A Study on the Radiation Hardness of Lead Tungstate Crystals [1]

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Abstract

This report presents recent progress of a study on the radiation damage in lead tungstate ($PbWO_4$) crystals. The dose rate dependence of radiation damage in $PbWO_4$ has been observed, confirming our early prediction based upon a kinetic model of color centers. An optimization of the oxygen compensation through post-growth thermal annealing, carried out in Shanghai Institute of Ceramics, has led to $PbWO_4$ crystals with significantly improved radiation hardness. A comparison between front versus uniform irradiations revealed that the later caused a factor of 2 to 6 times more severe damage. A measurement of a preliminary batch of lanthanum doped $PbWO_4$ crystals indicates that the La doping seems not a determine factor for $PbWO_4$ radiation hardness improvement. Finally, a TEM/EDS analysis confirmed our previous conjecture that the radiation damage in $PbWO_4$ crystals is caused by oxygen vacancies.

I. Introduction

Because of its high density and fast decay time, lead tungstate ($PbWO_4$) crystals were chosen by the CMS experiment to construct a precision electromagnetic calorimeter at LHC [1]. Our previous studies on $PbWO_4$ crystals revealed that $PbWO_4$ crystals suffer from non-negligible radiation damage after a dose as low as 10 rad [2], but the scintillation mechanism of $PbWO_4$ is not affected by the radiation, i.e. the loss of light output is due only to the absorption by radiation induced color centers [3]. We also proposed that the damage in $PbWO_4$ is caused by structure related defects, such as oxygen vacancies [2], and the level of the damage is dose rate dependent because of the recovery observed at room temperature [4].

In this report, we present progress in our understanding on the radiation damage in $PbWO_4$ crystals. Section II describes the dose rate dependence and result of an optimization of the oxygen compensation, carried out at Shanghai Institute of Ceramics (SIC). A comparison of different irradiation patterns is presented in Section III. Section IV discusses measurement result of a preliminary batch of lanthanum doped $PbWO_4$ crystals. A TEM/EDS analysis, which reveals the nature of $PbWO_4$ radiation damage, is presented in Section V. This work was carried out in a collaboration with SIC. As a result of this work, crystals of significantly improved radiation hardness have been produced at SIC. This work is also a part of an ongoing effort aiming at developing radiation hard $PbWO_4$ crystals for CMS at LHC [5].

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II. Dose Rate Dependence and Optimization of Oxygen Compensation

In our previous study, we predicted that the level of radiation damage in $PbWO_4$ crystals is dose rate dependent, which is a consequence deduced from a simple model of color center kinetics developed in our previous crystal research [4]. We also pointed out that the radiation resistance of $PbWO_4$ crystals may be improved by oxygen compensation through post-growth thermal annealing in an oxygen-rich atmosphere [3, 4]. Following this, a series of experiments was carried out, aiming at understanding the dose rate dependence and optimizing the annealing conditions for oxygen compensation.

Table 1
$PbWO_4$ Samples Tested for Oxygen Compensation

ID	Dimension (cm)	Date	Annealing
BGRI 1	$2.3 \times 5 \times 2.3$	1/97	-
SIC 93	$2.5 \times 5 \times 2.5$	1/97	-
SIC 115-1	$2 \times 5 \times 2$	1/97	O_2-1
SIC 121-1	$2 \times 5 \times 2$	1/97	O_2-1
SIC 117-1	$2 \times 5 \times 2$	1/97	O_2-2
SIC 122-1	$2 \times 5 \times 2$	1/97	O_2-2
SIC 115-2	$2 \times 5 \times 2$	1/97	Air-1
SIC 121-2	$2 \times 5 \times 2$	1/97	Air-1
SIC 116-2	$2 \times 5 \times 2$	1/97	Air-2
SIC 117-2	$2 \times 5 \times 2$	1/97	Air-2
SIC 152-2	$2 \times 5 \times 2$	8/97	Optimized O_2
SIC 153	$2 \times 5 \times 2$	8/97	Optimized O_2

A total of twelve 5 cm $PbWO_4$ samples were studied in this investigation. Table 1 lists the dimension, date of delivery and the condition of the post-growth thermal annealing. Samples were prepared in 6 groups of 2 each for each annealing condition, ranging from no annealing at all, two kinds of annealing in air: Air-1 and Air-2, to three kinds of annealing in oxygen: O_2-1, O_2-2 and

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final optimized O_2. In order to test reproducibility, each pair samples in a group of specific annealing condition was cut from different boles. In the no annealing pair, samples were grown in different institutes: SIC and Beijing Glass Research Institute (BGRI). In addition, two samples from the same bole were treated with different annealing conditions, such as 115-1 and 115-2 were treated in oxygen and air respectively. All samples, except BGRI 1, were grown at SIC.

