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THE LUMINESCENCE PROPERTIES OF $MgUO_4$

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The luminescence of $MgUO_4$ has been investigated. Emission and excitation spectra as well as the decay time and the quantum efficiency of the emission were measured at 4.2 K. The temperature dependence of the emission spectrum and the emission intensity was studied. The results show that in $MgUO_4$ the emission originates from uranate centres near defects. These centres act as optical traps. Even at 4.2 K about 90% of the excitation energy is lost non-radiatively by trapping at killer sites. These are most probably due to the presence of U^{5+} ions.

1. Introduction

In the course of our study of concentrated uranate systems we already reported on the luminescence properties of Ba_2CaUO_6 [1]. For this compound it was found that even at 4.2 K energy migration plays an important role and that the emission, after excitation into the intrinsic uranate centres, occurs from uranate centres near defects. When the temperature is raised the luminescent traps get emptied and trapping at killer sites becomes important.

In our laboratory the structure sensitivity of the luminescence of uranate groups in diluted systems is also investigated [2]. So we became interested in the role of crystal structure on the luminescence properties of the concentrated uranates. We therefore decided to investigate the luminescence properties of $MgUO_4$.

In this compound the U^{6+} ion is surrounded by six oxygen ions. The distorted uranate octahedra form linear chains by sharing edges, resulting in a much shorter U–U distance in $MgUO_4$ (3.6 Å) than in Ba_2CaUO_6 (6.2 Å). The two oxygen ions which do not participate in the edge sharing have a considerably shorter distance to the U^{6+} ion than the other four (1.92 Å and 2.16–2.20 Å, respectively) [3]. The uranate group in $MgUO_4$ can, therefore, be regarded as a uranyl group with four equatorial oxygens. It is likely that the luminescence spectra will resemble those of uranyl compounds and that energy migration as reported for Ba_2CaUO_6 will occur.

2. Experimental

Powders of $MgUO_4$ were prepared by firing intimate mixtures of basic magnesium carbonate and uranyl acetate (both Merck p.a.) for a few periods of 25 h at 1000°C in an oxygen atmosphere. Samples were checked by X-ray powder analysis. The set-up for the optical experiments has been described elsewhere [1]. A Leiss double grating monochromator was used. The resolution was 0.2 and 0.4 nm for the emission and excitation spectra, respectively. The spectrum of fig. 1 was measured with a Perkin–Elmer MPF 2A spectrofluorimeter. The resolution was ±2 nm. The quantum efficiency of the luminescence was measured using Zn_2SiO_4 : Mn^{2+} as a standard.

3. Results

At LHet $MgUO_4$ shows an orange photoluminescence with a quantum efficiency of approximately 10%. The luminescence intensity decreases with increasing temperature and is quenched completely at 30 K.

In fig. 1 the emission spectrum, measured at 6 K with low resolution (2 nm), is shown. This spectrum gives a good overview of the vibrational structure in the emission spectrum. The assignment of the vibrational structure is given in table 1, mainly in terms of $U-O_I$ vibrations. Here O_I denotes the oxygen ions which have a short distance (1.92 Å) to the uranium ions. The frequency of the i.r. active bending mode ν_d (246 cm^{-1}) is taken from Ohwada [4]. To obtain the frequency

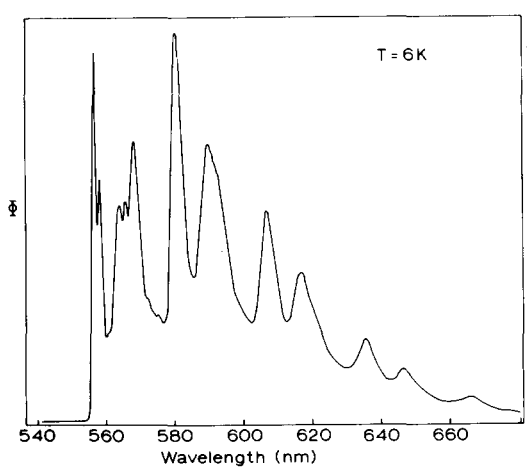

Fig. 1. Emission spectrum of $MgUO_4$, measured with low resolution (2 nm). The excitation wavelength is 400 nm. Φ denotes the spectral radiant power per constant wavelength interval in arbitrary units.

