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Luminescence of Pb²⁺ in SrTiO₃

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The luminescence of $Sr_{1-x}Pb_xTiO_3$ powder samples is reported for several values of x. In all cases, except $x = 1$, the self-trapped exciton (STE) emission of $SrTiO_3$ is accompanied by an overlapping emission band at lower energy due to a center involving Pb^{2+}. The relative emission intensities of these individual bands vary with temperature and Pb^{2+} concentration. The bandgap energy is decreased in the samples doped with 50% and 100% Pb^{2+}, which is explained by the increased Pb^{2+} wave-function overlap. It is concluded that the luminescence due to Pb^{2+} centers involves decay from conduction band levels to the ground level of Pb^{2+}. This level appears to be situated just above the valence band. A broad-band luminescence of the same origin is found in $PbTiO_3$. In addition, evidence for free exciton emission is observed.

Introduction

The luminescence properties of the Pb^{2+} ion ($6s^2$ configuration) are diverse. Usually they are described by the $^1S_0-^3P_{0,1}$ transitions which originate from the $6s^2-6s6p$ interconfigurational transition.[1] It has been shown that the Jahn–Teller effect in the ground state complicates the situation considerably.[2] On the other hand, it is known that a complication of different origin arises if the excited states of the host lattice or the surroundings of the Pb^{2+} ion are at about the same energy as the levels of the $6s6p$ configuration of the Pb^{2+} ion. Examples are the Pb^{2+} ion in $CaWO_4$ and the compounds $PbMoO_4$ and $PbWO_4$. The optical transitions are now characterized as charge-transfer transitions.[3]

In this view, it seems interesting to study the luminescence of Pb^{2+} in the perovskite $SrTiO_3$. In the perovskite $CaZrO_3:Pb^{2+}$ the optical transitions of Pb^{2+} are still of the $6s^2-6s6p$ type, since the bandgap of $CaZrO_3$ is very large.[4] The bandgap of $SrTiO_3$ is much smaller.[5] The bottom of the conduction band of $SrTiO_3$ consists mainly of Ti 3d orbitals. It will be interesting to find how the excited levels of the Pb^{2+} ion are situated relative to this conduction band. An advantage of the system $Sr_{1-x}Pb_xTiO_3$ is that this can be investigated for several values of x and even for $x = 1$ ($PbTiO_3$).

The luminescence of $SrTiO_3$ is known and has been ascribed to self-trapped exciton recombination on the titanate octahedron. The energy band structures of $SrTiO_3$ and $PbTiO_3$ have recently been reported.[6]

Experimental Section

Polycrystalline powders of composition $Sr_{1-x}Pb_xTiO_3$ (weighed in values: $x = 0, 2 \times 10^{-3}, 7 \times 10^{-3}, 2 \times 10^{-2}, 6 \times 10^{-2}, 50 \times 10^{-2}, 1$) were prepared by firing intimate mixtures of $SrCO_3$ (Merck, E.L.), $PbCO_3$ (Merck, Z.A.), and TiO_2 (freshly prepared from ammonium titanyl oxalate, Johnson Matthey, specpure) in air
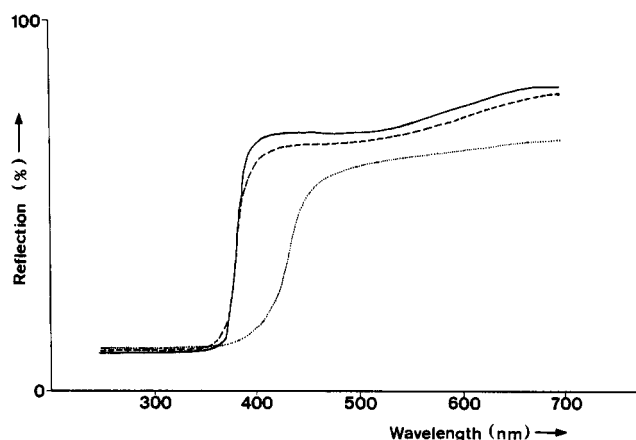

Figure 1. Diffuse reflectance spectra at RT of $Sr_{1-x}Pb_xTiO_3$, for $x = 0$ (solid line), $x = 6 \times 10^{-2}$ (dashed line), and $x = 1$ (dotted line).

for 2 h at 1200 °C and 2 h at 1300 °C, followed by an additional grinding and firing in oxygen for 2 h at 1100 °C. For $PbTiO_3$ an excess of 8% PbO was weighed in, and a firing procedure of 1 h at 350 °C and 4 h at 750 °C in air was sufficient. The samples were checked to be single-phase by X-ray diffraction. The lead-containing samples were yellowish.

