

Optical properties of scheelite and raspite PbWO_4 crystals

Minoru Itoh

Department of Electrical and Electronic Engineering, Faculty of Engineering, Shinshu University, Nagano 380-8553, Japan

Masami Fujita

Japan Coast Guard Academy, Wakaba, Kure 737-8512, Japan

(Received 15 June 2000)

Reflection spectra of lead tungstate (PbWO_4) crystals with scheelite and raspite structures have been measured at 6 K in the spectral range from 3 to 25 eV. The optical constants of both phases have been derived through the Kramers-Kronig analysis. The absorption spectra thus obtained exhibit a strong doublet exciton structure at around 4.30 eV for the scheelite phase and a weak exciton band at 3.75 eV for the raspite phase. The scheelite sample gives rise to a luminescence band peaking at 2.80 eV, while the raspite sample emits a band at 2.25 eV. The decay behaviors of these bands are found to be similar to each other. The 2.80- and 2.25-eV luminescence bands are intrinsic to the respective phases. The above results are discussed on the bases of a recent band-structure calculation of scheelite PbWO_4 and of a difference in crystal structure between the two phases. Furthermore, it is suggested that the controversial “green” luminescence in scheelite is due to the raspite-type inclusions introduced by thermal stress during the crystal growth.

I. INTRODUCTION

Lead tungstate, PbWO_4 , is a quite unique material because it possesses two stable structural modifications under normal conditions. As illustrated in Fig. 1,^{1,2} one is a scheelite-type (or stolzite-type) structure belonging to the space group $I4_1/a$, and the other is a raspite-type (or wolframite-type) structure with the space group $P2_1/c$. In the scheelite structure, W ions are in tetrahedral O-ion cages and isolated from each other. A Pb ion is surrounded by eight oxygen ions. In the raspite structure, the coordination number of W is six and WO_6 octahedra form a chain by edge sharing. Each Pb ion is coordinated to seven oxygen ions. The volume difference of the unit cells of these two structures is merely about 0.5%. The raspite PbWO_4 has not yet been successfully prepared in the laboratory and is obtained as a natural crystal, which transforms irreversibly to the scheelite around 400 °C.

In recent years, PbWO_4 has attracted much interest because of plans to use it as a scintillation detector at the Large Hadron Collider in CERN.^{3,4} For scheelite PbWO_4 crystals, there have been numerous investigations on the luminescent properties.^{3–17} In general, two emission bands, called “blue” and “green” bands, are observed, depending strongly on the photon energy of exciting light or the temperature of sample. Measurements of the reflection spectra, however, have been much more limited.^{18,19} Very recently, the electronic structures of this material have been calculated in the framework of density functional theory using a relativistic linearized-augmented-plane-wave technique.²⁰ On the other hand, no detailed optical investigation has been made on raspite PbWO_4 , except for preliminary reports by Alov²¹ and us.²²

In the present study, we have measured the reflection spectra of PbWO_4 crystals of scheelite and raspite phases in the energy range from 3 to 25 eV with the use of synchrotron radiation as a light source. The optical constants are derived through the Kramers-Kronig analysis. The luminescence

spectra and decay kinetics have also been investigated for both phases. On the basis of these results, the optical properties of scheelite- and raspite-structured PbWO_4 will be discussed in terms of the differences in crystal and electronic structures between the two phases.

II. EXPERIMENT

A large ingot of a scheelite PbWO_4 crystal was grown using the Czochralski melting technique at the Institute of Solid State Physics, Russian Academy of Sciences. With a reference of their luminescence characteristics, the scheelite samples ($\sim 3 \times 3 \times 2$ mm³ in size) used in the present study were carefully selected from a large number of crystals cleaved from the ingot. The raspite PbWO_4 was a natural crystal ($\sim 1 \times 0.2 \times 0.2$ mm³ in size) found in Broken Hill, Australia. The crystal structures of scheelite and raspite

