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On the Photoluminescence of Semiconducting Titanates Applied in Photoelectrochemical Cells

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We report on the photoluminescence of the semiconducting titanates TiO_2 (rutile), $SrTiO_3$, $MgTiO_3$, $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$, and $La_2Ti_2O_7$, which are known to act as photoanodes in a photoelectrochemical cell. For all materials, except TiO_2 (rutile), self-trapped exciton emission from a titanate group is observed at LHeT. The importance of the self-trapped excited state is discussed and related to the photoelectrochemical behavior of these semiconducting titanates. © 1985 Academic Press, Inc.

1. Introduction

The photoelectrolysis of water using *n*-type semiconducting metal oxide anodes has been studied extensively during the last decade (*1*). By far the most popular materials are titanates, e.g., TiO_2 (rutile), $SrTiO_3$, and $BaTiO_3$. In these semiconducting titanates, the conduction band has mainly titanium 3*d* character and the valence band oxygen 2*p* character. The bands are separated by a wide gap of at least 3 eV, so that these materials absorb only UV radiation. The optical absorption corresponds to an $O^{2-} \rightarrow Ti^{4+}$ charge-transfer (C.T.) transition.

Recently, there has been renewed interest in the luminescence of semiconducting titanates. Nakato *et al.* (*2*) studied the electroluminescence of semiconducting electrodes in a photoelectrochemical cell. The luminescence observed for TiO_2 was interpreted to be due to surface-trapped holes. Ihrig *et al.* (*3*) have discussed the cathode luminescence of $BaTiO_3$, $SrTiO_3$, and TiO_2. For $SrTiO_3$ they report a double-emission band peaking at 425 nm. Aguilar and Agullo-Lopez (*4*) reported the X-ray luminescence of $SrTiO_3$. They observed a single-emission band peaking at 500 nm. In both cases the luminescence is interpreted as a fundamental transition of local character in the TiO_6 octahedron.

In a previous report (*5*) one of us compared these results on the luminescence of semiconducting titanates with those on compounds with isolated titanate groups. The luminescence of the isolated titanate group is characterized by a broad emission band with a Stokes shifts of 1.5–2.0 eV. In compounds with high concentrations of these groups an additional emission is often observed at longer wavelengths, which is ascribed to oxygen-deficient groups. Results on the luminescence of isolated titanate groups have been reviewed by Kröger (*6*) and Blasse (*7*).

As Blasse (*5*) already mentioned, the

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results in Ref. (*3*) favor strongly an interpretation in terms of direct recombination of conduction band electrons and valence band holes. Because of the very small Stokes shift (0.5 eV) of this emission in $SrTiO_3$ compared to those reported for isolated titanate groups (1.5–2.0 eV), it seems likely that the transition from isolated titanate groups to semiconducting titanates influences the luminescence properties drastically. Assuming that the 425-nm emission in $SrTiO_3$ reported in Ref. (*3*) is intrinsic, Blasse (*5*) was inclined to ascribe the 500-nm emission reported in Ref. (*4*) to defect titanate groups, the more so because this luminescence was observed on Verneuil-grown crystals which are known to deviate from molecularity. This is in complete analogy with a previous study on $LiNbO_3$ (*8*). The luminescence of $LiNbO_3$ is very sensitive to the Li/Nb ratio. Therefore, it was suggested to investigate the $SrTiO_3$ luminescence as a function of composition.

The results of these investigations are presented in this paper, together with the results on the luminescence of $MgTiO_3$, TiO_2, $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$, and $La_2Ti_2O_7$. All these titanates show semiconducting behavior and are known to act as photoanodes in a photoelectrochemical cell. $MgTiO_3$ (*9*) with the ilmenite structure and $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ (*10*) with the hollandite structure were studied as photoanodes by ourselves and $La_2Ti_2O_7$ was studied by Campet *et al.* (*11*). By investigating all these materials, we aimed to find a relation between the photoelectrochemical properties and the luminescence properties of these semiconducting titanates.

2. Experimental

The titanates were prepared by usual ceramic techniques using high-purity metal oxides and carbonates as starting materials. The TiO_2 used in these preparations was obtained by thermal decomposition of ammonium titanium oxalate $[(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O]$ (AmTiOx) (Merck, Optipur) at 1000°C. Firing of the samples was performed between 1100 and 1300°C in air. Because the commercially obtained AmTiOx turned out to contain traces of several transition-metal ions (e.g., Cr, Mn) we prepared our own AmTiOx. Titanium tetrachloride [$TiCl_4$; Fluka AG, puriss. ≥99% (Cl)] was distilled and subboiled in a dry-nitrogen atmosphere. The purified $TiCl_4$ was added to an ammonium oxalate solution. The precipitate AmTiOx was dried and subsequently decomposed at 1000°C. The TiO_2 thus obtained was used only for the luminescence measurements.

