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Flux-grown $ScPO_4$ single crystals exhibit a number of luminescence bands in their x-ray-excited luminescence spectra - including sharp lines arising from rare-earth elements plus a number of broad bands at 5.6 eV, 4.4 eV, and 3 eV. The band at 5.6 eV was attributed to a self-trapped exciton (STE) [1], and it could be excited at 7 eV and higher energies. This luminescence is strongly polarised (P = 70 %) along the optical axes of the crystal and exhibits a kinetic decay time constant that varies from several ns at room temperature to ~10 μs at 60 K and up to ~1 ms at 10 K. It is assumed that the STE is localized on the Sc ions. The band at 3 eV can be excited in the range of the $ScPO_4$ crystal transparency (decay time = 3 to 4 μs.) This band is attributed to a lead impurity that creates different luminescence centers. At high temperatures, the band at 4.4 eV is dominant in the x-ray-excited TSL and afterglow spectra. Its intensity increases with irradiation time beginning at zero at the initial irradiation time. The 4.4 eV band does not appear in a fast process under a pulsed electron beam, showing that accumulation is necessary for its observation. A sample of $ScPO_4$ doped with vanadium exhibited a prevalent band at 4.4 eV at T = 480 K.
Keywords: Scandium orthophosphate, self-trapped exciton, luminescence.

INTRODUCTION

Scandium orthophosphate is a material with a number of promising applications due to its resistance to radiation, high chemical durability, hardness, and good optical properties. The material has potential applications in thermoluminescence dosimetry and frequency control and as an optical material and laser host. In particular, $ScPO_4$ in both pure and doped forms, is a promising phosphor/scintillator due to the rich nature of its luminescence spectra under [redacted] $ScPO_4$ in a series of experimental investigations.

The $ScPO_4$ crystal structure was determined in Ref. [1]. It can be viewed as consisting of eightfold-coordinated Sc ions with four oxygens at a short distance (0.2153 nm) and with four additional oxygen ions at a somewhat longer distance (0.2260 nm). Each of these discrete lengths are tetrahedrally oriented orthogonal to each other. Therefore, it can be assumed that the Sc ions form bonds with the oxygen ions through two sets of d orbitals ($d\gamma$ and d_ε) that are each tetrahedral and orthogonal to one another. The phosphorus ion is fourfold-coordinated with oxygen ions in a slightly distorted tetrahedron. Each unit cell contains four molecules. The structure is tetragonal zircon-type with unit cell parameters: a = 0.6574 nm and b = 0.5791 nm.

A combination of optical and photoelectric methods has previously been used by Trukhin [2] to investigate SiO_2, GeO_2, $AlPO_4$ and $GaPO_4$ crystals and to study their intrinsic properties. In the case of Sc-containing crystals, similar investigations were reported in Ref. [3] for Sc_2O_3 where it was shown that the intrinsic absorption edge of scandium oxide is determined by the d states of scandium, and no exciton states were found.

Single crystal of $ScPO_4$ were grown using a flux method [4] in tightly covered platinum crucibles containing lead pyrophosphate as the flux [1]. After soaking for 16 h at 1360 °C, the

crucibles were cooled at a rate of 1 °C/h to 900 °C and then directly to room temperature. The $Pb_2P_2O_7$ flux was then dissolved in boiling HNO_3. A series of $ScPO_4$ crystals from nominally pure to deliberately doped with Cu, Yb, Fe, V, Eu, Mn, and Tm with a doping level of about 1 wt % were studied. The crystals were of different dimensions not exceeding ~80 mm^2. Samples of desired thickness were cleaved with the use of a sharp chisel. All of the resulting sample plates were parallel to the optical axis, whose direction was determined by the use of a polarising microscope. The degree of polarization of the x-ray-excited luminescence was determined by the use of an analyser containing 8 silica glass plates of 1 mm thickness and maintaining the Brewster angle with respect to the luminescence beam.

