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Luminescence decay of PbWO_4 crystals under different excitation conditions

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Abstract

This paper reports the decay kinetics of the intrinsic blue luminescence from self-trapped excitons in lead tungstate excited by a Nd:YAG laser. The kinetics exhibits some complicated features, depending strongly on the experimental conditions, such as laser power, sample temperature, and one- or two-photon excitation. The result indicates that the self-trapped excitons interact with each other under high-density excitation, thereby shortening the decay time of the blue luminescence. Furthermore, a noticeable rise component is observed under two-photon excitation in the temperature range of 50–150 K. The contribution of radiation-induced defect centres in the process of energy transfer from Pb sites to WO_4 sites is discussed.

1. Introduction

Recent requirements for high-speed performance of scintillation detectors regard the luminescence decay time of a scintillating material as a crucial parameter in many applications. Lead tungstate, PbWO_4 (PWO), is a promising candidate for use in fast scintillation detectors because its decay time is in the nanosecond domain at room temperature. In fact, PWO has been approved as an electromagnetic calorimeter in high-energy physics [1–3]. It is also promising as a medical imaging sensor used in PET (positron emission computed tomography) [4]. The luminescence spectrum of PWO consists of two main bands [5]: the ‘blue’ one peaking around 2.8 eV and the ‘green’ one peaking between 2.3 and 2.5 eV. The blue luminescence is an intrinsic feature of PWO, and is generally ascribed to the radiative decay of a self-trapped exciton (STE) that locates on the regular WO_4 group. The green luminescence is of extrinsic origin; its cause is still under consideration [5, 6]. Impurity-doping effects have been extensively studied with a view to improving scintillation characteristics of PWO over the past decade or so [7].

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Luminescence decay of PWO has been investigated by many researchers [1–3, 8–17]. The decay kinetics of the blue luminescence was observed under x-ray or γ -ray excitation at room temperature by Belsky *et al* [8], who found that the decay curve can be fitted by a sum of three exponentials, with lifetimes $\tau = 3.6, 12,$ and 155 ns. They further revealed that the green luminescence has a slow decay time of more than $1 \mu\text{s}$. Similar results were also reported by Lecoq *et al* [1] and Nikl *et al* [9]. At low temperatures, however, there are some discrepancies among the results observed by different groups. Nikl *et al* [9] found by using an excimer laser that the blue luminescence exhibits a single-exponential decay with $\tau = 5.6 \mu\text{s}$ at 4.2 K. A similar single exponent with $\tau = 3.5 \mu\text{s}$ was reported by Tamulaitis *et al* [11] under the one-photon excitation with the fourth-harmonic light of a Nd:YAG laser at 77 K. Millers *et al* [16] studied the decay kinetics of PWO excited with a pulsed electron beam in the temperature range $T = 100$ – 300 K. Their decay curve at 100 K was not described by a single exponent; i.e., there appeared a fast ($\tau < 4 \mu\text{s}$) component in the early stage. Furthermore, they observed a rise component of the blue luminescence, with a rise time $\tau_r = 100$ ns. The present authors [17] found that the blue luminescence consists of three decay components ($\tau = 0.2, 1.5,$ and $5.6 \mu\text{s}$) even at 8 K, when PWO is excited by the fourth harmonics from a Q -switched Nd:YAG laser.

In the present study, the luminescence decay of PWO has been investigated with the use of a Q -switched Nd:YAG laser as an exciting source under different experimental conditions, in order to clarify the origin of the discrepancies mentioned above. The result indicates that the interaction between STEs plays an important role under high-density excitation, which shortens the decay time of the blue luminescence at low temperatures. Furthermore, a noticeable rise component is observed in the range $T = 50$ – 150 K. On the basis of this result, the contribution of radiation-induced defect centres in the process of energy transfer from Pb sites to WO_4 sites is discussed in connection with the existing model of energy transfer [5].

