

Investigations on the Luminescence of Titanium-Activated Stannates and Zirconates

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The luminescence of several titanium-activated stannates and zirconates with spinel, perovskite, K_2NiF_4 , pyrochlore, and fluorite structure is reported. For most compounds two emissions are observed, one blue and one yellow. Some compounds show only yellow emission and there is one compound with only blue emission. These results can be explained by one model, based on the occurrence of two different titanate centres, viz., a regular center and a defect center.

Introduction

In a previous paper (1) the luminescence of $La_2MgSn_{1-x}Ti_xO_6$ has been reported. In this system with ordered perovskite structure all stannate and titanate octahedra are isolated from each other if the order would be complete. It was shown that a violet emission originates from the isolated titanate octahedra. There is, however, a partial disorder of Mg^{2+} and Sn^{4+} (or Ti^{4+}) and as a result some of the Ti^{4+} ions have one or more Sn^{4+} neighbors instead of only Mg^{2+} neighbors. These defect titanate centers show a blue-green luminescence.

In this paper the luminescence of a number of titanium-activated stannates and zirconates is reported. In these compounds the stannate and zirconate octahedra are not isolated but share corners or edges. Some of these compounds have already been investigated by Kröger (2). He found two different emissions, one blue and one yellow, upon excitation with 254 and 313 nm radiation, respectively. Blasse (3) investigated the system $Mg_2Sn_{1-x}Ti_xO_4$ and proposed a model for the two emissions observed and for the concentration quenching of the luminescence. The present work consists partly of more detailed measurements on

compounds that have already been investigated by Kröger and Blasse and partly of an extension to new compounds. The first group of compounds consists of $Mg_2Sn_{1-x}Ti_xO_4$, $Sr_2Sn_{1-x}Ti_xO_4$, $CaZr_{1-x}Ti_xO_3$, and $BaZr_{0.99}Ti_{0.01}O_3$. The second group consists of $Y_2Sn_{2-x}Ti_xO_7$, $La_2Sn_{1.98}Ti_{0.02}O_7$, $Y_2Zr_{1.98}Ti_{0.02}O_7$, and $CaO-Zr_{0.99}Ti_{0.01}O_2$. Stannates and zirconates were chosen as host lattices because of the VI-coordination of Sn^{4+} and Zr^{4+} by oxygen ions and also because of the ionic radii of Sn^{4+} and Zr^{4+} which are not too different from that of Ti^{4+} ($r_{Ti^{4+}} = 0.61 \text{ \AA}$, $r_{Sn^{4+}} = 0.69 \text{ \AA}$, $r_{Zr^{4+}} = 0.72 \text{ \AA}$ (4)). In this way we can be sure that we are dealing with luminescence from the titanate octahedron.

Experimental

$Mg_2Sn_{1-x}Ti_xO_4$ was prepared from high-purity $MgCO_3$, SnO , and TiO_2 at $1250^\circ C$ in air. In order to investigate the influence of stoichiometry on the luminescence properties we prepared a $Mg_2Sn_{0.99}Ti_{0.01}O_4$ sample with 5 mole % excess of MgO and a sample with 5 mole % excess of SnO_2 , and also $Mg_2Sn_{0.99}Ti_{0.01}O_4$ under different firing conditions (N_2 or O_2).

$\text{Sr}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$ was prepared from high-purity SrCO_3 , SnO , and TiO_2 at 1200°C in air.

CaTiO_3 was prepared from high-purity CaCO_3 and TiO_2 at 1200°C in air. $\text{CaZr}_{1-x}\text{Ti}_x\text{O}_3$ was prepared by firing a mixture of $\text{Ca}[\text{ZrO}(\text{C}_2\text{O}_4)_2]$ and $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ at 1200°C in air, according to a method described in (5).

$\text{BaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$ was prepared from high-purity BaCO_3 , $\text{ZrOCl}_2 \cdot 7\text{H}_2\text{O}$, and TiO_2 at 1200°C in air.

$\text{Y}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$, $\text{Y}_2\text{Ti}_2\text{O}_7$, and $\text{La}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$ were prepared from high-purity Y_2O_3 or La_2O_3 , SnO , and TiO_2 at 1350°C in air. We did not succeed in preparing pure $\text{La}_2\text{Ti}_2\text{O}_7$.

The preparation of $\text{Y}_2\text{Zr}_{1.98}\text{Ti}_{0.02}\text{O}_7$ has been described elsewhere (6). Calcia-stabilized zirconia was prepared from high-purity CaCO_3 and ZrO_2 , in the ratio of 16 mole % CaCO_3 to 84 mole % ZrO_2 . The mixture was fired for several hours at 1500°C in air and quenched to room temperature. Titanium was added in the form of TiO_2 .

