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ENERGY TRANSFER BETWEEN OCTAHEDRAL TUNGSTATE AND URANATE GROUPS IN OXIDES WITH PEROVSKITE STRUCTURE

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Energy transfer between tungstate and uranate groups in oxides with perovskite structure is reported. The critical distance for this process is about 25 Å. Evidence is given for energy transfer between tungstate groups. In this case the critical distance is estimated to be about 8 Å.

1. Introduction

Efficient green emission has been reported for the octahedral uranate group in ordered perovskites with general formula $A_2BB'O_6$ (A = Ca, Sr, Ba; B = Mg, Ca, Sr; B′ = Te, W) [1]. The excitation spectrum of this luminescence shows two bands in the UV region. The one at lower energy arises from direct excitation of the uranate group. The band at higher energy is broad and arises from excitation of the tungstate groups, followed by energy transfer to the uranate group. Emission spectra show that, dependent on the host lattice, this energy transfer does not always quench the tungstate emission completely. Upon excitation in the tungstate host lattice groups at 77 K the compounds $A_2BW_{0.997}U_{0.003}O_6$ (A_2B = Ba_2Ca, Ba_2Sr and Ca_2Mg) show green uranate as well as blue tungstate emission. The tungstate emission of perovskites with A_2B = Ba_2Mg and Sr_2Mg, however, is completely quenched by 0.3% uranium. In the compounds mentioned excitation of the tungstate group can be followed by one or more of the following processes:

a. radiative emission from the tungstate group with probability P^r_W,
b. non-radiative decay; this process is neglected, because the measurements were made at temperatures where the quantum efficiency is high,
c. transfer of the excitation energy to another tungstate group with probability P_{WW},
d. transfer of the excitation energy to a uranate group with probability P_{WU}; this process is followed by radiative emission from the uranate group.

It is the purpose of this paper to report on energy transfer in ordered perovskites according to process *d*, but as a consequence a study of process *c* has been included.

2. Experimental

Energy transfer was studied in the ordered perovskites $A_2BB'O_6$ and, in more detail, in $Sr_2MgTe_{1-x-y}W_xU_yO_6$ ($y = 0.003, 0.01 \leqslant x \leqslant 0.75$). Samples were prepared as described before [1]. The presence of tungsten and uranium in the tellurium host lattice does not change the crystal structures nor the lattice parameter. All measurements were performed as described before [1].

3. Results and discussion

Our results indicate that we are not dealing with radiative transfer. With increasing uranium concentration no reduction of the tungstate emission band in the spectral overlap region was observed.

The theory of non-radiative energy transfer has been given by Förster [2] and later, in an extended form, by Dexter [3]. We consider only energy transfer by electric dipole–dipole interaction in view of the allowed nature of the transitions involved and the large distances between the relevant centres (see below). The probability of dipole–dipole energy transfer from a tungstate to an uranate group is given in good approximation by the following expression:

$$P_{WU}(dd) = 0.63 \times 10^{28} \frac{Q_U}{r_{WU}^6 \overline{\tau}_W} \frac{1}{E^4} \int F_W(E) f_U(E)\, dE \qquad (1)$$

where the values of the constants have been inserted, r_{WU} is in Å units, τ_W in seconds, E in eV and Q_U, which is related to the oscillator strength, P_U, of the absorption transition in the uranate group in cm^2eV [4].

If the probability of tungstate emission ($P_W^r = \tau_W^{-1}$) equals the probability of energy transfer from a tungstate to a uranate group (P_{WU}), eq. (1) yields:

$$R_c^6 = 0.63 \times 10^{28} \frac{Q_U}{E^4} \int F_W(E) f_U(E)\, dE \qquad (2)$$

R_c is called the critical distance at which $P_{WU} = P_W^r$. The value of R_c is not very sensitive to small changes in the spectral overlap or the oscillator strength.

The uranium concentration in our samples amounts to 0.3 mol%, so that concentration quenching can be neglected [5]. If the probabilities of non-radiative decay and tungstate-tungstate energy transfer are negligible, the ratio P_W^r/P_{WU} will be equal to the ratio of the quantum efficiencies of the tungstate emission and the uranate emission. This ratio will not depend on the tungsten concentration as long as the uranium concentration is fixed and the assumptions mentioned remain valid. In fig. 1 the ratio of the quantum efficiencies is given as a function of the tungsten concentration for excitation with 4.13 eV (tungstate excitation). Up to about $x = 0.1$ this ratio