As was pointed out in our previous study [2], the damage in $PbWO_4$ crystals was thermally annealable. By placing a $PbWO_4$ crystal in an oven of 250°C for two hours, all radiation induced color centers are fully eliminated. This property of $PbWO_4$ crystals is very useful for practical purpose: measurements may be cross-checked and verified in different laboratories. The result presented in this section has been cross checked at Paul Scherre Institute (PSI) irradiation facility. Our standard procedure of $PbWO_4$ measurement thus started with a complete thermal annealing.

All irradiations were carried out at Caltech. A 0.5 curie ^{137}Cs source was used for testing 5 cm long samples, and a 50 curie ^{60}Co source was used for testing full size samples. All samples in Table 1 were wrapped with aluminum foil, and were placed at a fixed distance to the radioactive source to receive defined dose rate. Samples were under irradiation all the time, except when measurements were carried out, which typically lasted for about 20 minutes to have transmittance and light output as function of integration time measured. Depending on light output a ^{137}Cs or ^{60}Co radioactive source was used to measure the absolute light output. Since the entire experiment building at Caltech is air-conditioned whole year, the systematic uncertainty of light output due to temperature variation is less than 0.3%. The overall systematic uncertainty of light output measurement is about 1% for samples of more than 10 p.e./MeV, and is increased to about 2%, when light output is about 5 p.e./MeV because of the uncertainties in the peak findings.

Figure 1 shows the entire history of the light output measurement for sample SIC 115-1. This experiment lasted for 20 days. The measured light output was normalized to that before irradiation, and was plotted as a function of the time of the measurement. The dose rate and integrated dose are also shown in the figure. There were periods when dose rate was shown as zero, indicating a recovery test. As shown in the figure, the level of $PbWO_4$ damage is dose rate dependent, and the fast recovery (in order of a few hours) was observed only when dose rate is 15.7 krad/h. This dose rate dependence is expected according to a simple model of color center kinetics [4]. If both annihilation and creation coexist, the color center density at the equilibrium depends on the dose rate applied. We define the light output at the equilibrium under certain dose rate when the second measurements carried out after 24 hours of the previous one shows no change of the light output. Because of this dose rate dependence, a proper specification for $PbWO_4$ radiation hardness would refers to a level of light output degradation under the dose rate expected at LHC. It is known that typical dose rate expected in the Barrel of $PbWO_4$ calorimeter is 17 to 30 rad/h, while it is up to 500 rad/h at the End-caps.

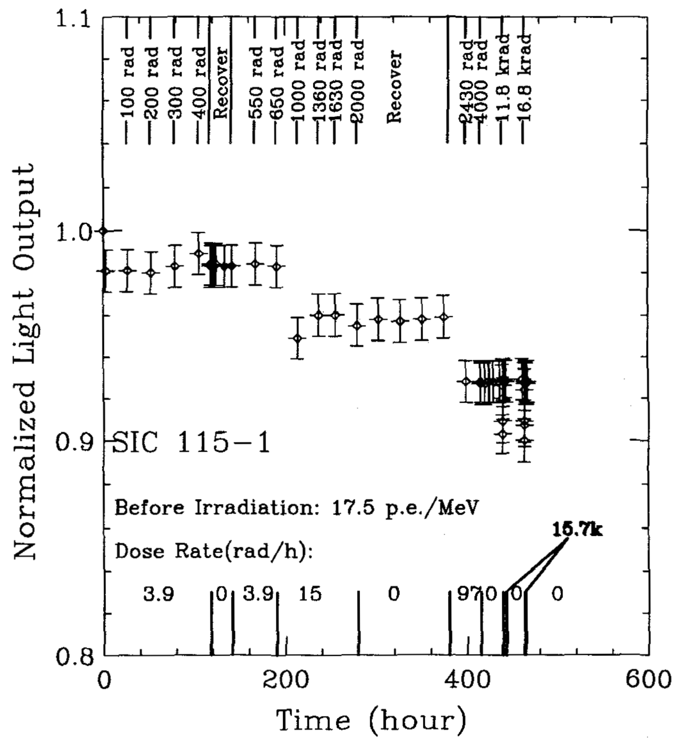

Fig. 1 The entire history of an experiment showing normalized light output as a function of dose rate.

We also found that samples treated with the same annealing condition had a similar radiation hardness, and there are clear correlations between the light out degradations and the annealing conditions. Figure 2 shows the normalized light output at the equilibrium under a specific dose rate for all samples, measured step by step for four dose rates: 15, 100, 480, 15.7k rad/h. It also shows that samples annealed under different conditions have much different behavior. Samples SIC 93 and BGRI 1, which were not annealed, have the worst radiation hardness. Samples annealed in oxygen is more radiation hard than that in air. Samples SIC 152-2 and SIC 153 which were annealed under the optimized oxygen conditions are the best. It was also clear that the effect of the post-growth thermal annealing to the radiation hardness of $PbWO_4$ crystals is reproducible, as evidenced by similar behavior of each pair of samples. This hints a key role of oxygen related defects in $PbWO_4$ radiation hardness.