Samples were checked by X-ray powder diffraction. Diffuse reflection spectra were recorded at room temperature on a Perkin–Elmer EPS-3T spectrophotometer. The luminescence measurements were performed on a Perkin–Elmer MPF-3L spectrofluorometer equipped with an Oxford CF 100 continuous He-flow cryostat. The emission spectra are corrected for the photomultiplier sensitivity. Excitation spectra are corrected for the transmission of the monochromator and the lamp intensity.

3. Results and Discussion

3.1. Diffuse Reflection Spectra

In Fig. 1 the diffuse reflection spectra of the titanates investigated are presented. From these spectra, the values of the band gap (E_g) can be estimated. This was done by extrapolating the steep slope in the curve to the long-wavelength side. They range from 3.0 eV for TiO_2 to 4.0 eV for $La_2Ti_2O_7$. In all cases the absorption can be assigned to an $O^{2-} \rightarrow Ti^{4+}$ C.T. transition (*7*). The absorption edge of the host lattice $SrZrO_3$ is situated at 5.4 eV (*6*).

For $MgTiO_3$, $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$, $SrTiO_3$, and $SrZr_{0.98}Ti_{0.02}O_3$ tails are observed in the reflection spectra, which extend into the visible. This absorption on the long-wave-

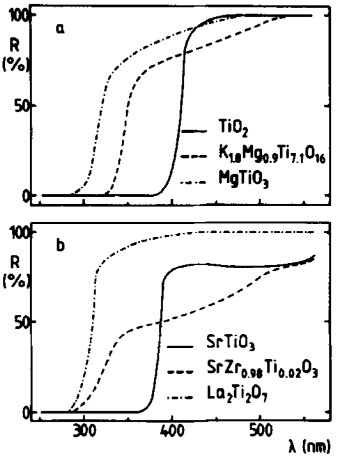

FIG. 1. Diffuse reflection spectra of (a) TiO_2, $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$, $MgTiO_3$, and (b) $SrTiO_3$, $SrZr_{0.98}Ti_{0.02}O_3$, $La_2Ti_2O_7$ recorded at room temperature.

length side of the intrinsic absorption edge originates from defect titanate centers, which are commonly present in titanates (*12*). In $MgTiO_3$ with the ilmenite structure a slight disorder between the Mg^{2+} and Ti^{4+} ions results in these defect titanate centers (*9*). In the hollandite $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ the titanium octahedra sharing a corner or edge with one magnesium octahedron can be designated as defect titanate centers (*10*). For $SrTiO_3$ and $SrZr_{0.98}Ti_{0.02}O_3$ such kind of cationic disorder cannot account for the defect titanate centers. In the perovskite structure there is only one possible crystallographic site for the titanium ion. According to Macke (*13*) the defect center consists of a titanium octahedron associated with one or more oxygen vacancies. It cannot be excluded, however, that the additional absorption is due to transition-metal impurities (*14*).

The value of the band gap E_g for $La_2Ti_2O_7$ deduced from the reflection spectrum (4.0 eV) is much higher than the value reported by Campet *et al.* (*11*). These authors used the photocurrent action spectrum and estimated E_g from the onset of the photocurrent resulting in a value of 3.2 eV. This discrepancy will be discussed below.

3.2. $SrTiO_3$ and $SrZr_{0.98}Ti_{0.02}O_3$

To investigate the luminescence of $SrTiO_3$ as a function of composition, we prepared several samples among which a sample fired with 2 mole% excess of TiO_2 and a sample where 2 mole% excess of $SrCO_3$ was used. Both samples were fired for 15 hr at 1250°C in air. The emission and excitation spectra of these two samples, $SrTiO_3$: 2% Ti, and $SrTiO_3$: 2% Sr, respectively, are shown in Fig. 2. The observed luminescence intensity of $SrTiO_3$: 2% Ti, is about four times as high as that of Sr TiO_3 : 2% Sr. Both samples show only one broad emission band with maxima at 500 and 520 nm, respectively. The excitation spectra of these emissions show broad asymmetrical bands with sharp edges on the long-wavelength side peaking at 370 and 380 nm, respectively. For both emissions the Stokes shift amounts to 0.9 eV. Although there is a small difference in the position of the emission maxima, we conclude that the emission originates from one and the same center in $SrTiO_3$: 2% Ti as well as $SrTiO_3$: 2% Sr.