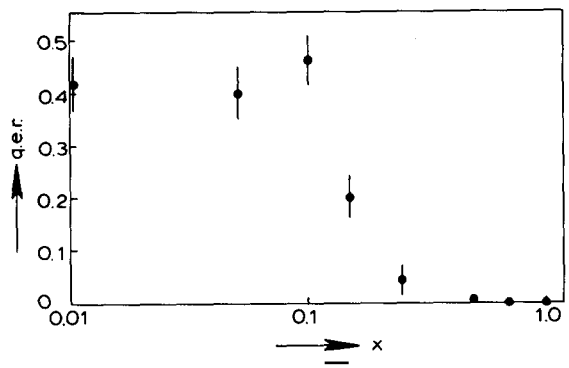

Fig. 1. The quantum efficiency ratio (q.e.r.) of the tungstate and uranate emission of $Sr_2MgTe_{1-x-0.003}W_xU_{0.003}O_6$ for excitation into the tungstate group at 295 K as a function of the tungsten concentration x.

is constant, so that P_{WW} is in fact negligible. The ratio is about 0.4. Together with the value of y this yields for the critical distance, R_c, the approximate value of 25 Å. For higher tungsten concentrations the ratio decreases drastically (see fig. 1). This is probably due to the occurrence of energy transfer between the tungstate groups mutually. Above $x = 0.1$ the average shortest W–W distance in the samples becomes less than twice the shortest W–W distance in the crystal structure (5.5 Å). In view of earlier work on tungstates [6,7] it is nevertheless surprising that tungstate-tungstate transfer proceeds over distances of this order of magnitude.

The critical distance for tungstate-uranate energy transfer has also been calculated with formula (2). The blue tungstate emission overlaps considerably with the uranate excitation band. In order to calculate the spectral overlap we have fit the high-energy side of the tungstate emission band with a gaussian. The spectral overlap between the tungstate emission and the uranate excitation band is 0.22 eV^{-1} and $E = 3.50$ eV. Table 1 gives the relevant results. The oscillator strength of the uranate absorption band is unknown. In the course of our study on the uranate luminescence we have found this absorption to be an allowed transition [5]. We assume the oscillator strength to be 0.05. The influence of the choice of P_U on the critical distance is shown in table 1. As is to be expected, the overlap at 5 K is smaller and so is the critical distance. The value of R_c obtained in this way agrees well with with that obtained from the quantum efficiency ratio. We conclude that energy transfer from tungstate to uranate proceeds over large distances.

The low-energy side of the tungstate excitation band has also been fit with a gaussian. The critical distance calculated for the tungstate-tungstate energy transfer is given in table 1 too. At 5 K this overlap is very small ($<10^{-7}$ eV^{-1}), so that the probability for energy transfer by dipole-dipole interaction between tungstate groups mutually will be low. Although the values for R_c at room temperature are not very

Table 1
Summary of the calculations of the tungstate-uranate energy transfer at 295 K and 5 K and the tungstate-tungstate energy transfer at 295 K for $Sr_2MgTe_{0.947}W_{0.050}U_{0.003}O_6$.

		W–U transfer				W–W transfer
T(K)		295	5.			295
Overlap (eV^{-1})		0.22	0.10_5			5×10^{-4}
E (eV)		3.50	3.50			4.03
$P_U = 0.01$	R_c(Å) =	19	17	$P_W^r = 0.01$	R_c(Å) =	6
= 0.05		25	22	= 0.05	=	8
= 0.1		28	24	= 0.1	=	9

reliable, the results of this calculation confirm the occurrence of tungstate-tungstate energy transfer deduced from fig. 1.

Finally we turn to the other perovskite systems. Table 2 shows the position of the maximum of the tungstate emission band in tellurium-diluted perovskites [8] and the position of the maximum of the uranate excitation band [5]. Comparing the given data with those of the perovskite Sr_2MgTeO_6 it is certain that in Ba_2MgWO_6 energy transfer from tungstate to uranate occurs over even larger distances than in the strontium compound (larger spectral overlap). This explains the absence of tungstate emission in Ba_2MgWO_6–U upon excitation into the tungstate groups. For the other perovskites the overlap will be less than in Sr_2MgTeO_6 and energy transfer will be restricted to smaller distances, so that the appearance of tungstate emission is not unexpected. In accordance with these results the intensity ratio of the short and long wavelength excitation bands of the uranate emission diminishes with decreasing overlap [5].

As a final remark we can state that we have given evidence for energy transfer between tungstate groups. This has been confirmed by the occurrence of concentration quenching of the tungstate emission in systems $A_2BTe_{1-x}W_xO_6$ [8]. These phenomena have not been reported before for tungstates.

Table 2
Position of the maxima of the uranate excitation band and the tungstate emission band in some ordered perovskites A_2BTeO_6.

A B	$U_{excitation}$ (eV)	$W_{emission}$ (eV)	Difference (eV)
Sr Mg	3.7	3.05	0.65
Ba Mg	3.4	2.95	0.45
Ba Ca	3.7	2.8	0.9
Ba Sr	3.6	2.6	1.0

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