The Influence of an Effective Charge on the Uranate Luminescence in the Ordered Perovskite Structure

M. E. AZENHA,* D. VAN DER VOORT, AND G. BLASSE

Debye Research Institute, University of Utrecht, P.O. Box 80,000, 3508 TA Utrecht, The Netherlands

The luminescence of the uranate group (UO_6^{6-}) in the ordered perovskites Sr_2MgWO_6, $SrLaMgNbO_6$, and $NaSrMgIO_6$ is investigated. The thermal quenching temperature of the uranate luminescence is related to the sign of the effective charge of the U^{6+} ion in the three perovskite lattices and a comparison with similar effects in the Eu^{3+} luminescence is made. © 1992 Academic Press, Inc.

1. Introduction

In our laboratory we are involved in a study of the luminescence of trivalent rare-earth (RE) ions in calcium and zirconium compounds (*1–4*). The main interest in this study concerns the influence of an effective charge at the Eu^{3+} ion on the quantum efficiency under charge-transfer (CT) excitation (q_{CT}). The results have been explained by a model which relates the sign of the effective charge to the shape and the position of the parabolae in the configurational coordinate diagram (*2*). It appears that a positive effective charge gives rise to a large relaxation in the CT state and a low q_{CT} value. For a negative effective charge the relaxation is predicted to be less and q_{CT} high.

In the case of the Eu^{3+} ion no emission is observed from the CT state, since this CT state decays nonradiatively to the levels of

the $4f^6$ configuration. It is of interest to check the proposed model (*2*) for a luminescent center which emits from the CT state itself. The uranate group shows absorption transitions to and emission transitions from the CT state (*5–9*). In this Brief Communication an attempt is made to study the luminescence of the uranate group in compounds with the perovskite structure (see Fig. 1) which offer an octahedral site to the U^{6+} ion with a different charge relative to the lattice. Hereto, the following systems are investigated: $La_2MgTiO_6 : U^{6+}$, $SrLaMgNbO_6 : U^{6+}$, $Sr_2MgWO_6 : U^{6+}$, and $NaSrMgIO_6 : U^{6+}$. In these systems the U^{6+} ion carries a different effective charge, viz., double positive ($U_{Ti}^{\cdot\cdot}$), single positive ($U_{Nb}^{\cdot}$), neutral (U_W^x), and single negative ($U_I^{\prime}$). The radii of the ions on comparable crystallographic sites are about equal (*10*).

It turns out that a positive effective charge on the U^{6+} ion gives rise to a low quenching temperature of the uranate luminescence, whereas the quenching temperature of the luminescence of the U^{6+} ion with a neutral

* Permanent address: Departamento de Química, Universidade de Coimbra, 3049 Coimbra, Portugal.

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● $= Ti^{4+}, Nb^{5+}, W^{6+}, I^{7+}$

◉ $= La^{3+}, Sr^{2+}, Na^{+}$

◎ $= La^{3+}, Sr^{2+}$
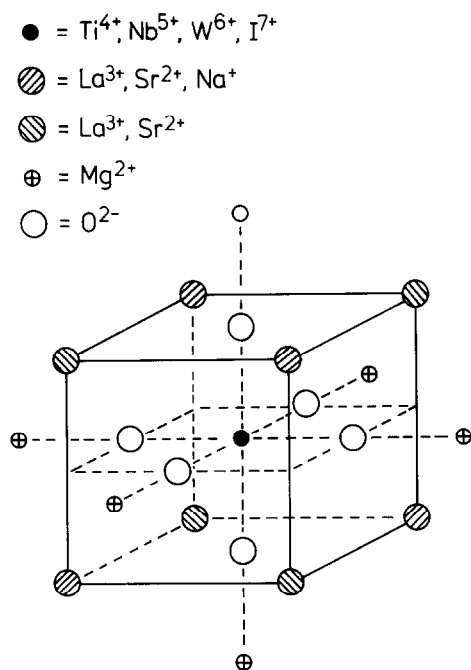
⊕ $= Mg^{2+}$

○ $= O^{2-}$

FIG. 1. Schematic representation of the ordered perovskite structure.

or negative effective charge is much higher. These observations are in agreement with the model proposed by us before (2).