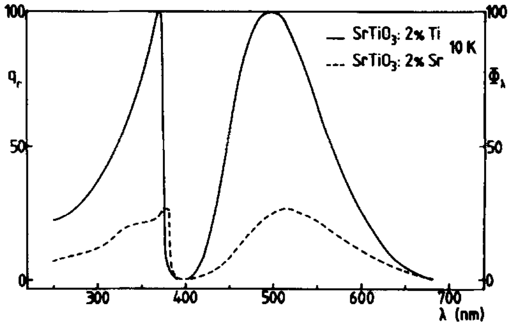

FIG. 2. Emission (right-hand side) and excitation (left-hand side) spectra of the luminescence of Sr TiO_3 : 2% Ti and $SrTiO_3$: 2% Sr at 10 K. The emission spectra were recorded for excitation at 370 nm. The excitation spectra were recorded for the emission wavelength at 480 nm. Here and in other figures Φ_λ denotes the photon flux per constant wavelength interval and q_r the relative quantum output, both in arbitrary units.

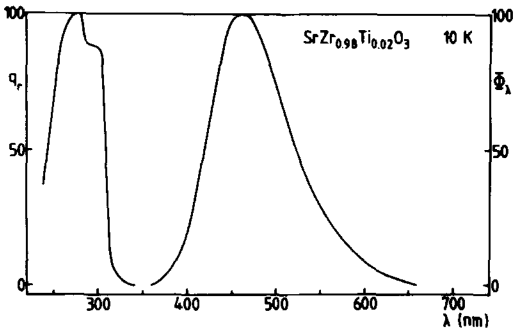

FIG. 3. Emission and excitation spectra of the luminescence of $SrZr_{0.98}Ti_{0.02}O_3$ at 10 K. The emission spectrum was recorded for excitation at 300 nm. The excitation spectrum was recorded for the emission wavelength at 440 nm.

Apart from a difference in intensity, the Sr/Ti ratio has practically no influence on the luminescence properties of $SrTiO_3$. Unlike the suggestion made before, there is thus no analogy with the luminescence properties of $LiNbO_3$ (*8*).

The emission observed by us is the same as the 500-nm emission reported by Aguilar and Agullo-Lopez (*4*) and was also reported earlier by Sihvonen (*15*) and Grabner (*16*). This suggests strongly that this emission is intrinsic.

The difference between this luminescence and that of an isolated titanate center can be illustrated by a comparison with the diluted, but analogous composition $SrZr_{0.98}Ti_{0.02}O_3$, which has the same perovskite structure as $SrTiO_3$. Assuming a statistical distribution of Zr^{4+} and Ti^{4+} over the octahedral sites, the greater part of the TiO_6 octahedra are isolated from each other. The emission and excitation spectra of the composition $SrZr_{0.98}Ti_{0.02}O_3$ are presented in Fig. 3. The excitation spectrum shows a broad band with a maximum at 280 nm. Only one emission band is observed peaking at 460 nm. The spectra closely resemble those of $BaZr_{0.99}Ti_{0.01}O_3$ reported by Macke (*13*). The emission can be assigned to a reverse $Ti^{4+} \rightarrow O^{2-}$ C.T. transition, occurring within a regular titanate octahedron (*13*). The Stokes shift of the emission is 1.5 eV.

The emission in $SrTiO_3$ corresponds in principle to the same $Ti^{4+} \rightarrow O^{2-}$ C.T. transition. The Stokes shift, however, is much smaller. Further, this luminescence is quenched rapidly, when the temperature is raised. Above 35 K hardly any emission is observed. Especially in view of the intrinsic nature of the luminescence, we assign this emission to a self-trapped exciton localized on a titanate group. The same conclusion was drawn by other authors (*4, 16*).

The temperature dependence of the luminescence will be further discussed below in connection with the observed luminescence from Cr^{3+} impurity centers.

3.3. $MgTiO_3$ and $MgTi_2O_5$

$MgTiO_3$ shows upon excitation with different energies more than one emission band. The strongest emission band together with its excitation spectrum is presented in Fig. 4. The emission band peaks at 410 nm. This emission was reported before by Villela *et al.* (*17*) at 77 K. The excitation spectrum consists of an asymmetrical band with a maximum at 265 nm.

