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Luminescence Spectroscopy of Eu^{3+} in Calcium Tartrate Tetrahydrate

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Abstract

Single crystals of calcium tartrate tetrahydrate doped with Eu^{3+} are readily grown by a gel technique. Luminescence spectroscopy shows that the Eu^{3+} ions occupy a set of energetically similar sites, with the majority of them having D_2 symmetry. This symmetry is due to small distortions of the original substitutional site caused by the necessity of a charge compensation. The decay curves of the luminescence from the $^5D_0$ level are in agreement with the spectral results and show that the various sites differ in the number of neighbouring O–H groups. In contrast to site-selection spectroscopy results on the same material doped with UO_2^{2+}, we find no evidence of a pseudo-continuous range of 'glassy' sites.

Introduction

Ions of transition metals, lanthanides and actinides are readily incorporated in large well-formed crystals of calcium tartrate tetrahydrate (CTTH) grown by the gel technique [1]. On the basis of the crystal structure [2], the in-doped ions can occupy two main sites in the lattice: an eight-fold coordinated substitutional site, or an elongated octahedral interstitial site. Previous ESR studies suggested the presence of Mn^{2+}, Cu^{2+} and Ni^{2+} ions in interstitial sites [3], and of VO^{2+} ions in at least three different sites [4]. However, the ESR technique is relatively insensitive for distinguishing between similar sites when several numbers of different sites are present. Recent site-selection spectroscopy results on UO_2^{2+}-doped CTTH [5] have shown the presence of at least five well-defined sites and of a pseudo-continuous range of sites analogous to that which has been found for UO_2^{2+} in glasses [6]. The majority of the sites appear to have an in-plane coordination number of five.

Nothing is known about the site or the sites occupied by trivalent rare earth ions in CTTH and it is therefore of interest to determine their interstitial or substitutional nature and to ascertain whether the spherical rare earth ions occupy glassy or distinct sites in this lattice.

In this contribution we report laser-excited luminescence spectra at 6 K and decay curves at 80 K for CTTH doped with Eu^{3+} ions. We found evidence that the dopant ions occupy a set of energetically similar sites and have obtained information about their geometry.

Experimental

Crystals of CTTH:Eu^{3+} of good optical quality were grown using a two-layer gel technique [7]. A 1.0 M aqueous solution of L-(+)-tartaric acid (Merck p.a.) was titrated with a 0.9 M solution of $Na_2O\cdot 3SiO_2$ (Fluka) to a pH of 2.5. The mixture was allowed to set at 33 °C. A solution of 0.7 M $CaCl_2\cdot 2H_2O$ (Merck p.a.) and 0.07 M $EuCl_3$ (Fluka) was carefully poured on top of the gel. After several weeks, large well-formed crystals appeared.

Luminescence spectra were measured using the 465.8 nm radiation from a Spectraphysics 164-03 Ar^+ laser, a 600 mm Hilger D460 monochromator, a RCA C31034 cooled photomultiplier and a Brookdeal 5C1 photon counting system. The spectral slit width was <2 cm^{-1} and did not limit the resolution achieved.

The decay curves were measured by exciting the samples every 0.1 nm around 525 nm with a Spectron SL2Q+SL3A Nd-YAG laser pumping Coumarin 500 in a Spectron SL4000 dye laser and detecting the luminescence at 615.2 nm using a Spex Minimate monochromator. The signals were averaged over about 1000 pulses with a modified PAR TDH-9 waveform eductor. The samples were

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maintained at 6 K in an Oxford Instruments CF100 flow cryostat (spectral measurements) and at 80 K in a simple laboratory-built cryostat (decay curves).

Results and Discussion

Luminescence Spectra

The luminescence spectrum of CTTH:Eu^{3+} at 6 K (Figs. 1, 2 and 3) shows several well-resolved groups of bands which are readily assigned to transitions from the non-degenerate $^5D_0$ level to the ^7F manifold. The very weak band centered around 17260 cm^{-1} is assigned to the transition to the $^7F_0$ non-degenerate level and therefore the structure present must originate from transitions in different sites in the lattice. Our high resolution spectrum (Fig. 1) allows us to identify at least eight clearly resolved components, with a total spread of about 35 cm^{-1}. The Eu^{3+} ion therefore occupies a set of energetically similar sites in this lattice. The total intensity of this transition is about 50 times less than the intensity of the magnetic dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition. This is consistent with the theory that the similar sites have a geometry whose crystal-field expansion does not contain A_{1p} terms [8].

