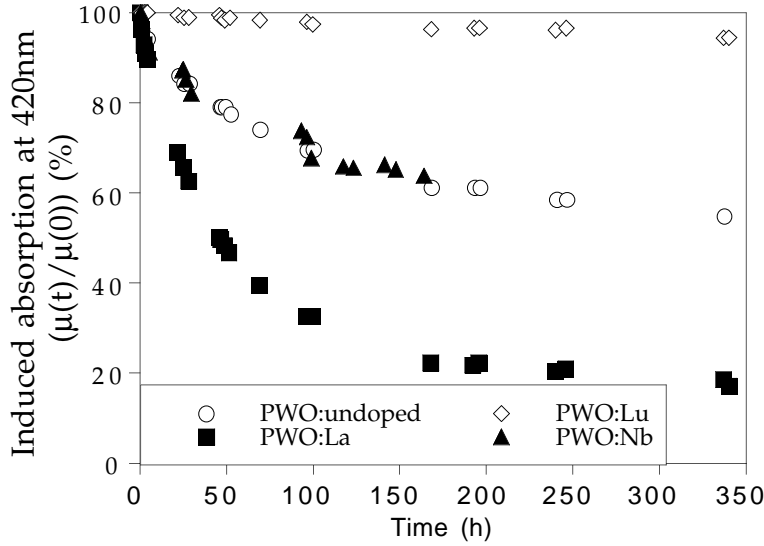


Fig. 7 Room temperature recovery of 3 CRYTUR and 1 BTCP crystals after 460Gy

The absorption spectrum of all samples after 460 Gy absorbed dose was systematically measured for 2 weeks after irradiation. Fig. 7 gives the shape of the recovery curves at 420 nm.

The parameters of the recovery process at four different wavelengths are extracted from a two exponential fit in the case of the PWO and PWO:La samples and from a single exponential fit for the PWO:Lu sample. The values of the recovery parameters at different wavelengths are reported in Table 3 where the a_0 and t_{mean} parameters are defined as follows:

follows:

$$\mu(t) = \sum_i a_i \cdot e^{-\frac{t}{t_i}} \quad ; \quad a_0 = \sum_i a_i \quad ; \quad t_{\text{mean}} = \frac{\sum_i a_i \cdot t_i}{\sum_i a_i} \quad (2)$$

The shorter recovery time at 390nm and 420nm is to be noted in La doped crystals [5]. On the other hand the time behaviour of Lu-doped crystal is practically stable on time. Though the colour centres induced by γ radiation in undoped as well as La and Lu doped PWO crystals are the same, their stability and as a consequence their relative concentration is different.

Recovery of Bogoroditsk crystals was also tested after low dose rate irradiation with the facility 5. The first light yield measurement could be made immediately after the end of the irradiation for a period of about 24h. La, Nb and Lu crystals were tested, and all the crystals were very stable during this period, with a recovery of less than 1%. It confirms our expectation that

with optimised raw material conditions the fast spontaneous recovery process (with time constant of the order of 1 hour or less) can be suppressed in all conditions of doping.

<u>Crystal ID</u> <u>wavelength</u>	a_1	t_1 hours	a_2	t_2 days	a_0	t_{mean} days
<u>PWO</u> <u>(undoped)</u> 390 nm	5.04	68.6	5.47	72	10.52	39
<u>PWO</u> <u>(undoped)</u> 420 nm	2.63	56.9	6.32	62	8.95	44
<u>PWO</u> <u>(undoped)</u> 550 nm	0.72	5.0	5.12	40	5.85	35
<u>PWO</u> <u>(undoped)</u> 685 nm	0.50	2.3	3.62	49	4.12	43
<u>PWO:La</u> 390 nm	3.72	42.4	1.77	35.25	5.49	12.5
<u>PWO:La</u> 420 nm	3.66	42.3	1.51	29.30	5.17	9.8
<u>PWO:La</u> 550 nm	2.83	44.7	1.71	55	4.54	22
<u>PWO:La</u> 685 nm	0.76	46.2	0.63	85	1.39	40
<u>PWO:Lu</u> 390 nm	6.9	282	---	---	6.9	282
<u>PWO:Lu</u> 420 nm	6.4	258	---	---	6.4	258
<u>PWO:Lu</u> 550 nm	3.5	137	---	---	3.5	137
<u>PWO:Lu</u> 685 nm	0.6	76	---	---	0.6	76

Table 3 - Room temperature recovery of (2 x 2 x 15 cm³) PWO crystals produced by CRYTUR

5-Conclusions

We have shown that doping long size (23cm) Lead Tungstate crystals with either Niobium or trivalent ions (Y, La, Lu) systematically improves several properties of this crystal, as long as the raw material is optimised accordingly. A much better optical transmission near the absorption edge yields significant increase of the collected light. All doped crystals are at least a factor 2 more radiation hard than undoped ones at all the doses and dose rates which have been investigated in this study. One to two days recovery time constants are shown for La doped, and to a lesser extent

Nb doped crystals for high irradiation dose and dose rate. At low dose rate no fast recovery process (about 1 hour) was observed for all conditions of doping.

All these results have been obtained on a sufficiently large statistical sample of full size crystals (23cm). Practical conclusions can therefore be drawn for the optimisation of crystal growth conditions for the CMS electromagnetic calorimeter.

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