Excitation with lower energy results in two other emissions, which must be extrinsic. These two emission bands are shown in

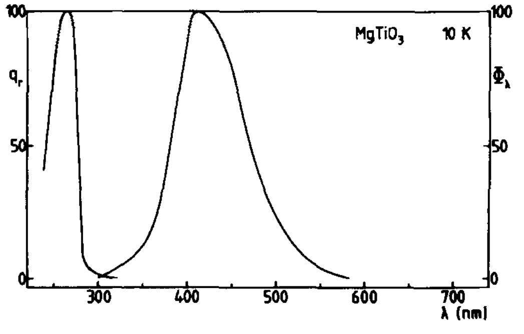

FIG. 4. Emission and excitation spectra of the stronger luminescence of $MgTiO_3$ at 10 K. The emission spectrum was recorded for excitation at 270 nm. The excitation spectrum was recorded for the emission wavelength at 420 nm.

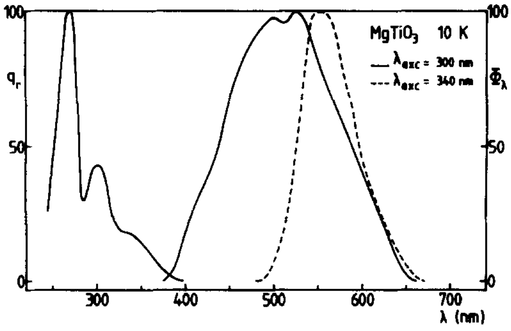

FIG. 5. Emission and excitation spectra of the weaker luminescence of $MgTiO_3$ at 10 K. The emission spectra were recorded for excitation at 300 nm (solid line) and at 340 nm (broken line). The excitation spectrum was recorded for the emission wavelength at 520 nm.

Fig. 5. Excitation with 300 nm gives an emission band peaking at 525 nm. Excitation with 340 nm results in a narrow emission band with a maximum at 550 nm. The excitation spectrum of the emission at 520 nm (see Fig. 5) shows two bands with maxima at 270 and 300 nm and a shoulder at 340 nm. From this excitation spectrum it is clear that the excitation band at 300 nm belongs to the broad-band emission at 525 nm, whereas the shoulder at 340 nm belongs to the narrow-band emission at 550 nm.

By observing three emission bands, we suspected a small amount of a second phase to be present in our sample. This second phase could be $MgTi_2O_5$ due to a low reactivity of MgO in the reacting mixture. To check this, we prepared a $MgTi_2O_5$ sample and measured the luminescence. The emission and excitation spectra are shown in Fig. 6. Only one emission band in observed peaking at 490 nm. The excitation spectrum of this emission shows one band with a maximum at 300 nm.

Comparison of Figs. 5 and 6 shows that one of the three emissions we observed in our $MgTiO_3$ sample can be attributed to a second phase, viz. $MgTi_2O_5$. The two remaining emission bands at 410 nm (see Fig. 4) and 550 nm (see Fig. 5) originate from the $MgTiO_3$ phase and are assumed to originate from regular and defect titanate octahedra. The shoulder at 340 nm in the excitation spectrum of the weaker emissions (see Fig. 5) coincide roughly with the tail in the reflection spectrum. This tail was attributed before to defect titanate centers, which result from a slight disorder between Mg^{2+} and Ti^{4+} ions. The emission at 550 nm can thus be attributed to defect titanate centers, whereas the emission at 410 nm originates from the regular titanate octahedra.

3.4. TiO_2, $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$, and $La_2Ti_2O_7$

We did not observe any titanate emission from our purified TiO_2 sample at liquid-helium temperatures. Only emission in the near infrared from an impurity center was observed. This suggests that the free electrons and holes recombine at impurity centers from where emission occurs. However, crystalline TiO_2 colloids in water luminesce in the ultraviolet as reported recently by Chandrasekaran and Thomas (*18*): TiO_2 suspensions in water show a weak emission centered at 375 nm which corresponds to the band gap of TiO_2. This might be due to free exciton recombination.