All samples were checked by X-ray analysis. The experimental set-up of the luminescence and decay measurements has been described elsewhere (1).

Results

1. $\text{Mg}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$. The compounds Mg_2SnO_4 and Mg_2TiO_4 have inverse spinel structure with cation distribution $\text{Mg}[\text{MgSn}]_4$ and $\text{Mg}[\text{MgTi}]_4$ and a certain degree of order between the octahedral ions (6). The SnO_6 and TiO_6 octahedra are coupled via edge-sharing. Mg_2SnO_4 and Mg_2TiO_4 are completely miscible and compositions with $x = 0.01, 0.2, 0.8$, and 1 have been investigated.

The emission spectra of $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ for excitation with 4.96 and 4.13 eV uv radiation are shown in Fig. 1. The results for the stoichiometric composition upon 4.96 eV excitation are essentially identical to those of Kröger and Blasse, but the yellow emission, excited with 4.13 eV radiation lies at higher energies, compared to the spectra of Kröger and Blasse. The position of the blue emission (maximum 2.62 eV) does not depend on

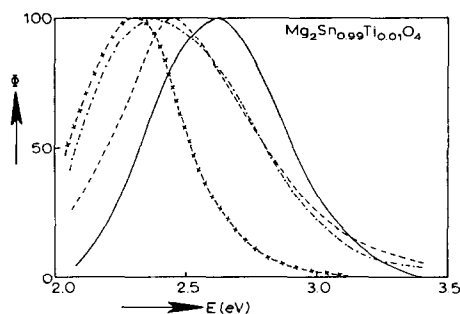


FIG. 1. Spectral energy distribution of the emissions of $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ at 5°K . Φ is the radiant power per constant energy interval in arbitrary units. Full line: stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$, excitation 4.96 eV. Dashed line: stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$, exc. 4.13 eV. Dash-dotted line: stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ fired in nitrogen atmosphere, exc. 4.13 eV. Dash-crossed line: nonstoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ 5% excess of SnO_2 , exc. 4.13 eV.

stoichiometry and preparation conditions. In the nonstoichiometric composition with 5% excess of SnO_2 the yellow emission lies at lower energies and is stronger than in the stoichiometric composition. The same effect is observed in the composition fired in a nitrogen atmosphere.

The excitation spectra of the blue emission and of the yellow emission in the stoichiometric composition, the nonstoichiometric composition and the composition fired in a nitrogen atmosphere are shown in Fig. 2 together with the diffuse reflection spectrum of unactivated Mg_2SnO_4 . The excitation band of the yellow emission in the stoichiometric composition lies at lower energy than the excitation band of the blue emission in the same composition. For the composition fired in a nitrogen atmosphere the excitation band of the yellow emission is shifted somewhat to lower energies with respect to the same band in the stoichiometric composition. In the excitation spectrum of the composition with excess of SnO_2 a new band appears at still lower energies.

Because of the possibility that the yellow emission in the nonstoichiometric composition originates from $\text{SnO}_2:\text{Ti}$, we prepared SnO_2 activated with 1 mole % TiO_2 . This sample does not luminesce at room tempera-

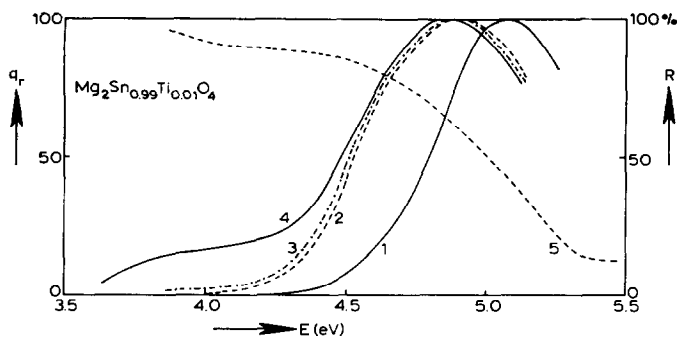


FIG. 2. Relative excitation spectra of the emissions of Fig. 1 and diffuse reflection spectrum of Mg_2SnO_4 . q , is the relative quantum output and R is the reflection. Curve 1: stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$, emission 2.95 eV. Curve 2: stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$, emission 2.38 eV. Curve 3: stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ fired in nitrogen atmosphere, emission 2.21 eV. Curve 4: nonstoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ 5% excess of SnO_2 , emission 2.21 eV. Curve 5: reflection spectrum of Mg_2SnO_4 .

