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One- and two-photon excited luminescence and band-gap assignment in $CaWO_4$

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Luminescence properties of $CaWO_4$ have been investigated using complementary one- and two-photon excitation techniques. Analysis of the thermal changes in the luminescence spectra indicates that the observed high-energy shift of the $CaWO_4$ emission maximum is mainly caused by a change of position of the intrinsic blue band. The thermal broadening and shift of this band can be interpreted satisfactorily in terms of a model of the luminescence center interacting with the vibrating crystalline environment. The characteristic parameters of the phonon system obtained from the experiment agree with those from earlier independent studies. Intense laser stimulation of $CaWO_4$ in the spectral region <505 nm (>2.45 eV) results in emission with spectral and kinetics features that are characteristic of the radiative decay of a WO_4^{2-} oxyanion complex in this crystal. The kinetics of luminescence decay under two-photon excitation changes with increasing excitation density due to exchange interaction of the elementary excitations. From a comparative analysis of the optical properties of $CaWO_4$ obtained in the course of two-photon and one-photon spectroscopic studies (absorption, reflection, one- and two-photon excitation spectra) it is concluded that the energy gap of the crystal is 5.2 ± 0.3 eV.

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I. INTRODUCTION

Calcium tungstate is a well-known single crystalline scintillation detector of ionizing radiation, first used in the years following Röntgen's discovery of x-rays.[1] Because of its excellent luminescence properties $CaWO_4$ has found practical importance in many optical applications as a phosphor, scintillation counter, laser material, etc. Therefore during more than a century calcium tungstate has been investigated thoroughly; starting with the early work of Kröger[2] who reviewed the luminescence properties of the tungstate family, a considerable amount of data on the spectroscopy of $CaWO_4$ has been collected by many investigators.[3–10] The planned use of $PbWO_4$ as a scintillator in detection systems of the Large Hadron Collider[11] has revived interest in tungstate materials and comparative experimental and theoretical studies of $CaWO_4$ have provided up-to-date information about its electronic structure,[12] excitation and relaxation processes,[13–15] and optical and luminescence properties.[16,17]

A new field of application emerged some years ago when the concept of cryogenic scintillation detectors was implemented for use in the search for interaction events caused by Dark Matter. The calcium tungstate scintillator is considered as a most suitable target material because of its capability to discriminate between electron and nuclear recoils by simultaneous detection of scintillation photons and phonons,[18] and optimization of its scintillation properties is becoming a primary focus of material and luminescence research.[19]

Single crystals of $CaWO_4$ with scheelite structure crystallize in tetragonal space group C_{4h}^6; it has two molecular units in the primitive cell. The result of single-crystalline x-ray-diffraction study by Hazen *et al.*[20] provides the following lattice parameters of $CaWO_4$: $a = 5.2429$ Å and $c = 11.3737$ Å. The Ca and W sites have S_4 point symmetry. The Ca cations are eightfold coordinated by oxygen in the form of eight-vertex polyhedra made up of elongated and compressed tetrahedra. The WO_4 groups have the shape of nearly regular tetrahedra, slightly compressed along the S_4 axis. The oxygen sites have only a trivial point symmetry and the crystal has an inversion center.

$CaWO_4$ is an intrinsic scintillator with high light yield, high quenching temperature and a broad structureless emission band centered at ~ 420 nm. It is generally accepted that the emission is due to electronic transitions of the charge-transfer type between oxygen and tungstate within the anion complex WO_4^{2-}, interpreted in the excited state as a self-trapped molecular exciton.[7,8,14–16] In addition to the main blue band, green luminescence can be detected with a relative intensity that is dependent on the type of excitation (UV-, X- or γ-emission, particles) and sample quality. This emission is attributed to extrinsic luminescence due to structure defects of the crystal lattice, such as WO_3 Shottky defects.[9,21] Grasser *et al.*[22] also suggested that apart from the WO_3 group, the Mo^{3+} impurity (i.e., MoO_4^{2-} group) can contribute to the green emission.

Investigations of luminescence kinetics of $CaWO_4$ have been reported in a number of papers.[4,5,7,23,24] Beard *et al.*[4] used α-particle excitation in the temperature range from 10 K to 375 K and observed first-order kinetics with a decay constant of 5 μs at room temperature that increases monotonically with decrease in temperature. Treadaway and Powell,[7] and later Blasse and Bokkers,[24] examined the behavior of luminescence decay under UV excitation and found

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a pronounced increase (by an order of magnitude) in the decay constant for temperatures below 20 K. The measured decay time was roughly twice the value obtained by Beard *et al.*[4] and this was explained by different types of excitation used[24]. Born *et al.*[5] obtained a shorter decay time with electron beam excitation compared with that measured under UV excitation. Overall these results are consistent with the characteristics of luminescence kinetics of $CaWO_4$ and the differences in the decay constants observed can be attributed to differences in excitation conditions. The effect of excitation density on luminescence decay has recently been analyzed for lead tungstate by Itoh *et al.*[25] and clarification of this issue for calcium tungstate is of interest.

Two-photon spectroscopy can provide new information concerning the nature of emission processes as it allows observation of states that are inaccessible by traditional one-photon spectroscopy.[26] For crystals with inversion symmetry both techniques are complementary owing to the selection rules that are very different: even parity transitions are allowed for two-photon spectra while odd-parity transitions are permitted in one-photon spectra.[27] Investigation of the two-photon induced process provides basic information about the nature of the excitonic states and band properties near the band-gap edge of the crystal that can be compared with those obtained under one-photon high-energy excitation. From a practical perspective two-photon excited luminescence has a critical advantage of allowing direct examination of luminescence from the interior of a bulk sample, permitting the homogeneity of the light yield from massive single-crystalline scintillators to be assessed.[28]

Bearing in mind the importance of such information for material science of scintillation detectors and because of the lack of pertinent studies for calcium tungstates we initiated comparative investigations of the luminescence properties of $CaWO_4$ induced by one and two-photon excitation (TPE) processes. Given recent progress in computational studies of the electronic band structure of $CaWO_4$ and other tungstates[12,29,30] it is believed that such experiments can be consistently interpreted in the frame of the theory of electronic band structure of crystals providing in turn quantitative parameters that are indispensable for the analysis of the theoretical results.

