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Scintillation characteristics of $PbWO_4$ single crystals doped with Th, Zr, Ce, Sb and Mn ions

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Abstract

In our previous papers we reported that La^{3+}, Gd^{3+}, Y^{3+}, and Lu^{3+} dopings significantly improve the optical and scintillation characteristics, including radiation hardness, of $PbWO_4$ single crystals. The hypothesis of Pb^{2+} deficiency in the grown crystals and its charge compensation by the mentioned trivalent ions occupying the Pb^{2+} sites has been proposed to explain the observed improvement. Under such assumption, tetravalent-ion doping may be as efficient as or even more efficient than trivalent-ion doping in improving $PbWO_4$ scintillator. Recently we extended the dopant ions to stable tetravalent ions (Th^{4+}, Zr^{4+}) and some other ions ($Ce^{3+,4+}$, $Sb^{3+,5+}$, Mn^{2+}). We have found that the tetravalent-ion (Th^{4+}) doping gives similar improvement compared with the trivalent-ion doping in consistency with the expectation mentioned above. The ions with two different possible charge states ($Ce^{3+,4+}$, $Sb^{3+,5+}$) gave finite but much less improvement than the trivalent and tetravalent ions. $Ce^{3+,4+}$ doping reduced the light yield significantly. Annealing of undoped PWO in PbO vapour was also studied to examine the possibility of reducing the Pb^{2+} deficiency.

1. Introduction

In our previous papers [1-3], we reported that La^{3+} doping dramatically improves the characteristics of lead tungstate PbWO$_4$ (or PWO) scintillating crystals including optical transmittance, decay time and radiation hardness. The mechanical stability against cracking is also improved significantly. La-doping was also discussed in several papers by other research groups at the International Workshop on Tungstate Crystals held in Rome in 1998 [4]. In order to understand the mechanism for the obtained improvement and thereby improve further this scintillator, we studied the effects of the other stable trivalent ions (Y^{3+}, Gd^{3+}, Lu^{3+}, Sc^{3+}) doped into PWO crystals. Comparing the obtained results with those for undoped PWO and divalent-ion (Cd^{2+}) and pentavalent-ion (Nb^{5+}) doped PWO, we confirmed [5] that not only La^{3+} but also the other trivalent ions such as Gd^{3+}, Y^{3+}, Lu^{3+} give significant improvement in transmittance, decay time and radiation hardness of PbWO$_4$ scintillating crystals. The obtained improvement has been tentatively explained in terms of the following hypothesis[6]: The two absorption bands at 350 and 420 nm can be due to the Pb^{3+}- and O$^-$-related defects, respectively, which should be created as a result of Pb^{2+} deficiency in the lattice during the growth and/or annealing process so as to recover the total charge balance in the entire crystal. Introduction of La^{3+} could compensate the Pb^{2+} deficiency, thereby reducing the densities of the Pb^{3+}/ O$^-$-related defects. Among the trivalent ions tested, Y^{3+} gave the best radiation hardness [5]. We also pointed out [5] that Y^{3+} (with segregation coefficient k=0.8) and Gd^{3+} (k=1.5) may be better than La^{3+} (k=2.5), and Lu^{3+} (k=0.3) from the viewpoint of uniform dopant concentration along the crystal length. Doping with the other ions of different charges (2+, 3+, 5+, etc) has also been studied in several institutes (for example see [7-9] and a review paper [10]). Nb^{5+} doping was intensively studied in the CMS group with an aim to cause oxygen leakage thereby reducing the densities of the Pb^{3+}/O$^-$-related defects, and was found [9] to give an apparently similar improvement to the typical trivalent-ion doping. However, the required level of Nb^{5+} concentration in the melt is by an order of magnitude larger than that of the trivalent ions because of the indirect nature of the charge compensation for the Pb^{2+} deficiency and the smallness of the segregation coefficient (k~0.4).

Although the smallness of the assumed Pb^{2+} deficiency (as small as or even smaller than 0.1 at.% [11,12]) makes difficult to detect the Pb^{2+} deficiency directly through the study of the microstructure of the grown crystals [5], a rather clear evidence has been obtained by Han et al. [13] from the observation of dielectric relaxation in PWO:La^{3+} crystals. They confirmed that the density of the mobile defects, which exist in undoped PWO, is reduced as the La^{3+} concentration is increased. The observed polarization is most probably due to the creation of $[2(\mathrm{La}_{Pb}^{3+})^{\cdot}\text{-}\mathrm{V}_{Pb}'']$ dipole complexes, and indicates the existence of Pb^{2+} deficiency (as mobile defects) in undoped PWO. La^{3+} ions should occupy the Pb^{2+} sites and form the $[2(\mathrm{La}_{Pb}^{3+})^{\cdot}\text{-}\mathrm{V}_{Pb}'']$ dipole complexes, thereby changing the mobile Pb^{2+}

vacancies to immobile ones. The improvement due to La^{3+} doping can be understood well if the mobile uncompensated Pb^{2+} vacancies should cause degradation in transmission and radiation hardness. However, it is to be noted that the defects related to the conjectured Pb^{2+} deficiency *may not be of a simple (i.e. point defect-like)* nature since they were not observed in ESR measurement [14].

If the hypothesis sketched above should be an at least qualitatively correct mechanism for the observed dramatic improvement in PWO due to the trivalent-ion doping, stable tetravalent-ion doping (entering Pb^{2+} sites) may be even more efficient. This is because two trivalent ions (for example, La^{3+}) have to come close to the Pb^{2+} vacancy *by chance to form the* $[2(La_{Pb}{}^{3+})^{\cdot}\text{-}V_{Pb}{}'']$ *dipole* complexes, while only one tetravalent ion (denoted here as R^{4+}) may be enough to form a similar dipole $[(R_{Pb}{}^{4+})^{\cdot\cdot}\text{-}V_{Pb}{}'']$ to make the Pb^{2+} vacancy immobile.

