A Study of the Optical and Radiation Damage Properties of Lead Tungstate Crystals

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ABSTRACT

A study has been made of the optical and radiation damage properties of undoped and niobium doped lead tungstate crystals. Data were obtained on the optical absorbance, the intensity and decay time of the scintillation light output, and the radioluminescence and photoluminescence emission spectra. Radiation damage was studied in several undoped and niobium doped samples using ^{60}Co gamma ray irradiation. The change in optical absorption and observed scintillation light output was measured as a function of dose up to total cumulative doses on the order of 800 krad. The radiation induced phosphorescence and thermoluminescence was also measured, as well as recovery from damage by optical bleaching and thermal annealing. An investigation was also made to determine trace element impurities in several samples.

1. INTRODUCTION

Lead tungstate ($PbWO_4$) is a new scintillating material which is of great interest for use in high energy electromagnetic calorimeters [1-2]. It has a very high density (ρ = 8.3 g/cm^3), short radiation length (X_o = 0.9 cm) and small Moliere radius ($R_M \approx$ 2 cm), and has a scintillation light output which peaks between 450-550 nm with a fast component decay time in the range from 2-15 ns. It is presently being considered for use in two large, high resolution electromagnetic calorimeters, one for the CMS experiment and the other for the ALICE experiment, at the Large Hadron Collider at CERN. In order to meet the stringent demands of these two experiments, the crystals are required to be of high purity, produce uniform light output, and, in the case of CMS, be resistant to radiation damage up to several megarads.

We have carried out a study of the optical and radiation damage properties of a number of undoped and niobium doped crystals obtained from sources in the former Soviet Union. A total of seven samples, measuring typically 2 × 2 × 21 cm^3, were measured in all. In this paper, we will mainly discuss the results for two particular samples (number 767 and 768), both of which are Nb doped, and were part of a group of crystals prepared for study by CMS. These two samples, which were grown under similar conditions, showed very different properties, particularly with respect to radiation damage. Other samples, both undoped and Nb doped, have shown similar behavior, some exhibiting good radiation hardness and others not. We will compare a number of differences in samples 767 and 768 in order to attempt to identify which of these properties could be relevant in determining the important optical and radiation damage properties of $PbWO_4$. Additional information on an undoped sample can be found in ref. [3]

2. OPTICAL AND RADIATION DAMAGE PROPERTIES

The initial (pre-irradiation) transmission spectra for samples 767 and 768, taken down the longitudinal axis of the crystals, are shown in Figure 1. Sample 767 showed a distinct absorption band in the region around 430 nm, while sample 768 exhibited only a shoulder. The transmission for sample 767 extends down to approximately 350 nm, while sample 768 starts to show significant absorption around this wavelength. Sample 767 also contained a small (~ 2 cm long) region of inhomogeneity near the center of the crystal at one end which produced much higher absorbance near the center than near the edges.

The spectral light output of both samples was compared by measuring the radioluminescence and photoluminescence emission spectra. The radioluminescence was measured using ^{60}Co gamma ray excitation, and the photoluminescence was measured using UV excitation at a wavelength of 315 nm. For sample 767, the photoluminescence was also measured for other excitation wavelengths from 250-350 nm, and no dependence of the emission spectrum on the excitation wavelength was found. Figure 2 shows the spectra measured for the two crystals after correcting for phototube quantum efficiency and monochromator grating efficiency. The radioluminescence peaks at around 515 nm for sample 767, while sample 768 shows a lower peak at around 486 nm. Although the photoluminescence appears to peak at longer wavelengths (527 nm for 767 and 513 nm for 768), at least