In this paper we report on the luminescence studies of $CaWO_4$ performed using high power pulsed laser sources for TPE of the luminescence and rudimentary spectroscopic techniques for one-photon excitation. Following an examination of the luminescence properties of calcium tungstate, particularly their temperature dependence, the TPE luminescence is compared with other spectroscopic properties of $CaWO_4$. These results are discussed within the current understanding of the energy-band structure of the material. Finally the main features of the kinetics of TPE luminescence are examined.

II. EXPERIMENTAL TECHNIQUE

Two samples were examined: (i) sample C, a polished (optical quality) section cut from a scintillation detector manufactured by SRC ‘‘Carat’’ (Lviv, Ukraine) and (ii) sample F, a fragment cleaved from a crystal ingot obtained from Dr. Y. Usuki (Furukawa Company, Japan). Both samples were grown by the Czochralski technique from the raw materials of 99.99% purity.

Two experimental configurations were used in the TPE luminescence studies. One experiment was carried out using fixed excitation wavelength comprising the third harmonic (355 nm) output of a Q-switched YAG laser (Continium Minilite II; pulse duration 5 ns; repetition rate 10 Hz; power density 20–40 $\mathrm{mW\,cm^{-2}}$). For excitation in the spectral region 450–600 nm a tunable laser source was used (parametric oscillator comprising a Quanta Ray MOPO 710, pumped by a Q-switched YAG laser; pulse half-width 3–4 ns; repetition rate 10 Hz; power density 2–12 $\mathrm{mW\,cm^{-2}}$). A detailed description of the two experimental systems can be found in Refs. 25 and 31, respectively.

Given the task of comparing the data obtained in the TPE luminescence study with the results of other experiments, the emission and excitation spectra of the $CaWO_4$ were measured in a wide spectral range using a 40-cm vacuum monochromator of the Seya-Namioka type in combination with a D_2 lamp (200 W). The band pass was adjusted to about 2 nm. The specimen was mounted on the copper holder of a closed cycle He cryostat operating in the temperature range 8–300 K. Luminescence was detected at a right angle to the exciting UV-light by means of a Nikon G250 monochromator and a Hamamatsu R4220 photomultiplier. The band pass of the analyzing monochromator was 5 nm. The luminescence spectra were corrected for the dispersion (λ^2 correction) and for the spectral response of the detection system.

The reflection spectra presented in this study were measured for sample F using a spectroscopic facility at UVSOR (for the experimental details see Ref. 32).

III. RESULTS AND DISCUSSION

A. Temperature dependence of $CaWO_4$ luminescence

The luminescence spectra of the $CaWO_4$ crystal samples C and F, excited by UV photons in the energy range 4.3–6.5 eV, shown in Figs. 1 and 2, respectively, explicitly demonstrate the effect of excitation energy on the emission spectrum. Under excitation with the low-energy photons mostly the extrinsic green emission band is observed, while the intrinsic blue band dominates at higher excitation energies (>5 eV). This effect is reflected in the luminescence light yield spectra of the crystals [Figs. 3(a) and 3(b)]. The excitation spectrum of the green component exhibits a band-like singularity located in the edge region of the excitation spectrum of the blue component, which gives evidence of the defect center emission. The relative intensity of the former band in the excitation spectrum is sample dependent and can provide an estimate of the content of such defects. It is noticeable that the dependence of changes in the emission spectra on the excitation energy in the region of the edge absorption is observed in $PbWO_4$ crystals[15,33,34] and it appears to be a common feature of the luminescence of tungstate crystals with a scheelite structure. The position of the green and blue emission bands also differs for the samples tested. As seen in Figs. 1 and 2, the emission bands measured at 8 K have

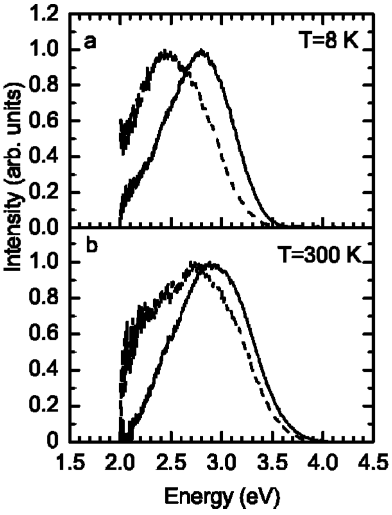

FIG. 1. Normalized luminescence spectra of $CaWO_4$, sample C, measured at $T=8$ K (a) and 300 K (b) under excitation with 4.49 (dashed line) and 5.16 eV (solid line) photons.

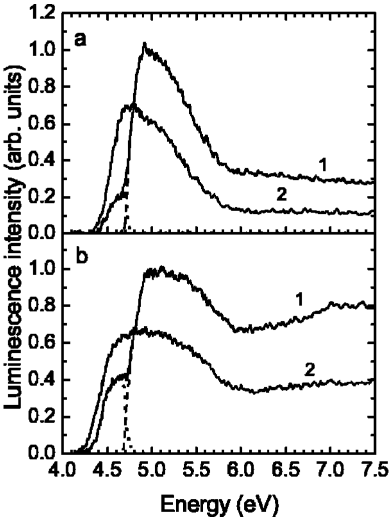

FIG. 3. Luminescence excitation spectra monitored at 2.95 eV for $CaWO_4$ [(a) sample C; (b) sample F]. Spectra are measured at $T=8$ K (1) and 300 K (2). The excitation spectrum at $T=8$ K is resolved into two components: the intrinsic (dashed line) and extrinsic (dotted line) emission.

extrinsic and intrinsic peaks located at 2.45(2.55) eV and 2.80(2.90) eV in sample C(F), respectively.

Temperature increase leads to a high-energy shift and broadening of the emission bands; at 300 K the maxima of the extrinsic and intrinsic emission bands are at 2.70(2.75) and 2.90(2.95) eV in sample C(F), respectively. The above observations suggest that the shift of the extrinsic green emission band with increased temperature is the consequence of an overlap of the excitation edge of the intrinsic emission with the nearby absorption band of the defect centers. This suppresses their excitation and results in the spectral redistribution of the emitted light in favor of blue emission (see also Ref. 13). Thermal changes in the luminescence excitation spectra of the crystals observed in the edge region support this interpretation [Figs. 3(a) and 3(b)]. At a temperature of 8 K, the luminescence excitation spectra exhibit a shoulder at 4.6 eV that is associated mainly with the excitation of the extrinsic green emission. As the sample temperature increases the onset of the excitation spectrum associated with the intrinsic emission shifts to lower energies and overlaps this defect band. This results in simultaneous excitation of the defect and intrinsic emissions. The onset of intrinsic blue emission occurs for excitation energies above 4.7 eV.

