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LEAD TUNGSTATE ($PbWO_4$) SCINTILLATORS FOR LHC EM-CALORIMETRY

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Abstract

This report describes the work carried out in order to analyse the properties of $PbWO_4$ crystals a scintillators and to determine the perspectives of their use in calorimetry in Large Hadron Collider (LHC) experiments. The scintillation mechanism in PWO crystals is explained and the properties connected with their use as scintillators are analysed both for undoped and Nb doped crystals. The specific problems concerning the physical parameters in the case of large scale production of PWO scintillators are discussed.

1. INTRODUCTION

Although the $PbWO_4$(PWO) compound was investigated as early as 1948 [1], it was considered of limited interest as luminophore due to its low light yield at room temperature. PWO is a crystal of the tungstate family which counts several high light yield but slow scintillators and luminophores like $CdWO_4$, $SrWO_4$ and $CaWO_4$. Due to a strong thermal quenching at room temperature, the $PbWO_4$ compound proved to have a very fast but relatively low light yield scintillation. The properties of this crystal make $PbWO_4$ a good compromise between cost and performance for high resolution electromagnetic calorimetry at the new generation of hadron colliders [2- 4].

$PbWO_4$ is a birefringent scheelite type crystal belonging to the space group I4 1/a [5] with tetragonal unit cell. Physico-chemical properties of PWO are given in Table 1.

Table 1. Physical and chemical properties of $PbWO_4$ crystals

Density (g/cm^3)	8.28
Radiation length (cm)	0.89
Molière radius (cm)	2.2
Melting point (°C)	1123
Hardness (Moh)	4
Refractive index along Z axis (λ = 632 nm)	2.16
Hygroscopic	no
Chemical activity	inert

All PWO crystals studied in this work were grown by Czochralski method from platinum crucibles of 120 mm diameter, in an atmosphere close to air in composition. The direction of crystal growth has a deviation from Z axis of about 19°. After crystal growth, the crystals were annealed with a low speed temperature variation so that the total time necessary to produce an ingot of Φ = 32 x 220 mm^3 is 140 hours (72 h of crystal growth and 68 h of annealing). Good quality crystals of Φ = 60 x 220 mm^3 were also grown, but the annealing process for the elimination of intrinsic stress lasts in this case much longer than for crystals of Φ = 32mm. The PWO crystal growth technology is very close to the one used for niobates and molibdates crystals which is well developed in many countries and particularly in Russia.

2. PWO SCINTILLATION MECHANISM

2.1. History

PWO is a scintillator for which a strong thermal quenching at room temperature and energy transfer mechanisms between radiating centres lead to a fast but low intensity scintillation at room temperature. Its luminescence properties are due not only to regular radiating centres but also to centres related to point structure host defects. The spectroscopy of PWO has been investigated by several authors in the past but many divergences still remain in the interpretation of the rather complex data.

The blue and green luminescence of PWO was studied for the first time by Kröger [1] and attributed to tungsten groups, surrounded by Pb^{2+} ions. Blasse and Brill [6] proposed that blue luminescence is caused by 6p - $6s^2$ transitions of Pb^{2+} ions or is due to a charge transfer transition between the tungsten group and Pb^{2+} ions. Van Loo [7] comes to the conclusion that the blue luminescence is caused by transition in isolated WO_4^{2-} groups and green luminescence which is the superposition of two bands, is caused by the transfer of an electron occupying an orbital with mainly Pb^{2+} character to an empty orbital of an adjacent WO_4^{2-} group with a predominantly d character. Blasse and Groenink [8] have found a polarisation of the green luminescence which they have interpreted as luminescence of isolated WO_3 groups. They have correlated the blue luminescence with regular WO_4^{2-} groups linked to the lead ions. Green luminescence in PWO has also been explained by Reut [9] as self trapped exciton radiation. Grasser [10] has found several luminescence bands, a blue one, two green, one yellow and two red. He explained green bands as intrinsic luminescence of relaxed excitons of (Pb-WO_4) type, yellow as WO_3 luminescence and red bands as F^--centres luminescence. These divergences in the interpretation of the data mainly reflect the fact that the luminescence characteristics of $PbWO_4$ crystals are very sensitive to the specific conditions of their synthesis. Even small changes of these conditions might induce large variations of emission and absorption spectra.