RESULTS

The measured absorption spectra for different samples are presented in Fig. 1. It can be seen that, in spite of essential differences in absorption value, in the range of optical

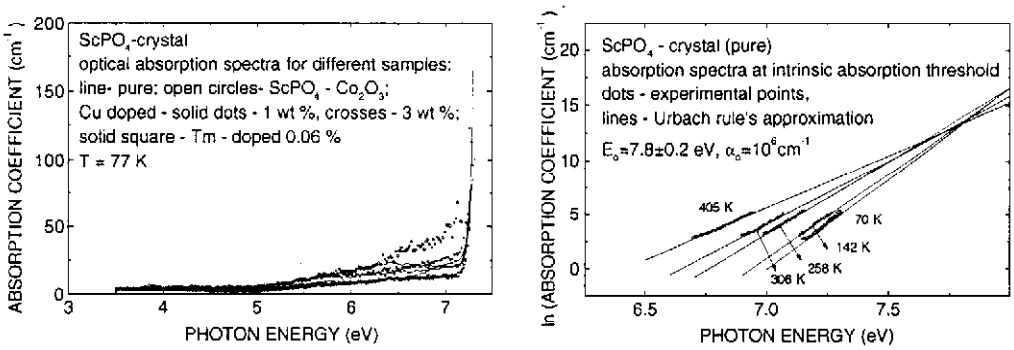


Fig.1
$ScPO_4$ crystal optical absorption spectra (left) and Urbach rule 's approximation (right).

transparency, the cut-off of transparency took place in the same energy range. Therefore, it was concluded that this represents the intrinsic absorption threshold, and attempts were made to check the correspondence of this threshold to the Urbach rule by measuring the absorption spectra in the range of the threshold using the thinnest samples at different temperatures. In Fig.1 (right) these data are presented in semilogarithmic coordinates, and it is apparent that there is good correspondence to the Urbach rule in the form corresponding to the model introduced by Toyozawa [7] for the case of strong exciton-phonon interactions. The equations expressing the Urbach rule are:

$$\alpha = \alpha_0 \exp[-\sigma(E_0 - E)/kT], \quad \sigma = \sigma_0 (2kT/\hbar\omega) \tanh(\hbar\omega/2kT) \quad (1)$$

The crossing point E_0 = 7.75±0.05 eV is located below the maximum of the broad structureless absorption band at 8.8 eV, whose position was estimated from the reflectivity spectra (not presented). Values of the parameter σ_0 = 0.63 and the crossing-point position both correspond to Toyozawa's criterion of a strong exciton-phonon interaction [7]. The value of $\hbar\omega$ = 70 meV may correspond to the range of optical phonons of $ScPO_4$. According to the theory [7], this may reflect the equality of the electron and hole effective mass involved in the exciton creation. It is significant that the Urbach's-rule parameters do not depend on impurities (See Fig.5) within experimental error.

The presently available single-crystal $ScPO_4$ samples exhibit a number of luminescence bands in the range available to our apparatus. In Fig. 2 (left), the x-ray-excited luminescence spectra obtained at different temperatures are presented. The outstanding questions are: (1.)

What is the nature of a given luminescence band - intrinsic or extrinsic? and (2.) By what processes is the luminescence excited?

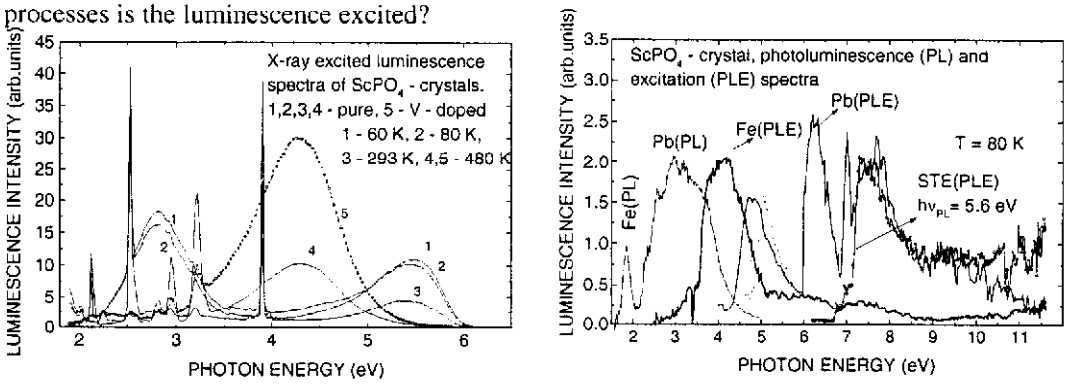
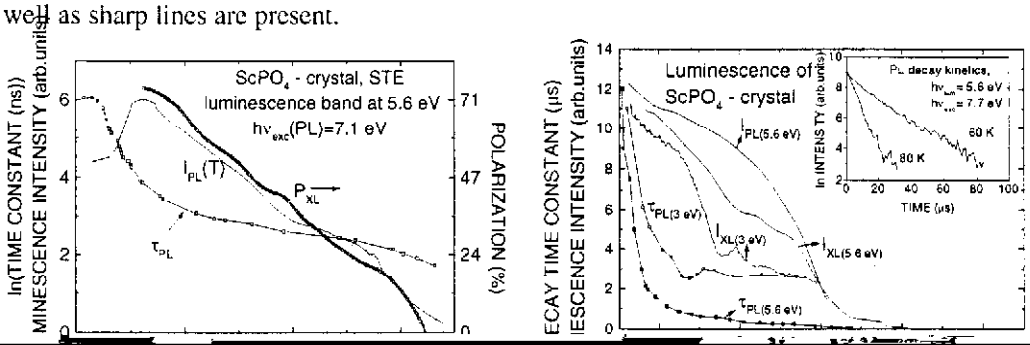