In order to check the new conjecture on the tetravalent-ion doping and thereby understand better the mechanism of the significant improvement obtained by trivalent-ion doping, we have extended the dopant ion species from previous ones (Cd^{2+}, La^{3+}, Gd^{3+}, Y^{3+}, Lu^{3+}, Sc^{3+}, Nb^{5+}), *whose results were described in* [1], to stable tetravalent ions (Th^{4+}, Zr^{4+}). We also included some other ions ($Ce^{3+,4+}$, $Sb^{3+,5+}$[15], Mn^{2+}) in the present study with the following motivations. Ce^{3+}, which belongs to the rare-earth elements similarly to Gd^{3+} and Lu^{3+}, is known to give fast scintillation (τ~30-40 ns) and/or improve radiation hardness in some scintillators (for example, Gd_2SiO_5:Ce [16]). $Sb^{3+,5+}$ was recently claimed to improve PWO by the research groups of Shanghai Institute of Ceramics [15, 17-19] and is worth checking in a deeper way by an independent investigation. Mn^{2+} is also *frequently used as a dopant to improve phosphors.* We will tentatively write Mn^{2+} for simplicity throughout the present paper although Mn ions may have other charge states of 3+, 4+, etc. In this paper, we will present the results obtained for the above-mentioned new dopant ions (Th^{4+}, Zr^{4+}, $Ce^{3+,4+}$, $Sb^{3+,5+}$, Mn^{2+}) with respect to transmittance in the short wavelength region, excitation-emission spectrum, light yield, decay time, radiation hardness, etc. We will also give the result of annealing an undoped PWO in PbO vapour in order to *reduce* Pb^{2+} *evaporation and/or recovering the* Pb^{2+} *deficiency during annealing.*

2. Test samples

All the test samples of PWO single crystals (see Table I for the list) were grown by Furukawa Co. in the same way (3-times crystallization [20] in the air by *the Czochralski method with a platinum crucible) by using raw material obtained* from the same source. They were annealed at 600 °C in the air for 6 hours, except for one undoped sample (PWO27, see Table 1), which was annealed in PbO vapour. Each sample was cut from an ingot with approximately 35 mm diameter and 80 mm length. The nominal purities of the starting raw materials (PbO and WO_3) were 99.99%. Dopant material was added into the melt in the third recrystallization process [20] with a concentration of 135 at.ppm in the melt for most of the dopant ions but $Sb^{3+,5+}$ which was added by 135 and 1350 at.ppm. The large concentration (1350 at.ppm) of Sb^{5+} was also tested because 135 at.ppm did not give sizable effects [21]: the similar feature was also found for Nb^{5+} doping [5]. True concentration of the dopant ions in the grown crystals is given in Table 1. It was either measured by the Inductively-Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) or calculated by using the known segregation coefficient. The impurities remaining in the grown crystals were analyzed by Glow Discharge Mass Spectroscopy (GDMS). From the results of impurity analysis carried out in more than 10 samples in the past, we can expect that the impurities were well controlled to be at similar level in all the studied samples. As seen in the typical result of impurity analysis given in [3] for La^{3+}-doped samples, most of the impurities are below 0.1 at.ppm level with no ones above 1 at.ppm level. Mo impurity, which induces very slow components in the luminescence [22-23], was less than 0.02 at.ppm level. Among the present new samples, only PWO:Ce had a tint of yellow, while the others were visibly colourless.

3. Measurements

Transmission and photoluminescence (excitation and emission) spectra were measured with a spectrophotometer (Hitachi 220 or U-2310) and a fluorescence spectrophotometer (Hitachi F4500), respectively. Phosphorescence spectra and its decay time were also measured with the F4500 by starting measurement 2 ms

after the exposure to UV light was stopped. We measured the scintillation intensity for ^{60}Co γ-rays by comparing the pulse height of the 1.25 MeV peak (the average of the 1.17 and 1.33 MeV photoelectron peaks) with the single photoelectron (p.e.) peak, which was calibrated with an LED pulser mounted at a distance from the photomultiplier. Each crystal was mounted with one of the largest faces on a 2-in. UV-sensitive photomultiplier tube (PMT, Hamamatsu R2259, with a bialkali photocathode and a silica window). The pulse height was analyzed with a PHA (LeCroy qVt) in the charge mode within 1 μs gate. We measured the decay time spectra within 1 μs by using the conventional single photoelectron technique with a Lecroy qVt and a fast 2-in. UV-sensitive PMT (Hamamatsu H3177, with a bialkali photocathode and a silica window). The obtained spectrum was fitted with two (three if necessary) exponentials superimposed on a constant background. Thermally stimulated luminescence (TSL) was measured in Milano: the apparatus used was described elsewhere [6,24].

Radiation damage was measured by irradiating the samples with ^{60}Co γ-rays at Japan Atomic Energy Research Institute (JAERI). Five cycles of irradiation followed by transmission measurement were carried out to cover the accumulated dose from 10^4 to 10^8 rad (10^2 to 10^6 Gy), by increasing the accumulated dose by a factor of ten per cycle. The obtained results in the new samples prepared for the present work (marked # in Tables 1 and 2) are compared with those in the old samples which were described in our previous paper [5]. The irradiation period for the new (old) samples was 1h, 1h, 2.5h(2.75h), 26h(18.5h), and 137h(70h) for 10^4, 10^5, $10^6(1.2\times10^6)$, 10^7, and 10^8 rad, respectively. The transmission measurement was carried out in 33h(56h), 34h(31h), 54h(42h), 30h(31h), and 33h(31h) after irradiation by 10^4, 10^5, $10^6(1.2\times10^6)$, 10^7, and 10^8 rad, respectively. Recovery of the radiation damages was also measured in 3.3d, 10.5d and 121d (2.3d, 9.3d, 24.3d and 205d for the old samples) after the 10^8 rad irradiation. To compare the radiation damage in samples having different thickness, we calculated the induced absorption coefficient μ_{ir} defined as

$$\mu_{ir} = (1/d)\,ln(T_o/T), \qquad (1)$$

where d is the thickness across which the transmittance T_o (before irradiation) and T (after irradiation) were measured.

4. Results

4.1 Tetravalent-ion (Th^{4+}, Zr^{4+}) doping

The transmission spectra of PWO:Th^{4+} and PWO:Zr^{4+} are compared in Fig.1a with the Pb-rich (essentially undoped) and trivalent-ion doped (PWO:Gd^{3+}80 at.ppm) samples. We see that Th^{4+} significantly improves the transmittance in the short wavelength region (330-450 nm) similarly to the trivalent ions. Absence of clear effects for Zr^{4+} doping may be due to that Zr^{4+} did not enter the crystal enough because of its too small segregation coefficient ($k<0.1$), or alternatively Zr^{4+} occupied interstitial sites due to its small ion radius (0.79A) compared with Pb^{2+} (1.20A).