2.2. New results and their interpretation

The γ-rays excited luminescence of $PbWO_4$ shows a broad and complex emission band extending from 370 to 500 nm, the shape of which directly depends on the W concentration in the melt [11,12]. This is an indication that the observed emission is actually the superposition of several luminescence bands and that their relative contribution to the total spectrum depends on stoechiometry related defects in the crystal. The luminescence band intensity and shape under photo or gamma excitation changes from the top to the bottom of an ingot [13] as a consequence of the progressive modification of the stoechiometry resulting in a gradient of radiating centres distribution in the crystal. The uniformity of the distribution of radiating centres in PWO crystals as well as their contribution to the total luminescence spectrum can be restored by additional doping of crystals where pentavalent cations substitute to the regular W^{6+} ions from the matrix [14,15].

The comparison of our data with those obtained by different authors for PWO and other tungstates, as well as data obtained from PWO crystals grown in different conditions, show that the blue luminescence band at 420 nm is always present in all tungstates. This observation strongly suggests that this band is related to the emission of regular WO_4^{2-} centres in these crystals. In addition to the blue luminescence at least two green and a red emission band were also noticed [11]. The spectra of $PbWO_4$ crystals luminescence are shown on Fig.1.

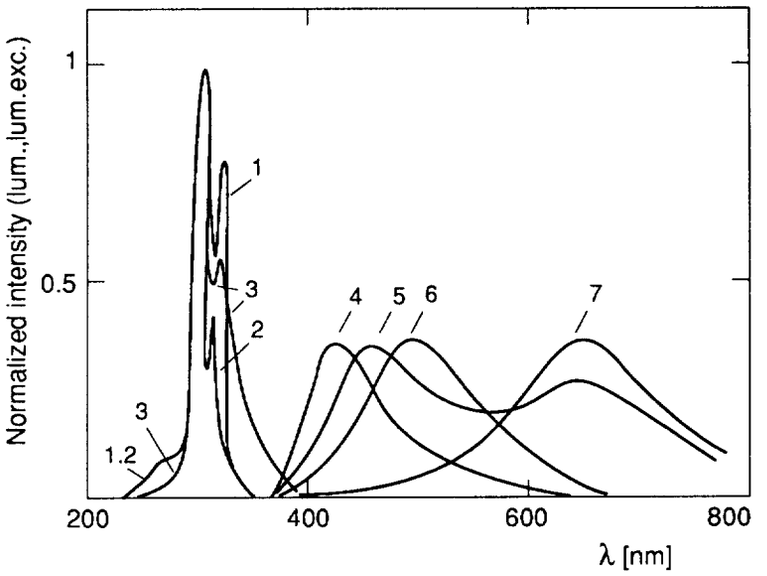

Fig.1. PWO excitation and luminescence spectra at T = 300 K: excitation for: 1. - λ_L = 420nm ; 2. - λ_L = 500nm ; 3. - λ_L = 650nm luminescence for: 4. -λ_{exc} = 275nm ; 5. - λ_{exc} = 308nm ; 6. - λ_{exc} = 325nm ; 7 - λ_{exc} = 350nm

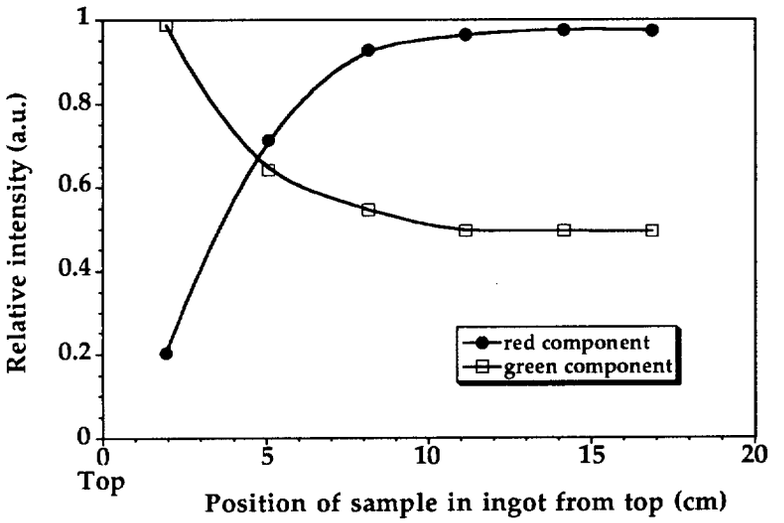

Fig.2. Normalised peak intensity of red and green luminescence versus position of several 2 x 2 x 1.7 cm^3 samples extracted from a 19 cm long PWO crystal, T = 300 K