Samples treated under the optimized oxygen annealing

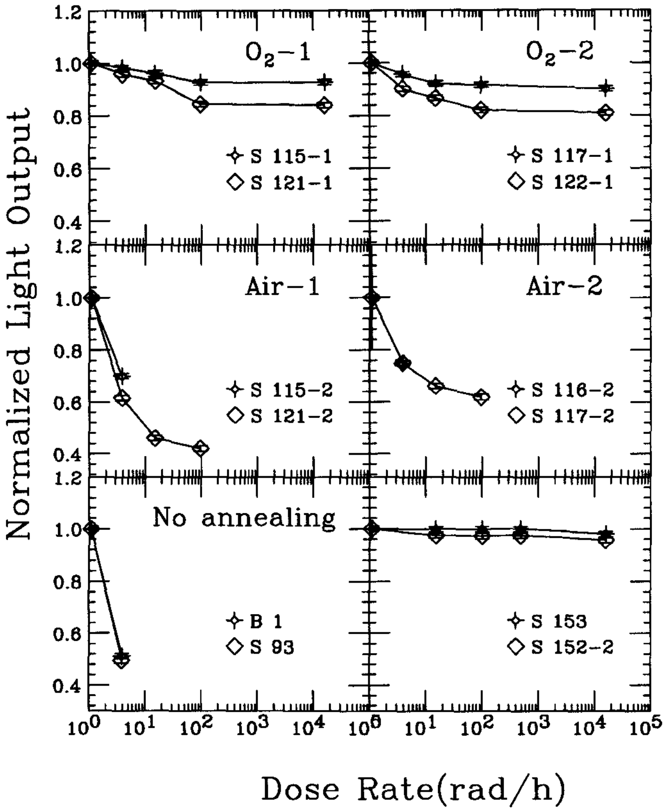

Fig. 2 Normalized light output at the equilibrium are shown as a function of the dose rate for six pairs of samples treated with different post-growing thermal annealing conditions.

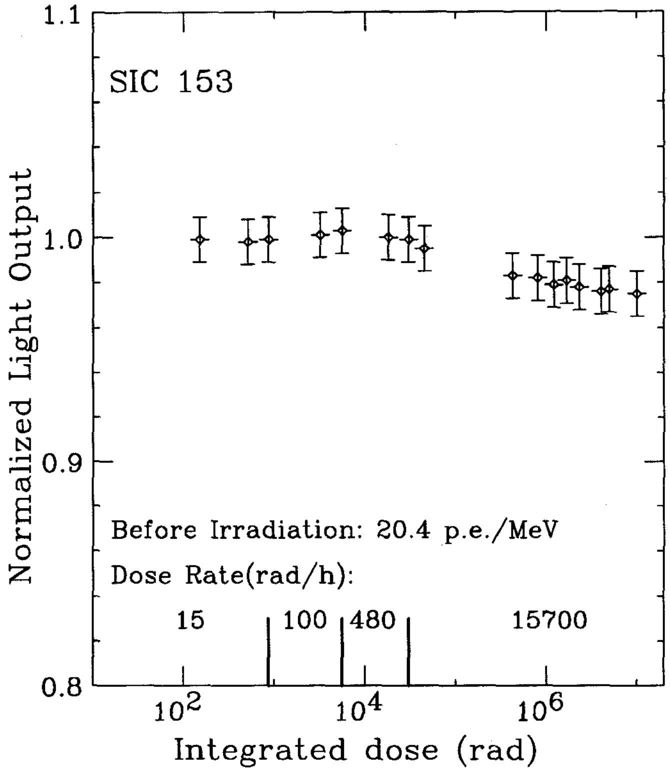

Fig. 3 The normalized light output of sample SIC 153 is shown as a function of integrated dose.

are radiation hard. Figure 3 shows the normalized light output of sample 153 as a function of integrated dose up to 10 Mrad. This sample showed no degradation in light output under a dose rate below 480 rad/h, and had only 2% degradation under an extremely high dose rate of 15.7 krad/h. The use of this unrealistic dose rate is to accelerate the experiment. The irradiation is continuing to accumulate an integrated dose of 20 Mrad, and we do not foresee any strange effect. Additional SIC $PbWO_4$ samples were treated with optimized annealing, and were tested at PSI. They were found to have a similar quality [5]. Samples of this quality certainly satisfy the most stringent radiation hardness specification for CMS to construct a precision $PbWO_4$ crystal calorimeter at LHC. Further effort, however, is to be made to transfer this annealing technology to treat full size crystals. It is believed that a similar optimization procedure would lead to full size samples with significantly improved radiation hardness.

III. Front Versus Uniform Irradiations

Several different irradiation patterns have been used in $PbWO_4$ investigations [5]. Two most common irradiation patterns are uniform and front irradiations respectively. In the front irradiation, the radiation is applied perpendicular to the small end of a long sample, as shown in Figure 4. In the uniform irradiation, the radiation was applied perpendicular to one long side face of the crystal, as shown in Figure 5. With a γ-ray irradiation source of ^{60}Co or ^{137}Cs, the uniform irradiation exposes the entire volume of the crystal, while the front irradiation only exposes a few cm at the front. A clear understanding of the difference between these two irradiation patterns will help in defining $PbWO_4$ radiation hardness specifications.