The main effect of temperature increase on the luminescence spectra of $CaWO_4$, a decrease in the emission intensity and spectrum broadening [Figs. 4(a) and 4(b)], is a typical characteristic of luminescence materials with intrinsic emission.[35] Under excitation with 6.2 eV photons, the integrated emission intensity remains almost unchanged at low temperatures and decreases significantly as the temperature

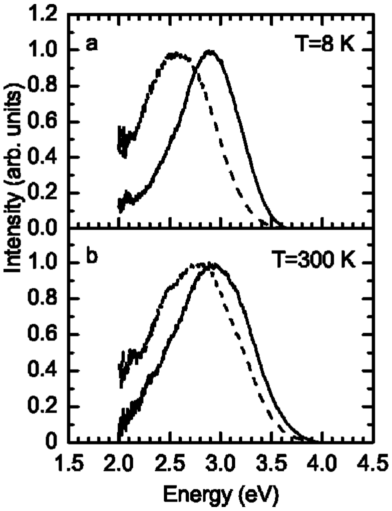

FIG. 2. Normalized luminescence spectra of $CaWO_4$, sample F, measured at $T=8$ K (a) and 300 K (b) under excitation with 4.59 (dashed line) and 5.16 eV (solid line) photons.

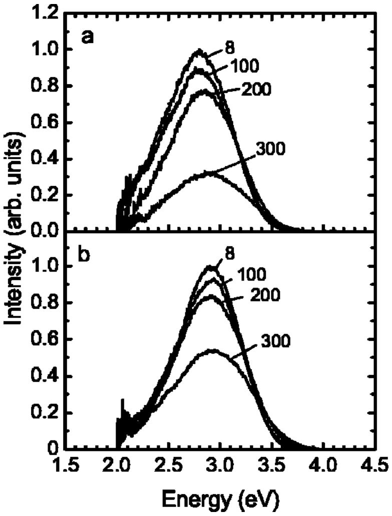

FIG. 4. Temperature dependences of the emission spectra of $CaWO_4$ excited at 6.20 eV [(a) sample C, (b) sample F]. The numbers adjacent to the curves represent temperature in K.

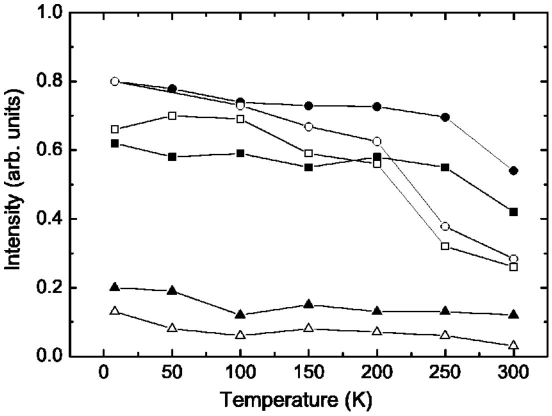

FIG. 5. Temperature dependence of the integrated luminescence intensity (circles), intensity due to intrinsic (squares) and extrinsic (triangles) emission bands of $CaWO_4$. Empty and solid symbols represent samples C and F, respectively. Luminescence is measured under 6.20 eV photoexcitation.

is raised. The temperature at which this significant change sets in is sample dependent; for sample C it starts above 200 K and for sample F above 250 K respectively.

A further feature to note is the high-energy shift of the emission peak with increased temperature when excitation is performed well above the luminescence excitation edge. Figure 4 demonstrates this well-recognizable signature of $CaWO_4$ luminescence.[7,17] Previous explanations of this effect are based on the composite nature of $CaWO_4$ luminescence. The intensity ratio and position of the intrinsic (blue) and extrinsic (green) components have been assumed to be temperature dependent, causing the fraction of green emission to decrease with increasing temperature and resulting in a concomitant blue shift of the detected luminescence spectrum. To test this model, we performed an analysis of the luminescence spectra using multi-Gaussian decomposition.

The presence of two Gaussian bands in the emission spectrum of $CaWO_4$ has been generally assumed.[8,16,17,21,22] It should further be mentioned that Bacci *et al.* have shown in recent studies[36] that the intrinsic blue luminescence of $PbWO_4$ has an internal structure (three bands) due to the Jahn-Teller effect. Since there are no apparent experimental indications of such internal structure of the blue emission in $CaWO_4$ the two-Gaussian decomposition was considered to be sufficient for the analysis of the luminescence spectra. However this does not eliminate the idea in itself; it could give a hint for understanding the sample-dependent change of the intrinsic emission band.

The results of this decomposition analysis are consistent for both samples, as summarized in Figs. 5 and 6. Figure 5 shows that the absolute intensity of both emissions decreases with temperature and, critically, changes in the integrated intensity of the blue emission with temperature replicate the temperature dependence of the integrated light yield observed. The position of the blue emission band peak almost coincides with the maximum of the luminescence spectrum [Fig. 6(b)], both of which undergo a gradual high-energy shift with increase in temperature. The magnitude of the shift (0.11 and 0.04 eV for samples C and F respectively) is consistent, within experimental error limits, with that observed experimentally for both samples (0.10 and 0.05 eV).

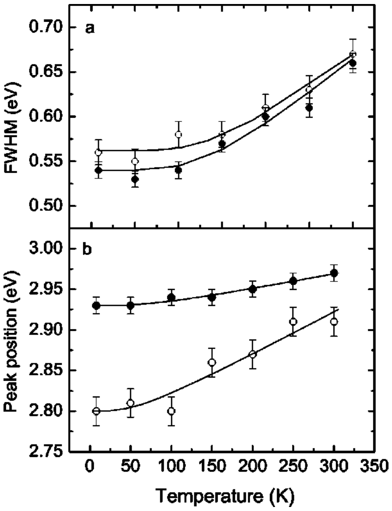

FIG. 6. Temperature dependence of intrinsic emission bands of $CaWO_4$; (a) full width at half maximum and (b) peak position of the intrinsic emission band as a function of temperature. Empty and solid symbols represent samples C and F, respectively. Solid lines show the best fitting to the Eqs. (1) and (2). Luminescence is measured under 6.20 eV photoexcitation.