TABLE I

POSITION OF THE MAXIMA OF THE EMISSION AND EXCITATION BANDS AT 5°K IN ALL COMPOSITIONS INVESTIGATED (ALL VALUES IN ELECTRON VOLTS)

Composition	Emission bands		Excitation bands	
	Exc. 4.96 eV	Exc. 4.13 eV	Em. 3.18 eV	Em. 2.20 eV
$\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$	2.62	2.44	5.07	4.85
$\text{Mg}_2\text{Sn}_{0.8}\text{Ti}_{0.2}\text{O}_4$	2.58	2.41	4.96	4.85
$\text{Mg}_2\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_4$	2.67	2.37	4.92	4.70
Mg_2TiO_4	2.81	2.44	4.66	4.56
$\text{SnO}_2:\text{Ti}$	2.38	2.38	—	4.08
$\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$	2.81	2.45	4.65	4.30
$\text{Sr}_2\text{Sn}_{0.95}\text{Ti}_{0.05}\text{O}_4$	2.77	2.43	4.60	4.27
Sr_2TiO_4	2.37	2.37	—	3.8
$\text{CaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$	2.90	2.60	4.77	4.40
$\text{CaZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$	2.88	2.61	4.70	4.30
CaTiO_3	2.68	2.68	—	3.97
$\text{BaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$	2.87	2.87	~4.4	~4.4
$\text{Y}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$	2.55	2.40	4.75	4.62
$\text{Y}_2\text{Ti}_2\text{O}_7$	—	Very weak	—	~4
$\text{La}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$	2.86	2.38	4.68	4.50
				4.13
$\text{Y}_2\text{Zr}_{1.98}\text{Ti}_{0.02}\text{O}_7$	2.3	2.3	—	4.6
$\text{CaO-Zr}_{0.99}\text{Ti}_{0.01}\text{O}_2$	2.4	2.4	—	4.45

ture but shows a yellow emission at liquid nitrogen temperature. This emission resembles the yellow emission of the nonstoichiometric composition. The excitation spectrum and the diffuse reflection spectrum show a band which

is situated at about the same position as the additional band in the excitation spectrum of the nonstoichiometric composition.

The emission and excitation spectra of $\text{Mg}_2\text{Sn}_{0.8}\text{Ti}_{0.2}\text{O}_4$, $\text{Mg}_2\text{Sn}_{0.2}\text{Ti}_{0.8}\text{O}_4$, and

Mg_2TiO_4 resemble those of the stoichiometric composition $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$. With increasing titanium concentration the blue emission band shifts to higher energies and the corresponding excitation band shifts to lower energies. The yellow emission remains at about the same position with increasing titanium concentration whereas the corresponding excitation band shifts to lower energies (see Table I).

In addition to the blue and yellow emissions all samples show a very weak red emission with a maximum at 1.88 eV upon excitation with 3.4-eV radiation. It is known (2, 7) that $\text{Mg}_2\text{TiO}_4:\text{Mn}^{4+}$ is an efficient red-emitting phosphor with a maximum of the emission at about 1.9 eV. An atomic absorption analysis (courtesy Mr. G. P. M. van den Heuvel of this laboratory) of the starting materials revealed the presence of Fe, Mn, and Cr in both MgCO_3 and TiO_2 (in MgCO_3 about 5 ppm of all three elements; in TiO_2 , 116, 12, and 10 ppm of Fe, Mn, and Cr, respectively).

The quantum efficiency of the blue emission decreases with increasing titanium concentration, as has already been found by Blasse (3). The quenching temperature of the blue emission also decreases with increasing titanium concentration from 600°K for $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ to 240°K for Mg_2TiO_4 . This is in agreement with the measurements of Blasse (3). The quenching temperatures of the yellow emissions are much lower. This

situation is different from that encountered in $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$ where the long-wavelength emission has a higher quenching temperature than the short-wavelength emission (1).

The results of the decay measurements as a function of temperature of the emissions of stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ monitored at different emission wavelengths, of the yellow emission of nonstoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ with 5 mole % excess of SnO_2 , and of the emission of $\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_2$ are presented in Fig. 3. At 5°K, the decay of the blue emission, excited with 4.96-eV radiation, can be described by the sum of two exponentials, with $\tau_1 = 2.5 \mu\text{sec}$ and $\tau_2 \approx 12 \mu\text{sec}$. At higher temperatures only the short decay time is left. With increasing temperature the value of this decay time increases up to 180°K and then remains approximately constant.