Table 2
Samples Tested for Front and Uniform Irradiations

ID	Dimension (cm)	Date	Annealing
SIC 85	2.0 × 20. × 2.3	8/96	O_2
SIC 135	2.0 × 23 × 2.3	5/97	O_2
SIC 136	2.0 × 23 × 2.3	5/97	O_2

A total of three full size samples were tested. Table 2 lists sample ID, dimension, delivery date and annealing conditions. These samples have a tapered shape with the small and large ends of 2 and 2.3 cm square respectively, and a length of 20 to 23 cm. Samples went through our standard procedure of thermal annealing and were irradiated at a fixed dose rate of 15, 100 and 480 rad/h.

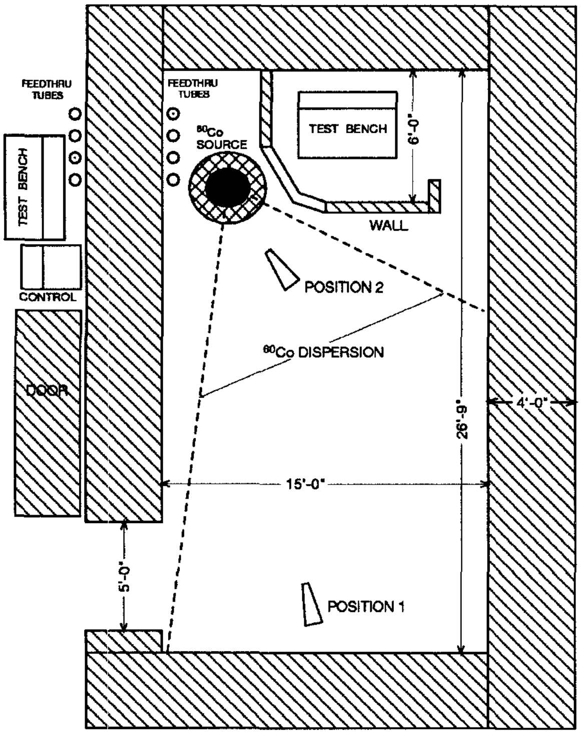

Fig. 4 A schematic of the front irradiation pattern.

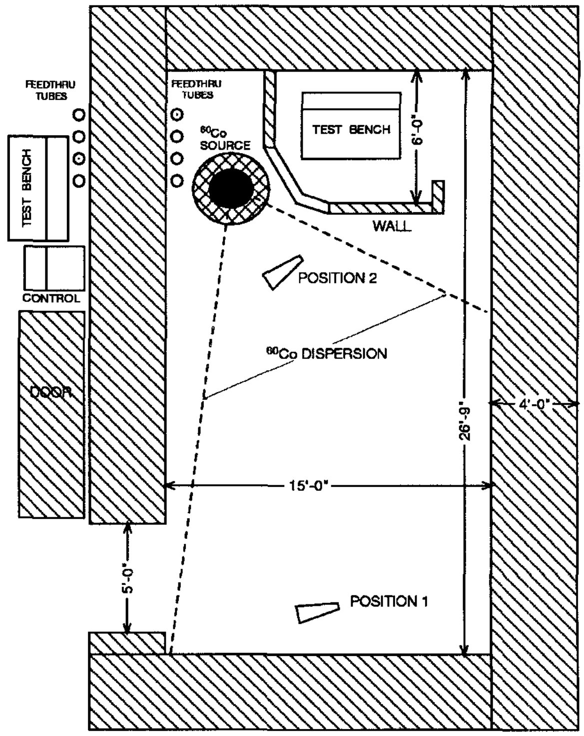

Fig. 5 A schematic of the uniform irradiation pattern.

At each dose rate, the light output of these samples were measured until reaching an equilibrium, as defined by no change of light output in 24 hours under irradiation. After that, the dose rate is increased to the next high level. The same procedure was followed for both front and uniform irradiations. We found that the light output degradation under uniform irradiation is a factor of 2 to 6 worse than that of the front irradiation. A typical result is shown in Figure 6 for sample 85, where the light output at the equilibrium under a specific dose rate, normalized to that before irradiation, are plotted as a function of dose rate. While this sample suffered from a damage of 2% at 15 rad/h under the front irradiation, it was increased to about 8% under the uniform irradiation. It is clear that the uniform irradiation caused much more severe damage, since the color centers in entire body of the crystal was created.

IV. Effect of Lanthanum Doping

The doping of lanthanum in $PbWO_4$ crystal is known to improve its UV cut-off edge of the transmittance [6]. In the process of developing rad-hard $PbWO_4$ crystals for CMS, we also recognized that lanthanum doping might be an alternative approach to reduce the density of oxygen vacancies. Since lanthanum doping is carried out by placing La_2O_3 powder in raw material, one molecule of La_2O_3 would replace two PbO molecules and, consequently, fills one oxygen vacancy. A preliminary batch of lanthanum doped sample was grown at SIC to test the effectiveness of the La doping. Table 4 lists the ID, dimension, annealing condition and the amount of lanthanum in the raw material. All samples were delivered in June, 1997.