The excitation-emission spectra in PWO:Th^{4+} and PWO:Zr^{4+} are given in Fig. 2 in comparison with the other samples. The peak excitation (or emission) wavelength of ~315 nm (~415 nm) is the same as in the other PWO samples (see Table 2). The second minor emission band in the red spectral region, which is characteristic to undoped PWO, is absent in PWO:Th^{4+}, while existing in PWO:Zr^{4+}. No very slow component (phosphorescence) was detectable. As for the decay time (see Table 2), the main component in PWO:Th^{4+} and PWO:Zr^{4+} was as short as or shorter than a few to ten ns as in all the other samples. While the decay time of undoped PWO usually consisted of three components, the third slowest component vanished when trivalent ions were doped [5]. Both PWO:Th^{4+} and PWO:Zr^{4+} gave a two-component decay spectrum as in the typical trivalent-ion doped PWO. The light yields of 40 p.e./MeV in PWO:Th^{4+} and 36 p.e./MeV in PWO:Zr^{4+} were as large as those in the other trivalent-ion doped samples (see Table 2).

The $\mu_{ir}(\lambda)$ spectrum is compared with the other samples in Fig. 3. The μ_{ir} at 420 nm, the emission peak wavelength, is compared in Fig. 4. From these figures we can see that Th^{4+} doping also gives significant improvement in radiation hardness similarly to the typical trivalent-ion doping. The radiation damage in PWO:Zr^{4+} is even enhanced compared with the undoped PWO.

4.2 $Ce^{3+,4+}$ doping

For $Ce^{3+,4+}$ doping, the transmission spectrum (see Fig.1) shows a sharper rise above the cutoff wavelength compared with the undoped PWO. However, the improvement in the transmittance in the short wavelength region (330-450 nm) is much less than that achieved by trivalent-ion doping. The reason for the absence of significant improvement in the transmission spectrum is probably related to the occurrence of the lowest 4f->5d absorption transition of Ce^{3+} in the present spectral region. As for the excitation-emission spectrum, the second minor emission peak in the red spectral region, which is characteristic to undoped PWO, disappears (see Fig. 2). These differences in both transmission and the excitation-emission spectra from undoped PWO indicate that Ce-doping by 135 at.ppm in the melt surely affects the characteristics of PWO. According to the ICP-AES analysis, the Ce concentration in crystal is as large as 29 at.ppm. Ce ions are expected to enter the Pb^{2+} sites, since the ion radius (Ce^{3+}~1.03A, Ce^{4+}~0.92A) is not very different from Pb^{2+}(1.20A).

With respect to the radiation hardness, PWO:Ce is between the typical trivalent-ion doped PWO and the undoped PWO (see Figs. 3 and 4). TSL glow curves have been studied to elucidate the relation between radiation hardness and radiation-induced trap levels. In the TSL glow curves after X-ray irradiation at room temperature, an intense peak is usually observed at 50 °C in undoped PWO. The amplitude of this peak is suppressed by at least 2 to 3 orders of magnitude in trivalent-ion doped PWO[25]. The low temperature TSL of undoped PWO features peaks at 50, 95 °K and composite structures in the region of 150-300 °K. Trivalent-ion doping usually suppresses such composite structures efficiently and enhances the 95 °K peak by again 2 to 3 orders of magnitude [25-27]. The TSL of PWO:Ce (see Fig. 5a) shows a substantial but insufficient suppression of the 50 °C peak (by only an order of magnitude), while the composite structures at higher temperatures is enhanced. In the low temperature TSL glow curves (see Fig. 5b), the main peaks observed at 50 and 95 °K with absence of peaks in the 150-300 °K region are in close agreement with the case of the trivalent-ion doping. These intermediate effects in the TSL glow curves are reasonably consistent with the results obtained for radiation hardness. Another distinctive difference of Ce doping from the trivalent-ion dopings (La^{3+}, Gd^{3+}, Y^{3+}, Lu^{3+}) is the reduction by half in light yield and the corresponding significant shortening of the decay time (see Table 2). These effects may be explained by the efficient non-radiative recombinations at the Ce-sites, which is supported by the absence of the Ce^{3+} emission even at low temperature (4.2 °K).

4.3 $Sb^{3+,5+}$ doping

As for $Sb^{3+,5+}$ doping, the concentration of 135 at.ppm in the melt did not improve sizably the transmittance in the short wavelength region but 1350 at.ppm gave a clear improvement (see Fig.1). As seen in Fig. 2, the excitation-emission spectrum of PWO:Sb1350 is different from that of PWO:Sb135 and rather resembles those of trivalent-ion doped PWO as typically seen in the disappearance of the second emission peak in the red spectral region. These differences observed between PWO:Sb135 and PWO:Sb1350 indicate that the former resembles undoped PWO, while the latter resembles the typical trivalent-ion doped PWO. A similar indication was also obtained from the TSL data. The TSL glow curve of PWO:Sb135 after X-ray irradiation at room temperature, given in Fig. 5a, shows substantial suppression in the 50 °C peak in comparison with undoped PWO, but by a factor less than one order of magnitude. However the 50 °C peak was further suppressed by another order of magnitude in PWO:Sb1350 with a higher Sb concentration (see Fig. 5c). This strong suppression in PWO:Sb1350 is similar to that in the typical trivalent-ion doped PWO and could explain the similar improvement in the transmittance in the short wavelength region and the disappearance of the second emission peak in the red spectral region.

The Sb concentration in the crystal may be much smaller than in the melt due to large vapour pressure of Sb. From an ICP-AES analysis, we obtained an Sb concentration of 90 at.ppm in PWO:Sb1350. Scaling of this number to PWO:Sb135 gives only 9 at.ppm, which is below the detection limit (33 at.ppm of Sb ions) in the present measurement. Although the segregation coefficient (k) is as large as 0.2, a substantial part of Sb added in the melt was lost by evaporation before starting crystal growth. For example in our Czochralski growth of PWO:Sb in Prague, 500 at.ppm in the raw material was reduced to 198 at.ppm in the sintrate before crystallization, and 41 at.ppm remained in the first part (crystallization ratio g=0.16) of the crystal. The observation in SIC[18] is qualitatively similar to ours while the crystal growth is done there by the Bridgman method instead of the Czochralski one.

The present PWO:Sb135 showed degradation in radiation hardness as shown in Fig. 3-4, while the reason is not yet clear. The poor radiation hardness is qualitatively understandable since the Sb concentration in the crystal may be insufficient as discussed in the preceding paragraph. The radiation hardness of PWO:Sb1350, which was grown most recently, remains to be measured. Although significant suppression of the 50 °C TSL peak seen in PWO:Sb1350 suggests similar charge compensation to that in typical trivalent-ion doped PWO, there is a big difference in the 100-270 °C region between PWO:Sb1350 and trivalent-ion doped PWO: The broad TSL peaks observed in PWO:Sb1350 are absent in the trivalent-ion doped PWO[25]. These large TSL peaks in the temperature region above 100 °C may indicate a possibility of poor radiation hardness of PWO:Sb1350 (see [6] for the correlations). The light yield of PWO:Sb1350 was as large as that of the undoped and trivalent ion-doped samples (see Table 2).