Table 1
Assignment of the vibrational structure in the emission spectrum of $MgUO_4$ at 6 K

λ (nm)	Difference from zero-phonon line a (cm^{-1})	Assignment *
556.6	0	zp line a
558.0	45	zp line b
564.1	239	a – ν_d
565.9	295	b – ν_d
568.1	364	
581 (br)	750	a, b – ν_s
590 (br)	1020	a, b – ($\nu_s + \nu_d$)
607 (br)	1490	a, b – $2\nu_s$
617 (br)	1760	a, b – ($2\nu_s + \nu_d$)
635 (br)	2230	a, b – $3\nu_s$
646 (br)	2490	a, b – ($3\nu_s + \nu_d$)
666 (br)	2950	a, b – $4\nu_s$

* zp = zero-phonon, ν_s is the symmetric stretching mode of the $U-O_I$ bond and ν_d is the bending mode of the $U-O_I$ bond; br = broad.

of the symmetric $U-O_I$ stretching vibration a Raman spectrum was recorded. The observed maxima are situated at 135 (s), 235 (sh), 275 (s), 360 (w), 410 (w), 530 (w) and 750 (s) cm^{-1}. The peak at 750 cm^{-1} is ascribed to the $U-O_I$ symmetric stretching vibration.

In fig. 2 the temperature dependence of the short wavelength part of the emission spectrum, measured with a resolution of 0.2 nm, is shown. At 1.4 K there are six zero-phonon lines. With increasing temperature the lines at shorter wavelengths disappear. The position of the zero-phonon lines is different in different samples of $MgUO_4$, for example 553.1, 553.6, 556.6 and 558.0 nm for sample I, 552.9, 553.1, 553.6 and 558.0 for sample II and 553.1, 553.6 and 558.0 nm for sample III, all measured at 4.2 K. Sample I and II were fired in an oxygen atmosphere, sample III in a nitrogen atmosphere. Data given in this paper relate to sample I.

The excitation spectrum of the orange luminescence of $MgUO_4$ consists of a broad band which extends from 550 nm till far into the uv region. The long wavelength part of the excitation spectrum, measured at 6 K, is given in fig. 3. The three sharp peaks at 551.6, 550.3 and 546.3 nm are considered to be zero-phonon transitions. Note that the zero-phonon lines in the emission spectrum are all situated at longer wavelengths than those in the excitation spectrum for all temperatures. It should be mentioned that in the diluted systems $A_2BWO_6-U^{6+}$ the zero-phonon line in the emission spectrum coincides with the zero-phonon line in the excitation spectrum [5].

The decay time of the total emission was measured at 4.2 K over 2 decades. At this temperature the decay curve is a single exponential within experimental error (τ = 100 μs).

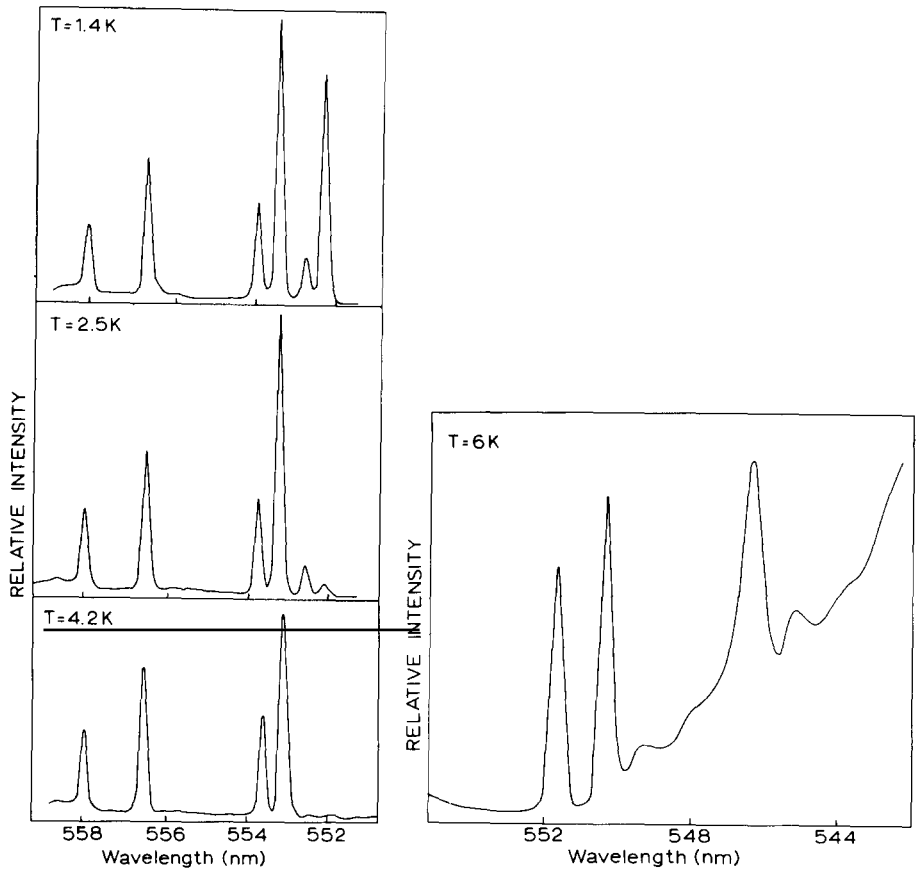

Fig. 2. The short wavelength part of the emission spectrum of $MgUO_4$ at different temperatures, measured with high resolution (0.2 nm). Excitation is in the region between 250 and 400 nm.