2. Experimental details

Two single crystals of PWO with different origins were prepared for the present experiment; one came from Dr Alov of the Institute of Solid State Physics of the Russian Academy of Science, Russia, and the other from Dr Usuki of the Materials Research Laboratory of Furukawa Company, Japan. Both were grown by the Czochralski technique from starting raw materials PbO and WO_3 with 99.99% purity. The former crystal was the same one as was used in the previous experiment [17]. The specimen, having a freshly cleaved surface, was mounted on the copper holder in a closed-cycle cryogenic refrigerator (Iwatani; CryoMini M310). The sample temperature was detected using a calibrated Au:Fe-versus-chromel thermocouple, and controlled within 1 K by an Iwatani TCU-4 controller.

The excitation source was a Q -switched Nd:YAG laser (Continuum; Minilite II), with a pulse duration of 5 ns and a repetition rate of 10 Hz. The fourth harmonics (4.66 eV) of the Nd:YAG laser correspond well to the onset of the band-to-band transition of PWO [13, 18, 19], thus resulting in one-photon excitation. The second harmonics (2.33 eV) fall into the transparent region, resulting in two-photon excitation. The laser light was focused by a fused-silica lens ($f = 100$ mm) on the sample surface. The power density was varied by using a suitable combination of filters.

Luminescence from the sample was analysed through a Nikon G250 monochromator, and detected by a photomultiplier tube (Hamamatsu Photonics; R106UH). The decay curves were recorded on a Tektronix 2440 digital storage oscilloscope operated in an averaging mode, and then fed into a computer in order to improve the signal-to-noise ratio by successive accumulation of the data.

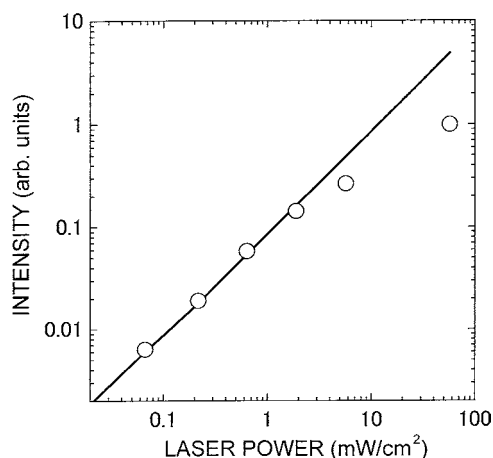


Figure 1. A log–log plot of the luminescence intensity against the laser power under one-photon excitation with 4.66 eV light at 8 K. The solid line represents a linear function of the excitation power, drawn to guide the eye.

3. Results

The luminescence spectra observed here were composed of a single band peaking at 2.80 eV for both samples (Alov and Usuki), irrespective of whether the crystals were one- or two-photon excited at $T = 8\text{--}300$ K. As mentioned in section 1, this blue luminescence arises from an STE localized on the WO_4^{2-} complex anion [5]. The absence of the green luminescence may suggest that the qualities of the present crystals are very good. No marked difference in decay kinetics of the blue luminescence was found between the two samples. We therefore describe the results obtained for Usuki's samples in this paper, unless stated otherwise.

In figure 1, the logarithm of the blue luminescence intensity is plotted against the logarithm of the power density under one-photon excitation with 4.66 eV light at 8 K. The laser power was varied from $60 \mu\text{W cm}^{-2}$ to 60 mW cm^{-2} on the sample surface. The solid line represents a linear function of excitation power. It appears that the luminescence intensity is proportional to the laser power, but shows a saturating tendency under high-density excitation.

Figure 2 shows the decay kinetics of the blue luminescence measured at various temperatures. The crystal was one-photon excited by a 4.66 eV light pulse with a power density of 60 mW cm^{-2} , at which the luminescence intensity is substantially saturated. One may see that all the decay curves are nonexponential, and are fitted by a sum of three components. For instance, the decay curve at 8 K consists of a fast component $\tau_f = 0.3 \pm 0.1 \mu\text{s}$, a medium component $\tau_m = 2.0 \pm 0.2 \mu\text{s}$, and a slow component $\tau_s = 5.6 \pm 0.2 \mu\text{s}$. The time-integrated intensities of the fast, medium, and slow components are in the ratio 1:11:32. At 300 K, the pulse shape of the fast component becomes almost identical to that of the exciting laser light. Using a deconvolution procedure, we get $\tau_f = 2 \pm 0.5 \text{ ns}$, $\tau_m = 11 \pm 2 \text{ ns}$, and $\tau_s = 110 \pm 30 \text{ ns}$. In this case, the time-integrated intensities of the fast, medium, and slow components are in the ratio 1:1:0.3. The result at 300 K is fairly consistent with that obtained previously by other groups [1, 8, 9] and also recently by us with the use of a femtosecond laser [20].