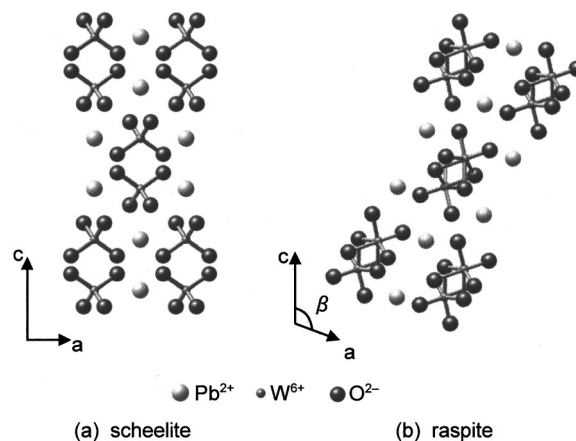


FIG. 1. Projections of (a) scheelite and (b) raspite structures of PbWO_4 along the b axis. For scheelite (Ref. 1), $a = b = 5.45$ Å, and $c = 12.02$ Å. For raspite (Ref. 2), $a = 5.56$ Å, $b = 4.97$ Å, $c = 13.56$ Å, and $\beta = 107.6^\circ$.

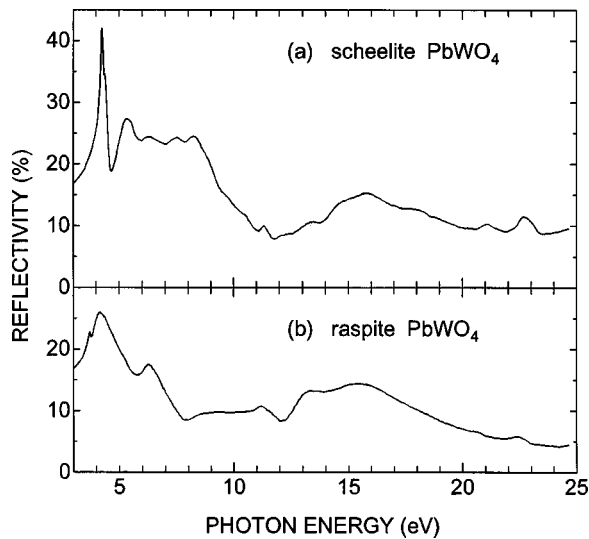


FIG. 2. Reflectivity spectra of (a) scheelite- and (b) raspite-structured PbWO_4 crystals obtained at 6 K.

samples were confirmed by the x-ray analysis. All the samples were colorless and transparent.

The present experiments were mainly carried out by using synchrotron radiation passed through a 1-m Seya-Namioka monochromator at beam line 1B of UVSOR in the Institute for Molecular Science, Okazaki. The specimens were mounted on the copper holder in a variable-temperature cryostat of He-flow type. Reflection spectra of near-normal incidence were measured using a photomultiplier tube coated with sodium salicylate. Photoluminescence was dispersed through a Spex 270M monochromator equipped with a charge-coupled device (CCD) camera (Princeton, LN/CCD-1152B). The registration system used here permitted us to get full excitation-emission information in a short amount of time; excitation energy was changed automatically by steps, and for each step the emission spectrum was registered. The emission spectra were corrected for the dispersion of the analyzing monochromator and for the spectral response of the detection system, and the excitation spectra were corrected for the intensity distribution of the incident light.

Decay kinetics measurements of luminescence were performed at Shinshu University. The fourth harmonics ($\hbar\omega = 4.66$ eV, pulse width=5 ns, average power=60 mW) from a Q-switched Nd:YAG (yttrium aluminum garnet) laser was used as an exciting light pulse. The 4.66-eV photon falls well above the fundamental absorption edges of scheelite and raspite PbWO_4 . The decay curves were recorded on a Tektronix 2440 digital storage oscilloscope operated with an averaging mode.

III. RESULTS

Figures 2(a) and 2(b) show the reflectivity spectra of scheelite and raspite PbWO_4 , respectively, in the energy range between 3 and 25 eV at 6 K. The absolute values of the reflectivity could not be obtained in the present experiment. This is because the cleaved surface of a scheelite sample was not flat, and the natural surface of a raspite sample was considerably smaller than the spot size of the incident light. The refractive index of the scheelite has been measured to be

