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Ultraviolet luminescence of ScPO$_4$, AlPO$_4$ and GaPO$_4$ crystals

Anatoly N Trukhin$^1$, Krishjanis Shmits$^1$, Janis L Jansons$^1$ and Lynn A Boatner$^2$

$^1$ Solid State Physics Institute, University of Latvia, 8 Kengaraga Street, LV-1063, Riga, Latvia
$^2$ Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6044, USA

E-mail: truhins@cfi.lu.lv

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Abstract
The luminescence of self-trapped excitons (STEs) was previously observed and described for the case of tetragonal-symmetry ScPO$_4$ single crystals. The subject band in this material is situated in the UV spectral range of ∼210 nm or ∼5.8 eV. In the present work, we are both expanding this earlier luminescence study and seeking to identify similar luminescence phenomena in other orthophosphate crystals, i.e., AlPO$_4$ and GaPO$_4$. These efforts have proven to be successful—in spite of the structural differences between these materials and ScPO$_4$. Specifically we have found that for AlPO$_4$ and GaPO$_4$, in addition to an α-quartz-like STE, there is a UV luminescence band that is similar in position and decay properties to that of ScPO$_4$ crystals. Potentially this represents an STE in AlPO$_4$ and GaPO$_4$ crystals that is analogous to the STE of ScPO$_4$ and other orthophosphates. The decay kinetics of the UV luminescence of ScPO$_4$ was studied over a wide temperature range from 8 to 300 K, and they exhibited some unusual decay characteristics when subjected to pulses from an F$_2$ excimer laser (157 nm). These features could be ascribed to a triplet state of the STE that is split in a zero magnetic field. A fast decay of the STE was detected as well, and therefore, we conclude that, in addition to the slow luminescence corresponding to a transition from the triplet state, there are singlet–singlet transitions of the STE. Time-resolved spectra of the slow and fast decay exhibit a small shift (∼0.15 eV) indicating that the singlet–triplet splitting is small and the corresponding wavefunction of the STE is widely distributed over the atoms of the ScPO$_4$ crystal where the STE is created.

(Some figures may appear in colour only in the online journal)

1. Introduction

ScPO$_4$ has a tetragonal zircon-type structure, and this material is frequently grouped together with the rare-earth orthophosphates (particularly those in the second half of the transition series) as well as tetragonal YPO$_4$. The orthophosphates in the first half of the rare-earth transition series have the monoclinic monazite structure and have been considered as a host ceramic material for radioactive waste storage [1]. The unit cell of the ScPO$_4$ zircon structure consists of four formula units, where each phosphorus atom is bonded to four nearby oxygen atoms, and each of the Sc atoms is surrounded by eight oxygen atoms [2]. The self-trapped exciton (STE) in ScPO$_4$ was initially described by Trukhin and Boatner [3, 4]. It exhibits a luminescence band in the UV range situated at ∼210 nm (∼5.6–5.9 eV). This band is broad even at liquid helium temperature with a FWHM of ∼0.7 eV.

This luminescence is excited above the intrinsic absorption threshold at 6.93 eV, belonging to the low energy side of the band at 8.93 eV. This luminescence is excited above the intrinsic absorption threshold at 6.93 eV, belonging to the low energy side of the band at 8.93 eV. The threshold obeys the Urbach–Toyozawa rule [3, 4] witnessed on direct creation of STEs. The specific nature of the triplet–singlet transitions was found for the STE luminescence in ScPO$_4$ based on the discovery of an effect related to triplet splitting in zero magnetic...
fields [3, 4]—i.e. a strong increase in the luminescence duration that is observed without a corresponding change in intensity. This luminescence is thermally quenched above 400 K [3, 4]. For a triplet state that is split in zero magnetic fields, the observation of faster components in addition to slow components is a characteristic feature. Since a slow component was clearly observed for the ScPO₄ STE luminescence, the identification and explanation of shorter components of the decay at liquid helium temperature is warranted. Additionally, since the details of the nature of the STE in ScPO₄ are still not fully understood, we have undertaken a search for similar luminescence effects in other orthophosphates—but with a crystal structure that differs from that of ScPO₄.