Because of the overlap of excitation and luminescence bands, the decay time constants under photo-excitation were determined by comparison of different parts of the decay curves at different excitations. As a result of the strong thermal quenching, the blue and green bands have a nonexponential

decay with a fast component at the initial part of the decay curve of about 2 ns decay time and longer components of respectively 5 ns, 9 and 15 ns for the blue and two green bands. The red band has a decay time of 38 ns at room temperature. The study of samples extracted from different positions along the growth axis showed that the intensity of green and red luminescence bands vary from the top to the bottom of a PWO ingot. These data are shown on Fig.2 and indicate that green and red luminescence are based on point defects with different origin. Recently [11,16] it was confirmed that the two green luminescence bands in PWO crystals are caused by (WO_3+F) centres. These centres are based on anion vacancy in the first co-ordinating sphere of W^{6+} ion and are similar in construction to impurity centres. They are radiation hard and stable in time. On the contrary [14] the red luminescence band is caused by complex defects based on heterovalent Pb ions (Pb^{3+} + V_k + F^+) created by W deficiency in the crystal. The instability of these centres under irradiation is a potential source of radiation damage in PWO crystals.

The excitation maximum (275 nm) for blue and green luminescence bands and the maximum in reflection spectrum noted by Grasser [10] and attributed to $^1S_0$ - $^1P_1$ transition in Pb^{2+} ions are situated in the same wavelength region. On the other hand the UV luminescence of Pb^{2+} ions observed in several Pb-doped and Pb - based crystals [17-22] is absent in PWO.

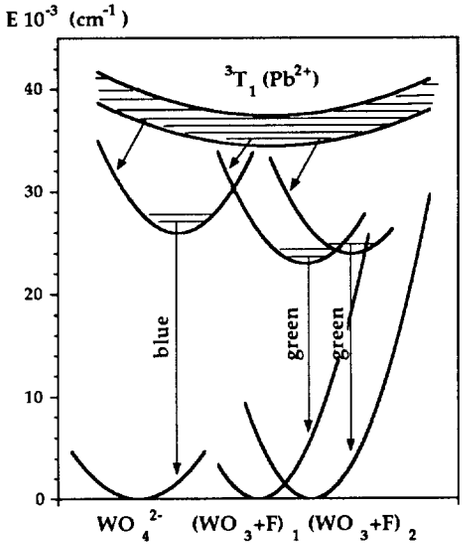

Fig.3. Scheme of energy transfer process in $PbWO_4$ scintillators

All the observations mentioned above led us to the conclusion that scintillation arises in $PbWO_4$ crystals due to the sensitisation of WO_4^{2-} and (WO_3 + F) centres luminescence by Pb^{2+} ions. The scheme of energy transfer processes is summarised in Fig.3. This scheme also illustrates possible limitations for a very high light yield in $PbWO_4$ scintillators. All radiating centres have a large Stokes shift and strong thermal quenching of luminescence. The main acceptors of energy from Pb^{2+} ions are regular WO_4^{2-} centres. Unfortunately they can not provide an important contribution

to the light yield due to the overlap of wave functions resulting in migration of excitation and quenching of the luminescence. Although (WO_3 + F) centres compete with WO_4^{2-} groups in energy transfer from lead ions and have an important contribution to the scintillation, they can not significantly contribute either to the light yield due to their limited concentration in the crystals. Furthermore, their influence is balanced by the presence of uncontrolled impurities which can also trap the excitation in a nonradiative way. These additional impurities are competitors to (WO_3 + F) centres in energy transfer from Pb^{2+} ions so the use of better raw material quality should lead to a more efficient energy transfer from Pb^{2+} ions to the luminescent centres $(WO_4)^{2-}$ and (WO_3 + F).