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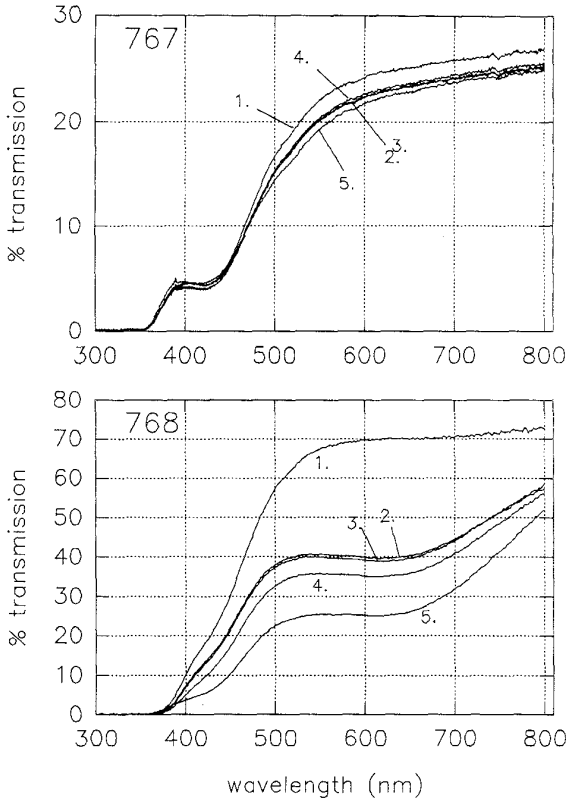

Fig.1: Longitudinal transmission spectra as a function of radiation dose for samples 767 and 768. Cumulative doses for 767 are 1 - initial, 2 - 2.6 Krad, 3 - 7.6 Krad, 4 - 18.2 Krad, 5 - 769 Krad. Dose rate was 120 rad/hr for doses 2 through 4 and 3.5×10^4 rad/hr for dose 5. Cumulative doses for 768 are 1 - initial, 2 - 2.4 Krad, 3 - 11 Krad, 4 - 20 Krad, 5 - 834 Krad. Dose rate for dose 2 through 4 was 132 rad/hr and 3.6×10^4 for dose 5.

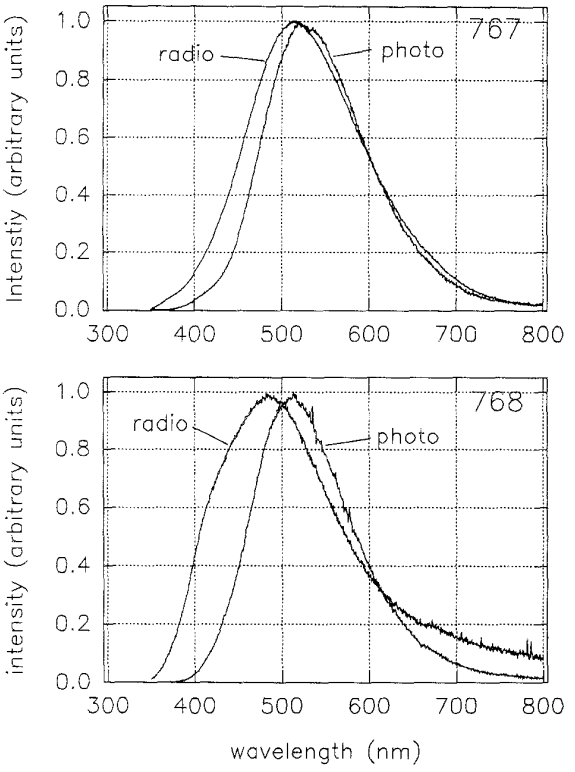

Fig. 2: Radioluminescence and photoluminescence emission spectra for samples 767 and 768. All spectra have been corrected for phototube quantum efficiency and monochromator efficiency and normalized to one at their peak.

part of this shift can be attributed to self absorbance in the crystal.

The decay time of the scintillation emission was measured for a number of samples using the single photon counting technique [4]. Figure 3 shows the decay time spectrum measured for sample 768. It is characterized by a very fast component with a time constant of 2.1 ns, a medium speed component with a time constant of 13.0 ns, and a slow component with a decay time of 348 ns, with relative amplitudes of 0.84, 0.12 and 0.04, respectively. In general, all samples showed this same three component spectrum with approximately the same decay times, although the amplitudes and time constants varied considerably from sample to sample. The amplitude of the slow component was typically $\sim$ 5% of the amplitude of the two fast components, but because of the long decay time, the total integrated light yield from the slow component was greater than that of the combined fast components.