The materials AIPO₄ and GaPO₄ are orthophosphates with the α-quartz structure. In comparison with silicon dioxide α-quartz, the structure is a repetition of Al(Ga) and P tetrahedrons. For both AIPO₄ and GaPO₄ crystals, a self-trapped exciton was discovered [5, 6] that is similar to that of the self-trapped exciton of silicon dioxide α-quartz. The luminescence band of the STE is situated in the visible spectral range. One distinguishing property of self-trapped excitons in crystals with the α-quartz structure is the existence of two types of STE—one that is approximately parallel to the c-axis and another that is approximately perpendicular to the c-axis of the crystal. This STE is related to Si(Al, Ga)–O bond rupture with creation of a bond between such non-bridging oxygen and a bonding oxygen on the opposite end of two types of STE—one that is approximately parallel to the c-axis and another that is approximately perpendicular to the c-axis of the crystal. This STE is related to Si(Al, Ga)–O bond rupture with creation of a bond between such non-bridging oxygen and a bonding oxygen on the opposite end of the channel, characteristic for α-quartz structure [5, 6]. For SiO₂, AIPO₄ and GaPO₄ crystals, the thermal quenching parameters, related to the oxygen–oxygen bond strength [5, 6], are different, and a two-step thermal dependence of the intensity of the STE luminescence was observed with a corresponding thermal dependence of the STE luminescence polarization [6]. The polarization of the luminescence is weak when both STEs are not quenched, and after one type is quenched, the remaining STE polarization is high (~60%). In the case of GeO₂ crystals with the α-quartz structure, both STEs have an equal thermal quenching parameter, and as result, the polarization of the STE luminescence is weak. The STE luminescence in crystals with the α-quartz structure is attributed to singlet–singlet and triplet–singlet transitions. The latter is evident through the effect of zero field splitting of the triplet state that exhibits a slow decay (~1 ms at 80 K) and a singlet–singlet transition evidenced by the detection of a very fast component of the STE luminescence (~2–3 ns). The estimated value of the singlet–triplet splitting of the STE in crystals with the α-quartz structure is on the order of 0.2 eV—consistent with an STE wavefunction that is spread over many atoms and not simply localized. The energetic yield of the STE luminescence in crystals with the α-quartz structure is relatively high, and a level of 25–30% of the absorbed energy of the ionizing irradiation is emitted through STE luminescence.

In the present work, an extended study of the UV luminescence of AIPO₄ and GaPO₄ crystals is carried out with the goal of comparing the results for these materials to those obtained previously for ScPO₄. These new studies have led to the discovery of a UV band in both AIPO₄ and GaPO₄ crystals, and the decay of the band at 210 nm is similar to that found for ScPO₄. Thus, while these result suggest that the UV luminescent STE in the orthophosphates is related to complex phosphate–oxygen ions, we should note that for the AIPO₄ and GaPO₄ crystals, we were able to detect the 210 nm band only under electron beam excitation—while for ScPO₄ it was possible to detect this band for different excitations i.e., using a hydrogen discharge source with a vacuum monochromator, an excimer F₂ laser (157 nm) and certainly under cathodeexcitation. Additionally, we carried out new studies of the fast luminescence of the STE in ScPO₄ that we were not able to perform in previous investigations because of technical problems, and we had found such a fast luminescence practically coinciding with the slow STE luminescence. This is consistent with a small singlet–triplet splitting of the STE.

2. Experimental details

Single crystals of SCPO₄ were grown using a flux method [7] in tightly covered platinum crucibles containing lead pyrophosphate as the flux. After soaking for 16 h at 1360 °C, the crucibles were cooled at a rate of 1 °C h⁻¹ to 900 °C and then cooled directly to room temperature. The PB₂P₂O₇ flux was then dissolved in boiling HNO₃. The SCPO₄ single crystals had different dimensions that did not exceed ~80 mm². The other orthophosphate samples investigated were hydrothermally grown pure GaPO₄ and either pure or Sc/Ga-doped AIPO₄ single crystals.