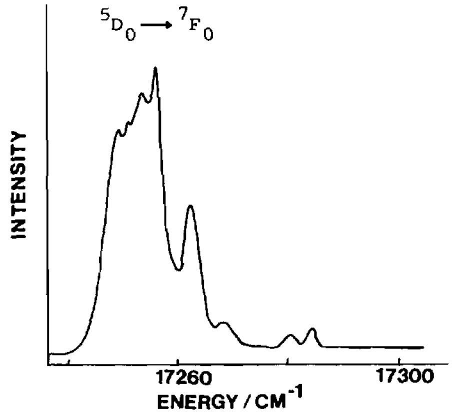

Fig. 1. Luminescence spectrum of CTTH:Eu^{3+} at 6 K in the 17240–17300 cm^{-1} region.

The two distinct groups of bands in the luminescence spectrum centered around 16900 and 16200 cm^{-1} (Figs. 2 and 3) are respectively assigned to the $^5D_0 \rightarrow {}^7F_1$ and the $^5D_0 \rightarrow {}^7F_2$ transitions. They are composed of three and five sets respectively of closely spaced but not well-resolved features. We assign each set of features to transitions to the Stark components of the $^7F_1$ and $^7F_2$ levels in different sites whose crystal-field splitting pattern is slightly different, thus leading to the barely resolved structure in the observed bands. It is evident that the symmetry of the majority of the sites is low enough to totally lift the $2J+1$ degeneracy of the levels.

The overall intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition is more than five times the overall intensity of the magnetic dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition and this suggests, in the framework of the dynamic coupling mechanism of hypersensitivity [9], that the geometry of the Eu^{3+} sites is such that the crystal-field expansion contains A_{3p} terms.

In the low-energy part of the spectrum, two structured groups of bands are present which are assigned to the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions, whose splitting patterns confirm the complete lift of the degeneracy of the levels by the crystal field. Another very weak band system centered around 17150 cm^{-1} (Fig. 2) is assigned to the $^5D_1 \rightarrow {}^7F_3$ transition. We note that luminescence from the $^5D_1$ level is very uncommon in this kind of material, due to the presence of high-energy O–H vibrations.

The similarity in size of Ca^{2+} (effective radius 1.12 Å) and Eu^{3+} (effective radius 1.07 Å) ions for eight-fold coordination by oxygens [10] as well as the tendency of Eu^{3+} to have a coordination number higher than six, suggest that the rare earth

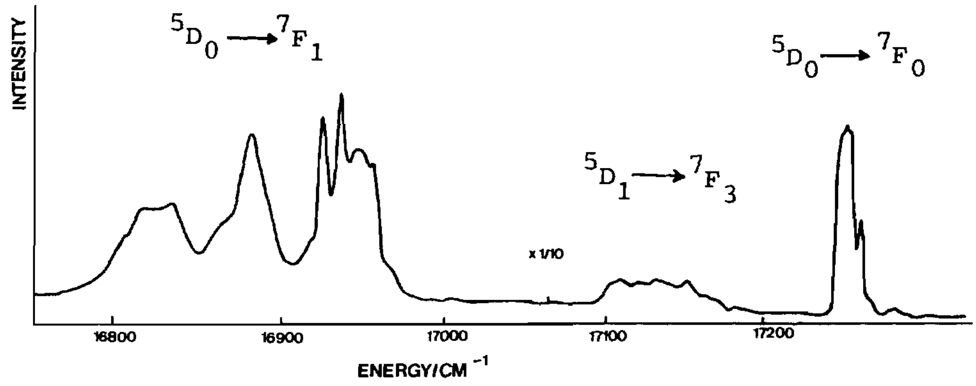

Fig. 2. Luminescence spectrum of CTTH:Eu^{3+} at 6 K in the 16800–17300 cm^{-1} region. The intensity scale is divided by 10 above 17070 cm^{-1}.