For reference, the decay kinetics of the blue luminescence in Alov's sample measured at 8 K under the same excitation conditions as in figure 2 is presented in figure 3. The decay curve can also be expressed as a sum of three components: $\tau_f = 0.2 \pm 0.1 \mu\text{s}$, $\tau_m = 2.0 \pm 0.2 \mu\text{s}$, and $\tau_s = 5.6 \pm 0.2 \mu\text{s}$. These values agree well with those for Usuki's

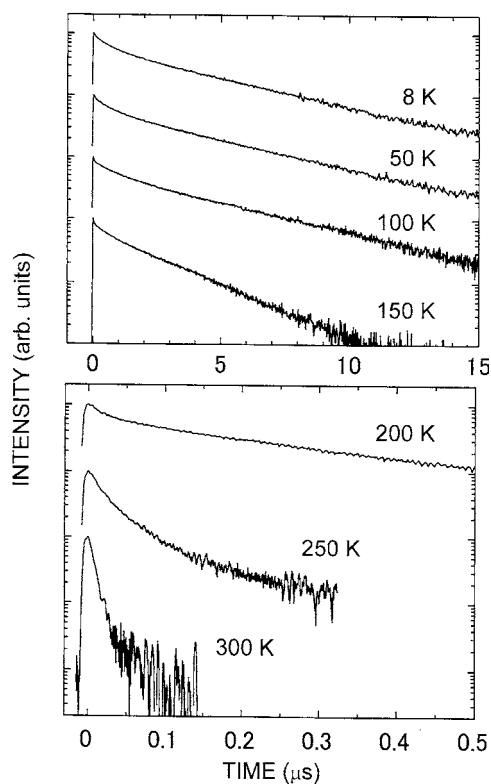


Figure 2. The decay kinetics of the blue luminescence measured at various temperatures. The crystal was one-photon excited by a 4.66 eV light pulse with a power density of 60 mW cm^{-2} , at which the luminescence intensity is substantially saturated.

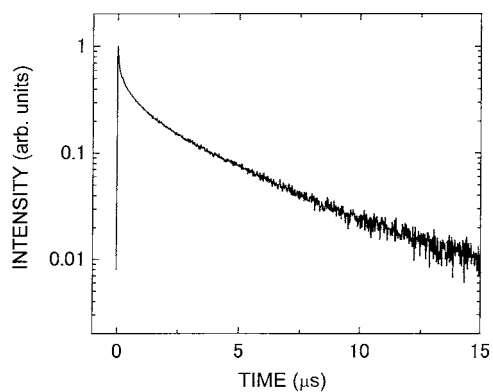


Figure 3. The decay kinetics of the blue luminescence in Alov's sample measured at 8 K under the same excitation conditions as in figure 2.

sample. One difference between the two samples is that the fast and medium components in figure 3 are more remarkable than those in figure 2; i.e., the time-integrated intensities of the fast, medium, and slow components of Alov's sample are in the ratio 1:5:9. This ratio (as well as the three decay times) is in good agreement with the results in our previous work [17].