We suppose that the above-mentioned composite structure of the intrinsic band provides support for the explanation of the minor sample-dependent variation of the peak position of this band. According to the model[36] its appearance is governed in a complex way by the number of parameters (Jahn-Teller coupling, ligand field, spin-orbit coupling) and it is assumed that these parameters can be sample dependent. This would result in different intensities of the separate peaks and hence in different shapes of the resultant intrinsic emission band.

As is seen in Fig. 5, the green emission band makes a minor contribution to the total emission (less than one-third), and the expected effect on the shape of the luminescence spectra is minor. Consequently the predicted change with temperature of the emission intensity and peak position of the single-Gaussian blue band closely follows that observed experimentally for the luminescence spectra of $CaWO_4$ crystals. We conclude that under photoexcitation of $CaWO_4$ using energies well above the luminescence excitation edge, the defect emission does not significantly influence the observed temperature dependence of the luminescence. Moreover, the observed features are predetermined by recombination processes associated with the intrinsic (blue) emission band.

To explain the observed temperature shift of $CaWO_4$ luminescence we adopted the model of a luminescence center in a vibrating crystalline environment that would provide the basis for a quantitative approach.[37] Recent studies of the temperature-induced effects in the luminescence of $ZnS:Mn^{2+}$ showed that such an approach can adequately explain the observed high-energy shift of the broad band emission of Mn^{2+} ions.[38] Using this theoretical approach, the expression for the temperature dependence of the half-width of the emission band is given as follows:

$$W(T)=W_0\sqrt{\coth(\hbar\omega/2kT)}, \tag{1}$$

where W_0 is the width of the band at 0 K and $\hbar\omega$ is the energy of the lattice vibrations that interact with the electronic transitions. The position change of the emission band with temperature can be written as:[37]

$$E(T)=E_0+CT^4\int_0^{\hbar\omega_D/kT} x^3dx/(e^x-1), \tag{2}$$

where E_0 is the energy of the transitions at 0 K, $\hbar\omega_D$ is the characteristic energy of acoustic phonons in the Debye model (cutoff energy) and C is a constant. These equations were employed in a numerical fit to the experimental data assuming that each emission band is associated with one type of luminescence center.

The result shown in Fig. 6(a) (solid line) can be fitted (two parameter least squares) to Eq. (1) on thermal broadening of the intrinsic emission band, yielding phonon energies of 45±3 meV and 42±2 meV for samples C and F, respectively. These values agree reasonably well within the uncertainties of the fitting procedure, and they are also consistent with the energy (44 meV) of the ν_2 internal vibration mode of the WO_4 tetrahedra in $CaWO_4$.[39]

Fitting of Eq. (2) to the experimental data was performed using the minimization by gradient method (MIGRAD algorithm) to minimize the sum of the least squared errors.[40] The Boltzmann distribution was numerically integrated using an extended version of the trapezoidal rule.[41] The best fits [Fig. 6(b), solid line] were obtained with values of the phonon cutoff energy ($\hbar\omega_D$) of 26±9 meV and 18±11 meV for samples F and C respectively. The comparatively large error is caused by high scatter and uncertainty associated with the evaluation of the energy position of the intrinsic emission band. Nonetheless, the numerical parameters are consistent with the value for the phonon cutoff energy of 22 meV obtained from measurements of the elastic constant of $CaWO_4$.[42] Overall these results indicate that the phonon interaction with the emitting WO_4^{2-} center is the dominating factor responsible for the line shift and temperature broadening of the $CaWO_4$ luminescence. We would like to point out that knowledge of the parameters of the phonon system is of importance for the development of cryogenic scintillation detectors and the present finding shows the possibility of making an assessment of these parameters from the results obtained by luminescence investigation.

B. Two-photon excited luminescence of $CaWO_4$

Intense laser excitation having a power density $>2\ \mathrm{mW\,cm^{-2}}$ in a spectral range significantly below the luminescence excitation edge (4.4 eV) stimulates blue luminescence in $CaWO_4$. Emission spectra for sample C were recorded under excitation with 2.58 eV photons (laser) and photons from a UV source (Fig. 7). The positions of the emission bands coincide, though the laser-induced luminescence spectrum exhibits noticeable narrowing compared with that obtained under high-energy excitation. This observation suggests that the emission is associated with cascade stimulation of intrinsic luminescence of $CaWO_4$. Luminescence measurements are known to be a convenient method for the detection of TPE phenomena in solids.[43] According to second-order perturbation theory the quadratic dependence of the emission intensity on the power density of the incident light signifies a TPE process.[44] Consequently the logarithm of the $CaWO_4$ blue luminescence intensity is proportional to the square of the power density of the incident light (Fig. 7, insert), and this quadratic dependence provides direct evidence that the emission is associated with a nonlinear two-photon stimulation process.

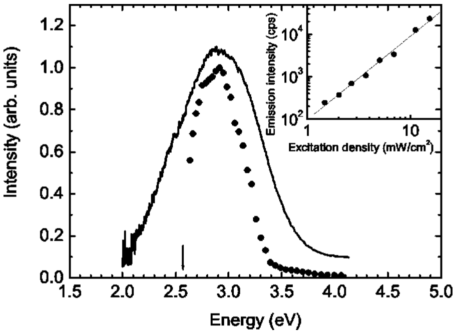

FIG. 7. Normalized luminescence spectra of $CaWO_4$ measured using different excitation at $T=300$ K. Circles, TPE luminescence (only the part of spectrum above the stimulation energy 2.58 eV, indicated by arrow, was measured); solid line, photoluminescence under excitation with 5.16 eV photons. The inset shows the intensity of the TPE luminescence in $CaWO_4$ as a function of the density of the incident light. The straight lines represents a fit to the experimental data points using a power law $I_{em}\sim I_{ex}^k$ with $k=2$.

The excitation spectrum of TPE luminescence (Fig. 8) was measured at two temperatures; at 300 K the spectrum exhibits an onset in the region of 505 nm (2.45 eV) and a peak at 465 nm (2.65 eV). Both the onset and peak shift to shorter wavelengths with decrease in temperature, and this "blue" shift is consistent with a thermal change in the energy band structure of the crystal, viz., broadening of the band gap.[26]

A search of the literature indicates that only a couple of two-photon studies have been conducted with tungstates.