Diffuse reflection spectra were measured with a Perkin-Elmer Lambda 7 spectrophotometer. Luminescence spectra were recorded with a SPEX DM3000F spectrofluorometer equipped with a liquid helium cryostat. All excitation spectra were corrected for the xenon lamp intensity, and emission spectra for the photomultiplier response. Decay times were measured using a Lambda Physik LPX 100 excimer laser (XeCl) as an excitation source. The excimer laser pumps a tunable dye laser, Lambda Physik LPD 3000 (DMQ). A pulse generator triggered this laser and a Tektronix 2440 oscilloscope simultaneously.

Results

The diffuse reflectance spectra of the diluted titanate systems $Sr_{1-x}Pb_xTiO_3$ ($x \le 6 \times 10^{-2}$) resemble that of undoped $SrTiO_3$ within experimental error; see Figure 1. $PbTiO_3$ shows a shift in absorption to longer wavelengths relative to the $SrTiO_3$ samples. This indicates a smaller bandgap. By extrapolating the steep slope in the reflectance spectra to the level of no absorption, bandgap energies were estimated to be 3.1 eV in the case of $SrTiO_3$, and 2.8 eV in the case of $PbTiO_3$. These results are in agreement with bandgap energies reported earlier.[5,6] For

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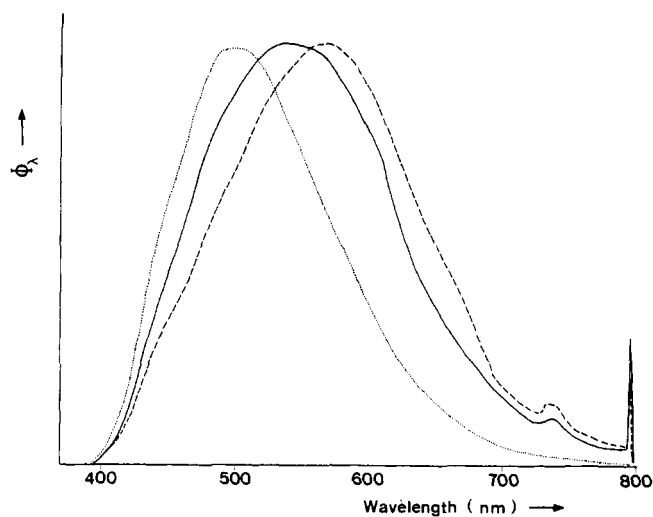
Figure 2. Emission spectra of $Sr_{1-x}Pb_xTiO_3$ ($x = 2 \times 10^{-2}$) excited at 315 (solid line) and 350 nm (dashed line), at 4.2 K. The spectrum of $SrTiO_3$ (dotted line) is shown for comparison.
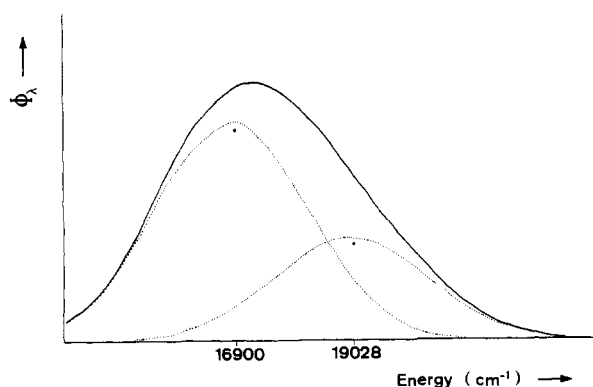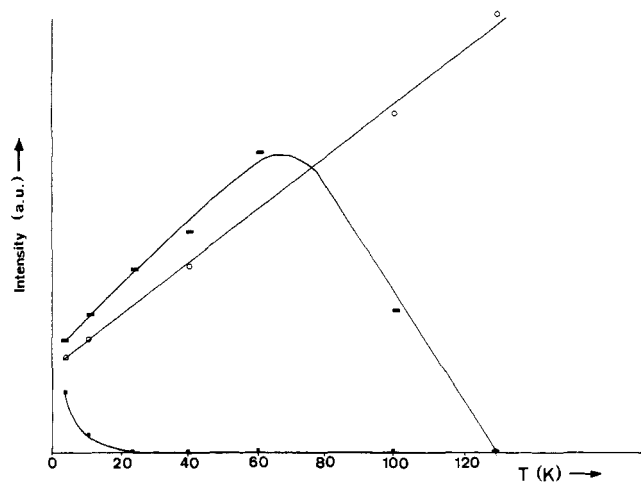