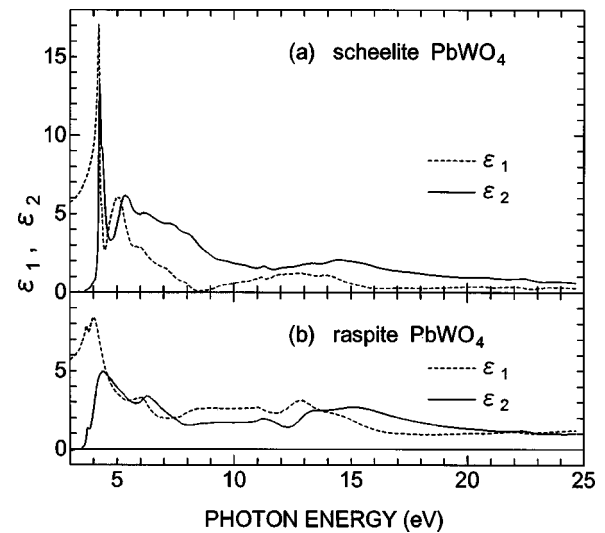


FIG. 3. The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of (a) scheelite- and (b) raspite-structured PbWO_4 , derived through the Kramers-Kronig analysis of the reflectivity spectra in Figs. 2(a) and 2(b), respectively.

2.16 at 632 nm (1.96 eV).⁴ Using this value, we obtained the reflectivity of Fig. 2(a). The reflectivity of Fig. 2(b) was also obtained by assuming that the refractive index of the raspite is the same as that of the scheelite.

For scheelite, one can clearly see a sharp peak at 4.25 eV and a high-energy hump at 4.38 eV.²² A similar doublet was also observed in the reflection spectrum for a cleaved surface by Shpinkov *et al.*,¹⁸ although our resolution is better.²³ Belsky *et al.*¹⁹ could not resolve the doublet structure in their reflection measurement at 300 K. For raspite, there appear a weak peak at 3.72 eV and a strong band at around 4.18 eV in the low-energy region.

The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of each phase were derived through the Kramers-Kronig analysis of the reflectivity spectra in Figs. 2(a) and 2(b). The obtained results are shown in Figs. 3(a) and 3(b). We also calculated absorption spectra for scheelite and raspite PbWO_4 , as shown in Figs. 4(a) and 4(b). For scheelite, a doublet structure peaking at 4.29 and 4.40 eV is seen. This doublet is most likely due to the lowest-exciton transitions. A hump is observed at 5.5 eV. There exist some structures in the energy region between 6 and 11 eV. A weak, but clear, peak appears at 11.3 eV. The absorption coefficient increases in the region above 12 eV, followed by a broad band at 15.8 eV. A doublet structure observed at 20.6 and 22.4 eV is certainly attributed to the $\text{Pb}^{2+} 5d \rightarrow 6p$ transitions. For raspite, a weak peak is observed at 3.75 eV. This lowest-energy peak is probably assigned to the exciton transition. Two broad bands are seen at 4.9 and 6.5 eV. As in the case of scheelite, a distinctive band is observed at 11.3 eV, and the absorption coefficient increases in the region above 12 eV, accompanying a broad band around 16.0 eV. The $\text{Pb}^{2+} 5d \rightarrow 6p$ transitions are also observable around 22 eV.

The contour plots of excitation-emission spectra of scheelite and raspite PbWO_4 measured at 6 K are shown in Figs. 5(a) and 5(b), respectively. The abscissa corresponds to the excitation energy, and the ordinate to the emission en-

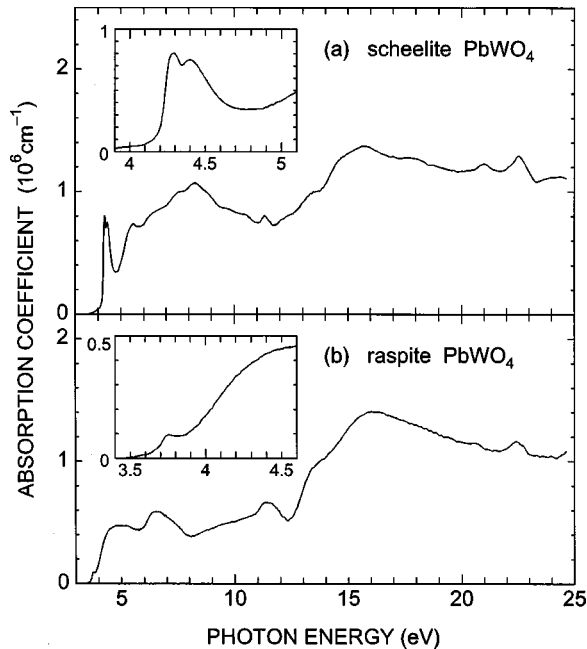


FIG. 4. Absorption spectra of (a) scheelite- and (b) raspite-structured PbWO_4 , derived through the Kramers-Kronig analysis of the reflectivity spectra in Figs. 2(a) and 2(b), respectively. The insets in (a) and (b) show the absorption spectra in the exciton-band region on an expanded scale.

ergy. The scheelite sample gives rise to an emission band which is asymmetric in shape and tails to the low-energy side. The peak position slightly depends on the excitation energy; it locates at 2.80 eV when excited in the range of 4.1–5.0 eV and at 2.75 eV when excited in the range above 5.5 eV. On the other hand, the raspite sample emits a single band with a Gaussian shape centered at 2.25 eV. Its peak position is independent of the excitation energy. The excitation threshold of the 2.25-eV band is about 3.6 eV.