Fig.2

$ScPO_4$ single-crystal luminescence spectra: (left) x-ray excited spectra; (right) - photoluminescence). Fe - luminescence of the iron center; Pb - assumed to be lead-related luminescence. Points at 5 eV correspond to the 3.5 eV sub-band excitation spectrum, but the line at 2.8 eV is a sub-band of the Pb-labelled curves. STE – self-trapped exciton luminescence [12].

In Fig.2, several sharp lines are seen that apparently belong to rare-earth elements, and these will not be considered further in this preliminary report. Primary attention here will be paid to an examination of the host materials' luminescence properties. The first consideration for the host-material luminescence would be excitation in only the intrinsic absorption range. The candidates for the intrinsic effects are the two bands at 5.6 eV and at 4.4 eV. In Fig.2 (right), the excitation spectra for the luminescence band at 5.6 eV are compared with the excitation spectra of other bands. This band can only be excited in the intrinsic range. Other luminescence bands shown in the figure have excitation bands below 6.9 eV. These exist in the "as-received" crystals and, therefore, can be ascribed to extrinsic luminescence centers. Now let us consider the other data for the 5.6 eV band. These are: the temperature dependence of the photoluminescence (PL) intensity, the PL decay time constant, and the luminescence polarization (Fig.3). The dependencies can be divided into three ranges: First, a range at 10 K, second a range at 40 to 270 K, and a third range at 270 to 400 K. In the first range, τ increases whereas the intensity decreases. This effect requires further study since a self-consistent explanation is not apparent at this time. In the second and third ranges, there is a good correspondence between $\tau(T)$, $I(T)$, and $P(T)$; and these ranges differ in the estimated activation energy. The third range is the range of the 5.6 eV-band thermal quenching. The activation energy for thermal quenching is estimated to be 0.22 eV. From the second temperature range, we estimate an activation energy of about 0.02 eV. In the following, we argue that the thermally activated reorientation of self-trapped excitons (STE) leads to a loss of polarization, decreasing the STE life time and a lost of amplitude due to interactions with defects. The degree of polarisation at 60 K is 70 to 10 % and the electric field vector of the luminescence is parallel to the optical **c** axe of the $ScPO_4$ crystal. The 5.6 eV band cannot be excited in a pure electron-hole recombination process since it was not observed in the thermo-stimulated luminescence. This provides good evidence for the excitonic nature of this luminescence band. In Fig.4 (right), the thermoluminescence curves are presented, and in Fig.4 (left), the thermoluminescence spectra are presented and compared to the x-ray-excited spectra. Together with the thermoluminescence studies, the thermo-stimulated electric depolarisation of the x-ray-excited sample has been obtained (not shown). For all of the TSL

peaks. we observed peaks in the depolarisation current. Therefore, the thesis of electron-hole recombination is valid. In the thermoluminescence spectra, broad bands at 3.4 and 4.4 eV as well as sharp lines are present.



Temperature dependencies for different luminescence band intensities and decay time constants as well as the 5.6 eV band polarisation in $ScPO_4$ crystals. In insertion PL decay kinetics.