4.4 Mn^{2+} doping

No sizable effect of Mn^{2+} doping was observed in any of the transmission spectrum, excitation-emission spectrum, light yield, decay time and radiation hardness when compared with undoped PWO (see Figs. 1-4 and Table 2). This may be due to too small Mn^{2+} concentration in the crystal (5.5 at.ppm, see Table 2), which should come from the small segregation coefficient (k=0.04).

4.5 Annealing in PbO vapour

The conjectured Pb^{2+} deficiency due to evaporation (see Introduction) could occur not only during crystal growth but also during annealing. To reduce the loss of Pb^{2+} during annealing, and even expecting a possible recovering of the Pb^{2+} deficiency by diffusion during annealing, an undoped PWO (PWO27) was annealed in PbO vapour. The same annealing condition (600 °C during 6 hours, see Section 2) was used as for the other samples. When PWO27 is compared with undoped PWO, no signifcant difference was observed in the transmission spectrum but a slight shift of the short-wavelength cutoff toward shorter wavelengths, excitation-emission spectrum (existence of the second peak in the red spectral region), decay time (3-components with the average τ_{av} = 8.2 ns), light yield (36 pe/MeV) and radiation hardness ($10^{5\text{-}6}$ rad). The obtained result indicates that the conjectured Pb^{2+} deficiency should naturally occur already before and during crystal growth, and it could not be recovered sizably during annealing in PbO vapour.

5. Summary and discussions

The obtained results can be summarized as follows:

(1) As for the tetravalent-ion doping, Th^{4+} doping gave a significant improvement in transmittance at short wavelengths, radiation hardness, etc. similar to the trivalent-ion (La^{3+}, Gd^{3+}, Y^{3+}, Lu^{3+}) doping. Zr^{4+} doping did not improve the transmittance in the short wavelength region but degraded the radiation hardness. The obtained result for Zr^{4+} doping suggests an overall resemblance of PWO:Zr^{4+} to undoped PWO. Zr^{4+} probably did not enter the crystal in a sizable amount, or entered mostly interstitial sites.

(2) Compared with the trivalent-ion doping, the $Ce^{3+,4+}$ doping caused less significant improvement in transmittance at short wavelengths, similar disappearance of the second emission peak in the red spectral region, improvement in radiation hardness to some extent, and reduction by half in light yield. Under the hypothesis of charge compensation as sketched in Introduction, the absence of big improvement in PWO:Ce may be related to probable oscillation of Ce ions between trivalent and tetravalent charge states, which may hinder formation of stable dipole complexes $[2(\mathrm{Ce_{Pb}}^{3+})^{\cdot}\cdot\mathrm{V_{Pb}}'']$, thereby failing in making the Pb^{2+} vacancy immobile.

(3) Large vapour pressure of Sb should lead to a significant loss of the dopant ions before the start of crystal growth, thus requiring a large concentration of dopant ions in the melt. $Sb^{3+,5+}$ doping by 1350 at.ppm (in the melt) gave an improvement in transmittance at short wavelengths similar to the typical trivalent-ion doping, suggesting the charge compensation by Sb doping. The significant suppression (by two orders of magnitude) of the 50 °C peak in the TSL curve

observed in this sample is similar to that seen in the typical trivalent-ion doped PWO and is consistent with the observed improvement in the transmittance. On the other hand, the TSL shows significant enhancement in the 100-300 °C region, which is completely different from the characteristic feature in the typical trivalent-ion doped PWO and may suggest degradation in radiation hardness [6]. Actually, we observed degradation in radiation hardness for Sb doping by 135 at.ppm in the melt, compared with undoped PWO, while measurement remains to be done for the increased Sb doping by 1350 at.ppm. If Sb doping causes degradation in radiation hardness, the reason is not yet clear, but may be related to the possible oscillation of Sb between two possible charge states (3+ and 5+) similar to the case of PWO:Ce (3+ and 4+).

(4) All the undoped PWO samples (PWO:Pb-rich, PWO27), PWO:Mn^{2+}, and PWO:Zr^{3+} got a tint of black after 10^8 rad irradiation. PWO:Sb135 got a tint of yellowish brown. Compared with the trivalent ion-doped PWO (PWO:La^{3+}, Lu^{3+}, Y^{3+}, Gd^{3+}) and PWO:Th^{4+}, the radiation damages of these four samples, as seen in μ_{ir} at 420 nm in Fig. 4, are not much larger at the dose level up to 10^6 rad, but much larger above 10^7 rad. However, even below 10^6 rad, PWO undoped or doped with Mn^{2+} or Zr^{4+} may not be good candidates for calorimeter materials, since the transmittance is poor in the 330-450 nm-region.

(5) No significant improvement was obtained by annealing the undoped PWO in PbO vapour. The obtained result indicates that the conjectured Pb^{2+} deficiency should naturally occur already before and during crystal growth, and it

could not be recovered during annealing in PbO vapour

Obtained results show that even the concentration of several tens at.ppm of not only trivalent ions (La^{3+}, Gd^{3+}, Y^{3+}, Lu^{3+}) but also tetravalent ion (Th^{4+}) in the crystal is enough to give significant improvement probably by charge compensation of the Pb^{2+} deficiency. The obtained new result for Th^{4+} doping is consistent with the hypothesis worked out by Nikl et al.[6], Han et al.[13], etc. on (1) the charge compensation of Pb^{2+} deficiency by trivalant (or tetravalent) ion doping and (2) the formation of stable dipole complexes which make the Pb^{2+} vacancy immobile. Compared with undoped PWO, $Ce^{3+,4+}$ or $Sb^{3+,5+}$ doping gives some improvement (in transmittance at short wavelength region and disappearance of the second emission peak in the red spectral region for Ce, Sb) and some degradation (in radiation hardness for Sb). This complicated result is different from the case of the other ions having a stable single charge state, and may be due to the oscillation of the ions between the two charge states. For further improvement of PWO scintillators, it should be worth studying in which part of the crystal growth and to which extent the Pb^{2+} deficiency is introduced. It should be also very important to make clearer the nature of the defects and colour centres induced by such a deficiency and their role in the processes of energy transfer and storage in PWO structure.