Both samples were irradiated using ^{60}Co gamma rays up to a maximum total dose of 769 krad for sample 767 and 834 krad for sample 768. In both cases, the initial irradiation was carried out at a low dose rate ($\sim$ 120-130 rad/hr) in order to study any rapid changes in either sample. As shown in Fig. 1, sample 768 damaged quickly, exhibiting a series of strong, broad absorption bands in the region between 400 and 700 nm, and continued to damage with increasing dose. This damage was similar to that which was observed in undoped samples [3]. On the other hand, sample 767 showed very little damage, both at the initial low dose rate, and at the higher dose rate up to the maximum dose. Other samples showed levels of damage which were in between samples 767 and 768.

The light output of samples 767 and 768 was measured before irradiation on a 2" dia. phototube (Hamamatsu R2059) and was determined to be $\sim$ 8 photoelectrons per MeV, and approximately independent of position along the crystal. After the initial dose, the light output from sample 768 was not measurable due to the increased self absorbance and interference from radiation induced phosphorescence. However, the light output from sample 767 was measurable even up to the maximum dose, as shown in Figure 4. The light output, measured approximately 30 minutes after the final dose, showed a slight decrease of about 15%, but recovered to its original

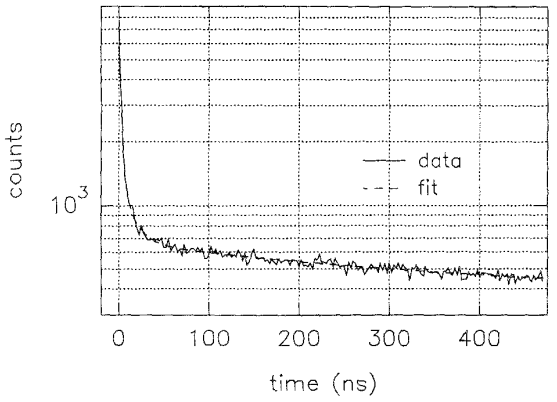

Fig. 3: Decay time of the scintillation emission for sample 768. A fit to the spectrum gives three components with times constants of 2.1 ns, 13.0 ns and 348 ns, with relative amplitudes of 0.84, 0.12, and 0.04, resp.

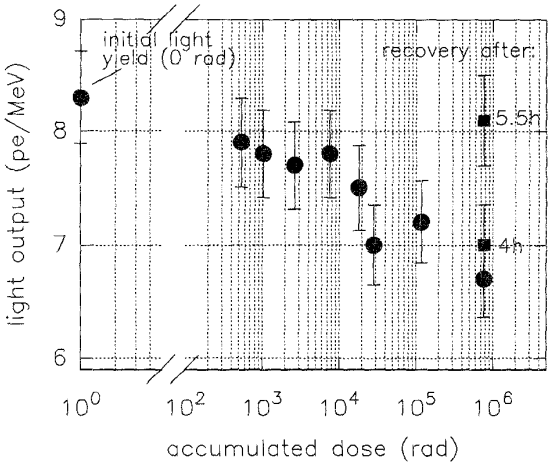

Fig. 4: Light output vs accumulated dose for sample 767. Except where indicated, all points were measured approximately 30 minutes after irradiation.

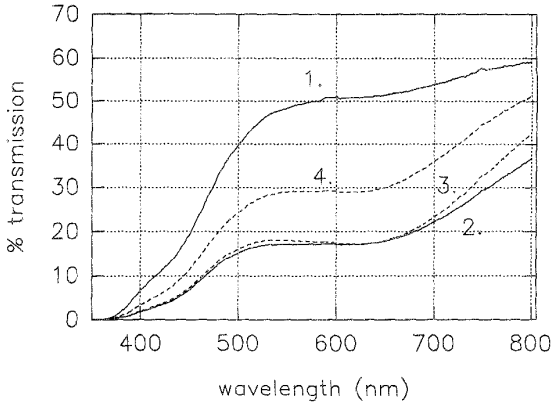

Fig. 5: Room temperature recovery for sample 768 kept in the dark. 1- initial, 2- 30 min after 1 Mrad, 3- 4 days recovery, 4- 18 days recovery.