Table 4
Samples Tested for the La Doping

ID	Dimension (cm)	Annealing	La (ppm)
SIC L-1	$2 \times 5 \times 2$	O_2	1960
SIC L-5	$2 \times 5 \times 2$	-	168
SIC L-6	$2 \times 5 \times 2$	-	84

We found that the La doping indeed improves the UV cut-off edge of the transmission, confirming early observation by Kobayashi *et al.* [6]. Figure 7 shows the longitudinal transmission of sample SIC L-5 , measured with a Hitachi U-3210 photospectrometer before irradiation and at the equilibrium under a dose rate of 15 and 100 rad/h. A very sharp rising at 340 nm was observed for both before and after irradiations, as compared to samples without La doping. A radiation-induced absorption band peaked at 420 nm, however, is clearly observed for this sample. The transmittance of the other La doped samples show similar feature, indicating that La doping alone does not improve sample's radiation hardness.

We also found that the peak of the emission spectra of La doped samples shifted from the green (500 nm) to the blue (420 nm), and the light output of these samples

Table 3
Trace Impurity Result (ppmw) Obtained by GDMS Analysis for Five La Doped $PbWO_4$ Samples

ID	Na	Al	Si	K	Ca	La	Mo	As	TE	Eu
L-6 (T)	9.1	0.2	0.3	1.4	0.8	2.7	1.3	0.93	0.2	4.3
L-6 (M)	2.7	0.04	0.4	0.7	2.9	38	0.92	0.19	0.01	2.1
L-6 (B)	1.9	0.1	0.2	0.5	6.2	85	0.84	0.13	0.02	1.5
L-4 (T)	1.4	0.4	0.5	5.9	0.05	2.8	1.8	3.9	0.2	1.2
L-4 (B)	0.2	0.7	0.6	0.4	0.38	590	0.68	0.64	0.1	0.6

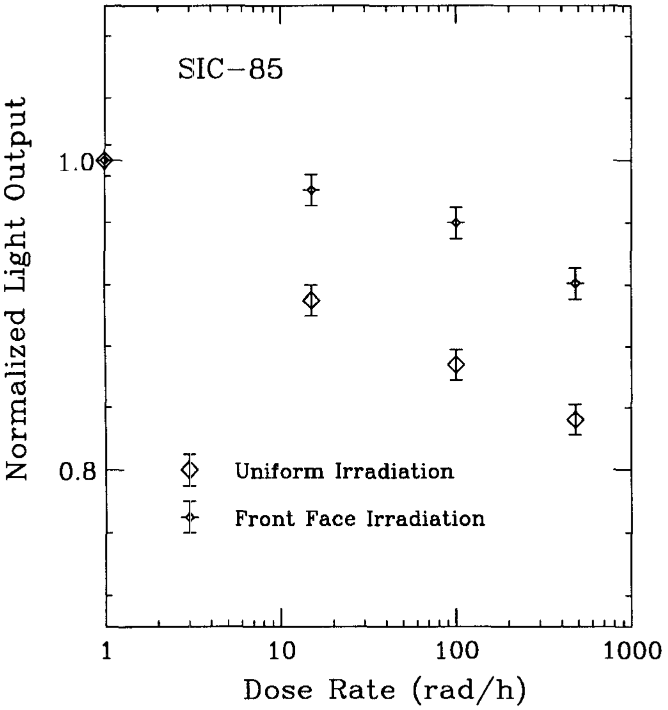

Fig. 6 Light output degradation in equilibrium is shown as a function of dose rate for uniform and front irradiations for sample SIC 85.

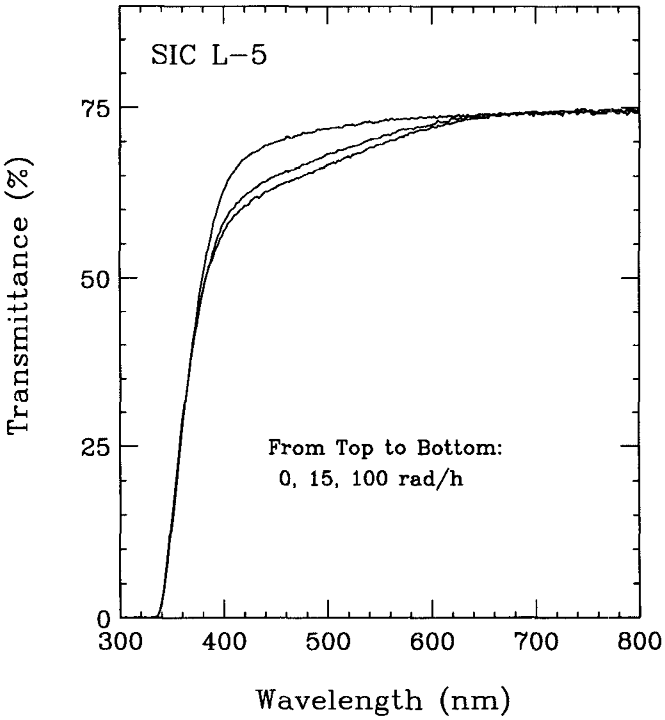

Fig. 7 Transmittance at the equilibrium under specific dose rate is shown as a function of wavelength for sample SIC L-5.