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References

1. M. Kobayashi et al., Nucl. Instr. Meth. A399(1997)261;
ibid. A404(1998) 149.
2. S. Baccaro et al., Phys. Stat. Sol. (a)160(1997)R5.
3. K. Hara et al., Nucl. Instr. Meth. A414(1998)325.
4. Proc. International Workshop on Tungstate Crystals, Rome, October 1998.
5. M. Kobayashi et al., Nucl. Instr. Meth. A434(1999)412;
"Radiation damage in doped PbWO$_4$ scintillating crystals", p.161 of [4].
6. M. Nikl et al., J. Appl. Phys. 82(1997)5758.
7. S. Baccaro et al., Phys. Stat. Sol. (a)164(1997)R9;
"Radiation hardness characteristics of PbWO$_4$ single crystals", Proc. International Conference on Inorganic Scintillators and Their Applications (SCINT97), Shanghai, September 1997, p.203.
8. M. Batenchuk et al., "On the principal possibility of improvement of PbWO$_4$ characteristics for scintillation applications", p. 49 of [4].
9. E. Auffray et al., Nucl. Instr. Meth. A402(1998)75.
10. M. Nikl et al., Nucl. Phys. B(Proc. Suppl.)78(1999)471.
M. Nikl, Phys. Stat. Sol. (a)178(2000)595.
11. P. Bohacek et al., "Stoichiometry and radiation damage of PWO crystals from melts of different composition", p.55 of [4].
12 K. Tanji et al., J. Cryst. Growth 204(1999)505.
13. B. Han, X. Feng, G. Hu, P.Wang, Zh.Yin, J. Appl. Phys. 84(1998) 2831.

14. V.V. Laguta et al., J. Phys. Cond. Mat. 10(1998)7293.

15. D.S. Yan: "Some important issues on quantity production and quality improvement and assurance of PWO crystals", p.7 of [4].

16 M. Kobayashi and M. Ishii, Nucl. Instr. Meth. B82(1993)85.

17. Y. Chen, C. Shi and G. Hu, J. Appl. Phys. 87(2000)1503.

18. Xi. Liu et al., Chin. Phys. Lett. 16(1999)761.

19. F. Nessi-Tedaldi et al., "Measurement of $PbWO_4$ crystals behaviour under irradiation", p.209 of [4].

20. Y. Usuki et al., "Development of PWO", Proc. Workshop on Scintillating Crystals, Tsukuba, April 1997, KEK Proceedings 97-9, p.207.

21. M. Kobayashi et al., "Radiation hardness of doped $PbWO_4$", to appear in Proc. Internationall Conference on Inorganic Scintillators and Their Applications (SCINT99), Moscow, August 1999.

22. M. Kobayashi et al., Nucl. Instr. Meth. A373(1996)333.

23. R.Y. Zhu, IEEE Nucl. Sci. NS-44(1997)468.

24. M. Martini et al., Phys. Rev. B60(1999)4653.

25. S. Baccaro et al., Radiation Effects and Defects in Solids 150(1999)15.

26. M. Nikl et al., Appl. Phys. Lett. 71(1997)3755.

27. M. Nikl et al., J. Appl. Phys. 87(2000)4243.

Figure Captions

Fig. 1 Comparison of the transmission spectra before irradiation for PWO:Pb-rich, PWO:Ce, Th, Zr, Gd80, Mn, Sb135, Sb1350, and PWO27 (annealed in PbO). The thickness across which the transmittance was measured is about 20 mm except for PWO:Sb1350 (10 mm), and PWO:Zr(40 mm); see Table 1.

Fig. 2 Excitation and emission spectra from the crystal surface for UV excitation in typical samples of PWO:Gd^{3+}, PWO:Th^{4+}, PWO:Zr^{4+}, PWO:$Ce^{3+,4+}$, PWO:Sb135, PWO:Sb1350, PWO:Pb-rich, PWO:Mn^{2+} and PWO27 (annealed in PbO). The contour of the emission intensity is plotted in the $(\lambda_{ex}, \lambda_{em})$ plane. The numbers attached to the contours give rough relative intensity.

Fig. 3 Spectra of the radiation-induced absorption coefficient μ_{ir} versus wavelength obtained at different accumulated doses: a) PWO:Gd^{3+}, b) PWO:Th^{3+}, c) PWO:Zr^{3+}, d) PWO:$Ce^{3+,4+}$, e) PWO:Sb135, f) PWO:Mn^{2+}, g) PWO27 (undoped, annealed in PbO vapour), and h) undoped PWO.

Fig. 4 Radiation-induced absorption coefficient μ_{ir} at 420 nm (the emission peak wavelength) versus accumulated dose is compared among different samples; (a) mainly for significantly radiation-resistant PWO, and (b) mainly for less radiation-resistant PWO. In (b) two typical significantly radiation-resistant PWO samples (PWO:La^{3+}, PWO:Nb^{5+}) are also shown for comparison. The recovery in 2.3d, 9.3d, 24.3d and 205d (or 3.3d, 10.5d, and 121d for some samples) after 10^8 rad irradiation is also given. The results of measurement carried out in Italy below 3x10^4 rad are also shown in (a) for PWO doped with Lu^{3+}, Y^{3+}, Gd^{3+}, and Nb^{5+} [5].

Fig. 5 (a) TSL glow curves of PWO(undoped), PWO:Ce and PWO:Sb135 after X-ray irradiation at room temperature; (b) TSL glow curves of PWO:Ce after X-ray irradiation at 10 and 60 °K; (c) Comparison of TSL glow curves after X-ray irradiation at the room temperature between PWO:Sb135 and PWO:Sb1350.

Table 1 List of doped PWO samples studied. The new samples tested in the present study after our previous paper [5] are marked #. The thickness across which the transmittance was measured is underlined. Dopant concentration in crystal was measured by ICP-AES (see text), unless otherwise indicated.