The decay of the yellow emission, excited with 4.13-eV radiation, can be described with one single exponential with $\tau \approx 8 \mu\text{sec}$ at temperatures below 50°K. At higher temperatures the decay can be described with the sum of two exponentials, one of which is of the same order of magnitude as the low-temperature decay time. The second decay time is much longer, with $\tau \approx 60 \mu\text{sec}$ at 50°K. The short decay time increases with increasing temperatures up to 100°K and then decreases. The longer decay time decreases steadily with increasing temperatures.

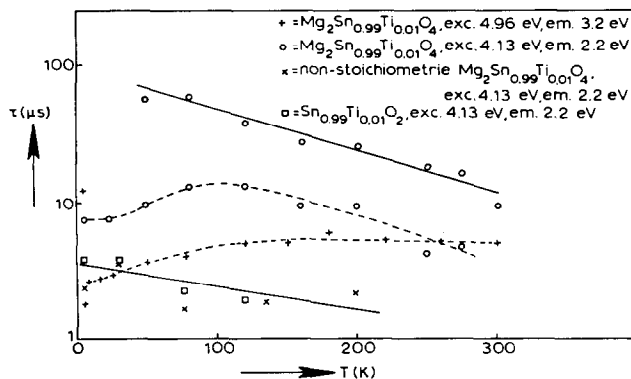


Fig. 3. The temperature dependence of the decay times of the blue and yellow emission of stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$, the yellow emission of nonstoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ with 5% excess of SnO_2 , and the yellow emission of $\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_2$.

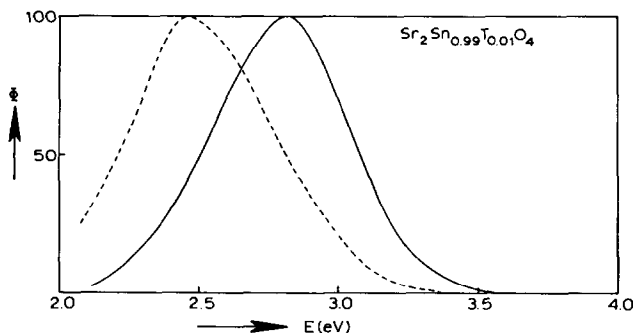


FIG. 4. Spectral energy distribution of the emission of $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ at 5°K . Full line: excitation 4.96 eV. Dashed line: excitation 4.13 eV.

The decay times of nonstoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ and of $\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_2$ are roughly the same in the temperature region of the measurements and can be described with one exponential. The decay time is about $4 \mu\text{sec}$ at 5°K and decreases with increasing temperature.

2. $\text{Sr}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$. Sr_2SnO_4 and Sr_2TiO_4 both have the K_2NiF_4 -structure, the relevant part of which consists of perovskite-like layers with corner-sharing octahedra. It turned out that Sr_2SnO_4 and Sr_2TiO_4 show a broad miscibility gap, so that only compositions with $x = 0.01, 0.05$, and 1 have been studied.

The emission spectra of $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ upon excitation with 4.96 and 4.13 eV uv radiation are shown in Fig. 4. The blue emission, excited with 4.96-eV radiation is the same as found by Kröger and has a

maximum at 2.81 eV. This maximum is situated at appreciably higher energy than the maximum of the blue emission in $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$. The yellow emission is situated at about the same energy as in stoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ (maximum, 2.45 eV).

The excitation spectra of the emissions of $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$, measured at 3.18 and 2.21 eV, are shown in Fig. 5, together with the diffuse reflection spectrum of unactivated Sr_2SnO_4 . The maximum of the excitation band of the blue emission lies at 4.65 eV, and the maximum of the long-wavelength excitation band lies at 4.30 eV.

The results for $\text{Sr}_2\text{Sn}_{0.95}\text{Ti}_{0.05}\text{O}_4$ are essentially identical with those of $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$, with a small shift (0.02–0.04 eV) of all bands to lower energies (see Table I). In Sr_2TiO_4 , the

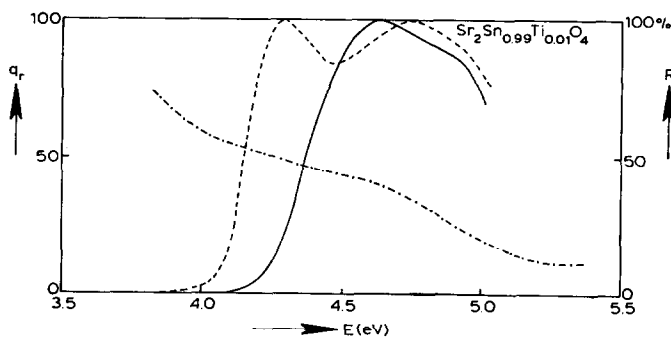


FIG. 5. Relative excitation spectra of the emissions of $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ at 5°K and diffuse reflection spectrum of Sr_2SnO_4 . Full line: emission 3.18 eV. Dashed line: emission 2.21 eV. Dash-dotted line: reflection spectrum of Sr_2SnO_4 .

blue emission has almost completely vanished and excitation with 4.48- and 4.13-eV radiation yields only the yellow emission with a maximum at 2.37 eV, whereas excitation with 5.5-eV radiation yields mainly the yellow emission with a shoulder at the high-energy side. The excitation band has a maximum at 3.8 eV. The absorption band in the diffuse reflection spectrum recorded at room temperature is situated at the same energy.