is sensitive to the La concentration, indicating that the La doping may change $PbWO_4$ scintillation. To verify this, the light output as a function of integration time was measured for each sample with two different ends coupled to the PMT. Figure 8 shows the result for sample SIC L-1. While the light output of La doped samples is indeed faster than samples without La doping, it depends on the end coupled to the PMT. A 30% more light was observed for sample SIC L-1 when after changing the end coupled to the PMT. This highly non-uniform light output was observed in all three La doped samples, but was not observed in any undoped sample.

Assuming the La doping affects $PbWO_4$ scintillation, this non-uniformity may caused by a non-uniform La concentration in the sample. A Glow Discharge Mass Spectroscopy (GDMS) analysis was carried out at Shiva Technologies West, Inc., California. Table 3 shows result of the trace analysis, in ppm weight, for five pieces of $PbWO_4$ samples: three pieces from the top, middle and bottom portion of sample SIC L6 and two pieces from two ends of another sample L4. As seen from this table, the La concentration is indeed not uniform in the sample. We thus conclude that the origin of this light output non-uniformity is due to very different La concentration in the sample caused by a segregation coefficient not equal one. Table 3 also indicates that while impurities of Na, K, Mo As and Eu moved to the top during growing process with a segregation coefficient of less than one, impurities of Ca and La stay at the bottom with a segregation coefficient of larger than one. Note, SIC uses modified Bridgman method to grow $PbWO_4$ crystals from bottom up.

Finally, the La doping seems not improve $PbWO_4$ radiation hardness. Figure 9 shows normalized light output at the equilibrium under specific dose rate for these La doped samples, and compared to sample 153 which is treated with optimized oxygen compensation. It is clear SIC 153 has much better radiation hardness

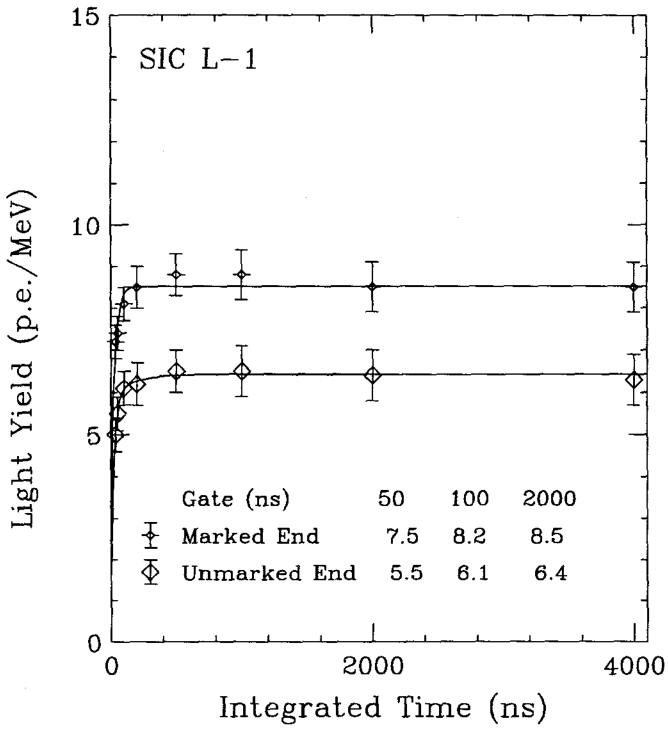

Fig. 8 Light output of sample SIC L-1 is plotted as a function of integration time, showing different amplitude when different end of the sample was coupled to the PMT.

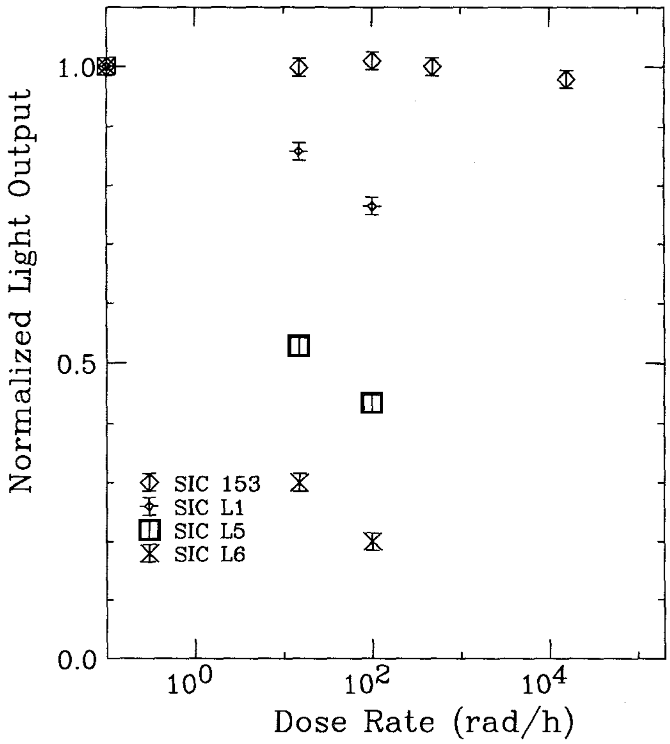

Fig. 9 Normalized light output at equilibrium is shown as a function of dose rate for three La doped samples, and compared to oxygen annealed sample SIC 153.