For the hollandite $K_{1.98}Mg_{0.9}Ti_{7.1}O_{16}$ we observed one emission band at LHeT. This

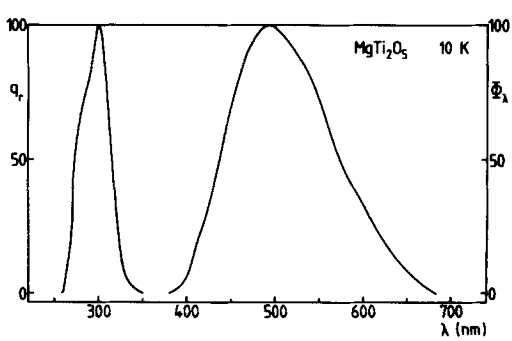

FIG. 6. Emission and excitation spectra of the luminescence of $MgTi_2O_5$ at 10 K. The emission spectrum was recorded for excitation at 300 nm. The excitation spectrum was recorded for the emission wavelength at 480 nm.

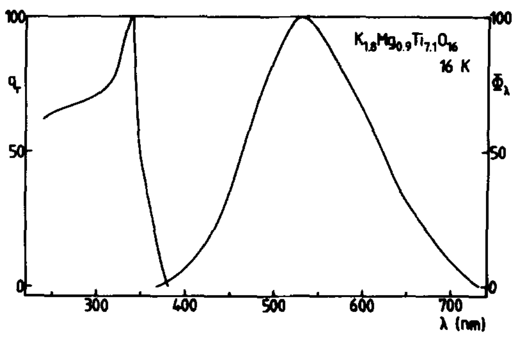

FIG. 7. Emission and excitation spectra of the luminescence of $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ at 16 K. The emission spectrum was recorded for excitation at 320 nm. The excitation spectrum was recorded for the emission wavelength at 520 nm.

emission with its excitation spectrum is shown in Fig. 7. The excitation spectrum shows again an asymmetrical band with a maximum at 340 nm. This corresponds well with the absorption edge observed in the reflection spectrum (see Fig. 1). The emission band peaks at 530 nm. The Stokes shift of this emission is 1.4 eV.

The luminescence spectra of $La_2Ti_2O_7$ are presented in Fig. 8. One emission band is observed with a maximum at 465 nm. The excitation band has its maximum at 270 nm. The Stokes shift of the emission (2.0 eV) is very large. Macke (*13*) investigated the composition $La_2Sn_{1.98}Ti_{0.02}O_7$, but as this author already pointed out, it is meaningless to compare the luminescence properties of $La_2Ti_2O_7$ with those of the diluted composition, because the crystal structures are different. $La_2Sn_2O_7$ has the pyrochlore structure, while $La_2Ti_2O_7$ has a block structure, which can be derived from orthorhombic deformed perovskites (*19*).

Let us return to the photoelectrochemical measurements which Campet *et al.* (*11, 20*) performed on $La_2Ti_2O_7$. As already pointed out, the band gap we derived from the reflection spectrum (4.0 eV) is much larger than the value these authors deduced from the photocurrent action spectrum (3.2 eV). They used an energy diagram proposed for precious metal pyrochlores and extended this to $La_2Ti_2O_7$ by inserting the 4*f* energy levels. Based on this extended energy diagram Campet *et al.* came to the conclusion that the photoactivity in $La_2Ti_2O_7$ may be attributed to LaO_8 centers. Our luminescence measurements show, however, that the lowest optically active center in $La_2Ti_2O_7$ is the TiO_6 octahedron.

3.5. Mn^{4+} and Cr^{3+} Emission

Band gap excitation or near-band gap excitation of the various titanates investigated resulted, apart from the titanate emission, in many cases in a line emission in the wavelength region 700–800 nm. The well-defined structure of these emissions left us to doubt that we are dealing with Mn^{4+} and Cr^{3+} ions. Samples which were intentionally doped with Mn^{4+} or Cr^{3+} showed the same emissions, but with higher intensity.

As an example the emission and excitation spectra of Mn^{4+} in $MgTiO_3$ are shown in Fig. 9. The sharp line at 700 nm with phonon sidebands can be assigned to the $^2E \rightarrow {}^4A_2$ transition on the Mn^{4+} ion (*17, 21*). The two bands with maxima at 550 and 330 nm in the excitation spectrum correspond to the $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ transitions on the Mn^{4+} ion, respectively (*17*). Emission

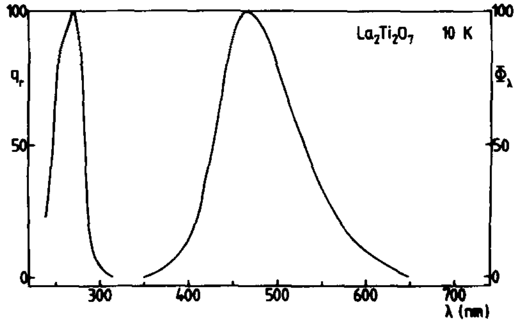

FIG. 8. Emission and excitation spectra of the luminescence of $La_2Ti_2O_7$ at 10 K. The emission spectrum was recorded for excitation at 275 nm. The excitation spectrum was recorded for the emission wavelength at 460 nm.