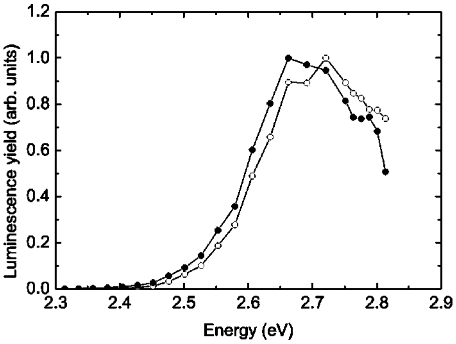

FIG. 8. Excitation spectra of TPE luminescence of $CaWO_4$ measured at $T=300$ (solid circles) and 77 K (empty circles).

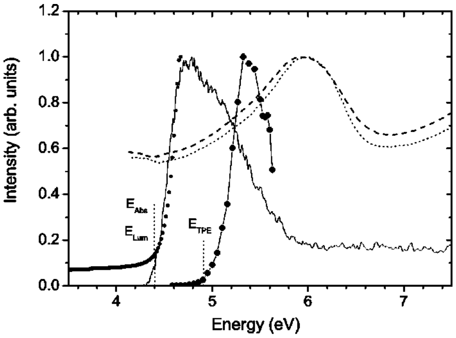

FIG. 9. Optical characteristics of the $CaWO_4$ crystal measured at $T = 300$ K. Line, excitation spectra of the photoluminescence monitored at 2.9 eV; dashed and dotted lines, reflection (300 and 10 K, respectively); circles, absorption; and circles with line, excitation spectrum of TPE luminescence. The abscissa value for the latter are twice the photon energy of the stimulation light. Vertical dashed lines indicate the spectral position of the onsets discussed in the text.

Unpublished results of measurements of two-photon absorption spectra were used by Abraham *et al.*[29] to estimate the energy band gap in $CdWO_4$, and Itoh *et al.*[25] examined the luminescence kinetics of $PbWO_4$ under two-photon excitation. In Fig. 9 we present a comparison of the results of TPE luminescence experiments with those obtained by one-photon spectroscopy of $CaWO_4$ (luminescence excitation, reflection and absorption spectra). From this figure, it is immediately evident that the excitation spectrum of TPE luminescence is located above the absorption edge and the onset of the luminescence excitation spectra (4.4 eV). However, the excitation spectrum is significantly below the 6.0 eV peak in the reflection spectrum which is usually interpreted as an exciton transition.[8,12] It is also of interest to compare these results with the experimental data obtained for other tungstates, namely, $CdWO_4$ and $PbWO_4$ (see Table I), from which it is evident that the position of the absorption edge consistently coincides with the onset of the luminescence excitation spectra. One can recognize a difference in the magnitude of the high-energy shift of the first reflection peak relative to the absorption edge: it is estimated to be 0.4–0.5 eV in $CdWO_4$ and $PbWO_4$ while being 1.6 eV in $CaWO_4$. This discrepancy persists also for the band-gap energy, and the general ordering of E_g is: $CaWO_4 > PbWO_4 > CdWO_4$. Finally, while the onset of the TPE process (Table I) correlates with the band gap energy in $CdWO_4$, there is a marked difference (almost 2 eV) in their positions for $CaWO_4$. This requires more detailed discussion concerning E_g.

To clarify this apparent inconsistency an analysis of the energy-band structure of $CaWO_4$ is required. It is commonly assumed that the $CaWO_4$ absorption edge is determined by electric dipole-allowed ${}^1A_1 \rightarrow {}^1T_2$ transitions. The ${}^1A_1 \rightarrow {}^3T_1$ or ${}^3T_2$ absorption transitions of lower energy are not observed in the excitation spectra due to strong spin selection violation. Recent computations of the electronic band structure of $CaWO_4$ (based on first principles) indicate that the top of the valence band and the bottom of the conduction band are predominantly defined by the $2p$ states of oxygen and the W $5d$ states, respectively.[12] Also, the calcium d states have noticeable density approximately 2 eV above the bottom of the conduction band, and the valence-band maxima and conduction-band minima are located at the Γ point. These calculations were performed using the one-electron approximation and did not account for exciton effects. Nevertheless, an excitonic model of the luminescence has been widely used to interpret the emission and excitation features of $CaWO_4$, and the first reflection peak of $CaWO_4$ at ~ 6 eV is usually interpreted as an exciton transition. The latter is based on measurements of the excitation spectra of phosphorescence[6] and thermoluminescence,[13] yielding a threshold formation energy of free carriers of ~6.5 eV and 7 eV respectively. The average value (~6.8 eV) has been adopted as the band-gap energy for the $CaWO_4$ crystal.[12]

In the above works[6,13] it has been suggested that the onset of excitation corresponds to the edge of Ca states since a hole residing on the tungstate group is paired with an electron in the Ca state. It should be noted that the phosphorescence is due to the recombination of spatially separated

TABLE I. Optical parameters of $CdWO_4$, $PbWO_4$ and $CaWO_4$ (data are given for $T = 300$ K unless otherwise indicated).

Parameter (eV)	$CdWO_4$	$PbWO_4$	$CaWO_4$
TPE onset (E_{TPE})	4.5±0.2 (Ref. 29)		4.9^a
Luminescence excitation onset (E_{lum})	3.7 (Ref. 54)	4.05 (Ref. 34)	4.4^a
	3.9 (Ref. 55)	3.7 (Ref. 15)	4.4 (Ref. 15)
Absorption edge (E_{abs})	3.8 (Ref. 56)	3.9 (Ref. 57)	4.4^a
	3.8 (Ref. 58)		4.3 (Ref. 59)
Reflection peak (E_{ref})	4.3 (Ref. 60)	4.3 (Ref. 61)	6.0^a
	4.3 (Ref. 55)	4.25^b (Ref. 32)	6.0 (Ref. 17)
Band-gap energy (E_g)	4.3 (Ref. 29)	4.6 (Ref. 17)	5.2 ± 0.3^a
	4.5^b (Ref. 17)	4.7^c (Ref. 13)	6.8 (Ref. 12)
			6.0^b (Ref. 17)

[a] Present study.
[b] LHeT.
[c] LNT.

charged particles and includes a long-lasting stage of migration to the emission centers. Since the model of tungstate luminescence assumes the emission center to be a closed-shell oxyanion complex WO_4^{2-} that can host only positive charge the above suggestion appears to be reasonably sound. Taking into account that *d* states of calcium exhibit noticeable density about 2–3 eV above the conduction-band minima[12] it is likely that published values of E_g are significantly overestimated.