The quenching temperature of the blue emission of $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$, measured by Kröger (2), is 450°K. The quenching temperature of the yellow emission is estimated to be 200°K in $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ and still lower in Sr_2TiO_4 .

Decay measurements as a function of temperature were performed on $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$. The excitation energies were 4.96 and 4.13 eV; the emission was monitored at about 3.1 and 2.2 eV. The values obtained, especially for the yellow emission, are too widely scattered to give the temperature dependence of the decay times. This is caused by the fact that the two emissions and the exciting lamp pulse cannot be separated satisfactorily so that the decay is always observed as the sum of three exponentials. The deconvolution of these decay curves yields large errors in the values of the individual decay times. The decay time at 5°K of the blue emission is about 5 μsec ; the decay time of the yellow emission is much longer, 20 to 50 μsec .

3. $\text{CaZr}_{1-x}\text{Ti}_x\text{O}_3$. CaZrO_3 and CaTiO_3 have a distorted perovskite structure with corner-sharing octahedra and show only partial miscibility just like Sr_2SnO_4 and Sr_2TiO_4 . Compositions with $x = 0.01, 0.05$, and 1 have been investigated.

The spectra of this system closely resemble those of $\text{Sr}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$. The blue emission lies at somewhat higher energy (maximum about 2.9 eV) and the maximum of the yellow emission is also shifted to higher energies (about 2.6 eV). The excitation bands show the same behavior (maxima about 4.75 and 4.35 eV for the short-wavelength and long-wavelength bands, respectively). In CaTiO_3 only the yellow emission is found. The maximum of this emission band lies at 2.68 eV; that of the corresponding excitation band is

at 3.97 eV (see Table I). These results are in agreement with the measurements of Grabner and Stokowski (8).

4. $\text{BaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$. Only BaZrO_3 activated with 1 at % Ti^{4+} has been investigated. This compound has the cubic perovskite structure. In $\text{BaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$, excitation with both 4.96 and 4.13 eV uv radiation yields the same emission with a maximum at 2.87 eV. This emission is very weak and can be observed at LNT and lower temperatures. The excitation band of this emission is very broad with a maximum at about 4.4 eV.

5. $\text{Y}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$, $\text{Y}_2\text{Ti}_2\text{O}_7$, and $\text{La}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$. $\text{Y}_2\text{Sn}_2\text{O}_7$, $\text{Y}_2\text{Ti}_2\text{O}_7$, and $\text{La}_2\text{Sn}_2\text{O}_7$ have the pyrochlore structure, whereas $\text{La}_2\text{Ti}_2\text{O}_7$ has a different structure (9). The pyrochlore structure can be thought of as an anion-deficient fluorite structure, in which the oxygen deficiencies are ordered in such a way that distorted corner-sharing octahedra are formed. The emission spectra of $\text{Y}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$ resemble those of stoichiometric $\text{Mg}_2\text{Sn}_{0.97}\text{Ti}_{0.01}\text{O}_4$. The blue emission peaks at 2.55 eV; the much weaker yellow emission, which also contains the blue emission band, peaks at 2.40 eV. The bands in the excitation spectra, however, are situated at much lower energies than in $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$. The excitation band of the blue emission peaks at 4.75 eV; that of the yellow emission peaks at 4.62 eV.

The blue emission is absent in $\text{Y}_2\text{Ti}_2\text{O}_7$, and the yellow emission is extremely weak.

The spectra of $\text{La}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$ resemble those of $\text{CaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$. The blue emission peaks at 2.86 eV; the yellow emission peaks at 2.38 eV. The maximum of the excitation band of the blue emission lies at 4.68 eV; the excitation spectrum of the yellow emission consists of two bands, one at 4.50 eV and one at 4.13 eV.

6. $\text{Y}_2\text{Zr}_{1.98}\text{Ti}_{0.02}\text{O}_7$ and $\text{CaO-Zr}_{0.99}\text{Ti}_{0.01}\text{O}_2$. These compositions also have an oxygen-deficient fluorite structure, but in this case the oxygen vacancies are statistically distributed.