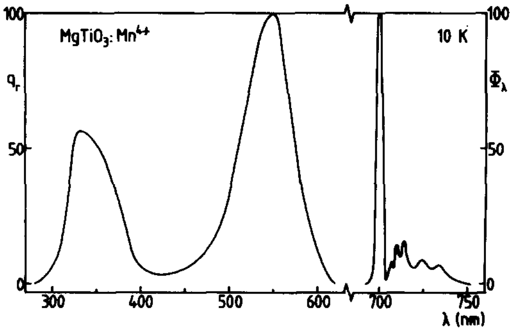

FIG. 9. Emission and excitation spectra of the luminescence of $MgTiO_3:Mn^{4+}$ at 10 K. The emission spectrum was recorded for excitation at 340 nm. The excitation spectrum was recorded for the emission wavelength at 700 nm.

from the ^2E state of Mn^{4+} was also observed in $SrTiO_3$. In this case, however, the zero-phonon line (*R*-line) was very weak in comparison with the phonon sideband. The maximum of the photon sideband was observed at 735 nm. This agrees well with the results of Stokowski and Schawlow (*22*).

As an example of the Cr^{3+} luminescence, the emission spectra of Cr^{3+} in $MgTiO_3$, $SrTiO_3$, and TiO_2 are shown in Fig. 10. In $MgTiO_3$ and $SrTiO_3$ the emission is assigned to the $^2E \rightarrow {}^4A_2$ transition on the Cr^{3+} ion (*21, 22*). The zero-phonon line (*R*-line) is observed at 732 nm in $MgTiO_3$ and at 794 nm in $SrTiO_3$. In TiO_2 the lowest lying electronic state of Cr^{3+} is, however, the $^4T_2$ state, which yields broad-band emission starting with a zero-phonon line (*23*), which is observed at 788 nm. Unfortunately, the spectral limit of our instrumentation makes it impossible to observe more than the higher-energy part of this emission band.

In $MgTiO_3$ the Cr^{3+} ion can occupy either a Mg^{2+} site or a Ti^{4+} site. These sites form an ordered arrangement (*24*). Since we observe one *R*-line in the emission spectrum, only one site is occupied by the Cr^{3+} ions. This we believe to be the Mg^{2+} site. The CrO_6^{9-} octahedron then shares a face with a TiO_6^{8-} octahedron. Due to the strong interaction between these two face-sharing octahedra, we prefer to denote this center as a $CrTiO_9^{11-}$ complex. Recently a similar center has been observed in $Ba_3SrNb_2O_9$ (*25*), i.e., $CrNbO_9^{10-}$. Its optical properties are similar to those described here for the $CrTiO_9^{11-}$ complex.

The data presented in Fig. 10 shows that in TiO_2 at LHeT the Cr^{3+} ions can be excited with band gap irradiation. At these low temperatures the Cr^{3+} ions in $MgTiO_3$ and $SrTiO_3$ are preferably excited in the crystal-field transitions of the Cr^{3+} ion. This supports our previous assumption, viz. that in TiO_2 band gap excitation leads to mobile charge carriers which are trapped by the Cr^{3+} impurity centers. At these low temperatures band gap excitation of $MgTiO_3$ and $SrTiO_3$ leads to localized excited states (self-trapped exciton) and no energy transfer to the Cr^{3+} centers is observed. As was mentioned before, the quenching temperature of the titanate emission in $SrTiO_3$ is low. In Fig. 11 the temperature dependence of this emission is given together with that of the Cr^{3+} emission. The decrease of the titanate emission intensity is accompanied by an increase of the Cr^{3+} emission intensity. The self-trapped exciton on the titanate group will dissociate at higher temper-

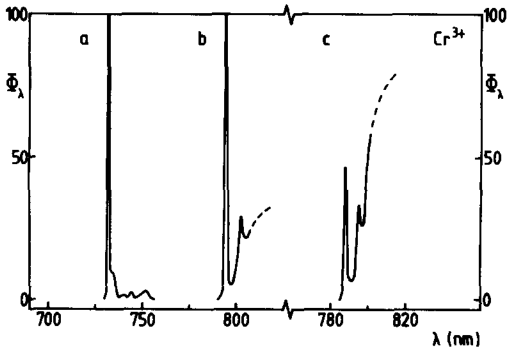

FIG. 10. Emission spectra of the luminescence of Cr^{3+} (a) In $MgTiO_3$ at 10 K, excitation at 368 nm (subband gap excitation); (b) In $SrTiO_3$ at 10 K, excitation at 400 nm (subband gap excitation); (c) In TiO_2 at 15 K, excitation at 360 nm (band gap excitation).