Summarising at the present stage of investigation, the direct connection between luminescence bands and possible radiating centres have been established. On this basis, improvements in crystal growth technology will be possible in order to obtain $PbWO_4$ crystals with a better light yield, increased radiation hardness and better uniformity of scintillation parameters. A first attempt was made by developing a new growth technology based on Nb doping [14, 15] to prevent the formation of defects based on Pb^{3+} in the PWO crystal. Nb^{5+} ion, because of its slightly smaller radius easily replaces W^{6+} ions, thus compensating the W ions deficiency and creating (NbO_3 + F^+) centres which are stable and similar to (WO_3 + F) centres. The red luminescence caused by defects based on Pb^{3+} ions is absent in these crystals. Although (NbO_3 + F^+) centres compete with (WO_3 + F) centres at the top of the crystal, they will progressively provide a compensation for tungsten groups deficiency when moving towards the bottom of the crystal. The global effect as it will be shown below, consists in possibly higher light yield, better uniformity and radiation hardness of doped crystals.

3. PROPERTIES OF RECENTLY PRODUCED PWO CRYSTALS

More than 100 crystals including 50 large size blocks of about 20cm in length, were systematically investigated in the present work in order to determine the influence of crystal growth conditions on their luminescence properties and radiation resistance.

3.1 Scintillation properties

The scintillation spectrum of $PbWO_4$ crystals is close to the one of BGO and is well matched to commonly used photodetectors: PMT, PIN-diodes and avalanche photodiodes (APD). A typical gamma-ray excited luminescence spectrum is shown in Fig.4. It is worth mentioning that the scintillation mechanism peculiarities provide a stability of the luminescence spectrum shape over a wide temperature range down to liquid nitrogen temperature.

An amplitude spectrum of ^{60}Co source (1.2 MeV) measured with a 1 cm^3 PWO scintillator is shown on Fig.5. The measured light yield is 40-45 photoelectrons/MeV. Assuming a quantum efficiency of the PM of 20% on the peak emission wavelength as given by Philips, we obtain a light yield of

200 - 225 photons/MeV. Dorenbos [23] has found for the same sample a light yield of 250 photons/MeV. When the light yield of large size crystals (about 20 cm in length) was measured with the same source mounted at the middle of the crystal, the light yield decreased by a factor of about 3. This difference is explained by poorer light collection as well as increasing light scattering and self absorption in long crystals.

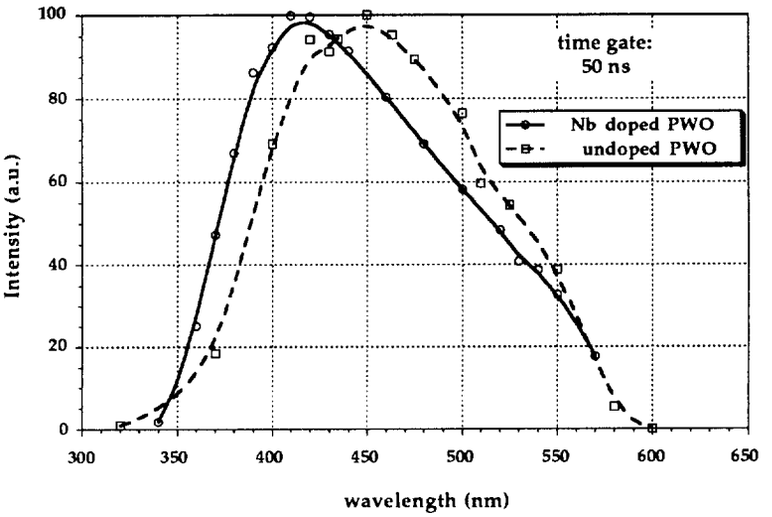

Fig.4. Radioluminescence spectra for undoped and Nb doped PWO crystals

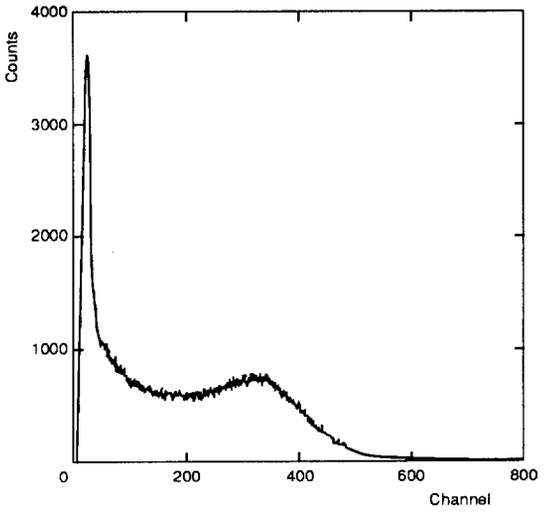

Fig.5. Amplitude spectrum of a PWO scintillator.
Sample 10 x 10 x 10 mm^3, PMT XP2262, source ^{60}Co, gain 10, shaping time 1μs, T = 300 K.
A single electron peak measured with the gain 80 had the peak position at channel 56.