Figure 3. Gaussian fit of the emission spectrum of $Sr_{1-x}Pb_xTiO_3$ ($x = 2 \times 10^{-2}$) excited at 350 nm at 4.2 K into two components.

$SrTiO_3$ doped with 50% Pb^{2+}, the bandgap was estimated to be 2.9 eV.

Figure 2 shows the emission spectrum of undoped $SrTiO_3$ when the sample is excited at 350 nm at 4.2 K. The moderately intense emission band is broad and has a maximum at 500 nm. This is consistent with results reported by Aguilar[7] et al.

The introduction of lead on strontium sites has a striking influence on the luminescence of $SrTiO_3$. Emission spectra of $SrTiO_3$ doped with 2% Pb^{2+} are shown in Figure 2, recorded at an excitation energy of 315 and 350 nm at 4.2 K. In all investigated samples $Sr_{1-x}Pb_xTiO_3$ ($x \leq 0.5$), the emission band is broadened and is shifted to lower energy. The emission spectra as well as the excitation spectra of all Pb^{2+}-doped $SrTiO_3$ show maxima at similar wavelengths. In addition, the emission spectra show a sharp line close to 800 nm, which is due to a Cr^{3+} impurity $^2E \rightarrow {}^4A_2$ emission, and a broader impurity emission at about 730 nm, which is probably due to the Mn^{4+} $^2E \rightarrow {}^4A_2$ transition.[8]

On an energy scale, the emission band of doped $SrTiO_3$ seems to be asymmetric, indicating more than one contributing site. Figure 3 shows that the broad band can be resolved into two Gaussians with maxima at 19 028 and 16 900 cm^{-1}. The former involves the self-trapped exciton

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Figure 4. Relative intensities of the 525 (black boxes, titanate), 590 (black rectangles, Pb^{2+} center) and 795 (open circles, Cr^{3+}) nm emission as a function of temperature of $Sr_{1-x}Pb_xTiO_3$ ($x = 2 \times 10^{-2}$) excited at 350 nm.
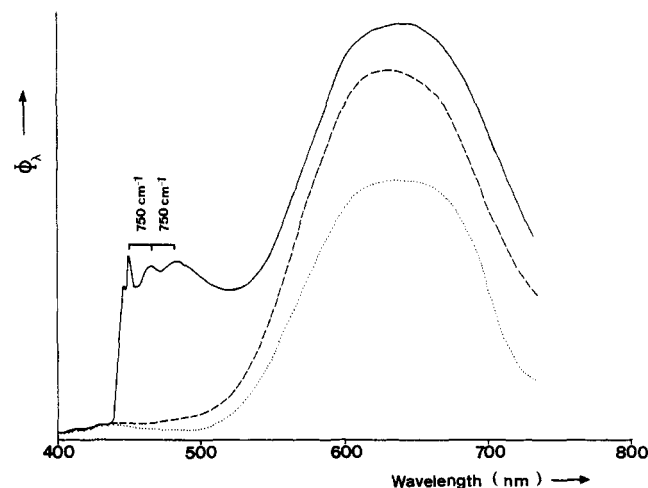
Figure 5. Emission spectrum of $PbTiO_3$, excited at 350 nm and recorded at 4.2 K (solid line), 30 K (dashed line), and 90 K (dotted line).
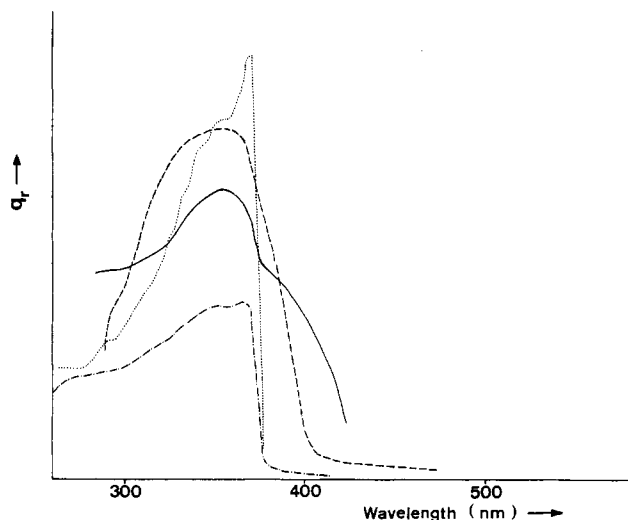
(STE) emission of the titanate group and is preferentially excited with an excitation energy of 315 nm. The latter is ascribed to centers involving Pb^{2+} and is preferentially excited at 350 nm. The higher emission intensity at shorter wavelength suggests that the surface layer contains less lead than the bulk.