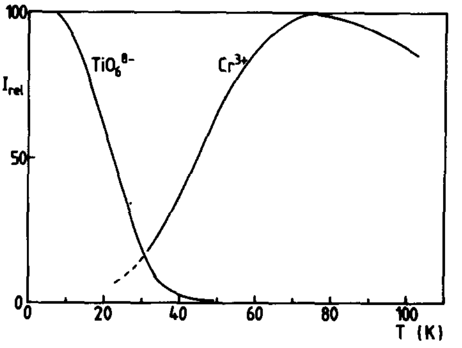

FIG. 11. Intensity of the titanate emission band (TiO_6^{8-}) and the Cr^{3+} emission of $SrTiO_3:Cr^{3+}$ as a function of temperature under band gap excitation.

atures and the charge carriers are captured by the Cr^{3+} centers, from where emission occurs. A similar behavior was not observed for $MgTiO_3$. The quenching temperature of the titanate emission in $MgTiO_3$ is about 100 K, but at this temperature the Cr^{3+} emission intensity is already decreasing due to thermal quenching as can be seen in Fig. 11. We assume that the Cr^{3+} center can capture the energy of the dissociated exciton on the titanate group, but that most of the energy will be lost nonradiatively.

A similar behavior is not expected for the Mn^{4+} luminescence in $SrTiO_3$. This is based on the excitation mechanism which Ghosh *et al.* (*26*) have given for the Cr^{3+} luminescence in $SrTiO_3$. The first step in this mechanism is the trapping of a hole by the Cr^{3+} ion, thus becoming Cr^{4+}. Subsequent capture of an electron results in a Cr^{3+} ion in its excited state. The Cr^{3+} ion in its ground state can trap a hole, because the ground state Cr^{3+} level lies above the oxygen valence band. The ground state Mn^{4+} level, however, lies close to or even within the oxygen valence band (*27*). This makes hole trapping by the Mn^{4+} ion not very probable. Thus, according to the mechanism described above, the Mn^{4+} ion cannot capture the excitation energy after dissociation of the exciton.

4. General Discussion

The results of the investigations of the luminescence of various titanates are summarized in Table I. There is a gradual change in properties. TiO_2 (rutile) is one extreme case: no self-trapped exciton is observed (probably because the self-trapped exciton does not exist at all) and band gap excitation results in emission from impurities. The other extreme case is $La_2Ti_2O_7$ with self-trapped exciton emission with a very large Stokes shift. We assume that these differences are due to the way in which the titanate octahedra are stacked, because this is an important factor which determines the electronic band structure. In connection with this it is interesting to note that the anatase modification of TiO_2 shows a broad-band green self-trapped exciton emission (*28*) which indicates that the transition from rutile to anatase favors the self-trapped exciton.

The results of Table I show that the importance of the self-trapped excited state increases in the sequence TiO_2 (rutile), $SrTiO_3$, $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$, $MgTiO_3$, $La_2Ti_2O_7$. This is illustrated by the simultaneous increase of the value of the Stokes shift and the quenching temperature of the titanate

TABLE I

SOME DATA ON THE LUMINESCENCE OF THE TITANATES UNDER STUDY

	E_g[a] (eV)	Maximum excitation band[b] (nm)	Maximum emission band[b] (nm)	Stokes shift (eV)	T_q (K)
TiO_2 (rutile)	3.0	—	—	—	—
$SrTiO_3$: 2% Ti	3.2	370	500	0.9	35
$SrTiO_3$: 2% Sr	3.2	380	520	0.9	35
$SrZr_{0.98}Ti_{0.02}O_3$	—	280	460	1.5	(150)
$K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$	3.4	340	530	1.4	70
$MgTi_2O_5$	3.6	300	490	1.7	100
$MgTiO_3$	3.7	265	410	1.7	100
$La_2Ti_2O_7$	4.0	270	465	2.0	120

[a] The values of the bandgap E_g were obtained from the diffuse reflection spectra recorded at room temperature.