Sample	Dopant (at.ppm) (in melt/in crystal)	Size (mm)	Notes	
PWO:La,#4	La^{3+}(135/202)	10x10x20	k=2.5, note(b),	[5]
PWO:Lu	Lu^{3+}(135/43)	10x10x45.2	k=0.31	[5]
PWO:Gd135	Gd^{3+}(135/208)	10x10x25.5	k=1.55	[5]
# PWO:Gd80	Gd^{3+}(80/ 123(a))	10x10x20		
# PWO:Gd60	Gd^{3+}(60/ 92(a))	10x10x40		
PWO:Y	Y^{3+}(135/108)	10x10x20.5	k=0.8	[5]
PWO:Sc	Sc^{2+}(135/7)	10x10x20.2	k=0.06	[5]
# PWO:Ce	$Ce^{3+,4+}$(135/29)	10x10x20	k=0.21	
# PWO:Sb135	$Sb^{3+,5+}$(135/<33)	10x10x20	k=0.2	
# PWO:Sb1350	$Sb^{3+,5+}$(135/90)	10x10x20		
# PWO:Zr	Zr^{4+}(135/<13)	10x10x40	k<0.1	
# PWO:Th	Th^{4+}(135/35)	10x10x20	k=0.26	
PWO:Pb-rich	Pb^{2+}(135)	10x10x20	~undoped PWO.	[5]
PWO:Cd	Cd^{2+}(135/41)	10x10x20.3	k=0.3	[5]
# PWO:Mn	Mn^{2+}(135/5.5)	10x10x20	k=0.04	
# PWO27	undoped	10x10x20	annealed in PbO (see text)	
PWO:Nb	Nb^{5+}(1350/670)	10x10x21		[5]

(a) Calculated from the segregation coefficient.

(b) From the same ingot as La2[2].

Table 2 Obtained result. The the new samples tested in the present study are marked #. λ_{ex} (or λ_{em}) denotes the excitation (emission) peak wavelength, and LY the scintillation light intensity for ^{60}Co γ-rays (see text). The i-th decay constant and its intensity (in percentage of the total intensity) are denoted as τ_i and I_i, respectively. $<\tau>_{av}$ gives the weighted sum of $\tau_i I_i$. The last column gives the existence of detectable phosphorescence peaks (seen at around 600 nm).

Sample	$\lambda_{ex}/\lambda_{em}$	LY	Decay constants (ns)				Phosph.
	(nm)	p.e./MeV	$\tau_1(I_1)$	$\tau_2(I_2)$	$\tau_3(I_3)$	$<\tau>_{av}$	
PWO:La,#4	308/410	31[5]	2.5(79%)	14(21%)		4.9	no
PWO:Lu	315/422	37[5]	4.1(75%)	9.7(25%)		5.5	no
PWO:Gd135	315/418	33[5]	3.3(81%)	22(19%)		6.9	no
# PWO:Gd80	315/415	39	1.3(49%)	6.5(51%)		3.9	no
# PWO:Gd60	315/415	39	5.6(100%)			5.6	no
PWO:Y	315/418	40[5]	3.3(75%)	11(25%)		5.2	no
PWO:Sc	312/410	37[5]	1.4(54%)	5.5(24%)	20(22%)	6.5	yes
# PWO:Ce	310/420	15	2.0(68%)	6.6(32%)		3.5	no
# PWO:Sb135	310/420	41	2.9(59%)	8.5(23%)	22(18%)	7.6	yes
# PWO:Sb1350	310/420	29	1.5(94%)	9.0(6%)		2.1	no
# PWO:Zr	315/420	36	2.9(52%)	12(48%)		7.1	no
# PWO:Th	315/415	40	3.1(41%)	8.2(59%)		6.1	no
PWO:Pb-rich	315/418	37[5]	1.5(61%)	8.9(26%)	29(13%)	7.0	yes
PWO:Cd	315/418	41[5]	1.6(60%)	8.2(26%)	26(14%)	6.7	yes
# PWO:Mn	312/415	26	1.7(51%)	9.6(38%)	46(11%)	9.5	yes
# PWO27	315/420	36	2.5(42%)	7.6(32%)	18(26%)	8.2	yes
PWO:Nb	318/422	26[5]	2.1(80%)	8.3(14%)	42(6%)	5.4	no