The F₂ laser (model PSX-100, manufactured by Neweks, Estonia) used here had a pulse energy of about 0.5 mJ with a duration of 5 ns. The F₂ laser light was passed through a copper tube filled with flowing nitrogen. The excitation laser (2 × 2 mm² beam) was located 1 m from the sample. Crystalline silicon dioxide (α-quartz) with a low level of luminescence was used as a window to pass the excitation laser light, and the measurements were carried out with the use of a helium refrigerator. The temperature range in this case was 8–300 K. Luminescence detection was performed using a grating monochromator with a photomultiplier tube (H6780-04) with a 50-Ω resistive load. Optical filters were employed for reducing the laser light for luminescence detection, and an oscilloscope (Teledyne TDS 2022B) was utilized for obtaining the decay curves. Each curve was averaged over 128 pulses. The time-resolved spectra were measured by recording the decay curve for each point of the PL spectrum over two time ranges—one in the ns range and the other in the µs range. The measured curves are shown in the figures ‘as recorded”—therefore, they directly reflect the error level. The discharge of the excimer laser produces a strong stray current in the measurement circuit, that distorts the signal for a short time duration. A pulsed beam of 6 kV electrons was used for the CL and time-resolved experiments, and the frequency of the 0.1 µs pulses was controlled in the 50 Hz–20 kHz range. A double-grating monochromator was used to analyze the cathode luminescence spectrum, and the luminescence-kinetics curves were collected during
20 min of irradiation with a multichannel analyzer. A photomultiplier tube with an S20 photocathode was used. A tungsten x-ray tube (10 mA, 40 kV) was utilized to excite the photoluminescence spectra. Additionally, optical reflection spectra were measured using a vacuum monochromator and a windowless discharge from a hydrogen light source. The reflections were measured with respect to a gold mirror. For luminescence spectra measurements also a CCD with the Andor monochromator was used.

3. Results

The luminescence spectrum (cathodoluminescence), photoluminescence excitation (PLE) spectrum, absorption spectrum (in the range of the intrinsic threshold), and optical reflection spectra are presented in figure 1. It is shown that the PL at $\sim 210$ ($\sim 5.75$ eV) is excited exactly in the range of intrinsic absorption of ScPO$_4$ at 6.93 eV [3, 4]. The decrease in the PLE above 7.5 eV can be related to a decrease in the penetrations depth, and it coincides with the position of the intrinsic absorption band at 8.8 eV (as estimated using the reflection spectrum). This intrinsic band apparently belongs to an exciton because of the low electric photoconductivity with respect to higher energy [3]. For comparison, we have also presented the PL and PLE of Al$_2$O$_3$ doped with scandium [8].

There is a PL band at 5.5 eV that starts just below the intrinsic absorption threshold of sapphire ($\sim 9$ eV [8]). Believing initially that, in fact, the UV band is associated with scandium, we decided to measure the luminescence of another orthophosphate material—i.e., berlinite (AlPO$_4$) doped with scandium. We found UV luminescence, however, not only in AlPO$_4$ doped with scandium but observed an even more intense UV band in pure AlPO$_4$. Accordingly, any correlation with the presence of Sc in alumina is apparently coincidental. We found a UV band both under F$_2$ laser and cathodoexcitation; however, since the intensity of the luminescence was quite small under F$_2$ laser excitation, we subsequently performed a series of cathodoluminescence measurements using other orthophosphates and compared the results to the UV luminescence observed for ScPO$_4$ (see figure 2). The data presented in figure 2 show that all of the studied orthophosphates exhibit a UV band in cathodoluminescence. The spectra measured at 80 K are presented in figure 3. In the samples of AlPO$_4$ and GaPO$_4$, there is an increased intensity of the ‘normal’ STE in the visible range, and the UV luminescence persists in all of the samples. It is known that the decay of the UV luminescence of ScPO$_4$ changes on cooling from a time constant of about 0.1 $\mu$s at 290 K to 3–4 $\mu$s at 80–65 K [3, 4], and the decay kinetics curves obtained at low temperature are presented in figure 4.

In all of the measured orthophosphates, the UV band kinetics changed in a similar way as a function of the temperature. By carrying out a check of the
Comparison of cathodoluminescence decay kinetics of the UV band in different orthophosphates. For ScPO₄ under the excitation of an F₂ laser at 157 nm, we observe a slow component on the order of 10 ms. This decrease is artificial because we were not able to record over the entire time range. The actual PL intensity dependence on temperature corresponds to signals obtained with a CCD and the Andor monochromator. There are no real changes in intensity below 40 K (see figure 5), and a flat line is observed.

An estimate of the fast component response, based on the level of the detection limit, is 0.5 ns, and this component decay is independent of temperature. Other decay components are in the µs time range. At 8 K, the corresponding time constants are 1.5 and 10 µs. The latter decreases on heating while the other component increases on heating, probably due to the disappearance of corresponding transitions. Both components merge at 25 K. These three decay components are assigned to a triplet state splitting in zero magnetic fields, as noted previously [3]. In the inset of figure 5, the time-resolved spectra are shown for both the slow µs component and the fast ns component. Both components produced practically coinciding spectra. The spectrum for the ns component is shifted (see the figure 5 inset) to higher energy—about 0.1–0.2 eV. This shift potentially corresponds to the singlet–triplet splitting of the STE in ScPO₄.

