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Luminescence in the System $Mg_4Ta_{2-x}Nb_xO_9$

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Detailed emission and excitation spectra and decay measurements of the luminescence of the system $Mg_4Ta_{2-x}Nb_xO_9$ are reported. In $Mg_4Ta_2O_9$ a new emission and excitation band at relatively low energy has been found. In the samples with a high niobium concentration ($x \geq 1$) a new weak orange emission has been observed upon long-wavelength uv excitation. A new interpretation of the results, based on the occurrence of different niobate or tantalate centers, is presented.

1. Introduction

The luminescences of $Mg_4Nb_2O_9$ and $Mg_4Ta_{2-x}Nb_xO_9$ have been reported by Wachtel (*1*) and Blasse and Bril (*2*), respectively. Wachtel measured only the emission excited with 4.89 eV (254 nm) radiation. Blasse and Brill found two different emissions upon excitation with short- and long-wavelength uv radiation. They ascribed these two emissions to different electronic transitions within one and the same niobate (or tantalate) octahedron.

Since the Nb^{5+} ($4d^0$) and Ta^{5+}($5d^0$) ions have no outer *d*-electrons, the luminescence properties of the niobate and tantalate octahedra may be compared to the luminescence of the titanate octahedron (Ti^{4+} has a $3d^0$ configuration). In two previous papers (*3*,*4*) it was shown that in most titanium-activated stannates and zirconates two emissions occur: One emission was ascribed to a regular titanate octahedron, the other to a defect titanate octahedron.

The work reported in this paper extends the previous luminescence measurements to lower temperatures and to more excitation wavelengths. The decay times of both emissions are measured from liquid helium temperature to room temperature. An interpretation of the results, based on the same model that is used in the case of the titanates, will be given.

2. Experimental

Samples were prepared by the usual ceramic techniques (*1*). The starting materials were high purity Nb_2O_5, Ta_2O_5, and $MgCO_3$. The firing temperature was 1450°C. All samples were checked by X-ray analysis. The experimental setup of the luminescence and decay measurements has been described in a previous paper (*3*).

3. Results

Samples with $x = 0$, 0.4, 1, 1.6, and 2 have been investigated. The emission, excitation, and diffuse reflection spectra of $Mg_4Nb_2O_9$ are represented in Figs. 1 and 2. Excitation with 4.96 eV radiation yields a fairly efficient blue emission, whereas excitation with 4.48 eV radiation yields a much weaker green emission. A very weak orange emission is found upon excitation with 4.0 eV radiation. The blue and green emission bands are in agreement with the results of Blasse and Bril (*2*). The excitation band of the blue emission has a maximum at 5.05 eV at 5°K and shifts appreciably to lower energies with increasing

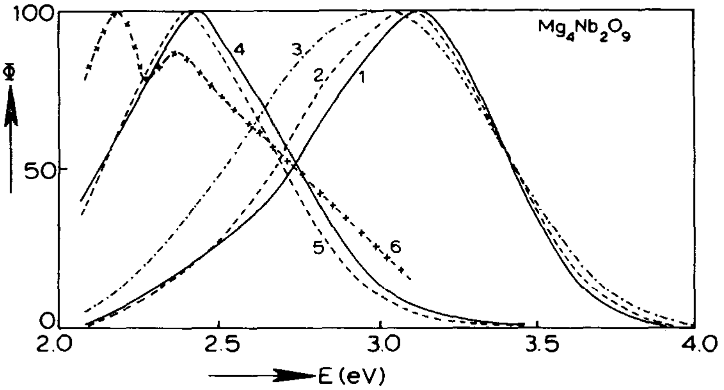

FIG. 1. Spectral energy distribution of the emissions of $Mg_4Nb_2O_9$ at several temperatures and excitation energies. Φ is the radiant power per constant energy interval in arbitrary units. Curve 1: excitation 4.96 eV, $T = 5°K$. Curve 2: excitation 4.96 eV, $T = 200°K$. Curve 3: excitation 4.96 eV, $T = 300°K$. Curve 4: excitation 4.48 eV, $T = 5°K$. Curve 5: excitation 4.48 eV, $T = 125°K$. Curve 6: excitation 3.88 eV, $T = 5°K$.