At higher temperature, the STE emission is quenched in favor of the Pb^{2+} involved emission. Whereas the STE emission is quenched at 35 K, the intensity of the lower energetic band increases up to 80 K and vanishes at 100 K (see Figure 4). The emission intensity due to Cr^{3+} increases as a function of temperature, in contrast to the Mn^{4+} emission intensity. This luminescence is quenched at 100 K.

The emission spectrum of $PbTiO_3$ shows differences with Pb^{2+}-doped $SrTiO_3$ (see Figure 5) and is very complicated. The luminescence intensity is an order of magnitude weaker than that of $SrTiO_3$ doped with lead. It is difficult to prove whether all features really belong to $PbTiO_3$, or that they are due to the fact that powder samples are used. Nevertheless, for several different samples, the same results were obtained. Starting at the shorter wavelength side, the following features can be distinguished:

Figure 6. Excitation spectra of the luminescence of $Sr_{1-x}Pb_xTiO_3$ for $x = 2 \times 10^{-3}$ (dotted line), $x = 2 \times 10^{-2}$ (dashed/dotted line), $x = 0.5$ (dashed line), and $x = 1$ (solid line) recorded at 4.2 K. The spectra are recorded at the maxima of the corresponding emission bands.

(i) A sharp line at 450 nm, coinciding with the bandgap energy. It is obvious to ascribe this line to free exciton emission.

(ii) A broad band with structure at 460 and 485 nm. It is tempting to assign these to phonon replicas of the free exciton emission because of the equal energy difference of 750 cm⁻¹, which equals the titanate stretching frequency. However, the emission intensity is too high to be due to these replicas solely. A contribution of bound excitons may also be involved.

(iii) A moderately intense broad band at 650 nm. Whereas the shorter wavelength features disappear rapidly by raising the temperature above 4.2 K, this band vanishes only slowly. At 100 K the intensity has decreased to 50%. It seems obvious that the band has an origin which is comparable to the Pb²⁺-involving emission band in SrTiO₃: Pb²⁺.

Figure 6 gives the excitation spectra of the emissions of $Sr_{1-x}Pb_xTiO_3$ for $x = 2 \times 10^{-3}$, 2×10^{-2}, 0.5, and 1, at 4.2 K. The steep character on the lower energetic site of the excitation spectrum of $Sr_{0.998}Pb_{0.002}TiO_3$ has vanished in the excitation spectrum of PbTiO₃. An intermediate case is shown in the spectrum of SrTiO₃ doped with 50% Pb²⁺.

Decay measurements performed on the 520-nm emission of $Sr_{0.98}Pb_{0.02}TiO_3$ and on the 450- and 650-nm emissions of PbTiO₃ indicate a decay time less than 15 ns, which may involve nonradiative decay.

Discussion

The luminescence of SrTiO₃ is well-known and has been ascribed to a self-trapped exciton on the titanate octahedron.[7] By introducing lead, one can expect luminescence from a different origin. The titanate octahedra can be influenced by neighboring Pb²⁺ ions or the Pb²⁺ ions can be active centers.