In connection with the above results, it must be noted that many other scheelite samples emit an additional band at around 2.36 eV when they are excited with photons in the narrow region between 3.95 and 4.11 eV, i.e., just below the exciton-band region. A typical result is shown in Fig. 6. It was also found that the low-energy tail part of the exciton doublet in the reflection spectra is somewhat deformed on these samples emitting the 2.36-eV luminescence, although the doublet structure itself is hardly affected.

Decay behaviors of the 2.80-eV luminescence in scheelite and of the 2.25-eV luminescence in raspite measured at 8 K are depicted in Fig. 7. The 2.80-eV luminescence decay is fitted by the sum of three exponentials; a fast decay time $\tau_f = 0.2 \pm 0.1 \mu\text{s}$, a middle decay time $\tau_m = 1.5 \pm 0.2 \mu\text{s}$, and a slow decay time $\tau_s = 5.6 \pm 0.2 \mu\text{s}$. The time-integrated intensities of the fast, middle, and slow components are in the ratio 1:5:11. Nikl *et al.*⁹ have found that the 2.80-eV luminescence exhibits a single exponential decay with a lifetime 5.6 μs at 4.2 K. A nearly exponential decay with a lifetime $\sim 4 \mu\text{s}$ has been observed by Millers *et al.*¹⁵ The present slow component is fairly consistent with these observations. Interestingly, the authors of Refs. 3 and 9 have reported that the 2.80-eV luminescence consists of three decay components at room temperature. The decay curve of the

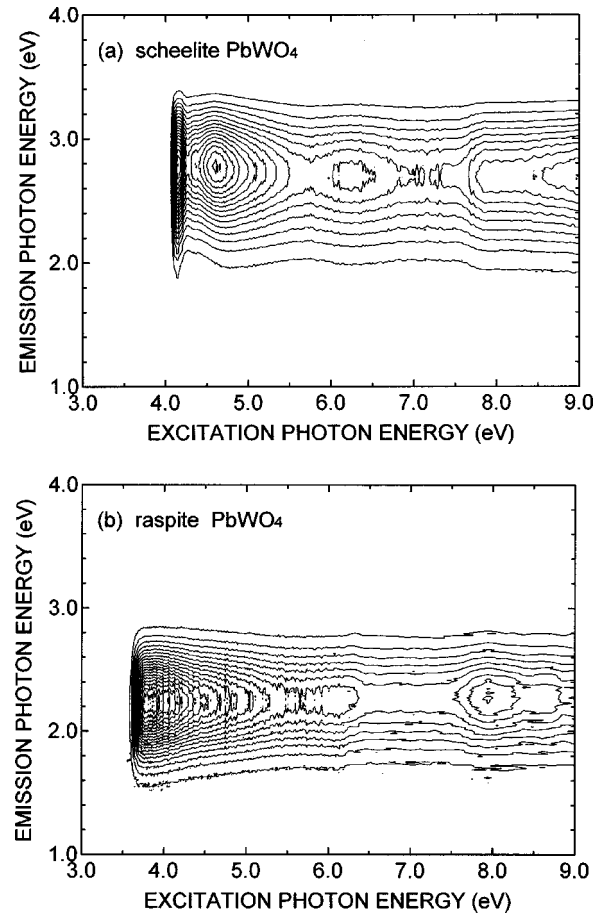


FIG. 5. Contour plots of excitation-emission spectra of (a) scheelite- and (b) raspite-structured PbWO_4 measured at 6 K. The abscissa corresponds to the excitation energy, and the ordinate to the emission energy.

2.25-eV luminescence is also triexponential, with $\tau_f = 0.4 \pm 0.1 \mu\text{s}$, $\tau_m = 1.9 \pm 0.2 \mu\text{s}$, and $\tau_s = 8.0 \pm 0.2 \mu\text{s}$. The time-integrated intensities of the fast, middle, and slow components are in the ratio 1:9:10.