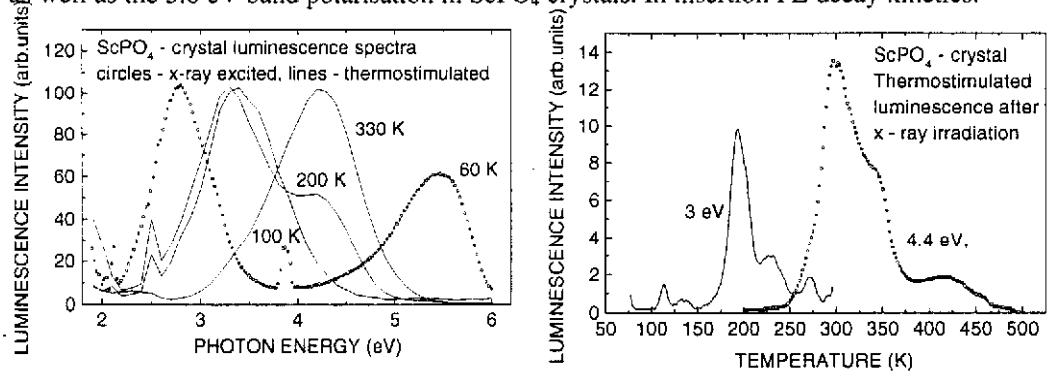


Fig.4

Thermostimulated luminescence (TSL) curves (right) and TSL luminescence spectra (left) for $ScPO_4$ crystal. (Monochromator slits were fully open).

The broad band at 3 eV that is visible in the PL and that was excited in the range of optical transparency of the $ScPO_4$ crystal (excitation at 5 eV with two sub-bands) falls into two bands that exhibit: different temperature dependencies of their intensity, separated excitation bands (Fig. 2), and different roles in thermostimulated luminescence. The low-energy sub-band is not seen in the TSL spectra. However, they may belong to the same impurity (probably lead), which creates luminescence centers of different types. The band at 3 can be excited in the range of the $ScPO_4$ crystal transparency. It life time (τ) is about 3 - 4 μs for excitation in this range. Ther is a correlation between τ of this band and that of 5.6 eV band for excitation in the intrinsic absorption range by either photons or x-rays (Fig.3). This effect is accounted for by overlapping of the 5.6 eV band with the excitation band of the blue luminescence. Therefore, 5.6 eV luminescence excites the centers responsible for luminescence at 3 eV. The same effect was observed for the red luminescence of an iron impurity in $ScPO_4$ crystals. (Fig.2).

At high temperature, the luminescence at 4.4 eV becomes dominant in the x-ray-excited and TSL spectra (Fig.4) as well as in the afterglow. The TSL and afterglow with the 4.4 eV band can be excited in the intrinsic range of the $ScPO_4$ crystal, however the excitation

transparency range gives only TSL, and we did not observe the afterglow. So, below optical gap this luminescence is not excited directly.

The luminescence intensity increases with the time of irradiation almost from zero at the initial time. The kinetics of this increase depend on the temperature. For room temperature, they are slow - increasing with saturation in one hour under x-rays. At higher temperatures (510K), this increase takes place in few minutes followed by a decrease (Fig.5). Such kinetics correspond to complex

of the crystal. The polarisation degree and orientation are independent of the conditions of observation (x-ray or TSL or afterglow in the time range of tens of minutes). The afterglow time dependence is changed with a change of the temperature from $t^{-0.3}$ at 330 K to t^{-2} at 510 K. A sample that was deliberately doped with vanadium exhibited the most predominant band at 4.4 eV at high temperature (480 K) in the PL, x-ray excited luminescence, and TSL. Impurities such as Eu^{3+} and Mn^{2+} reduce the luminescence band at 4.4 eV but it does not disappear in samples not deliberately doped with vanadium.

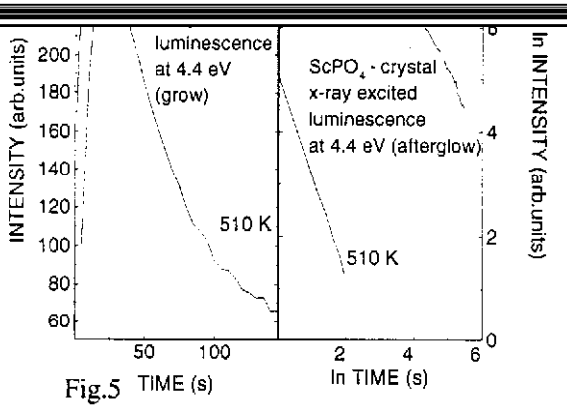


Fig.5 Kinetics of 4.4 eV luminescence band in $ScPO_4$ crystal.