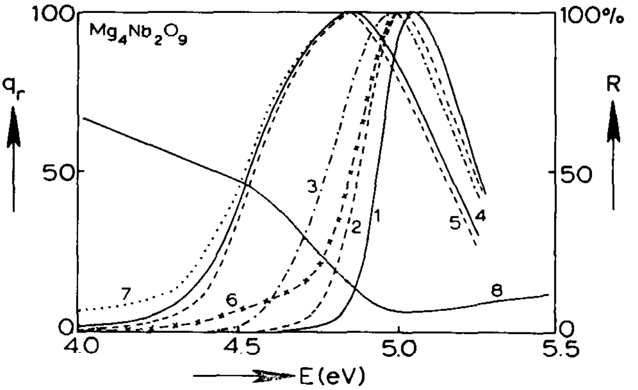

FIG. 2. Relative excitation spectra of $Mg_4Nb_2O_9$ at several temperatures and emission energies and diffuse reflection spectrum at room temperature. q_r is the relative quantum output and R the reflection. Curve 1: emission 3.10 eV, $T = 5°K$. Curve 2: emission 3.10 eV, $T = 200°K$. Curve 3: emission 310 eV, $T = 300°K$. Curve 4: emission 2.48 eV, $T = 5°K$. Curve 5: emission 2.48 eV, $T = 125°K$. Curve 6: emission 2.48 eV, $T = 200°K$. Curve 7: emission 2.21 eV, $T = 5°K$. Curve 8: reflection spectrum.

temperature. The room temperature spectrum is the same as that found by Wachtel (*1*). The excitation band of the green emission is situated at lower energies than the excitation band of the blue emission. From the temperature dependence of this band it can be estimated that the quenching temperature (as defined by Kröger (*5*)) of the green emission is about 200°K. According to Wachtel the quenching temperature of the blue emission is about 450°K. In the excitation spectrum of the orange emission, a weak additional excitation region at low energy is observed.

Figures 3 and 4 show the emission, excitation, and diffuse reflection spectra of $Mg_4Ta_2O_9$. Excitation with 5.53 eV radiation yields a weak, very broad, blue emission composed of two bands with maxima at about 2.9 and 2.5 eV. These values were obtained with a Gauss-fit computer program. Excitation with 4.37 eV radiation yields a still weaker blue-green emission with a maximum at about

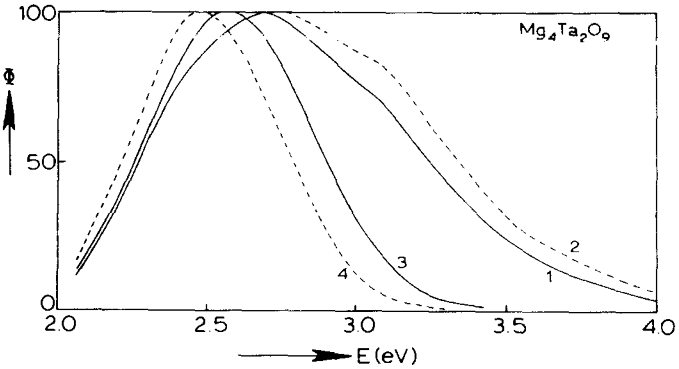

FIG. 3. Spectral energy distribution of the emissions of $Mg_4Ta_2O_9$ at several temperatures and excitation energies. Curve 1: excitation 5.53 eV, $T = 5°K$. Curve 2: excitation 5.53 eV, $T = 77°K$. Curve 3: excitation 4.37 eV, $T = 5°K$. Curve 4: excitation 4.37 eV, $T = 77°K$.