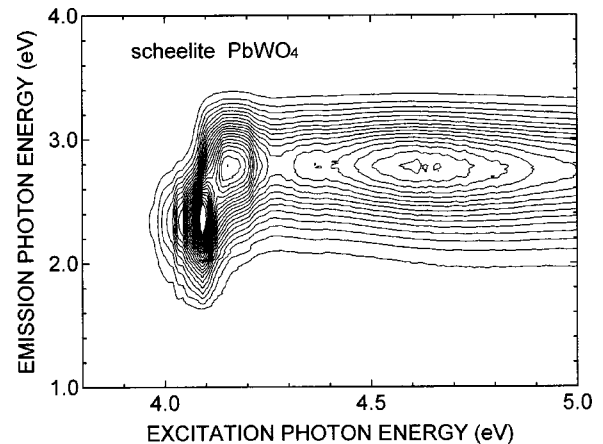


FIG. 6. Contour plot of a typical example of the coexistence of the 2.80-eV (“blue”) and 2.36-eV (“green”) emission bands in scheelite PbWO_4 measured at 6 K. The abscissa corresponds to the excitation energy, and the ordinate to the emission energy.

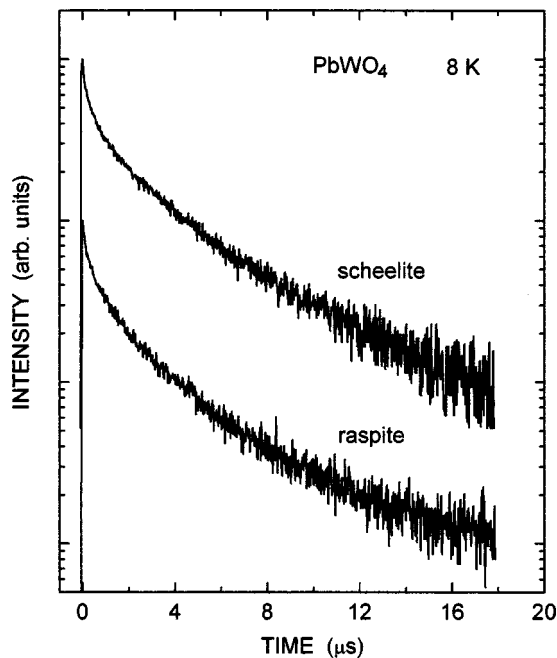


FIG. 7. Decay profiles of the 2.80-eV luminescence in scheelite and of the 2.25-eV luminescence in raspite. The excitation was made at 8 K with 4.66-eV photon pulses from a Q -switched Nd:YAG laser.

IV. DISCUSSION

The recent electronic structure calculation of scheelite PbWO_4 (Ref. 20) has indicated that the valence band is mainly described by the $2p$ state of O^{2-} ions, and the conduction band is dominated by the $5d$ state of W^{6+} ions. However, it has also been pointed out that the $\text{Pb } 6s$ state and $\text{Pb } 6p$ state have appreciable contributions throughout the valence band and conduction band, respectively. The valence-band width is calculated to be 5.5 eV. The $\text{Pb } 6s$ state forms a well-defined narrow band 1 eV below the bottom of the valence band.

The lowest exciton transition of scheelite in Fig. 4(a) is connected to an electronic excitation from the mixed $\text{Pb}(6s)\text{-O}(2p)$ ground states to the mixed $\text{Pb}(6p)\text{-W}(5d)$ excited states. In other words, a part of the scheelite exciton consists of the $6s \rightarrow 6p$ transition of Pb^{2+} ions. According to this model, the doublet structure can be explained in terms of the crystal-field splitting of the $\text{Pb } 6p$ levels with S_4 point symmetry. The present value (0.11 eV) of the splitting of the exciton band is comparable to 0.06–0.14 eV in lead halides,²⁴ although their cation sites have the C_S point symmetry. The present interpretation is different from that by Zhang *et al.*,²⁰ who have suggested the possibility that this doublet arises from the energy difference of the topmost valence bands at the Σ and Δ points of the Brillouin zone. The absorption coefficient of scheelite rises sharply at 5.0 eV on the high-energy side of the exciton doublet, which undoubtedly corresponds to the interband edge. No obvious symptom of the indirect transition predicted by Zhang *et al.*²⁰ could be found in the present experiment.