Impurities can play a competitive role with respect to charge carrier trapping.

DISCUSSION

There is a small shift between the position of the intrinsic absorption threshold and the photoconductivity threshold, and thus, we can conclude that there is exciton creation by light in this energy range (See Fig.6). This is in agreement with the observation of the host-material luminescence band at 5.6 eV, which is excitable in the intrinsic absorption range only and cannot be excited in a pure

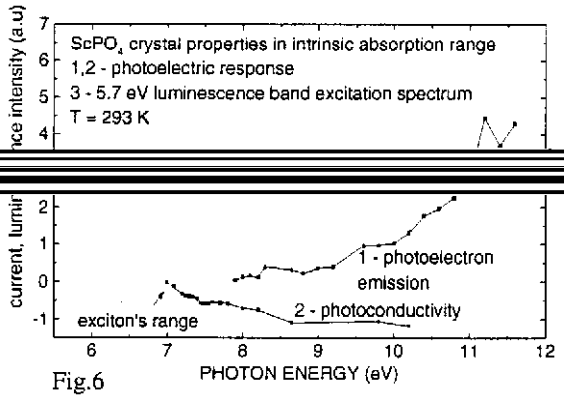


Fig.6 Intrinsic properties of $ScPO_4$ crystal [12].

about 1 eV, therefore it can be ascribed to a self- trapped exciton (STE). A transfer through hopping mobility was not verified because of the very effective mechanism of energy transfer through ultraviolet luminescence reabsorption by, for example, iron and lead centers.

Measurements of the degree of polarization of the luminescence band at 5.6 eV and its temperature dependence show that the orientation of the STE can be changed by temperature. We can determine that the energy gap in $ScPO_4$ crystal has a value of 7.2 eV at 293 K from the data shown in Fig.6. The lack of STE luminescence in TSL shows that there is no charge-

carrier self-trapping or, if such process self-trapping or, if such process exist, there is no creation of a STE from the recombination of a free carriers or there is a sufficiently high barrier for charge-carrier self-trapping.

The stability of the intrinsic absorption-tail position, in spite of a vanadium impurity substitution for phosphorus, suggests that scandium states are responsible for the tail. In previously studied $AlPO_4$ and $GaPO_4$ crystals [8], the tail positions differ in each case. Therefore the PO_4 energetic states should be higher. The d orbital of Sc can be responsible for lowest excited states of the $ScPO_4$ crystal. This is consistent with the point that the STE is localised on Sc ions since its luminescence parameters correspond well with those reported for the Sc-impurity luminescence in Al_2O_3 [11].

The growth of $ScPO_4$ crystals with the use of a lead-containing material assures some contamination with lead in the final samples. We have ascribed the broad luminescence band to lead impurities because of the similarity with the luminescence of lead oxide glasses as well as with the luminescence of lead phosphates [10]. There are at least two types of luminescence centers to participate in different recombination processes. One with a band at 2.8 eV is not seen in the afterglow at 80 K (it cannot participate in the TSL peak at 200 K because it is thermally quenched at that temperature). Only centers responsible for the sub-band at 3.4 eV participate in the recombination processes. If we also assume that, in the case of $ScPO_4$ crystals, the Pb^{++} ions are the origin of all these centers, then different surroundings of these ions would give different trapping capabilities for the charge carriers.

Finally we comment on the nature of the luminescence band at 4.4 eV that appears only in the electron-hole recombination process. It is detectable from RT to 550 K. The fact that it can be excited in the range of transparency of the $ScPO_4$ crystal by the creation of a TSL peak at 480 K shows the extrinsic nature of this luminescence. Also, the correlation with the vanadium impurity supports this point of view. However this band is seen in all of the available samples regardless of their purity. It can be excited with a high energetic yield by continuous excitation with a high-density electron beam. This band belongs to an anisotropic defect, which cannot be excited directly in range of the crystal's transparency. Therefore, it exist only under high-energy excitation.

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