Fig. 3. The long wavelength part of the excitation spectrum of the orange luminescence of $MgUO_4$, measured with a resolution of 0.4 nm. The emission wavelength is about 600 nm.

Table 2
The values of ΔE for the six different zero-phonon lines in $MgUO_4$. ΔE in the second column has been calculated from the spectra at 4.2 K; for the first two values the emission spectrum at 1.4 K has been used. In the third column the ΔE values found be plotting $\ln(1/I - 1/I_0)$ vs. $1/T$ have been given.

λ (nm)	ΔE (cm^{-1})	ΔE (cm^{-1})
552.2	20 ± 8	–
552.7	36 ± 8	–
553.1	49 ± 8	–
553.6	65 ± 8	58 ± 3
556.6	163 ± 8	154 ± 10
558.0	208 ± 8	180 ± 30

The temperature dependence of the intensity of the zero-phonon lines was measured. Due to instrumental limitations this was not possible for all lines. In all cases the curves follow the relation $1/I = 1/I_0 + C\exp(-\Delta E/kT)$. In this expression I_0 is the intensity at 0 K, estimated by extrapolating the curves towards 0 K. The values of ΔE obtained have been given in table 2.

4. Discussion

The luminescence properties of $MgUO_4$ show a great resemblance with those of Ba_2CaUO_6. In both compounds none of the zero-phonon lines in the emission and excitation spectrum coincide. In addition the zero-phonon lines at the shorter-wavelength part of the emission spectrum disappear with increasing temperature. This means that the luminescence mechanism in $MgUO_4$ can be described in the same way as for Ba_2CaUO_6 [1]. Excitation takes place in the intrinsic uranate centres. The excitation energy migrates through the lattice (probably along the linear chains) till it is trapped at uranate centres near defects, which have slightly lower energy levels. These are the centres from which the luminescence originates. When the temperature is raised the traps get emptied one by one. This results in a decrease of the luminescence intensity.

There is a striking difference, however, between $MgUO_4$ and Ba_2CaUO_6, viz. the quantum efficiency at 4.2 K, which is 10% and 80%, respectively. The low efficiency in $MgUO_4$ is ascribed to excitation energy migration to killer sites, where the energy is lost non-radiatively.

Though the emission of $MgUO_4$ originates from uranate centres near defects, the vibrational structure of the emission can be described reasonably well with the vibrational frequencies of the intrinsic centres. This indicates that the uranate centre is only slightly influenced by the defect. A strong progression in the $U-O_I$ symmetric stretching mode is observed. This is characteristic of compounds containing uranyl groups [6] and points to a large similarity between the uranyl group and the uranate centres in $MgUO_4$.

The long value of the radiative decay time (100 μs) means that we are dealing with a parity-forbidden electric-dipole transition [7,8]. The decay time at 4.2 K is regarded as a radiative one in view of the experimental accuracy. At 4.2 K two of the six zero-phonon lines have disappeared, three have their maximum intensity, and one is already decreasing. Since only one exponential is observed in the decay curve, we assume that the influence of non-radiative losses is negligible in comparison with the experimental accuracy.

The three sharp lines in the excitation spectrum of $MgUO_4$ (fig. 3) are ascribed to three zero-phonon lines of the intrinsic uranate group. In Ba_2CaUO_6 only one zero-phonon line was found in the excitation spectrum. The presence of three zero-phonon lines in $MgUO_4$ may be due to a splitting of the first excited state as a consequence of the low site symmetry of the uranium ion in $MgUO_4$, viz. C_{2v}

instead of O_h in Ba_2CaUO_6. Such a splitting of the first excited state has also been found in other compounds where the site symmetry of the uranium is low, for example β-Li_4WO_5 : U^{6+} [9].