$\text{Y}_2\text{Zr}_{1.98}\text{Ti}_{0.02}\text{O}_7$ and $\text{CaO-Zr}_{0.99}\text{Ti}_{0.01}\text{O}_2$ show only a weak yellow luminescence at temperatures below 100°K, with a maximum between 2.3 and 2.4 eV. The excitation spectra consist of very broad bands, with maxima at

4.6 eV ($\text{Y}_2\text{Zr}_{1.98}\text{Ti}_{0.02}\text{O}_7$) and 4.45 eV ($\text{CaO-Zr}_{0.99}\text{Ti}_{0.01}\text{O}_2$). The position of the excitation bands coincides with the position of the bands in the diffuse reflection spectra.

All results of the luminescence measurements are compiled in Table I. For more figures with the emission, excitation, and reflection spectra see (10).

Discussion

We shall show that the luminescence properties of all systems under investigation can be described with the model developed for $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$ (1). The apparent deviations can be satisfactorily explained by the specific properties of the several compositions.

In titanium-activated oxidic phosphors, absorption and emission processes are due to charge-transfer transitions within the titanate octahedron. For $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$ an approximate assignment of the levels involved could be given. In these compositions two titanate centers are present, a regular center and a defect center. For $x \geq 0.3$, energy transfer from the regular to the defect center occurs, probably by dipole-dipole interaction from the relaxed excited state. It could be shown that for large values of x all energy is transferred to the defect center, so that only emission from the defect center is observed in $\text{La}_2\text{MgTiO}_6$.

This model can be applied without modifications to $\text{Sr}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$, $\text{CaZr}_{1-x}\text{Ti}_x\text{O}_3$, and $\text{Y}_2\text{Sn}_{2-x}\text{Ti}_x\text{O}_7$. The blue emission originates from the regular titanate center and the yellow emission from a defect titanate center. In the undiluted titanates the blue emission has completely vanished. This is ascribed to energy transfer from the regular to the defect titanate center. There can only be efficient energy transfer if there is a nonzero spectral overlap of the emission band of the regular center and the excitation band of the defect center (11). From Figs. 4 and 5 it can be seen that the spectral overlap of the blue emission band and the excitation band of the yellow emission in $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ is very small. The same holds for $\text{CaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$ and

$\text{Y}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$. It is not possible to determine the spectral overlap in a direct manner in the compositions with $x = 1$ since the blue emission is absent in these compositions. It can be argued, however, that the spectral overlap increases with increasing values of x . First, Table I shows that the position of the excitation band of the yellow emission shifts to lower energy with increasing titanium concentration. Second, it may be assumed that the blue emission band shifts to higher energy with increasing values of x , in analogy to the situation in $\text{Mg}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$ (see Table I) and $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$ (see 1). It is therefore likely that for $x = 1$ there is a sufficient spectral overlap for the transfer to occur.

The nature of the defect center cannot be the same for $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$ on the one hand and $\text{Sr}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$, $\text{CaZr}_{1-x}\text{Ti}_x\text{O}_3$, and $\text{Y}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_7$ on the other. In $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$ the defect center was thought to be due to a partial disorder of Mg^{2+} and Sn^{4+} (Ti^{4+}) ions, so that some titanate centers have one or more Sn^{4+} neighbors instead of only Mg^{2+} neighbors. As a consequence, the quenching temperature of the defect emission is higher than that of the regular emission. In the other three systems it is just the reverse. This is in agreement with a model for the defect center consisting of a titanate octahedron associated with one or more oxygen vacancies. More arguments that corroborate this model will be presented below.

The assignment of the two emissions in $\text{La}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$ is the same as in $\text{Y}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$. $\text{La}_2\text{Ti}_2\text{O}_7$ has a different crystal structure than $\text{La}_2\text{Sn}_2\text{O}_7$. It is therefore meaningless to compare the luminescence properties of $\text{La}_2\text{Sn}_{1.98}\text{Ti}_{0.02}\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$.

The interpretation of the results for the system $\text{Mg}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$ is complicated by the occurrence of luminescent $\text{SnO}_2:\text{Ti}$. The presence of SnO_2 in nonstoichiometric $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ with 5% excess of SnO_2 is evident when the emission and excitation spectrum and the decay time of the yellow emission in this composition are compared with the results for $\text{SnO}_2:\text{Ti}$. It may be assumed that the samples of $\text{Mg}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$ of Kröger and Blasse contained some SnO_2

because of an incomplete reaction during the preparation. Wilke (12) has shown that the formation of pure Mg_2SnO_4 is impossible unless SnO is used as a starting material.