Although some improvement of the light yield was observed for small crystals extracted from the top of PWO:Nb ingots with a Nb concentration of about 300 ppm, this improvement has not been found so far for full size PWO:Nb scintillators. The reason could be that tungsten and lead oxides used

as raw materials for the growth of PWO:Nb full size crystals were not specially selected and certified. After a few centimetres of growth the amount of uncontrolled impurities can become as large or even greater by natural segregation than the amount of Nb, and therefore compete or compensate the effect of the doping in long crystals. The requirements on the purity of initial mixture for growth should be therefore revised if one is expecting a light yield increase from Nb doping for large size crystals. We also noted that a small concentration of Nb ions in the crystals of about 300÷500 ppm is enough to improve the uniformity of long crystals as well as their radiation resistance.

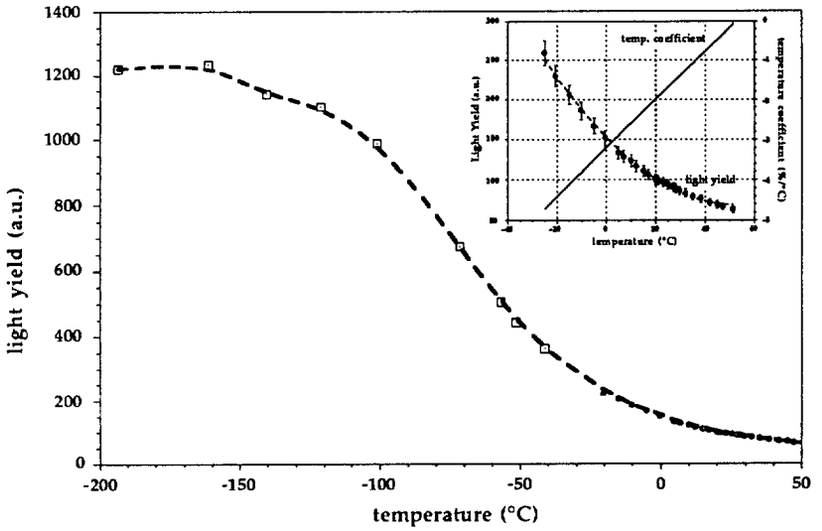

Fig.6 PbWO4 temperature dependence of light yield

The longitudinally measured transmission spectra of undoped and Nb doped crystals are different. Nb doped crystals have a slightly lower absorption in the 350 - 450 nm region of spectrum due to the decrease of Pb^{3+} based defects concentration. Moreover they have a smaller dispersion of longitudinal measured transmission. Nevertheless, a wide absorption band is still present around 420nm and reabsorbs in a non radiative way part of the emitted light. An improvement of the light yield and uniformity can therefore be expected from a reduction of the absorbance at this critical wavelength. A dedicated research work has been started for the understanding of the origin of this absorption band.

PWO scintillators have a relatively high temperature dependence of light yield due to the origin of radiating centres and the strong thermal quenching [15]. The temperature dependence of light yield in the range extending from -193°C to +50°C. is given on Fig. 6. The value determined for the temperature coefficient at 20 °C is -1.98 %/°C.

Because of the quenching and the superposition of several emitting centres, the scintillation decay curve is not exponential but can be well fitted by three exponentials. Typical decay curve of undoped PWO crystals is given in Fig.7. More than 90 % of the light is emitted in less then 100 ns. For PWO:Nb crystals in which only blue and green radiating centres exist, scintillation decay is faster and is well fitted by two exponentials with average decay times of 3 and 14 ns and a contribution to the total decay of

roughly 55% and 45% respectively. Fig.8 shows the temperature dependence of the mean decay time of PWO in a range extending from -193°C to +50°C. Going from +25°C to +15°C, the mean decay time increases from 10 to 12 ns only. In the same temperature range, the light yield increases by 20% [15]. Possible consequences on the radiation sensitivity of the crystal need of course to be studied in detail.