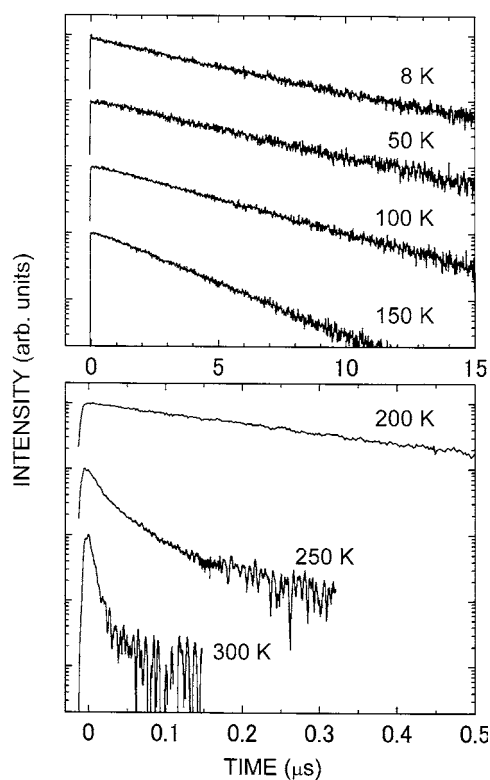


Figure 4. The decay kinetics of the blue luminescence measured at various temperatures. The crystal was one-photon excited by 4.66 eV light with a power density of 0.6 mW cm^{-2} , at which the luminescence intensity shows a linear power dependence.

Figure 4 shows the decay kinetics of the blue luminescence measured at various temperatures under one-photon excitation with a power density of 0.6 mW cm^{-2} . This laser power is relatively weak, and falls into the region where the luminescence intensity shows a linear power dependence, as seen in figure 1. The decay can be well described by a single exponent at 8 K. We get $\tau = 5.4 \pm 0.2 \mu\text{s}$, in good agreement with the result obtained by Nikl *et al* [9]. It should be noted that this value also coincides with the slow decay time ($\tau_s = 5.6 \mu\text{s}$) observed under high-density excitation. One may recognize a weak rise component just after the pulse excitation in the temperature range $T = 50\text{--}150 \text{ K}$. The decay curve becomes nonexponential above 150 K. The luminescence decay at 300 K consists of three components, with the same decay times as at 300 K in figure 2.

In figure 5, the logarithm of the blue luminescence intensity is plotted against the logarithm of the power density under two-photon excitation with 2.33 eV light at 8 K. The laser power was varied from 10 to 90 mW cm^{-2} . The solid line represents a quadratic function of the excitation power. The luminescence intensity is proportional to the square of the power density. The result ensures that the luminescence is indeed induced by two-photon absorption.

Figure 6 displays the decay kinetics of the blue luminescence measured at various temperatures under two-photon excitation by a 2.33 eV light pulse with a power density of 30 mW cm^{-2} . At 8 K, the transient response shows a single-exponential decay, with $\tau = 6.5 \pm 0.2 \mu\text{s}$. Interestingly, the rise component ($\tau_r \approx 0.3 \mu\text{s}$) is more clearly observed in the range $T = 50\text{--}150 \text{ K}$, as compared to the case of one-photon excitation (figure 4). This

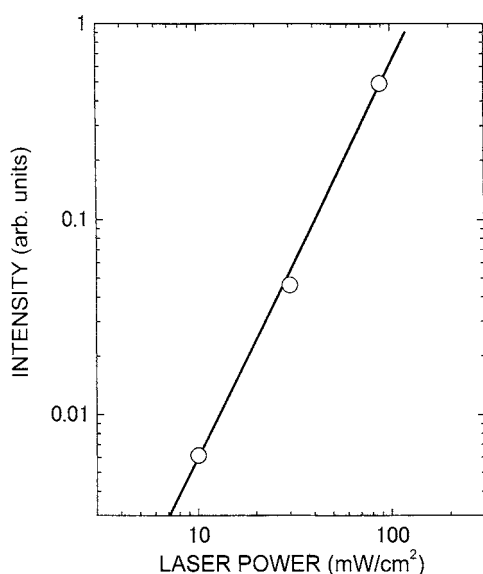


Figure 5. A log–log plot of the luminescence intensity against the laser power under two-photon excitation with 2.33 eV light at 8 K. The solid line represents a quadratic function of excitation power, drawn to guide the eye.

rise front becomes most remarkable around 100 K, and disappears above 200 K. The decay curve at 300 K is described by a sum of two or three exponents.