Based on the foregoing arguments we suggest that the 6.0 eV peak reflects the joint density of the O $2p$ and W $5d$ states. This would support the interpretation that the exciton transition of $CaWO_4$ is located at energies less than 6.0 eV and that its oscillator strength is too small to be observed even at low temperatures (see Fig. 9). Additionally it should be noted that the first reflection peak in $CaWO_4$ is unusually broad and exhibits an extended low-energy tail, in contrast with the results of $PbWO_4$ (see Fig. 4 in Ref. 32).

Given the results of the measurements of TPE spectra, it should be possible to reconcile the spectroscopic results obtained by revising the value of the energy gap of $CaWO_4$. Because of inversion symmetry of the crystalline lattice, the direct band-to-band absorption transitions must be parity forbidden for the two-photon absorption of $CaWO_4$ at the Γ point.[27] From a classical perspective the TPE spectrum should start in the energy region just below the energy gap of the crystal[26] since a strong electron-phonon coupling results in a shift of the two-photon excitation edge towards lower energy.[45] Assuming that the difference between the onset of the TPE spectrum and E_g is about 0.3 eV, we suggest an estimate for the value of the energy gap of $CaWO_4$ to be $\sim$5.2 eV. The value of 0.3 eV is derived from the typical difference in the spectral position of the energy gap and the TPE spectrum onset in halide crystals.[26,45,46] Such a shift, unless quantified, introduces substantial uncertainty in the analysis and it may therefore be more prudent to specify a range between 4.9 eV and 5.5 eV for the energy gap of $CaWO_4$. Despite this large uncertainty, the main point we wish to make is that, on the basis of the interpretation of the experimental and theoretical results discussed above, the energy gap of calcium tungstate appears to be at a significantly lower value than the previously accepted value of 6.8 eV.

Let us finally consider how this finding agrees with the data on the energy structure of $CaWO_4$. With the new value of band gap taken as $\sim$5.2 eV the absorption band overlapping the first reflection peak can be interpreted as a direct transition at the Γ point starting from the valence band with predominantly O $2p$-states and terminating at W $5d$-states. The higher energy structure, appearing above 7 eV, is likely to be due to transitions from the valence band to the upper part of the conduction band dominated by Ca $3d$-states. A comparison of the calculated density of the states with the reflection spectra of $CaWO_4$ (see Fig. 16 in Ref. 12) also gives a fairly reasonable qualitative correlation when the threshold of the former aligns with this new value of E_g.

In the context of this discussion it is worth noting the results of a recent study of bismuth-doped $CaWO_4$ (Ref. 47) where the decay kinetics were found to undergo a significant change when the excitation energy was varied from 4.4 to 5.5 eV. The emission resulting from excitation in the Bi^{3+} absorption band (4.4 eV) is due to radiative decay of a WO_4^{2-} complex perturbed by Bi^{3+} ion whereas excitation at 5.5 eV results in emission that is characteristic of intrinsic emission of $CaWO_4$ caused by radiative decay of excitons self-trapped at regular WO_4^{2-} oxyanion complexes. The decay kinetics of the latter are complex, indicating that both types of emission centers are excited. The energy range above 5 eV was identified as a fundamental absorption region of calcium tungstate that is in line with our interpretation.

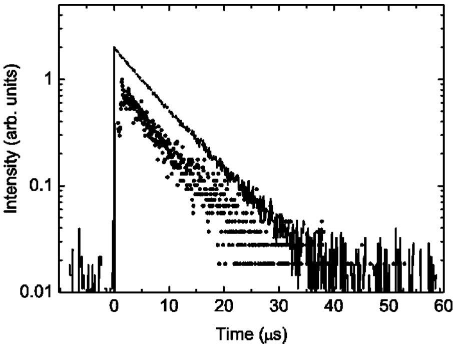

FIG. 10. Decay kinetics of the TPE luminescence of $CaWO_4$ measured at $T = 300$ K under excitation with 2.58 eV photons (sample C, dots) and 3.49 eV photons (sample F, line).

C. Luminescence decay time under two-photon excitation

As mentioned above, the measurements of the decay kinetics of TPE luminescence were performed using experimental apparatus in two laboratories with different excitation conditions: sample C was excited with 2.58 eV photons (power density 2–12 $mW\,cm^{-2}$) generated by an optical parametric oscillator while a third harmonic of a YAG laser ($E_{ex} = 3.49$ eV, power density 20–40 $mW\,cm^{-2}$) was used for excitation of sample F. Despite these differences, the decay kinetics of both samples are similar (Fig. 10), exhibiting a singular exponential decay with decay constants $\tau = 8.1 \pm 0.5$ μs and 7.6 ± 0.2 μs at 300 K for samples C and F respectively. These values are greater than that observed under particle excitation (5 μs at 300 K) by Beard *et al.*;[4] on the other hand Koepke *et al.*[48] resolved two decay components having time constants of 0.6 μs and 9.2 μs at room temperature using an excimer laser ($\lambda = 308$ nm) as excitation source, where the long lived component dominated the emission.

The measured luminescence decay time decreases significantly with increasing temperature (Fig. 11) in the elevated temperature region, while in the low-temperature region the changes are less pronounced. The decay kinetics retain a single-exponential character with decrease in temperature, and at 8 K the decay constant for sample F is 15.1 ± 0.2 μs. Given the model of the WO_4^{2-} molecular complex as the emitting center in $CaWO_4$ (implying that the lower ${}^3T_1$ and ${}^3T_2 \rightarrow {}^1A_1$ spin-forbidden transitions account for the intrinsic luminescence) the temperature dependence of the

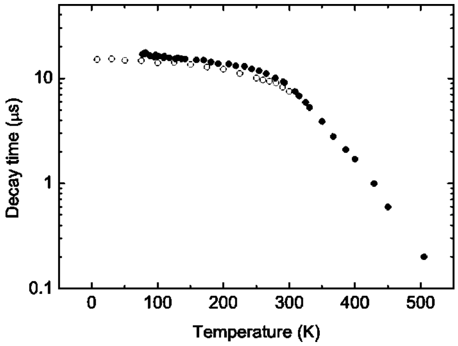

FIG. 11. Temperature dependence of the decay time of the TPE luminescence of $CaWO_4$ measured under excitation with 2.58 eV photons (sample C, solid circles) and 3.49 eV photons (sample F, empty circles).

kinetics of the luminescence can be interpreted in terms of a conventional three-level model of the emission center in tungstates.[10,24] Since our examinations do not extend below 8 K, in this study we did not endeavor to carry out modeling of the luminescence dynamics that is very sensitive to the value of decay constant in the milli-kelvin range; we refer to the model elaborated thoroughly by Mürk *et al.*[13] and more recently by Nikl *et al.*[14]

At 77 K the measured luminescence lifetime of sample C was found to be 17.0 ± 0.7 μs. This value is essentially the same as that reported by Grasser *et al.*[9] who used UV excitation, and comparable to that (~ 15 μs) measured under pulse x-ray excitation at 100 K.[49] It is noticeably that decay time of sample C is consistently larger than that measured for sample F at all measurement temperatures, as seen in Fig. 11.