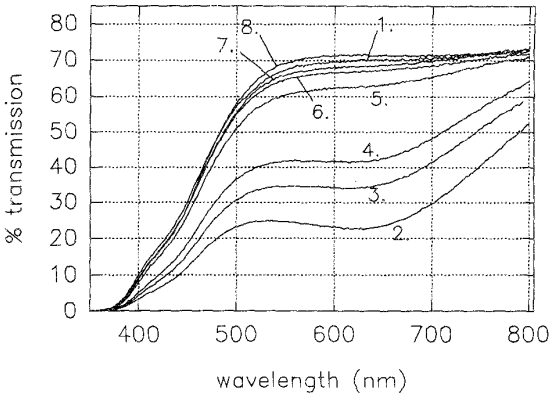

Fig. 6: Effect of optical bleaching on sample 768. Longitudinal transmission curves correspond to: 1- initial; 2- immediately after a total dose of 834 krad; optical bleaching: 3- 5 hours at 700 nm; 4- 12 hours at 700 nm; 5- 5 hours at 600 nm; 6- 10 hours at 600 nm; 7- 7 hours at 640 nm; 8- 2 hours of thermal annealing at 200°C.

value within 5.5 hours.

Sample 768 damaged much more than 767, but showed a natural recovery in its transmission when kept in the dark at room temperature, as shown in Figure 5. Other samples which damaged showed a similar behavior, with a recovery time characterized by a time constant of $\sim$ 160 hours. Recovery in sample 768 could also be induced by optical bleaching using light in the 600-700 nm range, as shown in Figure 6. Several hours of bleaching with 700 nm light produced significant recovery when applied immediately after irradiation. Further recovery was induced by several additional hours of bleaching with 600 nm and 640 nm light, but a certain level of permanent damage remained. However, after bleaching, thermal annealing for two hours at a temperature of 200 °C produced more recovery, and resulted in a transmission which was actually slightly higher than its original value.

Figure 7 shows the radiation induced phosphorescence in samples 767 and 768 as a function of time starting approximately 10 minutes after gamma ray doses of 0.7 and 1.0 Mrad, respectively. The apparent lower phosphorescence intensity in sample 768 was at least partly due to its higher induced absorption. The magnitude of the phosphorescence intensity was rather weak in both samples, which made it difficult to determine the actual emission spectrum. In fact, for lower radiation doses applied at lower dose rates, as indicated in Fig. 1, the phosphorescence intensity after irradiation was barely measurable. Using a series of edge cutoff filters with higher dose exposures, it was possible to determine that the phosphorescence emission peaks at $\sim$ 500 nm, which is approximately the same wavelength as the radioluminescence and photoluminescence. The time constant for

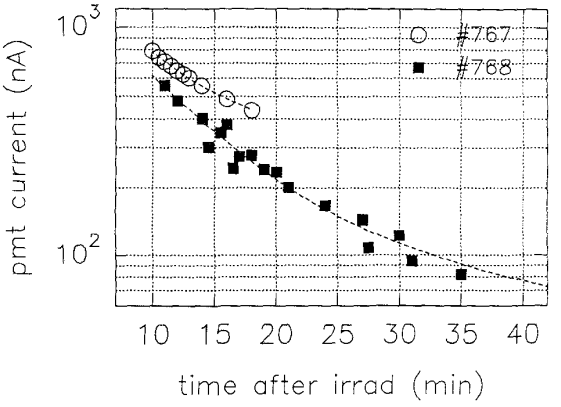

Fig. 7: Phosphorescence intensity vs time for samples 767 and 768 after gamma ray doses of 0.7 and 1.0 Mrad, resp.