than all La doped samples. Note, this batch of the La doped samples is preliminary. Effort will be made to dope lanthanum uniformly in $PbWO_4$. As discussed above, the La doping indeed improves transmittance of the crystal, and may help in reducing oxygen vacancies, the La and other tri-valent doping experiment will continue until a final conclusion is drawn.

V. Lead Tungstate Damage Mechanism

Crystal defects, such as oxygen vacancy, are known to cause radiation damage for other oxide scintillators. In BGO, for example, three common radiation induced absorption bands at 2.3, 3.0 and 3.8 eV with consistent widths were found in a series of 24 doped samples [7], indicating defect-related color centers, as shown in Figure 10.

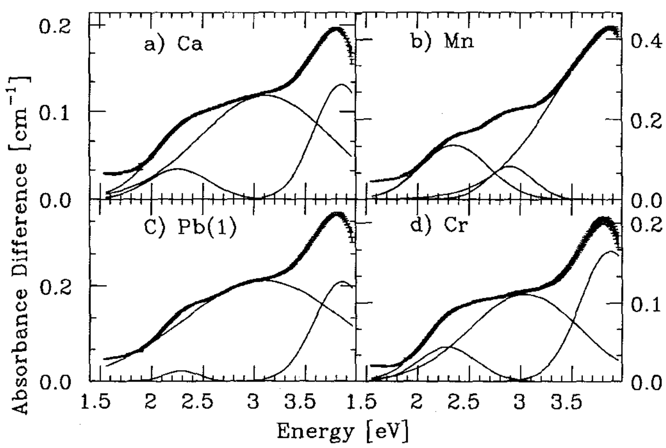

Fig. 10 The radiation-induced absorption is shown to be decomposed to three common absorption bands for four BGO crystals doped with different dopants.

In our previous work, we concluded that $PbWO_4$ damage is caused by structure related defects, such as oxygen vacancies [2]. This conclusion was reached based upon material analysis carried for a batch of $PbWO_4$ crystals grown in Bogoroditsk Techno-Chemical Plant (BTCP), Russia, and SIC. We first did GDMS analysis in Charles Evens & Associates, California. A survey of 76 elements, including all of the lanthanides, indicates that there are no obvious correlations between the detected trace impurities and crystal's susceptibility to the radiation damage. This indicates an important role of defects, such as oxygen vacancies which can not be determined by GDMS. We then did Particle Induced X-ray Emission (PIXE) and quantitative wavelength dispersive Electron Micro-Probe Analysis (EMPA) in Charles Evans & Associates, and found that crystals with poor radiation hardness had a deviated stoichiometric W/Pb ratio.

As discussed in Section II, we have observed significant improvement of radiation hardness of $PbWO_4$ crystals by oxygen compensation through post-growth thermal annealing in an oxygen-rich atmosphere. This is a pragmatic approach to develop radiation hard $PbWO_4$

crystals, but is not a direct observation of oxygen vacancies in the crystal. To directly observe oxygen vacancies, one must be able to measure complete stoichiometric ratio of Pb:W:O in $PbWO_4$ samples. Efforts have been made along this line. X-ray Photoelectron Spectroscopy (XPS) was tried at Charles Evens & Associates [8]. It, however, was found to be very difficult due to the systematic uncertainty in oxygen analysis. Effort has also be made to directly identify oxygen vacancies by Electron Paramagnetic Resonance (ESR) and Electron-Nuclear Double Resonance (ENDOR) through observing unpaired electrons. It, however, was also difficult to reach a quantitative conclusion.