2. Experimental

The measurements described in this paper were performed on powdered samples. The following starting materials were used: $UO_2(CH_3COO)_2 \cdot 2H_2O$, $SrCO_3$, Na_2CO_3, WO_3, H_5IO_6, $MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ (all Merck, p.a.), Nb_2O_5 (Janssen Chimica, 99.99%), TiO_2 (Janssen Chimica, 99.9%), and La_2O_3 (Highways Int., 99.997%). The following compositions were prepared: $Sr_{0.006}La_{1.994}MgTi_{0.997}U_{0.003}O_6$, $Sr_{1.003}La_{0.997}MgNb_{0.997}U_{0.003}O_6$, $Sr_2MgW_{0.997}U_{0.003}O_6$, and $Na_{0.997}Sr_{1.003}MgI_{0.997}U_{0.003}O_6$.

All powders were prepared according to usual solid state techniques. The starting materials were mixed in stoichiometric

amounts, except for H_5IO_6, of which a 30 mole% excess was used. All firing procedures were carried out in air. A first firing was performed for the titanate, niobate, and tungstate powders at 1100°C for 8 hr, followed by a second firing for 8 hr at 1200°C for the tungstate and at 1400°C for the titanate and the niobate powders.

In the first firing of the iodate powder the temperature was slowly increased up to 200°C and was maintained for 2 hr. Then the temperature was increased toward 400°C and maintained for 4 hr. A second firing was carried out for 4 hr at 400°C. The crystal structure of the powders was checked by X-ray powder diffraction and was found to be of the perovskite type.

The luminescence spectra were recorded using a SPEX Fluorolog spectrofluorometer equipped with a 450-W xenon lamp as a light source and a helium flow cryostat for measurements down to 4.2 K (LHeT). Luminescence spectra at temperatures above 300 K (RT) were carried out by placing the samples in a cell which was temperature controlled by a programmable West 2050 temperature controller.

3. Results and Discussion

The luminescence spectra of Sr_2Mg $WO_6 : U^{6+}$ have been reported before (5, 11) and were used for comparison with the other systems. We could reproduce the results from Refs. (5, 11). At RT the emission consists of a broad structureless band with a maximum at about 500 nm. At LHeT the emission band shows vibrational structure (see Fig. 2b). A progression is observed in the symmetric stretching mode of the UO_6^{6-} octahedron ($\nu_s = 800$ cm^{-1}, see also (11). From the low-temperature spectra the value of the Huang–Rhys parameter S can be estimated to be about 1. The Stokes shift at RT amounts to about 2300 cm^{-1}. At about 340 K the intensity of the uranate emission
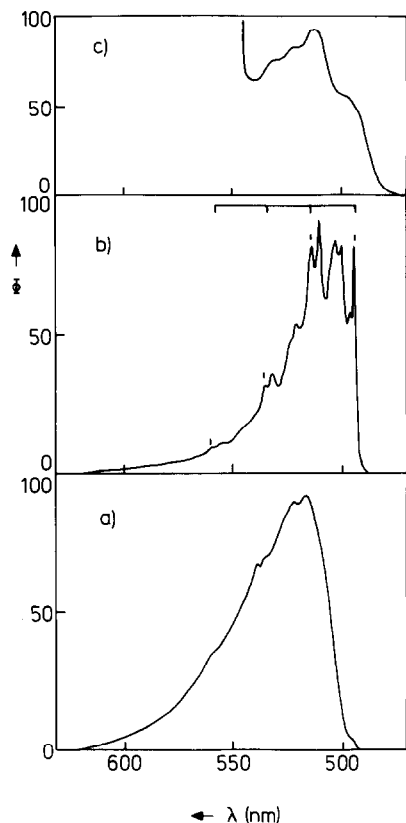
FIG. 2. Emission spectra of the UO_6^{6-} group at LHeT in: (a) $SrLaMgNbO_6$ (λ_{exc} = 345 nm, (b) Sr_2MgWO_6 (λ_{exc} = 345 nm), and (c) $NaSrMgIO_6$ (λ_{exc} = 340 nm). Φ gives the spectral radiant power per constant wavelength interval in arbitrary units. The progression in ν_s (b) is indicated at the top of the figure.

is half of that at LHeT ($T_{1/2}$ = 340 K, see Fig. 3).