In Fig. 4(a) the absorption spectrum of scheelite shows a composite structure between 5 and 11 eV. Since the calculated valence-band width is 5.5 eV, this structure can be primarily attributed to the transitions from the valence band

to the bottom of the conduction band. A narrow band at 11.3 eV is assigned to the isolated $\text{Pb } 6s$ state. It is likely that the structures above 12 eV are mainly ascribed to electronic transitions from the valence band to the high-lying states in the conduction band.

No electronic structure calculation has been made for raspite PbWO_4 . However, because of the sameness of the constitutive elements, the electronic structures of raspite are expected not to be so different from those of scheelite. From Figs. 4(a) and 4(b), it is obvious that a main difference of the absorption spectra in both phases is in the exciton transitions. The exciton transition in raspite is very weak. This result suggests that the Pb contributions to the top of the valence band and the bottom of the conduction band are small in raspite compared to those in scheelite. That is to say, the raspite exciton is a molecular-type exciton of the WO_6 -anion complex with mainly covalent bonding within the oxocomplex. Our speculation may be reasonable in view of the fact that the cation coordination is remarkably different between the two forms, i.e., the coordination sphere consisting of Pb and eight O ions in scheelite is a slightly distorted cubelike arrangement, while the coordination polyhedron of Pb and seven O ions in raspite is rather irregular in shape.²

The band-gap energy of raspite is located around 4.0 eV at which the absorption coefficient rises sharply in Fig. 4(b). Similarly to the case of scheelite, the distinctive $\text{Pb } 6s$ band is also seen at 11.3 eV, and some structures between 4 and 11 eV are likely due to the transitions from the valence band to the bottom of the conduction band. Furthermore, there are close similarities in the absorption spectra above 12 eV for scheelite and raspite samples, indicating that the electronic band structures of both phases are, as a whole, similar to each other.

Let us now discuss the origin of the luminescence bands in scheelite and raspite PbWO_4 . All scheelite samples investigated here give rise to the luminescence band at 2.80 eV. This luminescence has been regarded as being an intrinsic feature of the scheelite sample.^{3–17} Such a conclusion is indeed supported by the present result that the 2.80-eV luminescence is stimulated with photons above the onset of the lowest exciton absorption band, as shown in Fig. 5(a). The 2.80-eV luminescence is ascribed to the radiative decay of excitons self-trapped (localized) on regular WO_4 groups in which four oxygen ions form the tetrahedron with a tungsten ion at the center. It was observed that the luminescence peak moves from 2.80 to 2.75 eV when the excitation energy is changed from the exciton-band to interband regions. The reason for this shift is not clear at present.

The raspite sample emits the 2.25-eV luminescence. This luminescence is stimulated with photons above the onset of the lowest exciton absorption band, as shown in Fig. 5(b). Such a result suggests an intrinsic nature of the 2.25-eV luminescence, but does not rule out the possibility that optically generated excitons may move about freely through the crystal and be trapped by some lattice imperfection from which the 2.25-eV photons are emitted. In Fig. 5(b), we cannot see any other luminescence. Therefore, if this possibility is realized, it has to be supposed that almost all excitons transfer their energy to imperfections before relaxing into self-trapped states. Such a supposition looks questionable, particularly in view of the strong exciton-phonon coupling in

lead tungstates. We ascribe the 2.25-eV luminescence to the radiative decay of excitons self-trapped on octahedral WO_6 groups in which a tungsten ion is surrounded by six oxygen ions. This assignment is consistent with the result of ZnWO_4 with raspite structure, where the intrinsic luminescence from WO_6 groups appears at around 2.5 eV.²⁵

From the above discussions, we can state that the scheelite and raspite samples give rise to the intrinsic luminescence bands at 2.80 and 2.25 eV, respectively. It is reasonable to believe that the difference in molecular structure between WO_4 and WO_6 groups results in the different relaxed configuration of the self-trapped excitons generated in scheelite and raspite crystals, leading to the difference in magnitude of a Stokes shift.