To test the hypothesis that the defect centers are formed by titanate octahedra with oxygen vacancies, we prepared $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ fired in a nitrogen and an oxygen atmosphere. It can be seen that the yellow emission band of the sample fired in a nitrogen atmosphere is shifted to lower energies with respect to the samples fired in air or in oxygen (Fig. 1). The long-wavelength excitation band (Fig. 2) shows a similar shift. The most important conclusion from this experiment is that the yellow emission is influenced by the firing conditions (in contrast to the blue emission). This is evidence for the model in which the yellow emission occurs from a titanate group associated with a defect. The simplest explanation of the phenomena observed is as follows. Since the long-wavelength emission is composed of two emission bands, one blue and one yellow, a shift of the maximum to lower energy means that the contribution of the yellow emission increases. The same argument holds for the excitation band. It is reasonable to assume that firing in nitrogen yields more oxygen vacancies than firing in an oxygen atmosphere. So the conclusion may be drawn that the yellow emission is associated with oxygen vacancies.

In contradistinction to Sr_2TiO_4 , CaTiO_3 , and $\text{Y}_2\text{Ti}_2\text{O}_7$ the compound Mg_2TiO_4 shows two emissions. From Table I it can be seen that the separation of the maxima of the blue emission band and the yellow excitation band in $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ is 2.23 eV and in Mg_2TiO_4 , 1.75 eV. For $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ and $\text{CaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$ this value is 1.49 and 1.50 eV, respectively. It seems reasonable to consider the aforementioned separation as a measure of the spectral overlap. As we have already seen, the spectral overlap in $\text{Sr}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ is practically zero. In view of the larger separation the spectral overlap in $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ and Mg_2TiO_4 must be even smaller. As a consequence there is less energy transfer and the blue emission in Mg_2TiO_4 is not quenched.

Nevertheless, there is appreciable concentration quenching in the system $\text{Mg}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$. This is demonstrated by the decrease of the quantum efficiency and the quenching temperature of the blue emission with increasing titanium concentration. The concentration quenching cannot be due to energy transfer from one regular titanate group to another, because of the extremely small spectral overlap that follows from the energy separation of the maxima (the Stokes shift) of 2.45 eV. It also hardly seems possible that energy transfer from regular titanate centers to defect titanate centers can cause such a large concentration quenching, although it may have some influence. Energy transfer from one regular titanate center to another is, however, possible if the emission does not originate from the level at which excitation takes place. In that case the excitation is followed by a non-radiative decay to a lower-lying level from which either emission to the ground state or energy transfer to the same level in another regular titanate center takes place. In the latter case the energy can migrate through the lattice until a "killer" site is reached where the energy is lost nonradiatively. The existence of a large number of excited levels is predicted by M.O. theory and confirmed by the decay experiments, which will be discussed below. Another argument for such a level is the combination of the large Stokes shift and the high quenching temperature of the blue emission in $\text{Mg}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$. From the configurational coordinate model it follows that a large Stokes shift should result in a low quenching temperature. The solution of this apparent contradiction is the assumption that more than one level is involved in the excitation and emission process. The absorption band of the level from which the emission originates is not observed experimentally. This is not surprising since the transition probability must be low in view of the observed decay time (3 μsec , see below). It is to be expected, however, that this absorption band overlaps appreciably with the blue emission band, so that energy transfer is possible.

The results of the decay measurements, in combination with the conclusions drawn from the measurements of emission and excitation

spectra, can be used to construct a descriptive model of the energy levels of the titanate octahedron in $\text{Mg}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$. The temperature dependence of the decay time of the blue emission of $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ (Fig. 3) can be explained by a three-level scheme (levels 1, 2, and 3 of Fig. 6). The probabilities for transitions to the ground state are p_{31} and p_{21} ; the transition probabilities, p_{23} and p_{32} , are assumed to be nonradiative. The energy difference between levels 2 and 3 is ϵ . If p_{21} , $p_{31} \ll p_{23}$, p_{32} the system decays with one decay time, τ , with

$$\tau^{-1} = p_{31}(1 + e^{\epsilon/kT})^{-1} + p_{21}(1 + e^{-\epsilon/kT})^{-1} \quad (1)$$

(see 13). For $T \rightarrow 0$, $\tau = 1/p_{21}$; for $T \rightarrow \infty$, $\tau = 2/(p_{21} + p_{31})$. If $p_{31} < p_{21}$, τ increases with increasing temperature, until the thermal quenching becomes effective; if $p_{31} = 0$, τ is at high temperatures ($kT \gg \epsilon$) twice as large as at low temperature. If relation (1) is fitted to the observed curve of Fig. 3, an approximate value of 2 meV is found for ϵ ; further $p_{21} = 3 \times 10^5 \text{ sec}^{-1}$ and $p_{31} < 0.1 p_{21}$. According to this model the intensity of the blue emission as a function of temperature ought to remain approximately constant until the thermal quenching sets in. Indeed, a less steep

slope of the I vs T curve is observed below about 200°K than above this temperature.