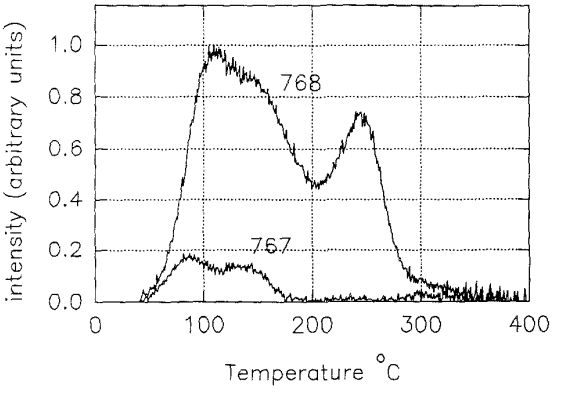

Fig. 8: Thermoluminescence spectra for samples 767 and 768.

the phosphorescence decay, as given by fitting the data shown in Fig. 7, was 6.0 minutes for sample 767 and 6.7 minutes for sample 768. However, measurements made on the phosphorescence starting within a few seconds after irradiation showed a more intense, rapidly decaying component which decays away by more than two orders of magnitude within approximately 1 minute. This would imply a much higher phosphorescence intensity during and immediately after irradiation than the data shown in Fig. 7 indicate.

Both samples also exhibited a weak thermoluminescence (TL), as shown in Figure 8. The thermoluminescence curves were obtained by exposing roughly 10 mg of each crystal to 1 Mrad of ^{60}Co gamma rays. The TL was then measured 10 minutes after irradiation from 40 °C to 400 °C at a heating rate of 2 °C /sec. The resulting spectra show that sample 768 has a stronger TL response than 767, implying a higher concentration of charge traps and luminescence centers. However, the TL signal in both samples is rather weak, and is roughly 3 or 4 orders of magnitude less in intensity than a typical sample of BaF_2. The longer lived phosphorescence observed in both crystals most likely arises from the two lowest temperature glow peaks. Sample 768 has at least 3 peaks at 110,150, and 245 °C, and sample 767 has at least 2 peaks at 90 and 140 °C. These data indicate that the lowest temperature trap has a depth of about 0.7 eV for both crystals, but to estimate the trap depths for the other peaks would require additional measurements.

A trace element analysis was performed on both samples using Particle Induced X-ray Emission (PIXE) and Glow Discharge Mass Spectroscopy (GDMS) in order to determine the stoichiometry of the crystals and to search for trace element impurities [5]. The results showed that both crystals were essentially stoichiometric $PbWO_4$, although there was an indication that the W/Pb ratio varied by $\sim$ 5% from one end of the crystal to the other. A survey of 77 elements showed similar levels of impurities in the few ppm to sub ppm level in both samples.

Element	Sample concentration (ppm)	
Sample	767	768
Na	9.6	1.8
Si	44.0	52.0
Ca	1.0	2.5
Nb	8.1	7.1
Mo	17.0	15.0

Table 1. GDMS analysis for samples 767 and 768

Table 1 lists the impurities detected in a portion of each sample, taken 3-5 mm below the surface of the crystal, at a level greater than 1 ppm. The lighter elements (Na,Si and Ca) could be present due to handling or treatment of the samples during earlier tests. The niobium levels of 7-8 ppm indicate that a substantial fraction of the niobium which was added to the initial melt (30 ppm) was lost during growth. Finally, it is interesting to note the high level of molybdenum in both samples. The presence of molybdenum has recently been shown to be a possible cause of phosphorescence in some samples [6]. Due to the long decay time of the phosphorescence, this emission may contribute to the apparent total light yield of crystals with high molybdenum content when measured in a dc mode, as opposed to a single photon counting mode. It is therefore of considerable interest to study the effect of molybdenum and other impurities in greater detail, and to try and correlate their presence with other properties, such as radiation hardness.

3. CONCLUSIONS

A study of a number of lead tungstate crystals has revealed a large sample to sample variation in many of their properties. The optical transmission varies considerably, and some samples show sizable regions of visible inhomogeneities. The radioluminescence spectra also vary from crystal to crystal, with the peak occurring in the 480-520 nm range. The scintillation decay time shows two major components in the 2-3 ns and 15-20 ns range, along with a third slow component in the several hundred nanosecond range. Some samples, which do not necessarily show the best optical transmission before irradiation, exhibit particularly good radiation hardness. Initial trace element analyses carried out on samples having very different characteristics have shown no high level impurity content and similar levels of trace element impurities. Further work is under way to attempt to correlate these results with the optical and radiation damage properties of these crystals.

4. ACKNOWLEDGMENT

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