4. Discussion

A recent study of the reflectivity spectra [18] clearly revealed that the lowest exciton band of PWO is mainly characterized by ‘cationic’ $6s^2 \rightarrow 6s6p$ transitions in Pb^{2+} ions. It is therefore believed that the excitons or electron–hole pairs generated optically on Pb^{2+} ions move to the regular WO_4 groups, at which the STEs are formed and emit blue luminescence, as proposed in previous works [5].

We shall first discuss why the decay kinetics of the blue luminescence changes with the excitation power at low temperatures. When the crystal is one-photon excited with a power density of 0.6 mW cm^{-2} , the decay is well described by a single exponent with $\tau = 5.4 \mu\text{s}$ (figure 4). On increasing the power density up to 60 mW cm^{-2} , however, the transient response of the blue luminescence becomes dramatically nonexponential; i.e., it is evident that the faster decay components grow in the early stage, as seen in figures 2 and 3. Such a sharpening of the decay profile suggests two possible explanations. One is the stimulation of the blue luminescence under high-density excitation; the stimulation, or light amplification, is a well-known phenomenon in lasing action [21]—this explanation predicts that the luminescence intensity is enhanced by high-density excitation, which is in contrast to the result of figure 1, however. The other is the appearance of a nonradiative decay process that is faster than the lifetime ($5.4 \mu\text{s}$) of the STE—this explanation is supported by the fact that the luminescence intensity shows a tendency to saturation at dense excitation. The most probable channel of nonradiative decay of STEs is the Auger process due to the interaction between them. In the Auger process, one STE recombines nonradiatively, and transfers its energy to another STE, which is consequently decomposed into a free electron and hole.

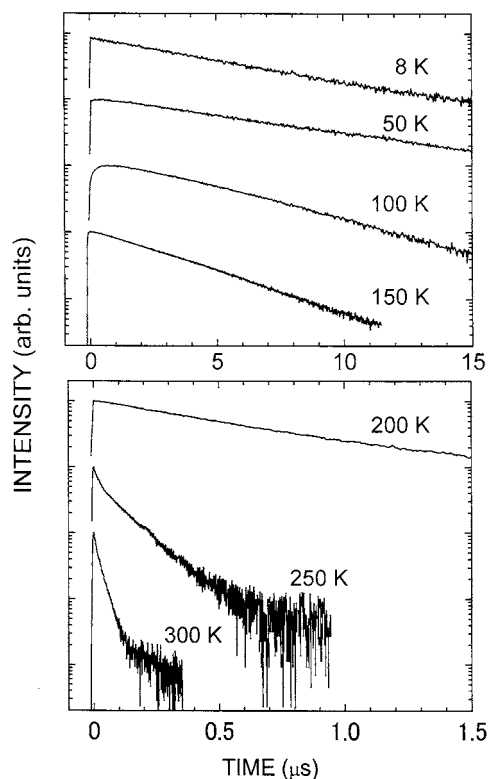


Figure 6. The decay kinetics of the blue luminescence measured at various temperatures under two-photon excitation by a 2.33 eV light pulse with a power density of 30 mW cm^{-2} , at which the luminescence intensity shows a quadratic power dependence.

Allowing for the effective depth of penetration of the 4.66 eV light being $7 \times 10^{-6} \text{ cm}$ [18], the excitation density being 60 mW cm^{-2} , and the repetition rate being 10 Hz, the number of free excitons (FEs) generated by a laser pulse is roughly estimated to be $1.2 \times 10^{21} \text{ cm}^{-3}$. This is about 1/10 of the number of PWO molecules per unit volume. Therefore, there are many chances that the STEs are adjacent to each other. Additional support for the STE–STE interaction has been obtained from the study of the luminescence decay kinetics in CeF₃ [22].

The STE–STE interaction is favourable at low temperatures, and results in Auger decay. At high temperatures, the STE–STE interaction becomes unimportant due to nonradiative quenching processes. The STE–STE interaction is characterized by the interaction time of about 300 ns which corresponds to τ_f at low temperatures. The interaction time is not so dependent on temperature, while the lifetime of the STE becomes shorter with increasing temperature, and is a few nanoseconds at 300 K. It is thus thought that the decay kinetics at 300 K depend little on the excitation density, because of the absence of STE–STE interaction. This is confirmed from a comparison of the results in figures 2 and 4.