The dependence of the $CaWO_4$ luminescence kinetics on excitation density is shown in Fig. 12. The emission decay time decreases gradually with an increase in the excitation intensity. Therefore we suppose that the difference in the emission decay constant observed is most likely to be caused by the difference in power density of the excitation light used in the two experiments (sample C, power density ~ 5 mW cm^{-2}, whereas a factor of 4–8 higher was used for sample F). The effect of the excitation density on the luminescence decay kinetics can be explained by assuming that the exchange interaction between elementary excitations introduces a competing nonradiative decay process.[50–53] Similar to that suggested by Itoh *et al.*[25] for lead tungstate the most probable mechanism of the exchange interaction under high-excitation density is Auger-decay of two excitons self-trapped on adjacent WO_4^{2-} oxyanion groups, which would result in the nonradiative relaxation of one self-trapped exciton and the decomposition of another.

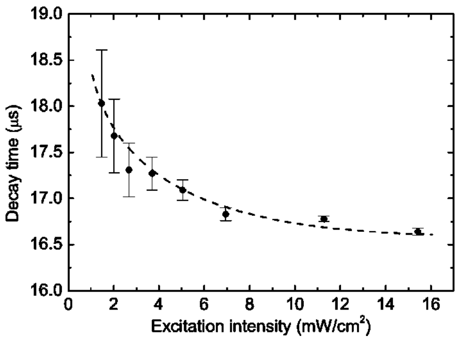

FIG. 12. Decay time of TPE luminescence of $CaWO_4$ as a function of the density of the excitation light at 2.58 eV, $T = 77$ K. Dashed line is shown for guide to the eye.

IV. CONCLUSIONS

In this study comparative investigations of the luminescence properties of calcium tungstate crystals have been performed using one- and two-photon excitation techniques. A detailed analysis of the temperature dependence of the luminescence spectra obtained under UV excitation shows that the observed high-energy shift of the $CaWO_4$ emission arises almost entirely from the position change of the intrinsic blue band, and not from the relative change in the intensity of the intrinsic and extrinsic bands, as suggested previously. The thermal changes in the intrinsic emission band of $CaWO_4$ are interpreted in terms of a model of electron-phonon interaction with the luminescence center. The luminescence kinetics of calcium tungstate examined under two-photon excitation were found to be fully consistent in terms of characteristics and decay constants with those observed in other luminescence experiments where high-energy excitation is used. This study has also demonstrated that the magnitude of the excitation density in the TPE luminescence experiment influences the kinetics of the luminescence decay, and this is due to an exchange interaction of elementary excitations similarly to the effect known for one-photon excitation.

The most significant result of the study is the outcome of a comparative analysis of the spectral characteristics of $CaWO_4$ obtained by investigation of the energy states that are inaccessible by traditional spectroscopy. From the results obtained we conclude that the previously used value of energy gap of $CaWO_4$ has been substantially overestimated and recommend that a value of $E_g = 5.2 \pm 0.3$ eV is adopted. This value is consistent with the main experimental results and also with the calculated scheme of energy band structure of the crystal. Finally, we suggest that the TPE luminescence technique has the advantage of allowing analysis of luminescence produced within the interior of large single-crystalline objects, whereas other luminescence methods can usually only probe a thin surface layer and consequently the luminescence measurements are strongly affected by surface effects. This capability is particularly important when considering the stringent requirements for quality inspection of cryogenic scintillating detectors that are to be used in search for rare events.

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[1] T.A. Edison, Nature (London) **53**, 470 (1896).

[2] F.A. Kröger, *Some Aspects of the Luminscence of Solids* (Elsevier, New York, 1948).

[3] J.R. Cook and K.A. Mahmoud, Proc. Phys. Soc. London, Sect. B **67**, 817 (1954).

[4] G.B. Beard, W.H. Kelly, and M.L. Mallory, J. Appl. Phys. **33**, 144 (1962).

[5] G. Born, A. Hofstaetter, A. Scharmann, and G. Schwarz, J. Lumin. **1/2**, 641 (1970).

[6] A.M. Gurvich, E.R. Il'mas, T.I. Savikhina, and M.I. Tombak, J. Appl. Spectrosc. **14**, 751 (1973).

[7] M.J. Treadaway and R.C. Powell, J. Chem. Phys. **61**, 4003 (1974).

[8] R. Grasser, E. Pitt, A. Scharmann, and G. Zimmerer, Phys. Status Solidi B **69**, 359 (1975).

[9] R. Grasser, A. Scharmann, and K.-R. Strack, J. Lumin. **27**, 263 (1982).

[10] G. Blasse, Struct. Bonding (Berlin) **42**, 1 (1980).

[11] P. Lecoq *et al.*, Nucl. Instrum. Methods Phys. Res. A **365**, 291 (1995).

[12] Y. Zhang, N.A.W. Holzwarth, and R.T. Williams, Phys. Rev. B **57**, 12 738 (1998).

[13] V. Mürk, M. Nikl, E. Mihokova, and K. Nitsch, J. Phys.: Condens. Matter **9**, 249 (1997).

[14] M. Nikl, P. Bohacek, E. Mihokova, M. Kobayashi, M. Ishii, Y. Usuki, V. Babin, A. Stolovich, S. Zazubovich, and M. Bacci, J. Lumin. **87-89**, 1136 (2000).

[15] V.V. Mikhailin, A.N. Belsky, I.A. Kamenskikh, V.N. Kolobanov, P.A. Orekhanov, I.N. Shpinkov, D.A. Spassky, and A.N. Vasil'ev, Nucl. Instrum. Methods Phys. Res. A **486**, 367 (2002).

[16] V. Nagirnyi *et al.*, Radiat. Meas. **29**, 247 (1998).

[17] V.N. Kolobanov, I.A. Kamenskikh, V.V. Mikhailin, I.N. Shpinkov, D.A. Spassky, B.I. Zadneprovsky, L.I. Potkin, and G. Zimmerer, Nucl. Instrum. Methods Phys. Res. A **486**, 496 (2002).