The second decay time at 5°K is an indication that the situation is more complicated. For a better understanding more measurements at temperatures below 5°K are needed.

The short component, τ_1 , of the decay time of the yellow emission of $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$ (Fig. 3) shows a similar temperature-dependent behavior as the decay of the blue emission. This can be explained in the same manner. The longer component, τ_2 , is an indication of the presence of two higher lying levels (levels 4 and 5 in Fig. 6), similar to the situation encountered in $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$ (*I*). Excitation takes place in level 5, followed by a fast relaxation to levels 2, 3, and 4. Emission is observed from level 2. The radiative transition probability $p_{21} = \tau_1^{-1} \approx 10^5 \text{ sec}^{-1}$. The longer component of the decay time is caused by the slow radiative and nonradiative transitions from level 4 to levels 2 and 1. The rates p_{42} and p_{41} are of the order of 10^4 sec^{-1} . In the case of $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$ about the same values for the radiative and non-radiative transition rates are found. So there is a large similarity between the energy-level scheme of Fig. 6 and the four-level scheme proposed for $\text{La}_2\text{MgSn}_{1-x}\text{Ti}_x\text{O}_6$. The most striking difference is the splitting of the lowest excited level in $\text{Mg}_2\text{Sn}_{0.99}\text{Ti}_{0.01}\text{O}_4$. The splitting might be related to the trigonal field that is present at the octahedral cation site in the spinel structure.

We shall now discuss the compositions $\text{BaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$, $\text{Y}_2\text{Zr}_{1.98}\text{Ti}_{0.02}\text{O}_7$, and $\text{CaO-Zr}_{0.99}\text{Ti}_{0.01}\text{O}_2$.

In $\text{BaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$ the yellow emission is absent and the blue emission is only observed below liquid nitrogen temperature. The absence of the yellow emission is thought to be due to a very low quenching temperature compared to $\text{CaZr}_{0.99}\text{Ti}_{0.01}\text{O}_3$. Blasse and Brill (*14*) have shown that in general the quenching temperature depends on the size of the surrounding cations. The quenching temperature decreases with increasing size of the surrounding cations. Since Ba^{2+} has a much larger radius than Ca^{2+} , the quenching temperature of the titanate emission in BaZrO_3 will be much lower than in CaZrO_3 .

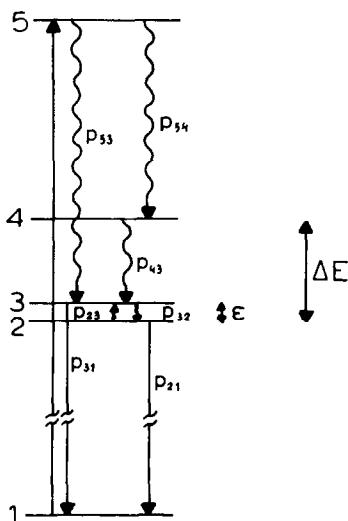


FIG. 6. Proposed energy-level scheme for $\text{Mg}_2\text{Sn}_{1-x}\text{Ti}_x\text{O}_4$ (see text).

The same effect has been observed for the tungstate emission in the series CaWO_4 , SrWO_4 , and BaWO_4 (2).

$\text{Y}_2\text{Zr}_{1.98}\text{Ti}_{0.02}\text{O}_7$ and $\text{CaO-Zr}_{0.99}\text{Ti}_{0.01}\text{O}_2$ show only yellow emission. It is known that these compositions with fluorite structure contain a high concentration of oxygen vacancies. Obviously, the concentration of defect titanate centers has become so high in these compositions that only defect emission can be observed.

As a conclusion we can state that the luminescence properties of titanium-activated stannates and zirconates can be described by a model with two different centers: a regular center and a defect titanate center. In many systems energy transfer from the regular to the defect center can be observed.

A comparison with similar systems, like vanadates, tungstates, and niobates, yields a similar behavior with respect to the occurrence of a regular and a defect center in the case of some tungstates (15–17) and niobates (18). Vanadates always show only one emission. The nature of these similarities and differences is not yet clear.

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