As mentioned before, the lowest absorption bands in scheelite and raspite are connected to the exciton transitions. If the exchange interaction between electron and hole is taken into account, the exciton states are split into a singlet-triplet mixed state and a pure triplet state.²⁶ The former is dipole active, and the latter is spin-forbidden for electric-dipole transitions. Because of the long radiative lifetimes, it can be thought that the lowest triplet state of self-trapped excitons is mainly responsible for the intrinsic luminescence bands in both scheelite and raspite PbWO_4 crystals. This agrees with the argument based on the molecular orbitals of a tetrahedral WO_4^{2-} cluster.²⁰

It has been well known³⁻¹⁷ that there appear two emission bands in scheelite crystals; one is the intrinsic “blue” band at 2.80 eV, and the other is the “green” band peaking between 2.30 and 2.45 eV. In the present experiment, too, the green emission band at 2.36 eV was often observed when some of scheelite samples were excited just below the lowest exciton absorption band, as shown in Fig. 6. The origin of the green band has still been controversial.

Two principal models have been proposed for explaining the appearance of the green band. Korzhik *et al.*¹⁰ pointed out the possibility that this band may be related to crystal defects on the surface (lack of oxygen, i.e., WO_3 groups). However, Kobayashi *et al.*¹² showed no significant effects of the surface on the luminescence spectra. Alternatively, they suggested that the green band is caused by Mo impurities, i.e., MoO_4 groups, in PbWO_4 . Although their model is appealing, we want to give a new conjecture for the cause of the green band in light of our results.^{21,22} The raspite sample exhibits the intrinsic emission band at 2.25 eV. This peak energy is very close to that of the green band in scheelite PbWO_4 . Such a similarity allows us to consider that the green band is related to the raspite-type inclusions existing in

synthetic crystals, which usually crystallize in the scheelite-type structure. The transformation from scheelite to raspite is expected to take place by thermal stress because of the very small volume difference between the two forms. The difference in peak energy between the green band and the raspite band is about 0.1 eV. Furthermore, the decay time ($\sim 8 \mu\text{s}$) of the raspite band is somewhat shorter than that ($\sim 15 \mu\text{s}$) of the green band.⁹ These differences may be understood by taking into account the environmental influence that the raspite-type inclusions are embedded in the scheelite host matrix.

The valence and conduction bands of the host scheelite crystal will be perturbed by the existence of locally deformed structural environments (raspite-type inclusions). As a result, new localized states, wave functions of which have mainly the character of a WO_6 group, are created in the energy region just below the band edge of the host crystal. This explains the result of Fig. 6 showing that the green band due to raspite inclusions is stimulated with photons in the narrow region of 3.95–4.11 eV, which is intermediate in energy between the exciton bands in raspite and scheelite.

V. SUMMARY

We have measured the reflection spectra of scheelite and raspite PbWO_4 at 6 K. Their absorption spectra are obtained by the Kramers-Kronig analysis. A clear difference is found on the exciton absorption bands. This is attributed to the difference in the Pb contributions to the valence and conduction bands between the two phases. The scheelite and raspite samples give rise to the intrinsic luminescence bands at 2.80 and 2.25 eV, respectively, with decay times of the order of μs . The different molecular structures of WO_4 and WO_6 groups leads to the difference in magnitude of a Stokes shift. The origin of the controversial green band is connected to the raspite-type inclusions in scheelite PbWO_4 .

ACKNOWLEDGEMENTS

The authors would like to express their sincere thanks to Dr. D. L. Alov for kindly providing them the scheelite and raspite samples and for stimulating discussions throughout the present study. They also acknowledge Mr. M. Horimoto and Mr. K. Hayakawa for the experimental assistance. M.I. is thankful to Professor M. Nikl for useful comments on the luminescent properties of PbWO_4 . The present work was partly carried out at the UVSOR facility under the Joint Studies Program of the Institute for Molecular Science.

¹L. Bragg and G. F. Claringbull, *Crystal Structures of Minerals* (G. Bell and Sons Ltd., London, 1965), p. 149.

²T. Fujita, I. Kawada, and K. Kato, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **33**, 162 (1977).

³M. Kobayashi, M. Ishii, Y. Usuki, and H. Yahagi, *Nucl. Instrum. Methods Phys. Res. A* **333**, 429 (1993).

⁴P. Lecoq, I. Dafinei, E. Auffray, M. Schneegans, M. V. Korzhik, O. V. Missevitch, V. B. Pavlenko, A. A. Fedorov, A. N. Annenkov, V. L. Kostylev, and V. D. Ligun, *Nucl. Instrum. Methods*

Phys. Res. A **365**, 291 (1995).

⁵F. A. Kröger, *Some Aspects of the Luminescence in Solids* (Elsevier, Amsterdam, 1948).