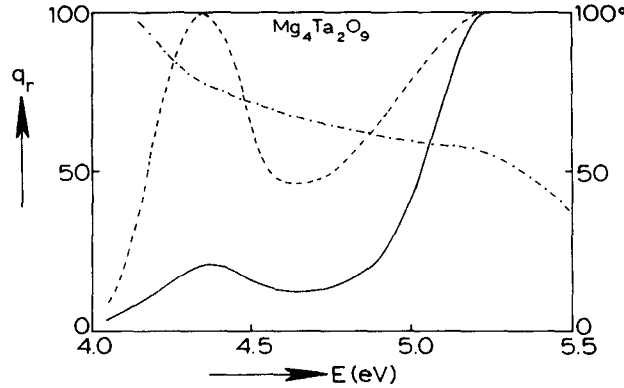

FIG. 4. Relative excitation spectra of $Mg_4Ta_2O_9$ at several temperatures and emission energies and diffuse reflection spectrum at room temperature. Full line: emission 3.26 eV, $T = 5°K$. Dashed line: emission 2.70 eV, $T = 5°K$. Dash-dotted line: reflection spectrum.

2.5 eV. Blasse and Bril (*2*) found a very-short-wavelength emission with a maximum at about 3.5 eV upon cathode-ray excitation and also found the band at 2.9 eV upon excitation with 4.96 eV radiation. The excitation spectra consist of two bands. The band at the high-energy side corresponds with the blue emission. The position of the maximum is not accurate due to the spectral restriction of our apparatus and is probably situated at much higher energy, as found by Blasse and Bril. In that case there is also better agreement with the optical absorption edge, found in the reflection spectrum at 5.8 eV (not visible in Fig. 4). The low-energy excitation band, not observed by Blasse and Bril, corresponds with the blue-green emission.

The emission and excitation spectra of $Mg_4Ta_{0.4}Nb_{1.6}O_9$ and Mg_4TaNbO_9 are almost exactly the same as the spectra of $Mg_4Nb_2O_9$. The maxima of the excitation bands of the blue emission are shifted somewhat to higher energies with increasing tantalum concentration and the luminescence intensity at 5°K of the blue emission increases with increasing niobium concentration.

In $Mg_4Ta_{1.6}Nb_{0.4}O_9$ (for the figures, see (*6*)) a mixture of tantalate and niobate emission bands is obtained. The relative intensity of these bands depends on excitation energy and temperature.

The results of the decay experiments are shown in Fig. 5. The decay of the blue emission can be described with a single exponential.

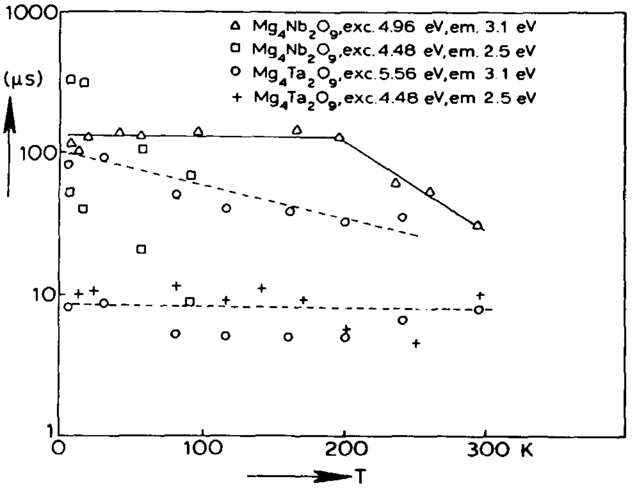

FIG. 5 The temperature dependence of the decay times of the blue and green emissions of $Mg_4Nb_2O_9$ and of the blue and blue-green emissions of $Mg_4Ta_2O_9$.

The decay time is 130 μsec at 5°K and remains constant up to 200°K. At higher temperatures, the decay time decreases and at room temperature a value of 30 μsec is found (Blasse and Bril found 25 μsec at RT (*2*)). The emission, excited with 4.48 eV radiation and measured at 2.5 eV, shows a decay which can be described with the sum of two exponentials. One of these is of the same order of magnitude as the decay time of the blue emission, the other is shorter (about 50 μsec at 5°K, decreasing to 9 μsec at 100°K).

