

THE NATURE OF THE EMISSION TRANSITION OF THE OCTAHEDRAL URANATE GROUP

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Decay times of the green luminescence of U^{6+} in oxides with perovskite structure are reported. The influence of the site symmetry is found to be considerable. The temperature dependence of the decay time gives evidence for a coupling of the electronic transition with a phonon of about 200 cm^{-1} in the excited state. The results show the emission to originate from a parity-forbidden transition, vibronically allowed by coupling with vibrations of ungerade symmetry.

1. Introduction

Recently we have reported the luminescence of hexavalent uranium in oxides with ordered perovskite structure [1]. These compounds show an efficient green luminescence. At present a more detailed study of the luminescence mechanism has been carried out. In this note we report on the nature of the transition responsible for the emission.

Up to now only the electronic transitions in the uranyl ion (UO_2^{2+}) have been discussed thoroughly [2,3]. In general its emission is assumed to be a spin-forbidden triplet-singlet transition [2]. Jørgensen, however, has argued that it has no meaning to speak about singlet or triplet states [4]. For a fluorescing level of $CaF_2:U^{6+}$ Manson et al. have measured the Zeeman splitting [5]. Their analysis shows the zero-phonon emission line to be a pure magnetic dipole transition. The emitting centre has been shown to have threefold symmetry. From the absence of electric-dipole intensity it is assumed to have a centre of symmetry. They could not decide definitely between a UO_2^{2+} and a UO_6^{6-} group as the emitting centre.

We are considering the luminescence of the UO_6^{6-} group in oxides with ordered perovskite structure. The emitting centre in this type of compounds occupies a site with inversion symmetry. As mentioned earlier this emission shows vibrational fine structure at low temperatures [1]. The vibronic lines can be assigned to a coupling of the electronic transition with

ungerade vibrational modes [6]. Together with the long decay time reported before, this points to a parity-forbidden electric-dipole transition.

The parity selection rule can be relaxed by a permanent non-centrosymmetric distortion or by coupling with ungerade vibrational modes. In this note the influence of the former is considered by studying the luminescence decay in a series of compounds with increasing deviation from cubic site symmetry, whereas the influence of the latter is found from the temperature dependence of the decay time.

2. Experimental

We have measured the decay time of $SrLaNaW_{0.997}U_{0.003}O_6$ and of compositions with the general formula $A_2BW_{0.997}U_{0.003}O_6$ ($A = Ca, Sr, Ba$; $B = Mg, Ca, Sr, Zn$). Powder samples were prepared and checked as described before [1]. $SrLaNaW_{0.997}U_{0.003}O_6$ was fired at $900^\circ C$ for about 7 hours. This is a new compound which is related to a series of ordered perovskites with cubic crystal structure reported by Brixner [7]. In contrast with these $SrLaNaWO_6$ has an orthorhombic structure. The lattice parameters are $a = 5.80\text{ \AA}$, $b = 5.67\text{ \AA}$ and $c = 8.08\text{ \AA}$. The samples were excited with a pulsed Xe-lamp (pulse width $\pm 1\text{ }\mu s$), along with a 366 nm Balzers narrow band interference filter. By using this combination we excite directly into the uranate group. The relevant

Table 1
Decay time of the luminescence of U^{6+} in oxides with perovskite structure at LNT. Mainly 366 nm excitation. All compounds contain 0.3 mol percent U^{6+}

Ba_2MgWO_6	255 μs	Ba_2MgWO_6	255 μs	$SrLaNaWO_6$	$\leq 155 \mu s$
Ba_2ZnWO_6	260 μs	Sr_2MgWO_6	245 μs	$Ba_2Li_{1.2}W_{0.8}O_6$	10 and 80 μs [12]
Ba_2CaWO_6	240 μs	Ca_2MgWO_6	220 μs		
Ba_2SrWO_6	200 μs				

absorption is an allowed transition. In the emission beam a Balzers broad band interference K3 filter was placed, which has a maximum transmission for the emission. The emission intensity was measured with a photomultiplier and the time dependence was displayed on the screen of a sampling oscilloscope. For averaging and storing of the signal use was made of a waveform eductor.

For $Ba_2MgW_{0.997}U_{0.003}O_6$ we have measured the temperature dependence of the decay time. The sample was mounted in a liquid helium flow cryostat (Oxford CF 100). The temperature could be adjusted between liquid HeT and RT by varying the flow rate.

The decay time of the other samples was measured at LNT. We used a home-made cryostat, which was cooled by thermal contact with a liquid nitrogen bath.

3. Results

In table 1 decay times are given for numerous compositions at LNT. The decay curves can be described by single exponentials. Only for $SrLaNaW_{0.997}U_{0.003}O_6$ a sum of several exponentials gives a better agreement with the experimental curve. The longest decay time was 155 μs , the others were shorter.

The temperature dependence of the decay time of $Ba_2MgW_{0.997}U_{0.003}O_6$ is given in fig. 1 together with the temperature dependence of the emission intensity. Note that the decay time decreases in a region where the emission intensity is constant.