[b] At LHeT.

emission in the same sequence. However, in the case of a very large Stokes shift the influence of temperature quenching in the excited state itself cannot be neglected.

Following Toyozawa we can distinguish two extreme situations after excitation (*29*). In one extreme case the excited state relaxes to its equilibrium state, lowering the energy of the system by E_{lr} (lattice relaxation). If E_{lr} is large enough, the excitation energy remains localized at that particular site accompanied by a distortion of the surroundings (self-trapped state). In the other extreme case the excitation energy can be transferred from one center to another, forming an exciton band of width $2B$, where $2B = 2\nu|J|$ (free state). Here ν is the number of nearest neighbors and J the transfer energy between nearest neighbors. The total energy of the system is in this case lowered by B (*29*).

It is obvious that in TiO_2 (rutile) we are dealing with the second case, whereas in all other titanates the lattice relaxation after excitation is large enough to localize the excited state if the temperature is low. Note in passing that the value of ν is higher in rutile ($\nu = 10$) than in all other structures under discussion.

The change from a localized to a delocalized excited state reported here for the titanate luminescence is not confined to closed-shell transition-metal complexes. A similar phenomenon has also been reported for the luminescence of the Bi^{3+} ion. These results have been reviewed recently by Blasse (*30*). In the compounds $Cs_3Bi_2Br_9$ and Rb_3BiBr_6, which both contain $BiBr_6^{3-}$ octahedra, the observed emission is essentially a $6p \rightarrow 6s$ transition on the Bi^{3+} ion. In $Cs_3Bi_2Br_9$, which is a semiconductor, we are dealing with free and bound exciton emission (*31*). In Rb_3BiBr_6 we are dealing with localized transitions on the Bi^{3+} ion (*32*). In the first compound the transfer energy J is much larger that E_{lr}, while the second compound shows the opposite case.

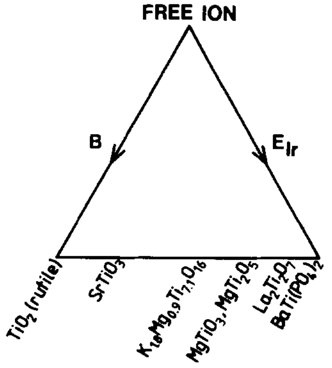

FIG. 12. Schematical representation of the gradual change from the free state (left) to the self-trapped state (right) in titanates. See text.

We can summarize our observations for the titanate luminescence schematically in a triangle given in Fig. 12. The top of the triangle presents the free ion state. Along the right-hand-side leg the lattice relaxation energy increases, along the left-hand-side leg the band width increases. It is obvious that TiO_2 (rutile) is near the lower left corner. The best example of a concentrated titanate system belonging near the lower right corner is probably $BaTi(PO_4)_2$. In this compound the TiO_6 octahedra are isolated from each other ($\nu = 0$), so that the transfer interaction should be negligible. This was indeed observed in the luminescence measurements (*33*). The compounds $MgTiO_3$, $MgTi_2O_5$, and $La_2Ti_2O_7$ are close to $BaTi(PO_4)_2$ in the lower right corner. We are inclined to place $SrTiO_3$ and $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ in between TiO_2 and $BaTi(PO_4)_2$, whereby $SrTiO_3$ is closer to TiO_2 than the magnesium hollandite.

In view of photoelectrochemical applications of these titanates the band width is the most relevant parameter. Figure 12 shows that B decreases in the sequence TiO_2 (rutile), $SrTiO_3$, $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$, $MgTiO_3$, $La_2Ti_2O_7$. Note that the decreasing value of B in this sequence is reflected by the increasing value of the band gap. A wider band will enhance the mobility of the charge carriers. From this point of view TiO_2 (rutile) should be one of the better photoanodes available. Also from an optical point of view, the values of the band gap E_g show, that TiO_2 (rutile) is the better choice, although the value of 3.0 eV is far too high for efficient solar energy conversion. But there are still other relevant parameters determining the behavior of photoanodes, among which the flat-band potential V_{fb} (*1*). The value of V_{fb} found for TiO_2 is not in favor of this material, since it is positive to the H_2-evolving level, so that one needs an additional bias (*1*). This shows again the complexity of the field of photoelectrochemical solar energy conversion.

In conclusion, we have shown that the luminescence of semiconducting titanates can be related to their photoelectrochemical properties.

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