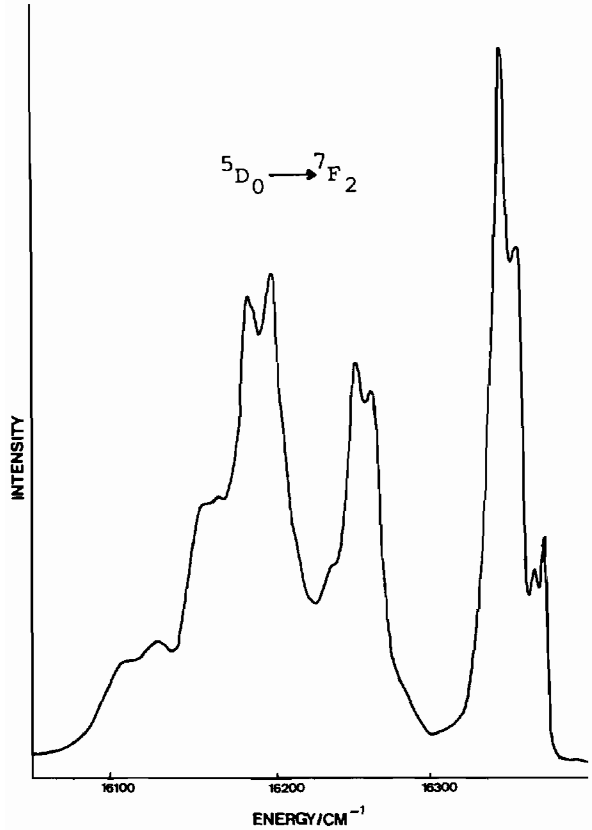

Fig. 3. Luminescence spectrum of CTTH:Eu^{3+} at 6 K in the 16 100–16 400 cm^{-1} region.

ion occupies a substitutional site in the CTTH lattice. The Ca^{2+} ion occupies in pure CTTH a site of nearly perfect D_{2d} symmetry [2]. For the dopant ion this geometry is ruled out by the spectral results because its symmetry is not consistent with the complete lifting of the $2J+1$ degeneracy of the levels [11]. The intensities of the luminescence transitions to the $^7F_0$ and $^7F_2$ levels are consistent with symmetries whose crystal-field expansions contain A_{3p} terms but not A_{1p} terms. Therefore D_2 is left as the only possible point group, at least for the majority of the sites. This point group is a subgroup of D_{2d} and therefore can originate from a distortion of the original Ca^{2+} site. This distortion is probably due to the necessity of charge compensation in the CTTH lattice in order to accommodate a trivalent ion like Eu^{3+}. We can predict that in CTTH several different charge compensation mechanisms are probably operative [5], such as the loss of protons from tartrate hydroxyl groups or from water molecules, or vacancies in the Ca^{2+} sites. This could account for the presence of a set of slightly distorted but energetically similar sites, mainly having D_2 symmetry, in qualitative agreement with our spectral results.

Decay Curves

The decay curves of the luminescence from the $^5D_0$ level have been measured at 80 K using excitation wavelengths differing by 0.1 nm in the region between 524.1 and 526.2 nm. These excitation wavelengths excite the Eu^{3+} ions to the $^5D_1$ level. The resulting decay curves appear to be exactly exponential, but the lifetimes deduced from them show a large variation in the range 0.34–0.55 ms. These results again agree with the presence of a set of similar sites for the dopant ion in CTTH, each of them being excited by a different wavelength. The lifetime of the $^5D_0$ level is strongly affected by the presence of neighbouring O–H groups whose high-energy stretching vibrations are very effective in providing an efficient non-radiative decay path. This large variation in the measured lifetimes is explained by the fact that several charge-compensation mechanisms can account for different numbers of neighbouring hydroxyl groups around the sites occupied by the rare earth ions. Therefore the decay curves are in complete agreement with the spectral results.

Conclusions

We have shown that the dopant Eu^{3+} ions do not occupy a single site in the CTTH lattice, but that the presence of a variety of charge-compensation mechanisms accounts for the rare earth ions occupying a set of energetically similar sites. The majority of these sites appear to have D_2 symmetry, which can be obtained by a small distortion of the original Ca^{2+} site.

The time evolution of the site-selective luminescence from the $^5D_0$ levels shows the presence of differing numbers of O–H groups around the dopant ions. The purely exponential decay curves are consistent with the spherical Eu^{3+} ions occupying distinct sites in the CTTH lattice and rule out the presence of pseudo-continuous glassy sites, which have been found in the case of CTTH:UO$_2^{2+}$. In this latter case, the cylindrical symmetry of the uranyl ions allows them to be randomly oriented in the lattice. This gives rise to very small differences in the energy of the excited states, leading to a pseudo-continuous range.

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