⁶*Proceedings of the International Conference on Inorganic Scintillators and Their Applications*, edited by P. Dorenbos and C. W. E. van Eijk (Delft University Press, Delft, 1996), Part IV.

⁷*Proceedings of the International Workshop on Tungstate Crystals*, edited by S. Baccaro, B. Borgia, I. Dafinei, and E. Longo (Università degli Studi La Sapienza, Rome, 1999).

- ⁸A. N. Belsky, V. V. Mikhailin, A. N. Vasil'ev, I. Dafinei, P. Lecoq, C. Pedrini, P. Chevallier, P. Dhez, and P. Martin, *Chem. Phys. Lett.* **243**, 552 (1995).
- ⁹M. Nikl, K. Nitsch, K. Polak, E. Mihokova, I. Dafinei, E. Auffray, P. Lecoq, P. Reiche, R. Uecker, and G. P. Pazzi, *Phys. Status Solidi B* **195**, 311 (1996).
- ¹⁰M. V. Korzhik, V. B. Pavlenko, T. N. Timoschenko, V. A. Katchanov, A. V. Singovskii, A. N. Annenkov, V. A. Ligun, I. M. Solskii, and J.-P. Peigneux, *Phys. Status Solidi A* **154**, 779 (1996).
- ¹¹G. Tamulaitis, S. Buračas, V. P. Martinov, V. D. Ryzhikov, H. H. Gutbrod, and V. I. Manko, *Phys. Status Solidi A* **157**, 187 (1996).
- ¹²M. Kobayashi, M. Ishii, K. Harada, Y. Usuki, H. Okuno, H. Shimizu, and T. Yazawa, *Nucl. Instrum. Methods Phys. Res. A* **373**, 333 (1996).
- ¹³R. Y. Zhu, D. A. Ma, H. B. Newman, C. L. Woody, J. A. Kierstead, S. P. Stoll, and P. W. Levy, *Nucl. Instrum. Methods Phys. Res. A* **376**, 319 (1996).
- ¹⁴V. Mürk, M. Nikl, E. Mihoková, and K. Nitsch, *J. Phys.: Condens. Matter* **9**, 249 (1997).
- ¹⁵D. Millers, S. Chernov, L. Grigorjeva, and V. Pankratov, *Radiat. Meas.* **29**, 263 (1998).
- ¹⁶M. Nikl, P. Straková, K. Nitsch, V. Petříček, V. Múčka, O. Jarolímek, J. Novák, and P. Fabeni, *Chem. Phys. Lett.* **291**, 300 (1998).
- ¹⁷M. Martini, F. Meinardi, G. Spinolo, A. Vedda, M. Nikl, and Y. Usuki, *Phys. Rev. B* **60**, 4653 (1999).
- ¹⁸I. N. Shpinkov, I. A. Kamenskikh, M. Kirm, V. N. Kolobanov, V. V. Mikhailin, A. N. Vasilev, and G. Zimmerer, *Phys. Status Solidi A* **170**, 167 (1998).
- ¹⁹A. N. Belsky, S. M. Klimov, V. V. Mikhailin, A. N. Vasil'ev, E. Auffray, P. Lecoq, C. Pedrini, M. V. Korzhik, A. N. Annenkov, P. Chevallier, P. Martin, and J. C. Krupa, *Chem. Phys. Lett.* **277**, 65 (1997).
- ²⁰Y. Zhang, N. A. W. Holzwarth, and R. T. Williams, *Phys. Rev. B* **57**, 12 738 (1998).
- ²¹D. L. Alov and S. I. Rybchenko, *Mater. Sci. Forum* **239-241**, 279 (1997).
- ²²M. Itoh, D. L. Alov, and M. Fujita, *J. Lumin.* **87-89**, 1243 (2000).
- ²³Our recent reflection measurements at 7 K have clarified that a clearness of this doublet structure is very sensitive to the surface treatment of crystals.
- ²⁴M. Fujita, M. Itoh, Y. Bokumoto, H. Nakagawa, D. L. Alov, and M. Kitaura, *Phys. Rev. B* **61**, 15 731 (2000).
- ²⁵H. Wang, F. D. Medina, M. S. Antonious, C. Párkányi, J. E. Haky, D. M. Baird, and Y. Zhou, *Chem. Phys. Lett.* **205**, 497 (1993).
- ²⁶Y. Onodera and Y. Toyozawa, *J. Phys. Soc. Jpn.* **22**, 833 (1967).