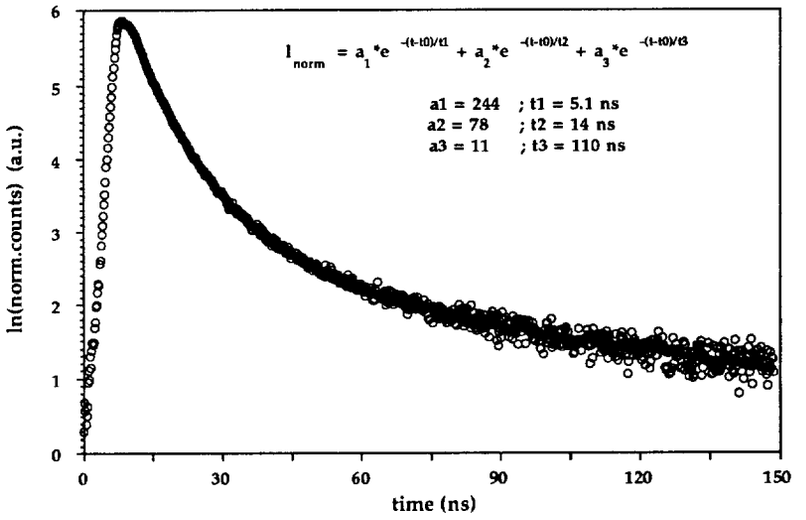

Fig.7 Typical scintillation decay of an undoped PWO crystal

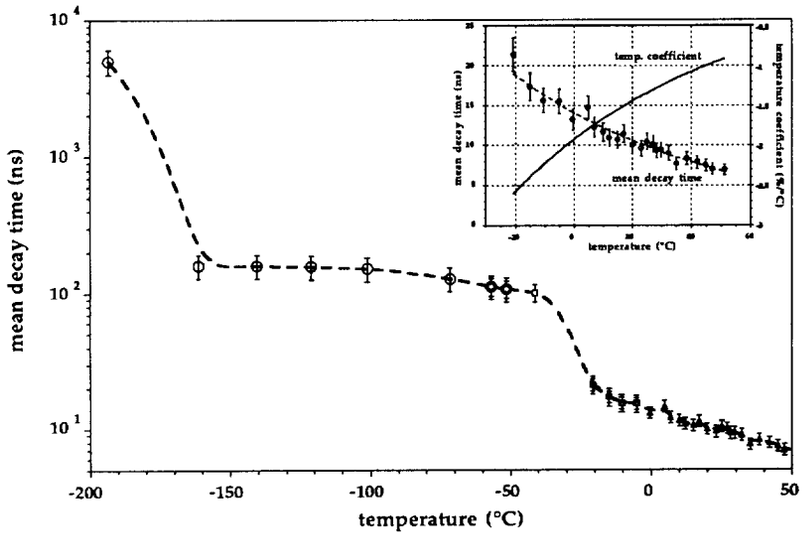

Fig.8 $PbWO_4$ temperature dependence of the mean decay time

Thermostimulated luminescence (TSL) measurements under UV excitation showed that the green luminescence radiating centres in PWO are responsible for the TSL emission in the -190°C to +50°C temperature range [24]. It indicates that these centres are also very effective in capture of free carriers created under high energy excitation. Preliminary measurements of TSL and thermostimulated conductivity (TSC) of X ray irradiated PWO crystals showed on the other hand that the recombination of trapped carriers

always occurs via the conduction band and that only shallow traps are active in PWO crystals. This last property explains the weak phosphorescence of PWO crystals after γ irradiation at high dose rates. Phosphorescence decay time of the order of a few hours was put in evidence in PWO crystals after a 10^4 Gy (1.2 MeV, ^{60}Co) γ-radiation dose [25, 26]. Nb doped crystals seem to have a shorter decay time of the phosphorescence [26], but the effect still needs to be confirmed especially for low radiation doses.

3.2. Radiation hardness

Undoped PWO crystals exposed to ^{60}Co gamma - irradiation present a global reduction of optical transmission, depending on the relative position of the sample in the crystal ingot. Average values of (4±1) m^{-1} after 600 - 700 Gy (3Gy/min) absorbed dose are normally measured for the absorption coefficient of radiation induced defects in the region of the luminescence emission peak.