[18] M. Bravin, M. Bruckmayer, C. Bucci, S. Cooper, S. Giordano, F. von Feilitzsch, J. Höhne, J. Jochum, V. Jörgens, R. Keeling *et al.*, Astropart. Phys. **12**, 107 (1999).

[19] J. Ninkovic *et al.*, Nucl. Instrum. Methods Phys. Res. A (to be published).

[20] R.M. Hazen, L.W. Finger, and J.W.E. Mariathasan, J. Phys. Chem. Solids **46**, 253 (1985).

[21] E.V. Sokolenko, V.M. Zhukovskii, E.S. Buyanova, and Y.A. Krasnobaev, Inorg. Mater. **34**, 611 (1998).

[22] R. Grasser, M.I. Himam, A. Scharmann, and J. Ströde, Phys. Status Solidi A **130**, K225 (1992).

[23] R. Grasser and A. Scharmann, J. Lumin. **12/13**, 473 (1976).

[24] G. Blasse and G. Bokkers, J. Solid State Chem. **49**, 126 (1983).

[25] M. Itoh, M. Horimoto, and M. Fujita, J. Phys.: Condens. Matter **15**, 193 (2003).

[26] D. Fröhlich and B. Staginnus, Phys. Rev. Lett. **19**, 496 (1967).

[27] M. Inoue and Y. Toyozawa, J. Phys. Soc. Jpn. **20**, 363 (1965).

[28] M. Casalboni, F.D. Notaristefani, R. Francini, U.M. Grassano, C. Musilli, and R. Pizzoferrato, Nucl. Instrum. Methods Phys. Res. A **228**, 581 (1985).

[29] Y.B. Abraham, N.A.W. Holzwarth, and R.T. Williams, Phys. Rev. B **62**, 1733 (2000).

[30] Y.A. Hizhnyi and S.G. Nedilko, J. Lumin. **102-103**, 688 (2003).

[31] V.B. Mikhailik, I.K. Bailiff, H. Kraus, P.A. Rodnyi, and J. Ninkovic, Radiat. Meas. (to be published).

[32] M. Fujita, M. Itoh, M. Horimoto, and H. Yokota, Phys. Rev. B **65**, 195105 (2002).

[33] M. 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 (1995).

[34] M. Itoh and M. Fujita, Phys. Rev. B **62**, 12 825 (2000).

[35] G. Blasse and B. C. Grabmaier, *Luminescence Materials* (Springer-Verlag, Berlin, 1994).

[36] M. Bacci, S. Porcinai, E. Mihokova, M. Nikl, and K. Polak, Phys. Rev. B **64**, 104302 (2001).

[37] B. Henderson and G.F. Imbusch, *Optical Spectroscopy of Inorganic Solids* (Clarendon Press, Oxford, 1989).

[38] J.F. Suyver, J.J. Kelly, and A. Meijerink, J. Lumin. **104**, 187 (2003).

[39] D. Christofilos, S. Ves, and G.A. Kourouklis, Phys. Status Solidi B **198**, 539 (1996).

[40] R. Fletcher, Comput. J. **13**, 317 (1970).

[41] S. Teukolsky, W. Vetterling, and B. Flannery, *Numerical Recipes in C* (Cambridge University Press, Cambridge, England, 2002).

[42] M. Gluyas, F.D. Hughes, and B.W. James, J. Phys. D **6**, 2025 (1973).

[43] W. Kaiser and C.G.B. Garret, Phys. Rev. Lett. **7**, 229 (1961).

[44] R. Braunstein, Phys. Rev. **125**, 475 (1962).

[45] J.J. Hopfield and J.M. Worlock, Phys. Rev. **137**, A1455 (1965).

[46] M. Casalboni, C. Cianci, R. Francini, U.M. Grassano, M. Piacentini, and N. Zema, Phys. Rev. B **44**, 6504 (1991).

[47] V. Nagirnyi, A. Kotlov, L. Jönsson, M. Kirm, and A. Lushchik, Nucl. Instrum. Methods Phys. Res. A (to be published).

[48] C. Koepke, A.J. Wojtowicz, and A. Lempicki, J. Lumin. **54**, 345 (1993).

[49] V. Pankratov, L. Grigorjeva, D. Millers, S. Chernov, and A.S. Voloshinovskii, J. Lumin. **94-95**, 427 (2001).

[50] M.A. Terekhin, A.N. Vasil'ev, M. Kamada, E. Nakamura, and S. Kubota, Phys. Rev. B **52**, 3117 (1995).

[51] K. Kimura and J. Wada, Phys. Rev. B **48**, 15 535 (1993).

[52] M. Nikl, J.A. Mares, M. Dusek, P. Lecoq, I. Dafinei, E. Auffray, G.P. Pazzi, P. Fabeni, J. Jindra, and Z. Skoda, J. Phys.: Condens. Matter **7**, 6355 (1995).

[53] K. Kimura, J. Electron Spectrosc. Relat. Phenom. **79**, 43 (1996).

[54] M.J.J. Lammers, G. Blasse, and D.S. Robertson, Phys. Status Solidi A **63**, 569 (1981).

[55] M. Itoh (unpublished).

[56] M.M. Chirila, K.T. Stevens, H.J. Murphy, and N.C. Giles, J. Phys. Chem. Solids **61**, 675 (2000).

[57] M. Itoh, H. Yokota, M. Horimoto, M. Fujita, and Y. Usuki, Phys. Status Solidi B **231**, 595 (2002).

[58] V. Nagirnyi, M. Kirm, A. Kotlov, A. Lushchik, and L. Jönsson, J. Lumin. **102-103**, 597 (2003).

[59] S. Baccaro, P. Bohacek, A. Cecilia, V. Laguta, M. Montecchi, E. Mihokova, and M. Nikl, Phys. Status Solidi A **178**, 799 (2000).

[60] V. Nagirnyi, E. Feldbach, L. Jönsson, M. Kirm, A. Kotov, A. Lushchik, V.A. Nefedov, and B.I. Zadneprovski, Nucl. Instrum. Methods Phys. Res. A **486**, 395 (2002).

[61] I.N. Shpinkov, I.A. Kamenskikh, M. Kirm, V.N. Kolobanov, V.V. Mikhailin, A.N. Vasil'ev, and G. Zimmerer, Phys. Status Solidi A **170**, 167 (1998).