### 4. Discussion

We have obtained new data on the spectral–kinetic properties of the STE UV luminescence in ScPO₄. We have identified similar UV luminescence in other orthophosphate crystals i.e., AlPO₄ and GaPO₄ in spite of the structural differences between these materials and ScPO₄. This represents an additional STE in AlPO₄ and GaPO₄ crystals which is analogous to the STE of ScPO₄. It exists beside previously studied STE in AlPO₄ and GaPO₄ crystals analogous to that of SiO₂ α-quartz [5, 6], possessing a luminescence band in the visible range of the spectra. The STE of α-quartz structured crystals is related to oxygen–oxygen bond creation, when the exciton is self-trapped. Such an exciton was not found in the structure of ScPO₄. The STE in ScPO₄ is related to the PO₄ molecular ion and therefore the second STE in AlPO₄ and GaPO₄ crystals is related to the PO₄ molecular ion as well. Possibly, such UV luminescence is a property of orthophosphates. Observation of the band at 210 nm after soldering, with use of orthophosphate acid, is an argument for that. However, the probability of such STE existence in AlPO₄ and GaPO₄ crystals is small, perhaps because of the high efficiency of exciton self-trapping in the style of α-quartz. Therefore, this ScPO₄-like STE we observe only in specific excitation with an electron beam, figure 2.

We have obtained new data on STE in ScPO₄ crystals. Specifically, in addition to the known [3] slow component of decay, we have obtained results for a fast (ns) component and two slower components (1.5 and 10 µs). The slow component...
decay is somewhat faster than the value obtained previously
(10 ms)—presumably related to technical factors as noted in
section 3. The fast (ns) component of the decay is ascribed to
singlet–singlet transitions and the slow components to
triplet–singlet transitions of the STE. It is difficult to
determine exactly a value of the decay that is not affected
by temperature, since in the range of temperatures below
200 K (where the intensity is practically unchanged),
the decay time constant is monotonically increasing on cooling.
Therefore, we can assume that at 150 K there is no additional
component of decay with the exception of the fast component,
and we can estimate the decay time constant at 100 K (1.5 µs)
where the occupation of the triplet state sublevels occurs
uniformly with temperature. The value of 1.5 µs exactly
coincides with one of the decay components at 8 K. This
last component of the decay exhibits an unusual temperature
dependence on heating. It becomes slower on heating and
then merges with a 10 µs component. The second component
exhibits a usual thermal dependence—accelerating on heating
and disappearing at 100 K. Accordingly, the behavior of
the triplet state STE splitting is normal for the case of
splitting in zero field [9, 10], where in addition to the slow
component (due to long a long residence on M = |0⟩), both
of the sublevels M = |−1⟩M = |1⟩ are radiative and decay at
8 K. (They possess two components in the µs range where
the sublevel is uniformly occupied.) Effects of the 1.5 µs
component slowing on heating may be due to occupation from
corresponding sublevels merging with another triplet sublevel
that is responsible for the 10 µs component.

The shift between the time-resolved bands corresponding
to the fast and slow components evidently corresponds to
a singlet–triplet splitting of the STE in ScPO₄. This shift is
small (0.1–0.2 eV) and would, therefore, correspond to large
spatial dimensions of the wavefunction of the STE.

An analytical model describing the peculiarities of the
luminescence decay kinetics was developed in [9] for the
case of quartz and GeO₂ cathodeexcitation. This model is
based on previous investigations of the STE in alkali halides (see references in [9]). At low temperatures, when the spin–lattice relaxation is frozen, the exchange between
the ZFS sublevel of the triplet state is ‘frozen’. Both values
of the zero field splitting D and E [9] could be real for the
UV luminescence of ScPO₄, and the observation of two
components in the µs range of time may show the existence
of zero field splitting with two radiative sublevels. Increasing
the temperature merges both sublevels—evident in figure 5
as the merging of τ₂ and τ₃. The sublevels occupation could then
be expressed using corresponding kinetic equations [9, 10],
written for the general case:

\[ \frac{dn_a}{dt} = - \left( \frac{1}{\tau_a} + \omega_b \right) n_a + \omega_a n_b; \tag{1} \]

\[ \frac{dn_b}{dt} = - \left( \frac{1}{\tau_b} + \omega_a \right) n_b + \omega_b n_a \tag{2} \]

where nᵢ (i = a, b) and τᵢ correspond to the population and
the radiative time constants of each sublevel, and ωᵢ is the
non-radiative transition rates from level i to the other level.