By comparing the luminescence of pure SrTiO₃ with the Pb²⁺-diluted SrTiO₃ an emission band consisting of two contributions is observed. The shorter wavelength contribution has a maximum at 525 nm and is ascribed to the self-trapped exciton on the titanate octahedron. The second contribution is ascribed to centers involving Pb²⁺. At 4.2 K, in the diluted samples, the first contribution

dominates. At higher temperature, the intensity contribution of the titanate decreases, and the contribution of the lead involved center increases. Above 30 K, the emission band can be described by one Gaussian, with a similar maximum as the Pb²⁺-involved luminescence component at low temperatures. Further, a higher lead content results in a higher intensity contribution from the lead-involved center. In the broad emission band from PbTiO₃ around 650 nm, no titanate component is observed and this luminescence can only be ascribed to Pb²⁺-involved centers.

It is well-known that the quenching of the self-trapped exciton emission is due to energy migration to quenching sites. This is most easily shown by adding some Cr³⁺. The luminescence intensity due to Cr³⁺ increases at the cost of the self-trapped exciton emission intensity.[8] In this work the same trend is observed for the Cr³⁺-impurity emission and the Pb²⁺-involved emission. From the further increase of the Cr³⁺ emission intensity (Figure 4), it seems that the quenching of the Pb²⁺-involved emission is also due to thermally activated detrapping of this center. In PbTiO₃ the quenching temperature is even higher.

In previous work it has been proposed that the optical transitions in such Pb²⁺-involved centers are due to charge-transfer transitions involving Pb²⁺–M (d⁰) charge transfer.[3] Since the self-trapped state can be described with an energy level just below the conduction band and the Pb²⁺-involved emission is of lower energy than the STE emission, the Pb²⁺ ground level is assumed to be situated just above the valence band (mainly oxygen 2p orbitals). The Pb²⁺ ion does not, or only slightly, seem to participate in the valence band. This is consistent with band structure calculations performed recently on the perovskite lead zirconium titanate (PZT).[6] At a sufficiently high lead concentration, the Pb²⁺ wave-function overlap will result in an upper valence band. From the excitation spectra (Figure 6) the differences in absorption edge are shown for several concentrations Pb²⁺. The sample doped with 50% Pb²⁺ shows a decrease in bandgap energy of 0.2 eV. In PbTiO₃ the bandgap energy is even more reduced.

This description of the optical transitions is similar to that used for the charge-transfer transitions in Pb²⁺-doped CaWO₄ and the compounds PbWO₄ and PbMoO₄. Next to an intrinsic blue luminescence an additional yellow Pb²⁺–tungstate or Pb²⁺–molybdate involved luminescence is observed.[3] The spectral position of the Pb²⁺-involved center is here dependent on the Pb²⁺ concentration. Since the luminescence of the lead centers in SrTiO₃ involves a transition from the conduction band (mainly titanium 3d orbitals) to the ground level of divalent lead, situated near the valence band, no concentration dependence on the spectral position can be observed, except for $x = 1$. The emission of the Pb²⁺ component in the above-mentioned example has a higher quenching temperature than the emission of the Pb²⁺-free compounds. This is similar to the present samples. The localized nature of the Pb²⁺-involved transitions in SrTiO₃ may explain this temperature behavior, which was mentioned above. However, it cannot be excluded that the quenching-temperature enhancement of the emissions from Pb²⁺-related centers is of a similar origin in all systems.

The possible observation of free exciton emission for PbTiO₃ is rather exceptional for oxides. It has also been observed for TiO₂.[9] Perhaps the reduced hole diffusion

rate in $PbTiO_3$[10] is related to the fact that the free exciton emission line is observed already in a powder sample, since the probability of nonradiative electron–hole recombination is reduced in this case. These observations need confirmation on the basis of single crystals.

The luminescence of the Pb^{2+}-involved center is not very efficient. The intensity of the $PbTiO_3$ emission is nearly an order of magnitude lower than that of $SrTiO_3$.

Therefore, the observed decay times are hard to interpret. However, the radiative decay times will certainly be short.

In conclusion, the introduction of $PbTiO_3$ into $SrTiO_3$ results in the appearance of new emissions due to interaction between the Pb^{2+} ions and the host lattice.

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