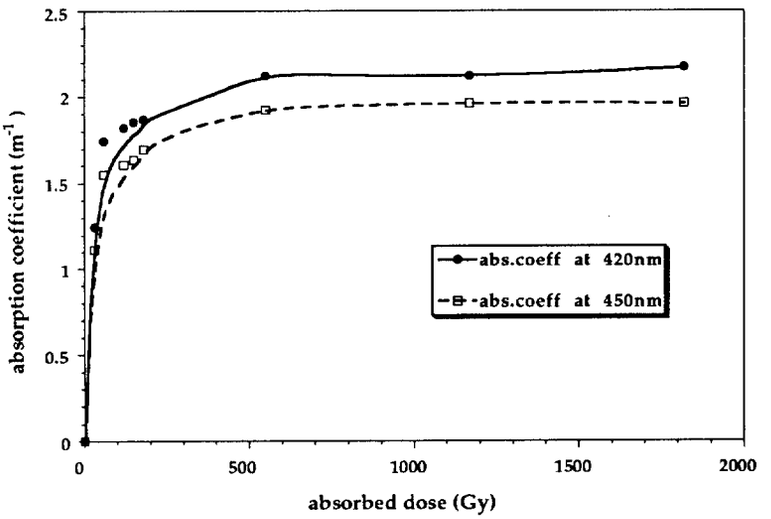

Fig.9 Evolution of absorption coefficient at λ = 420 nm and λ = 450 nm with radiation dose in Nb doped $PbWO_4$ crystals

The absorption is rather constant in a large fraction of the crystal, but smaller in the first few centimetres near the seed and larger in the last few centimetres on the bottom side. The damage is almost uniformly distributed as a function of the wavelength. One can barely distinguish two absorption bands at around 420 nm and 600 nm [15], the last one being attributed to Pb^{3+} based defects. On the other hand, PWO crystals doped with 0.1% Nb where Pb^{3+} defects are compensated, show a considerable improvement in radiation hardness : the radiation induced absorption coefficient is reduced to values of less than 2 m^{-1} in the region of the luminescence maximum ; the saturation is reached at a dose of about 500 Gy radiation dose (Fig.9) ; the absorption bands with maxima at 420 nm and 600 nm are not present anymore, even after a dose of 700 Gy. Moreover, Nb doping provides an uniformisation of radiation hardness along the ingot. Fig.10 gives the values of the nonuniformity in radiation induced absorption coefficient at 420nm along a Nb doped and an undoped PWO crystal.

Radiation resistance tests were also made for a full size PWO:Nb scintillator (L = 180 mm) in a 500 MeV e^- beam at LIL CERN. At $2 \cdot 10^3$ Gy, the radiation induced absorption coefficient had typical values of 0.3 m^{-1} and the damage completely recovered at room temperature after 2 months. A 10^4 Gy radiation dose led to the same unstructured absorption spectrum with values of about 3±1 m^{-1}. The distribution of radiation damage along the crystal corresponds to the Monte Carlo evaluation for 500 MeV showers (Fig.11).