4. Discussion

The emission of the compounds studied shows vibrational fine structure at lower temperatures. We can distinguish a well-defined one-phonon part. It follows from our assignment that the vibrational modes involved are the ungerade internal modes of the UO_6^{6-}

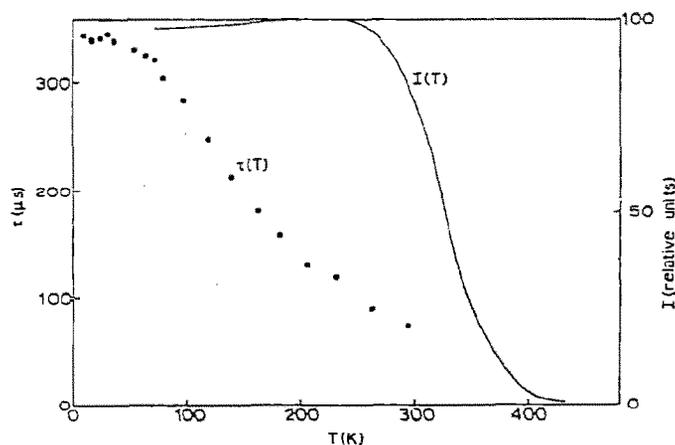


Fig. 1. Temperature dependence of the decay time τ and the intensity I of the green emission of $Ba_2MgW_{0.997}U_{0.003}O_6$. Mainly 366 nm excitation.

group [6]. Vibrational spectroscopic studies of compounds with ordered perovskite structure have shown that we may consider the UO_6^{6-} group as an isolated molecular group with its own internal vibrational modes, corresponding with those for an octahedron [8,9]. For such a group there are three modes with "ungerade" symmetry, viz. $\nu_3(T_{1u})$, $\nu_4(T_{1u})$, and $\nu_6(T_{2u})$. Coupling of the pure electronic transition with one of the three ungerade modes is an indication for a parity-forbidden electric-dipole transition.

A static removal of the centre of symmetry can also relax the parity selection rule. For the given compounds vibrational spectroscopic results are available [10]. From these we learned that an increasing broadening of the two IR active bands appeared from top to bottom in table 1. A broadening of these bands is due to a deviation from cubic symmetry which lifts the threefold degeneracy of these modes. A deviation from inversion symmetry may be the result. We see from table 1 that in the series A_2BWO_6-U the decay time decreases with increasing deviation from cubic symmetry.

Note that the measurements were made for a concentration where concentration quenching is negligible and at a temperature where temperature dependent radiationless decay can be neglected [6].

For $\text{SrLaNaW}_{0.997}\text{U}_{0.003}\text{O}_6$ we have found more than one decay time. This is the result of the presence of UO_6^{6-} groups with different surroundings. In the IR spectrum of this compound a weak additional absorption band is observed at the same frequency where the $\nu_1(\text{A}_{1g})$ is observed in the Raman spectrum. This points to the mixed occupation of the larger cation sites by Sr^{2+} and La^{3+} ions which causes a deviation from inversion symmetry at the site of the hexavalent ion [11]. A great variety of luminescent centres with different surroundings is the result. This explains the relatively short decay times and the occurrence of more than one decay time.

It is interesting to note that in $\text{Ba}_2\text{Li}_{1.2}\text{W}_{0.8}\text{O}_6\text{-U}$, a compound with perovskite-like structure, two decay times have been found, viz. 10 and 80 μs [12]. Due to the sequence of the BaO_3 layers in this crystal structure here are two different sites for the hexavalent metal ions, both with site symmetry C_{3v} . These short decay times extend the relation of table 1.

Further evidence for the presence of a parity-forbidden transition can be gained from the temperature dependence of the decay time. First of all one should note that the influence of the temperature on the decay time differs markedly from that on the luminescence intensity (fig. 1). While the latter is still constant, the former decreases. The excitation takes place by an allowed electronic transition. The slight temperature dependence of this process can be neglected. With increasing temperature the occupation of vibrational levels in the excited electronic state increases. The possibility for coupling with an ungerade vibration in the excited state becomes larger. The parity-selection rule will be more relaxed dynamically and a decrease of the decay time is the result. The temperature dependence of the transition probability for a vibronically allowed transition is contained in a factor $[\exp(h\nu_a/kT) - 1]^{-1}$, as described by Di Bartolo [13]. Here ν_a is the frequency of the phonon which is involved in the coupling.

Analysis of the results with this relationship gives a very good agreement for temperatures below 120 K.

We have succeeded in a fit using a ν_a of about 200 cm^{-1} . This ungerade vibration is probably the $\nu_6(\text{T}_{2u})$ internal mode. This vibration is IR inactive. The frequency of this mode found from the vibrational pattern in the emission of $\text{Sr}_2\text{MgW}_{0.997}\text{U}_{0.003}\text{O}_6$ (240 cm^{-1}) is a little higher than the ν_a frequency [6]. This difference can be explained by the fact that the latter corresponds to a vibrational mode in the excited state.

In conclusion we may state that we have given strong evidence for a parity-forbidden transition in the emission of the UO_6^{6-} group. It is possible that for the UO_2^{2+} group the electronic transition responsible for the luminescence has to be considered in the same way.

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