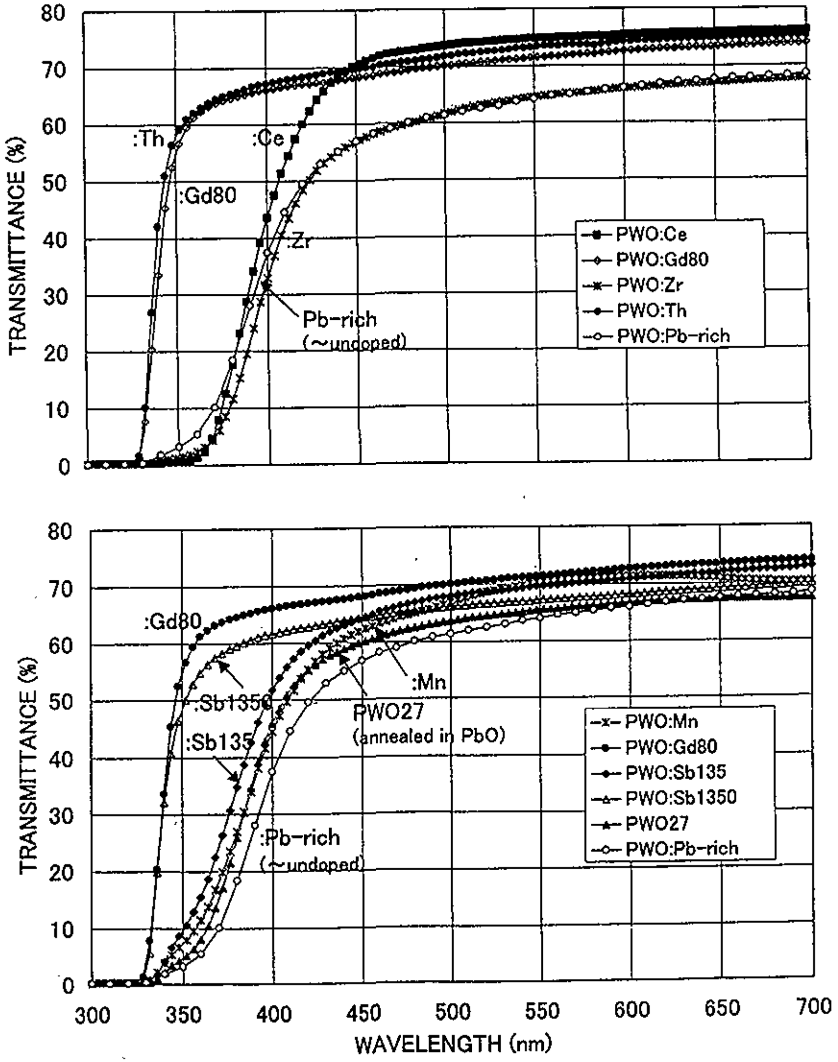

Fig. 1

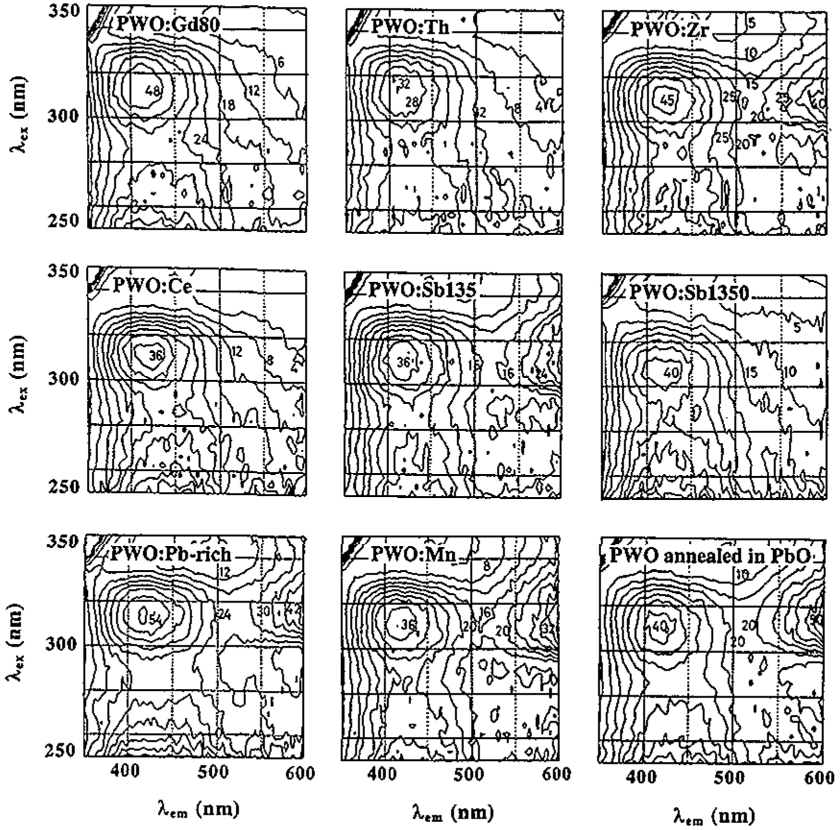
PWO:Gd80
PWO:Th
PWO:Zr
PWO:Ce
PWO:Sb135
PWO:Sb1350
PWO:Pb-rich
PWO:Mn
PWO annealed in PbO
350
300
250
λ_{ex} (nm)
400
500
600
λ_{em} (nm)

Fig. 2

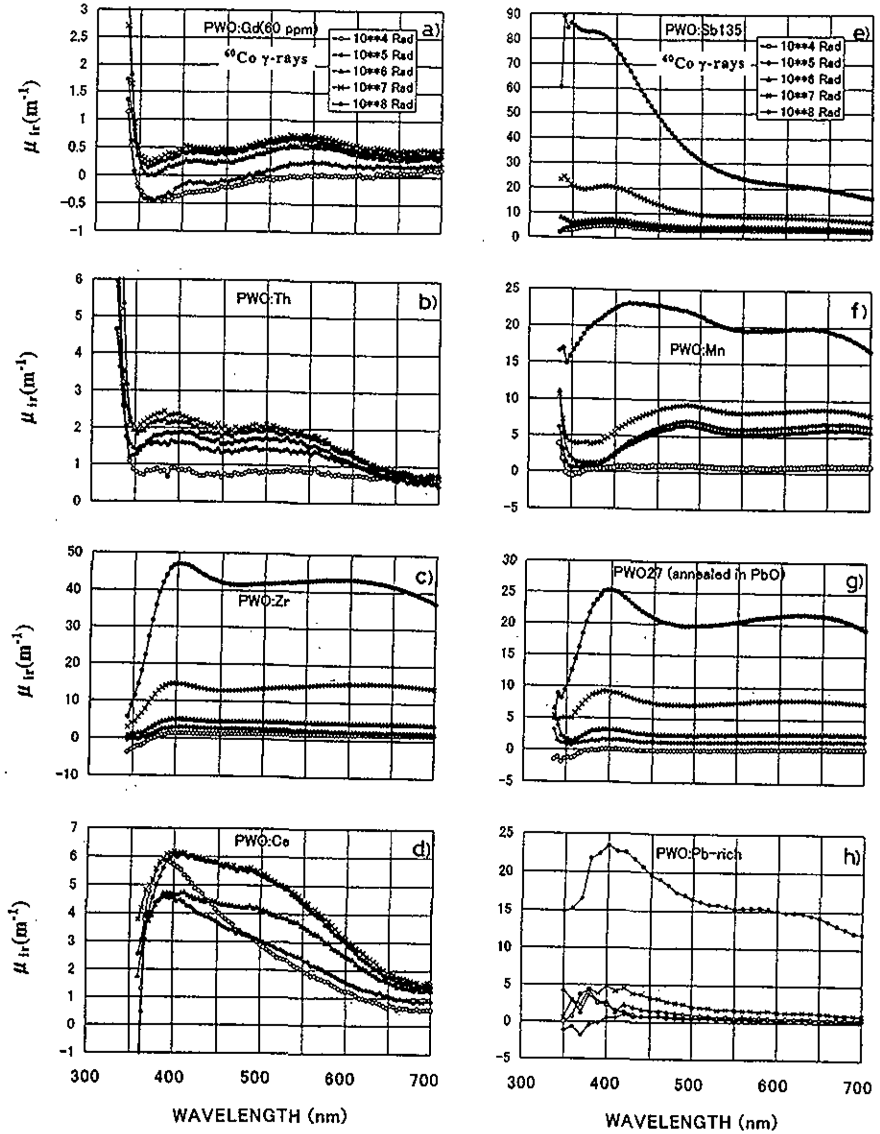
PWO:Gd(60 ppm)
^{60}Co γ-rays
10**4 Rad
10**5 Rad
10**6 Rad
10**7 Rad
10**8 Rad
a)
PWO:Th
b)
PWO:Zr
c)
PWO:Ce
d)
PWO:Sb135
e)
PWO:Mn
f)
PWO27 (annealed in PbO)
g)
PWO:Pb-rich
h)
μ_{ir}(m^{-1})
300
400
500
600
700
WAVELENGTH (nm)