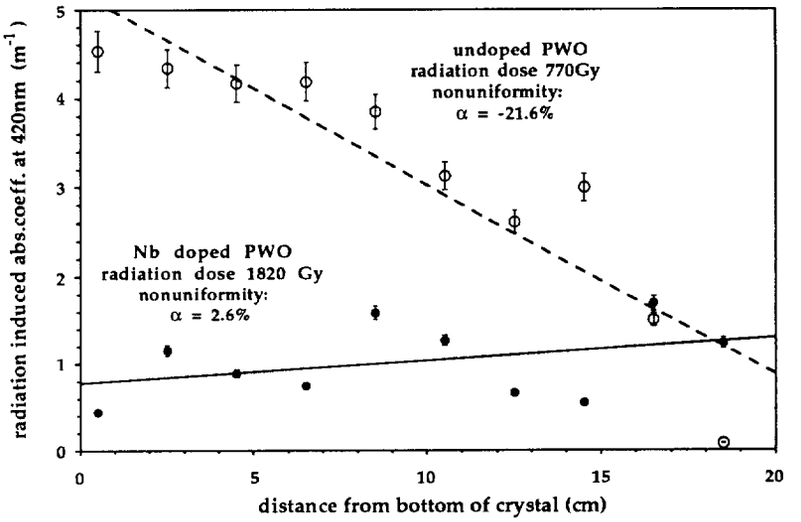

Fig.10 Radiation damage uniformity along large PWO crystals

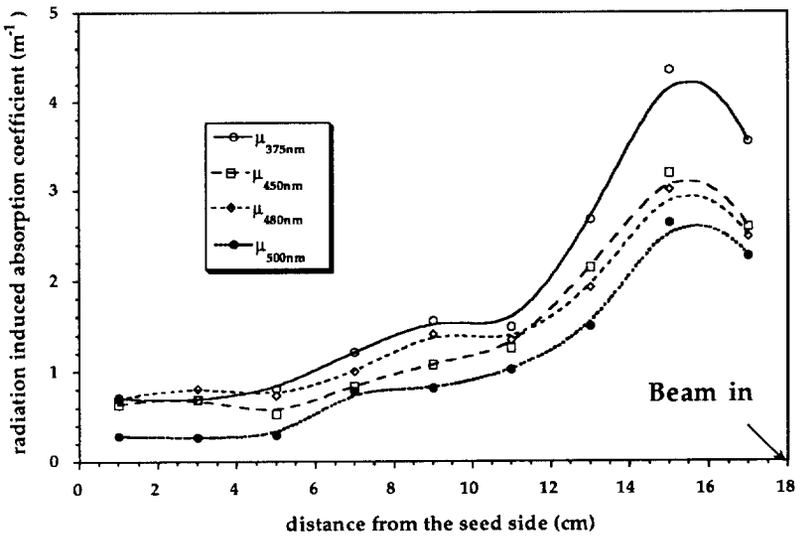

Fig.11 Radiation damage in a PWO:Nb crystal after 10 Mrad at LIL/CERN

Under neutron irradiation, the photoluminescence spectrum is not significantly affected and a very slight decrease of transparency is observed. The radiation induced absorption coefficient is equal to 0.086±0.05 m^{-1} per

10^{13} fast neutrons cm^{-2} which is equivalent to an attenuation length of approximately 1.2 m at 10^{14} neutrons cm^{-2} [27].

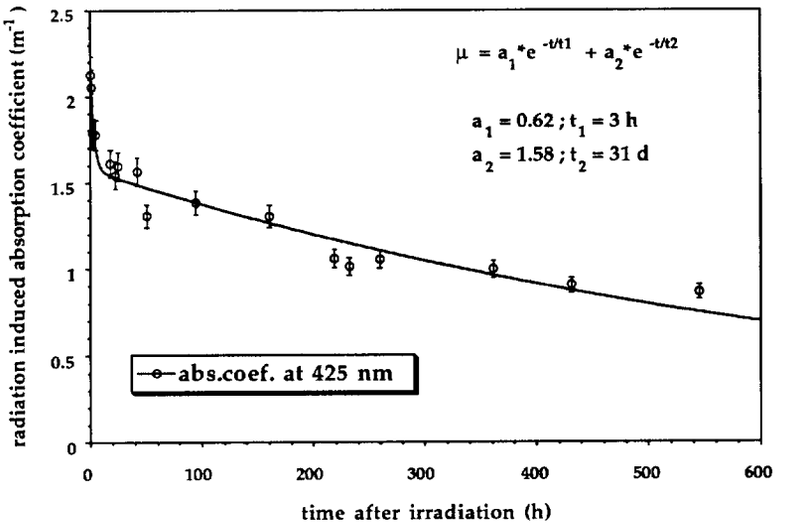

Fig.12 PWO:Nb room temperature recovery after 1820 Gy radiation dose

An important recovery of radiation damage at room temperature was noticed for PWO:Nb crystals whatever the source of irradiation. Fig.12 shows the room temperature recovery after a 1820 Gy irradiation by ^{60}Co source. A double exponential function best fits the recovery with time constants of 3 hours and 31 days respectively.

4. CONCLUSION

Due to its high density, short decay time, and good radiation hardness, PWO is a good candidate for electromagnetic calorimeter for the future high energy physics experiments. Moreover, the large existing infrastructure for mass production (particularly in former Soviet Union) triggered the choice of this crystal for the CMS experiment at LHC.

The mechanism of scintillation is established and Nb doping has proven to enhance the optical uniformity and radiation hardness of large crystals.

Nevertheless, the light yield of large PWO crystals is only marginally acceptable and a strong R&D program has to start in order to define the production parameters for increased and stable light yield on PWO crystals.

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