La_2MgTiO_6 : U^{6+} shows no emission at RT. At low temperatures a yellowish emission band with a maximum at about 550 nm is observed which is the same as reported for Y_6UO_{12} (12). Also the excitation spectrum corresponds to that of Y_6UO_{12}. Since La_6UO_{12} (13) and Y_6UO_{12} (14) are isostructural, these spectral features are ascribed to a second phase of composition La_6UO_{12}. From this we conclude that the amount of U^{6+} which enters the La_2MgTiO_6 phase is very low.

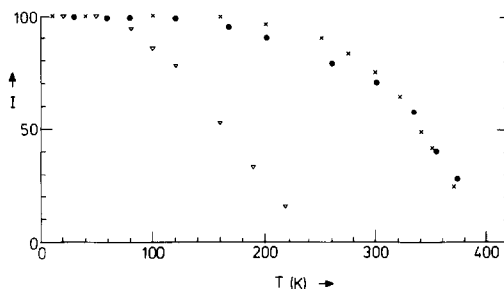FIG. 3. Integrated intensity of the uranate emission as a function of temperature in $SrLaMgNbO_6$ ($\triangledown$), Sr_2MgWO_6 ($\times$), and $NaSrMgIO_6$ ($\bullet$).

$SrLaMgNbO_6$: U^{6+} also shows no luminescence at RT. At low temperatures two emission bands are observed. A weak yellowish emission, which is identical to the one observed in the titanate sample, is ascribed to U^{6+} in La_6UO_{12} (present as a second phase). A green emission with a maximum at about 515 nm (see Fig. 2a) is ascribed to the U^{6+} ion in $SrLaMgNbO_6$. The excitation spectrum of this emission is given in Fig. 4 and consists of a relatively weak band with a maximum at about 450 nm
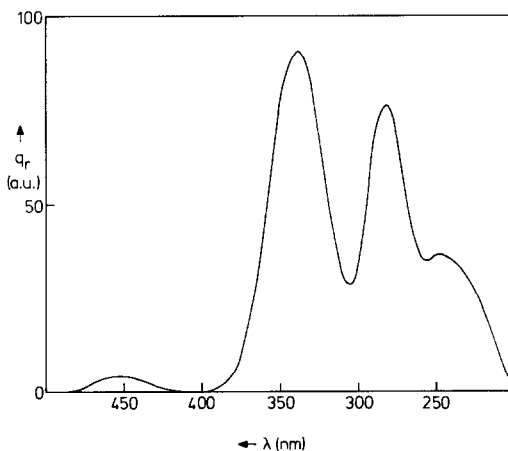

FIG. 4. Excitation spectrum of the uranate emission in $SrLaMgNbO_6$ at LHeT. Emission wavelength is 515 nm. q_r gives the relative quantum output in arbitrary units (a.u.).

and stronger bands with maxima at about 340, 280, and 245 nm. Bleijenberg has discussed the origin of the CT bands within the UO_6^{6-} group (15). According to that work we ascribe the strong excitation bands at 280 and 340 nm to electric-dipole CT transitions and the weak band at 450 nm to a magnetic-dipole CT transition. The excitation band at 245 nm is ascribed to the niobate group, since after excitation into this band not only uranate emission is observed, but also a broad emission band with a maximum at about 380 nm. The latter emission is ascribed to the niobate group. These results point to energy transfer from the niobate group to the U^{6+} ion. The emission band of the UO_6^{6-} group in $SrLaMgNbO_6$ shows poor vibrational structure at LHeT. The Stokes shift of the UO_6^{6-} emission amounts to 2800 cm^{-1}. The shape of the emission band suggests that there is some inhomogeneous broadening as is to be expected in view of the charge compensation. The value of S is derived to be about 1.5, but this value has to be considered as a rough estimate. The increase of the value of S for U^{6+} in the niobate lattice relative to the tungstate lattice is in agreement with the increasing Stokes shift. A striking difference between the uranate luminescence in the tungstate and the niobate is the drastic decrease of the value of the quenching temperature: the quenching temperature of the uranate emission ($T_{1/2}$) in the niobate is only 165 K (see Fig. 3).