Fig. 3

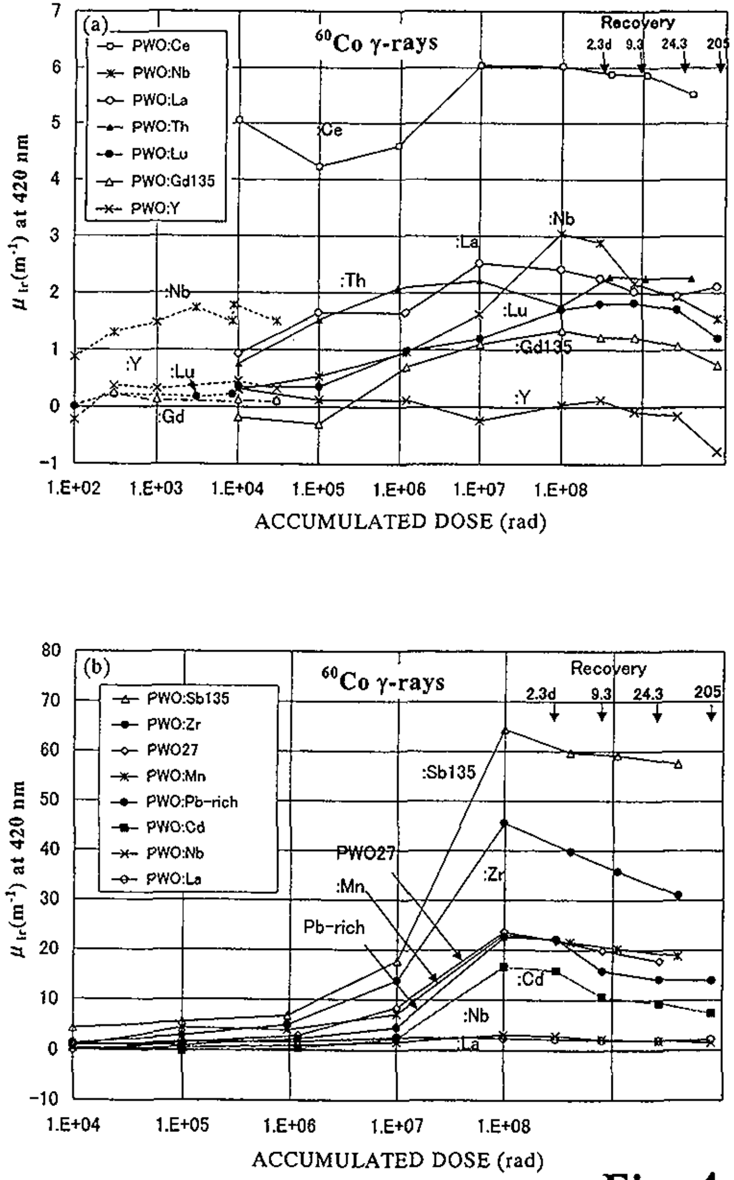
(a)
PWO:Ce
PWO:Nb
PWO:La
PWO:Th
PWO:Lu
PWO:Gd135
PWO:Y
⁶⁰Co γ-rays
Recovery
2.3d
9.3
24.3
205
:Ce
:La
:Nb
:Th
:Lu
:Gd135
:Y
:Gd
μ tr(m⁻¹) at 420 nm
ACCUMULATED DOSE (rad)
1.E+02
1.E+03
1.E+04
1.E+05
1.E+06
1.E+07
1.E+08
(b)
PWO:Sb135
PWO:Zr
PWO27
PWO:Mn
PWO:Pb-rich
PWO:Cd
PWO:Nb
PWO:La
⁶⁰Co γ-rays
Recovery
2.3d
9.3
24.3
205
:Sb135
PWO27
:Mn
:Zr
Pb-rich
:Cd
:Nb
:La
μ tr(m⁻¹) at 420 nm
ACCUMULATED DOSE (rad)
1.E+04
1.E+05
1.E+06
1.E+07
1.E+08

Fig. 4

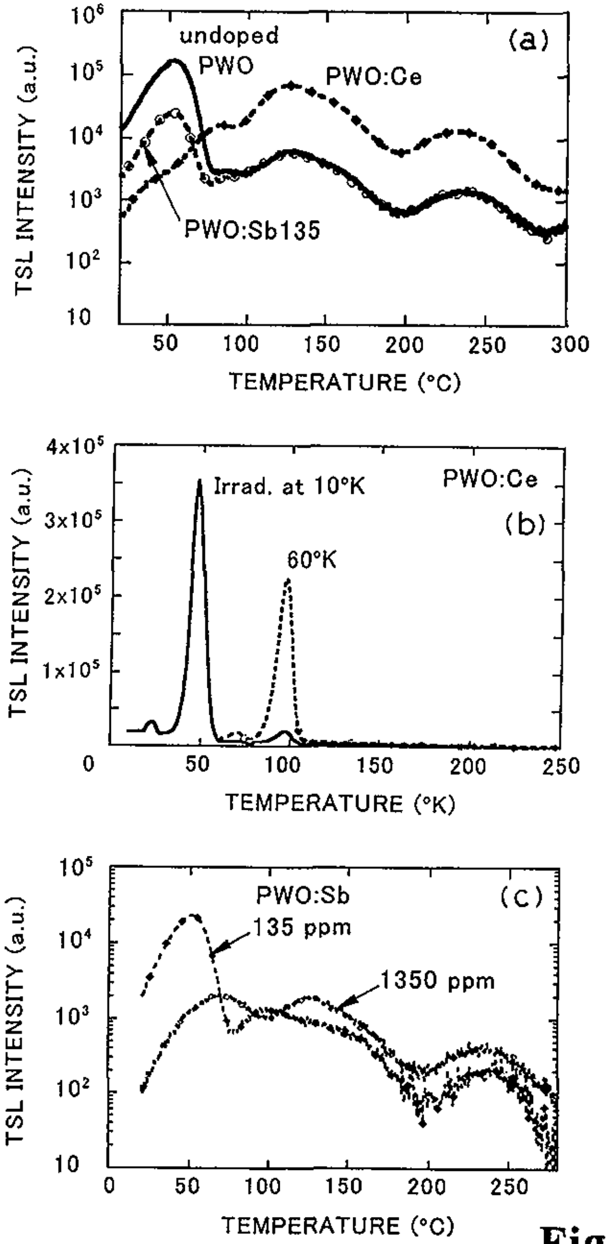
(a)
undoped PWO
PWO:Ce
PWO:Sb135
TSL INTENSITY (a.u.)
TEMPERATURE (°C)
(b)
PWO:Ce
Irrad. at 10°K
60°K
TSL INTENSITY (a.u.)
TEMPERATURE (°K)
(c)
PWO:Sb
135 ppm
1350 ppm
TSL INTENSITY (a.u.)
TEMPERATURE (°C)

Fig. 5