In fig. 4 an energy level diagram for the luminescence process in $MgUO_4$ is shown. For simplicity only one luminescent trap has been drawn. The difference between the lowest excited state of the intrinsic uranate centre and that of a defect centre is denoted as ΔE. The ΔE values are equal to the energy difference between the position of the lowest-zero-phonon line in the excitation spectrum and the position of the zero-phonon lines in the emission spectrum. If the diagram, shown in fig. 4, is valid, the luminescence intensity of a given trap should vary with temperature according to $1/I = 1/I_0 + c \exp(-\Delta E/kT)$. The ΔE values found in this way should correspond to those derived from the spectra. In table 2 both ΔE values are given for the traps emitting at 553.6, 556.6 and 558.0 nm. They are in good agreement with each other, which confirms the proposed model.

It is difficult to determine the chemical nature of the luminescent traps. By measuring the emission spectra of different samples of $MgUO_4$ we found that part of the zero-phonon lines in the emission spectrum depends on sample history and another part does not. The zero-phonon lines at 553.1, 553.6 and 558.0 nm are found in each sample, whereas the lines at 556.6 and 552.9 are only found in sample I and II, respectively. This seems to indicate that the emitting uranate groups belong to two types, viz. a group consisting of uranate centres disturbed by lattice imperfections and a group of uranate centres disturbed by impurities.

The killer sites, where the excitation energy is lost non-radiatively, are most probably U^{5+} ions. Compounds like $MgUO_4$ easily become non-stoichiometric by loss of oxygen [10]. In fact our samples show a weak, very broad absorption band between 500 and 1400 nm in the diffuse reflectance spectrum. Compounds containing both U^{6+} and U^{5+} ions also show such a very broad absorption band in this spectral region [11], which cannot be easily ascribed to either the U^{5+} ion or the uranate centre. We propose that this absorption is due to an intervalence charge transfer (IVCT) transition between U^{5+} and U^{6+}. These transitions are often ob-

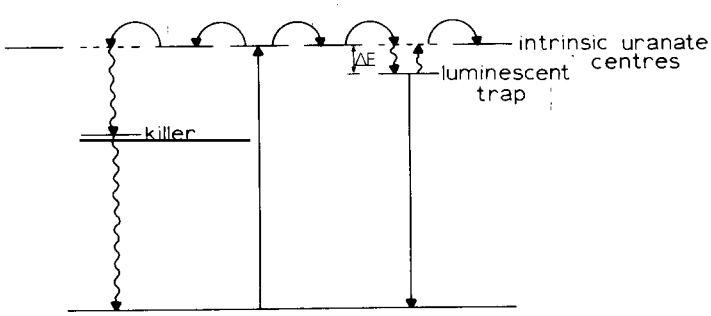

Fig. 4. Schematic energy level scheme for the luminescence process in $MgUO_4$.

served in compounds containing ions in two different valencies, e.g. Tb^{3+}, Tb^{4+} [12]. The spectral overlap between the emission of $MgUO_4$ and the IVCT absorption is good enough to yield efficient energy transfer when the excitation energy, after migration through the lattice, reaches a killer site consisting of a central U^{5+} ion with its nearest U^{6+} neighbours.

Thus in $MgUO_4$ the greater part of the excitation energy reaches the killer sites, whereas in Ba_2CaUO_6 most of the excitation energy reaches the luminescent traps. In the latter compound the U^{5+} concentration must be much smaller than in $MgUO_4$, because for Ba_2CaUO_6 no absorption was found in the near-infrared region of the diffuse reflectance spectrum. It is likely that the difference in quantum efficiency between these two compounds arises mainly from the difference in U^{5+} concentration. It should, however, be emphasized that in this model it is in fact the ratio of the concentrations of luminescent traps and killer sites which determines the quantum efficiency. We have tried to vary the U^{5+} concentration in $MgUO_4$ by firing in different atmospheres. The diffuse reflectance spectrum in the near-infrared region showed, however, no clear differences between the different samples nor did the quantum efficiency of the luminescence within the experimental accuracy.

We also investigated some other uranate compounds, e.g. Li_4UO_5 and Y_6UO_{12}. Both show energy migration and luminescence from traps at low temperatures. The quantum efficiency of Y_6UO_{12} is so low that at 4.2 K hardly any luminescence can be observed. This compound also shows the above-mentioned absorption band in the diffuse reflectance spectrum. The quantum efficiency of the luminescence of Li_4UO_5 was not measured but seems to be very high.

We conclude that the luminescence properties of all kinds of uranates with different crystal structure resemble each other strongly in certain aspects. All compounds show efficient energy migration and luminescence from traps at low temperatures. The main difference between them is found in the quantum efficiency at low temperatures which is determined by the concentration ratio of the luminescent traps and the killer sites.

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