Beside the STE–STE interaction, there may be another nonradiative decay channel of STEs. A FE approaches neighbouring sites of an STE. Auger decay becomes possible in such a case, too: the annihilation of a FE and the ionization of the neighbouring STE. This process will also lead to nonexponential decay, as well as a saturation tendency, of the blue luminescence.

Let us now discuss the appearance of the rise component in figure 6. There are two points to be considered. Such a rise front appears (i) at around 100 K and (ii) under two-photon excitation. As regards (ii), we should say more exactly that the observed rise front is more remarkable under two-photon excitation than one-photon excitation. The rise front of the blue luminescence has also been observed by Millers *et al* [16] under electron beam irradiation. They obtained $\tau_r = 100$ ns at 100 K, which is a little smaller than our value (0.3 μ s).

When the excitons or electron–hole pairs are produced, some of them travel to trap centres, then jump back to the conduction or valence band, and finally recombine at the WO_4 site through radiative transition. It is likely that such a trapping process causes a delayed rise of the blue luminescence. It is well known [23] that PWO tends to be naturally ‘lead deficient’, because of the increased evaporation of PbO from the melt during the crystal growth in air. The Pb^{3+} and/or O^- centres may be created as a result of the charge compensation for Pb^{2+} vacancies, although their existence has not been confirmed by the recent EPR experiment [24]. According to [25], the Pb^{3+} and/or O^- centres could act as trap defects for the energy transfer from Pb sites to WO_4 sites.

The above model, however, cannot explain the present result that the rise component is not observed at 8 K, in spite of the suggestion that Pb^{3+} and/or O^- centres exist. It should be, therefore, supposed that the pre-existing centres do not play a significant role in the processes of energy transfer and storage. We propose that different centres, which are efficient as ‘trap defects’, are produced by the irradiation above 50 K, although their details are not clear at present. The production of radiation-induced defects causes the rise front of the blue luminescence. When the sample is warmed, an electron or a hole is quickly released from the radiation-induced defect centre through a thermal activation process, which leads to the disappearance of the rise front at 300 K in figure 6. In this connection, it is interesting to note the recent experimental result observed by using a femtosecond laser [20]; i.e., the blue luminescence has a rise component with $\tau_r = 60 \pm 30$ ps even at room temperature. In other words, the trapping process is still preventing the transfer of the excitation energy at room temperature in the picosecond domain.

When PWO is two-photon excited with a 2.33 eV light pulse, an electron and/or a hole composing an STE localized on the regular WO_4 group has a chance to be re-excited into the conduction and/or valence band by another 2.33 eV photon. This is a kind of two-step cascade process. The re-excited carriers are again trapped by the defect centres. Such a cascade process will be repeated within the pulse duration, and result in an enhancement of the rise component under two-photon excitation. This explanation is somewhat speculative, because the rise time (300 ns) is much longer than the excitation pulse width (5 ns). The observed difference in rise component between one- and two-photon excitation may be related to the difference between the sample volumes excited. The mean migration length of free carriers before their radiative recombination is probably longer under two-photon excitation than under one-photon excitation. This is another possible explanation for the present result.

5. Summary

The luminescence decay of PWO was investigated by using a Q -switched Nd:YAG laser at $T = 8$ –300 K. The decay kinetics of the intrinsic blue luminescence exhibited some complicated features, depending strongly on the experimental conditions. It was pointed out that the STE–STE (or FE–STE) interaction plays an important role in the decay kinetics under high-density excitation at low temperatures. We proposed that radiation-induced defects are produced above 50 K, and contribute to the process of energy transfer by free carriers. The nature of the radiation-induced defects still remains to be established. From the present results,

it is naturally understood that the previous decay data are mutually consistent, irrespective of the excitation method, as long as the experiments were performed at room temperature [1, 8, 9, 20].

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