The decay of the blue tantalate emission can be described with the sum of two exponentials. The longer of the two decay times is 100 μsec at 5°K and decreases steadily to 25 μsec at 250°K. The shorter of the two corresponds with the decay time measured for the blue-green tantalate emission and remains practically constant at about 8 μsec in the whole temperature region of the measurements. (Blasse and Bril found a decay time of 6 μsec for the uv emission at RT (*2*)).

4. Discussion

Contrary to the assumption of Blasse and Bril (*2*), but in agreement with our model for the luminescence of titanium-activated stannates and zirconates (*3*, *4*), we postulate that the blue and the green emission in $Mg_4Nb_2O_9$ are due to two different niobate centers, viz., a regular and a defect niobate center. This implies that the efficient blue emission originates from the regular niobate center and the weaker green emission from the defect niobate center. $Mg_4Nb_2O_9$ and $Mg_4Ta_2O_9$ have an ordered corundum structure in which the pentavalent cations form pairs by face sharing of their coordination octahedra (*7*). The defect niobate center could be formed by a partial disorder of the Mg^{2+} and Nb^{5+} ions on the cation sites so that there are also Mg^{2+}–Nb^{5+} pairs instead of only Nb^{5+}–Nb^{5+} pairs. This assumption for the green luminescence of $Mg_4Nb_2O_9$ is sustained by the luminescence properties of $Mg_4Sb_2O_9$:Nb (*8*). The structure of $Mg_4Sb_2O_9$ can be deduced from the ilmenite structure, $MgTiO_3$, an ordered corundum structure with Mg^{2+} and Ti^{4+} layers, by replacing Ti^{4+} at random by $\frac{1}{3}Mg^{2+}$ and $\frac{2}{3}Sb^{5+}$ (*9*). In this structure there are no face-sharing pairs of antimonate octahedra. The emission spectrum of $Mg_4Sb_2O_9$:Nb resembles very much the green emission of $Mg_4Nb_2O_9$. The excitation band of $Mg_4Sb_2O_9$:Nb has about the same spectral position as the excitation band of the green emission in $Mg_4Nb_2O_9$.

The orange emission is probably due to another defect niobate center, perhaps a niobate center associated with an oxygen vacancy. The position and shape of this emission band are not in agreement with any of the possible impurities like manganese, chromium, or other transition metal ions. The width of this band is roughly the same as the width of the other niobate emission bands.

The blue niobate emission shows no concentration quenching, so that there is no energy transfer from one regular niobate group to another. This is to be expected in view of the very small spectral overlap of the blue emission band and the corresponding excitation band. The spectral overlap of the blue emission band and the excitation band of the green emission is larger so that energy transfer from regular to defect niobate centers might be possible. The long-wavelength tail in the spectra of the blue emission at low temperatures seems to indicate that there is indeed some energy transfer.

The situation in $Mg_4Ta_2O_9$ is more complicated. It is probable that the uv emission observed by Blasse and Bril upon cathode-ray- or very-short-wave uv excitation is the regular tantalate emission. There are two additional emissions in $Mg_4Ta_2O_9$, one at 2.9 eV, also found by Blasse and Bril, and a new one at 2.5 eV with the corresponding excitation band at 4.35 eV. In analogy to the green and orange emission in $Mg_4Nb_2O_9$ we suppose that both emissions are due to defect tantalate centers, one of which is formed by a partial disorder of Mg^{2+} and Ta^{5+} while the other is formed by tantalate octahedra associated with oxygen vacancies. It is to be expected that there is energy transfer from the regular center to the center with the 2.5 eV emission. If in our sample the concentration of defect tantalate centers is much larger than in the sample of Blasse and Bril, this could be the reason that in our sample the uv emission is quenched by energy transfer from the regular to the 2.5 eV defect center.

The emission and excitation spectra of $Mg_4Ta_{1.6}Nb_{0.4}O_9$ show a number of bands, originating both from tantalate and niobate centers. It is also possible, that some of these bands are due to Ta–Nb pairs instead of Ta–Ta pairs and Nb–Nb pairs. The ratio of the intensities of these bands depends on temperature and excitation or emission wavelength, which can be due to different temperature quenching of the various emissions or to energy transfer from one center to another. The spectra are, however, too complicated to decide which mechanism is dominant in this case.