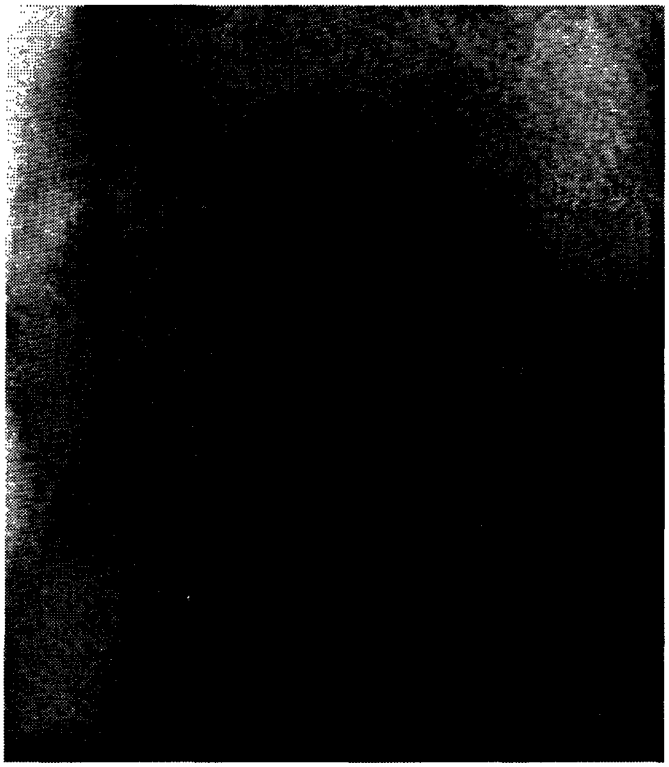

Fig. 11 High resolution TEM picture of a $PbWO_4$ crystal, showing lattice structure.

By using Transmission Electron Microscopy (TEM) coupled to Energy Dispersion Spectrometry (EDS), a localized stoichiometry analysis was possible to identify oxygen vacancies. A TOPCON-002B Scope was first used at 200 kV and 10 μA. Samples were made to powders of an average grain size of a few μm, and then placed on a sustaining membrane. With a spatial resolution of 2 Å, the lattice structure of $PbWO_4$ crystals was clearly visible. Figure 11 is a high resolution TEM picture, showing lattice structure.

Figure 12 shows a TEM picture taken for a sample with poor radiation hardness. Some black spots of a diameter of 5 – 10 nm were clearly seen in the picture. On the other

Fig. 12 TEM picture of a $PbWO_4$ crystal with poor radiation hardness, showing clearly the black spots of ϕ5–10 nm related to oxygen vacancies.

hand, samples with good radiation hardness show stable TEM picture with no black spots (Figure 13).

Table 5
Localized (ϕ0.5 nm) Stoichiometry Analysis by TEM/EDS

As Grown Sample

Element	Black Spot	Peripheral	$Matrix_1$	$Matrix_2$
O	1.5	15.8	60.8	63.2
W	50.8	44.3	19.6	18.4
Pb	47.7	39.9	19.6	18.4

The Same Sample after Oxygen Compensation

Element	$Point_1$	$Point_2$	$Point_3$	$Point_4$
O	59.0	66.4	57.4	66.7
W	21.0	16.5	21.3	16.8
Pb	20.0	17.1	21.3	16.5

By employing a TEM with EDS system, a localized stoichiometry analysis was carried out at SIC. The system is a JEOL JEM-2010 scope and a Link ISIS EDS. The spatial resolution of this system allows a localized stoichiometry analysis in a region of a diameter of 0.5 nm [9]. An as grown sample was first analyzed, and black

Fig. 13 TEM picture of a $PbWO_4$ crystal with good radiation hardness, showing no black spots.

spots were observed. Points inside and surrounding the black spots were analyzed as well as points far away from the black spots. The uncertainty of the analysis is typically 15%. The result of this analysis is listed in Table 5, where atomic fractions (%) at these areas are shown. The result shows a deviation from the atomic stoichiometry of O:W:Pb = 66:17:17 in the center of these black spots, pointing to a severe deficit of oxygen component. In the peripheral area, the oxygen deficit is less, but still significant. There is no oxygen deficit observed in the area far away from the black spots. This analysis thus positively identified oxygen vacancies in $PbWO_4$.

As a comparison, the same sample after oxygen compensation was re-analyzed. No black spot was found. The result of the analysis is also listed in Table 5. In all randomly selected points no stoichiometry deviation was observed. This analysis thus clearly identified oxygen vacancies in $PbWO_4$ samples of poor radiation hardness, and confirmed our early conjecture on $PbWO_4$ radiation damage mechanism.

VI. Summary

A brief summary of the investigation carried out in this report is listed below.

1. The level of radiation damage in $PbWO_4$ crystals is dose rate dependent — a confirmation of our prediction published in reference [4].

2. The oxygen compensation through post-growth thermal annealing is effective in improving $PbWO_4$ radiation hardness, and has led to 5 cm $PbWO_4$ samples of significantly improved radiation hardness. The effect of annealing to the radiation hardness of $PbWO_4$ crystals is reproducible.

3. The light output degradation under uniform irradiation is a factor of 2 to 6 worse than that of the front irradiation. Since the later checks the quality of entire body of the crystal, so should be used for $PbWO_4$ specification.

4. Investigation on a preliminary batch of La-doped samples indicates that the La doping does improve the UV cut-off edge of the transmission and cause a fast light output, but seems not making $PbWO_4$ crystal rad-hard. Investigation on La doped sample will continue to reach a final conclusion.

5. The $PbWO_4$ damage mechanism is understood as due to the structure related defects, e.g. oxygen vacancies, which were clearly identified by localized stoichiometry analysis by TEM/EDS. This also explains the effectiveness of the oxygen compensation in improving the radiation hardness of $PbWO_4$ crystals

VII. Acknowledgements

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