The sample $NaSrMgIO_6$: U^{6+} shows a green emission band at RT with a maximum at about 510 nm. At low temperatures another structured emission arises in the longer wavelength region which is identical to the emission of MgO : U^{6+} (16). Apparently the amount of U^{6+} which can be incorporated into the iodate lattice is limited. From the intensity of the uranate emission after excitation into bands of the same nature (CT electric-dipole) an estimate of the partition of U^{6+} over the two lattices can be

TABLE I

DATA ON THE LUMINESCENCE OF THE U^{6+} ION IN THE ORDERED PEROVSKITE STRUCTURE

Compound	Emission maximum (nm, estimated)	Stokes shift (cm^{-1})	$T_{1/2}$ (K)
SrLaMgNbO$_6$	515	2800	165
Sr$_2$MgWO$_6$	500	2300	340
NaSrMgIO$_6$	510	—	350

Note. Also see text.

made. It appears that only some 10% of the U^{6+} ions are incorporated into the perovskite lattice. In the discussion we confine ourselves to the emission band at 510 nm. The shape of the excitation spectrum of this emission is comparable to that of the uranate emission in $SrLaMgNbO_6$. The magnetic-dipole CT transition was also weakly observed, but the exact position could not be derived from the spectrum because the light output of the xenon lamp strongly fluctuates in the region of this transition. As a matter of fact the excitation band of the niobate group is lacking. From these spectral results we conclude that the 510-nm emission band is due to the uranate emission in the perovskite lattice of $NaSrMgIO_6$. The uranate emission in $NaSrMgIO_6$ shows hardly any structure at low temperatures (see Fig. 2c). Due to the strongly interfering emission of MgO : U^{6+} we were not able to make an estimate of the Huang–Rhys parameter S and of the Stokes shift. The quenching temperature of the uranate emission is very high and amounts to about 350 K (see Fig. 3). The results for the uranate luminescence in the perovskites studied are summarized in Table I.

The model presented before (2) predicts that for an effective charge on the luminescent ion which varies from positive to negative the Stokes shift should decrease and the quenching temperature should increase. An inspection of Table I shows that this trend is indeed observed. This is the first direct

proof that the presence of an effective charge at the site of a luminescent ion influences its luminescence properties. Especially the variation of the quenching temperature is an interesting effect. The difference in $T_{1/2}$ between the iodate and the tungstate is not significant, but the quenching temperature of the niobate is substantially lower than the two other cases. These results indicate that the excited CT state expands if the effective charge increases. The same effect as described here for U^{6+} in the ordered perovskite structure was recently observed in this laboratory (17) for the scheelite and fergusonite structure, where the U^{6+} ion is in four coordination.

It is satisfying to find that the model which explains the influence of an effective charge on the luminescence properties of the Eu^{3+} ion is also able to do so for another ion with CT transitions. This suggests that the model proposed before (2) is generally valid for ions which show luminescence in which CT transitions play a role. In fact it was already applied before in the case of $Al_2O_3 : Ti^{4+}$ (18). The difference between Eu^{3+} and U^{6+} is that in the former case excitation is into the CT state which then feeds an emitting state of another configuration, whereas in the latter case excitation and emission are from the CT state involved. This makes a direct observation of the effect under study possible.

4. Conclusions

Although it is difficult to dissolve large amounts of U^{6+} in ordered perovskites with aliovalent ions, this study shows convincingly that an effective charge on the U^{6+} ion has a drastic influence on the luminescence properties of the uranate group. This can be

explained by a model proposed before for Eu^{3+} (2). The spectral measurements on U^{6+}, however, are of a more direct nature.

Acknowledgments

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