From these kinetic equations, two exponential components
can be obtained with two decay time constants τₛ and τᶠ,
where the temperature dependence is given by the following
expressions, [9, 10]:

\[ \frac{1}{\tau_S} = \frac{1}{2} \left\{ \frac{1}{\tau_a} + \frac{1}{\tau_b} + \omega_a + \omega_b \right\} \]

\[ - \left[ \left( \frac{1}{\tau_a} - \frac{1}{\tau_b} + \omega_a - \omega_b \right)^2 + 4\omega_a\omega_b \right]^{1/2} \]; \tag{3} \]

\[ \frac{1}{\tau_F} = \frac{1}{2} \left\{ \frac{1}{\tau_a} + \frac{1}{\tau_b} + \omega_a + \omega_b \right\} \]

\[ + \left[ \frac{1}{\tau_a} - \frac{1}{\tau_b} + \omega_a - \omega_b \right]^2 + 4\omega_a\omega_b \right\}^{1/2}. \tag{4} \]

As in previous cases [9, 10], the best fitting procedure was
obtained by introducing the Orbach process. If a low-lying
excited spin manifold exists near the ground-state manifold,
the Orbach process dominates the relaxation pathway. Given
an excited spin manifold at an energy Eₐ above the ground-state manifold, the spin system is promoted into the
excited spin manifold by the absorption of a phonon and
returns to another spin state of the ground-state manifold as
another phonon Eₜ of slightly different energy is emitted. For
low temperatures, the Orbach process relaxation rate varies
exponentially with inverse temperature: νₑ = exp(−Eₑ/(k_B*T)),
where k_B is the Boltzmann constant, νₑ is the temperature
independent rates of non-radiative transitions, and Eₑ is the
energy separation between each sublevel and the additional
state. If the two sublevels are degenerate, then νₑ/νₐ = 2, [9].

From a fitting of the experimentally determined data, the
resulting dependences τₛ = τ₁ and τᶠ = τ₂ are obtained and
presented in figure 5 with the appropriate parameters given
in the caption. A fitting for τ₃ was not performed. We should
emphasize that the fitting procedure is good over a wide range
of νₑ and Eₑ. (The larger the value of Eₑ, the smaller the
value of νₑ. Thus, some independent source of the values
of those parameters is required.) The nature of the ZFS
is determined by the crystal-field, spin–orbit interaction, and
spin–spin interactions. The parameters obtained for the UV
luminescence of ScPO₄ are: τₙ = τ₁ = 2 × 10⁻⁴ s; τₖ = τ₂ =
10⁻³ s; νₑ = 10⁷ s⁻¹; νₕ = 6 × 10⁷ s⁻¹ being close to the
relation νₑ/νₕ = 2; νₑ = 0.013 eV; Eₑ = 0.011 eV. τ₃ was
not used for the simulation because it merges together with
τ₂. The Eₑ values are high, but are in agreement with those
known from the literature (see e.g. [9, 10]). The difference
is too big for estimation of zero field splitting parameters
of triplet state D and E. For that, ODMR studies of STE in ScPO₄
are needed.

5. Conclusions

A UV band at 210 nm was observed in several orthophosphate
crystals that is ascribed to the PO₄ complex. The STE in
ScPO₄ exhibits singlet–singlet and triplet–singlet transitions.
The triplet state of the STE is split in zero magnetic fields producing two radiative sublevels and one metastable sublevel. The singlet–triplet splitting of the STE is about 0.15 eV, indicating that the corresponding wavefunction is spatially distributed with an electron component on the Sc ions and a hole component on the PO$_4$ complex. Observations of the UV band in other orthophosphates similar to the case of ScPO$_4$ lead us to assume that the PO$_4$ complex ion is responsible for the STE. The large spatial dimensions of the wavefunction lead to the hypothesis that the PO$_4$ complex is responsible for the hole component of the STE and the electron component is distributed in space. In AlPO$_4$ and GaPO$_4$ crystals, the center responsible for UV luminescence is apparently similar to the case of the STE in ScPO$_4$.

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