A comparison with the luminescence properties of the system $YTa_{1-x}Nb_xO_4$ (*10*), which contains niobate and tantalate tetrahedra, yields several similarities, viz., the occurrence of two emissions and the relative position of the maxima of the tantalate and niobate excitation and emission bands. There is, however, a marked difference. In $YTa_{1-x}Nb_xO_4$ the regular niobate emission band does not depend on the niobate concentration, whereas in $Mg_4Ta_{2-x}Nb_xO_4$ it does. This difference can be related to the occurrence of the Nb–Nb pairs in $Mg_4Ta_{2-x}Nb_xO_4$.

The relatively long decay time of the regular niobate emission is an indication that in emission we are dealing with a forbidden transition. From the reflection spectra we know that the absorption transition is allowed. We can conclude, therefore, that the emission does not originate from the level into which excitation takes place, but from a lower-lying level. A similar situation is encountered and accounted for in the case of the titanate emission (*3*, *4*), although the decay time of the regular titanate emission is somewhat shorter (10 μsec in $La_2MgSn_{1-x}Ti_xO_6$ and 3 μsec in $Mg_2Sn_{1-x}Ti_xO_4$). Because of the position of Ti, Nb, and Ta in the periodical system the spin-orbit coupling increases in the series Ti, Nb, Ta. As a consequence one would expect in the case of a spin-forbidden transition the shortest decay time for the tantalate emission and the longest for the titanate emission. The decay time of the regular tantalate emission has only been measured at room temperature and therefore cannot be compared to the other two. The decay time of the regular niobate emission is, contrary to the prediction based on the spin-orbit coupling, much longer than the decay time of the regular titanate emission. Since the transition in the case of the titanate emission is only spin-forbidden, we assume that the transition corresponding to the regular niobate emission is not only spin-forbidden, but also symmetry-forbidden.

It is possible, that pulsed excitation with 4.48 eV radiation in $Mg_4Nb_2O_9$ yields both the blue and the green emission. The long decay time is in that case due to the blue emission, whereas the short decay time corresponds with the green emission. The fact that the decay time of the defect emission is shorter than the decay of the regular emission is probably caused by the lower symmetry of the defect center. The transition is then no longer symmetry-forbidden.

An interpretation of the decay times of the defect tantalate emissions is not feasible, since a comparison with the regular tantalate emission is not possible.

The conclusion can be drawn that in analogy to the model developed for the luminescence of titanium-activated phosphors, the luminescence properties of the system $Mg_4Ta_{2-x}Nb_xO_9$ can be described with three different centers, one regular and two defect niobate or tantalate centers. The system is not very appropriate for the study of energy transfer from tantalate to niobate centers because of the complexity of the spectra of the samples with small niobate concentration.

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References

1. A. Wachtel, *J. Electrochem. Soc.* **111**, 534 (1964).
2. G. Blasse and A. Bril, *J. Solid State Chem.* **3**, 69 (1971).
3. A. J. H. Macke, Thesis, Utrecht, 1976, Chap. II; submitted to Phys. Status Solidi.
4. A. J. H. Macke, Thesis, Utrecht, 1976, Chap. III; *J. Solid State Chem.* **18**, 337 (1976).
5. F. A. Kröger, "Some Aspects of the Luminescence of Solids," p. 202, Elsevier, Amsterdam (1948).
6. A. J. H. Macke, Thesis, Utrecht, 1976, Appendix.
7. E. F. Bertaut, L. Corliss, F. Forrat, R. Aléonard, and R. Pauthenet, *J. Phys. Chem. Solids* **21**, 234 (1961).
8. G. Blasse, *J. Chem. Phys.* **48**, 3108 (1968).
9. G. Blasse, *Z. Anorg. Allg. Chem.* **331**, 44 (1964).
10. G. Blasse and A. Bril, *J. Lumin.* **3**, 109 (1970).