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Luminescence of Octahedrally Coordinated Eu^{2+} in $Rb_2MP_2O_7$ (M = Ca, Sr)

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In this paper we report on the excitation and emission spectra of the octahedrally coordinated Eu^{2+} ion in $Rb_2M^{2+}P_2O_7$, with M^{2+} = Ca^{2+} and Sr^{2+}. The Eu^{2+} emission in these materials is characterized by a very large Stokes shift and, for phosphates, an unusually low energy of the emitted photons - the broad Eu^{2+} emission bands peak at 628 nm and 585 nm for $Rb_2CaP_2O_7$ and $Rb_2SrP_2O_7$, respectively. At this point, we ascribe the Eu^{2+} emission in these materials to a normal, although extreme, $4f^6 5d^1 \rightarrow 4f^7[^8S_{7/2}]$ transition.

Introduction

In a recent paper (1) we have investigated the peculiar luminescence of divalent europium in $Cs_2CaP_2O_7$ and $Cs_2SrP_2O_7$ which is characterized by both an extremely large Stokes shift and a high quenching temperature. For those systems we presented arguments that the emission is due to an extreme case (with respect to the observed Stokes shift and the emission wavelength) of standard Eu^{2+} d-f transition, and not due to the so-called anomalous emission from an excitonic state.

Dorenbos has compiled and analyzed the archival literature of the optical properties of Eu^{2+} in a large number of host materials (2), and finds an average value for the Stokes shift of the Eu^{2+} emission in solids is 1350 cm^{-1} (0.16 eV). For $Cs_2CaP_2O_7$ and $Cs_2SrP_2O_7$ we find a Stokes shift for the Eu^{2+} emission of about 1.0 eV, resulting in the lowest reported emission wavelength for a phosphate (1).

Here we report on an extension of our studies on octahedrally coordinated Eu^{2+} ions in diphosphates by investigating the Eu^{2+} luminescence in $Rb_2CaP_2O_7$ and $Rb_2SrP_2O_7$.

Experimental Details

Polycrystalline samples of Eu^{2+} activated $Rb_2M^{2+}P_2O_7$ were synthesized by classic solid-state reaction techniques. Starting materials used were analytical grade Rb_2CO_3 (10 mole% excess) $CaCO_3$, $SrCO_3$ and $(NH_4)_2HPO_4$ (10 mole% excess) and Eu_2O_3. The samples were heated at 300 C for one hour in air and then heated twice at 800C for 5 hrs in a slightly reducing atmosphere with intermediate grindings. In both materials, the XRD pattern confirmed the formation of phase pure material. Since the final products were found to be hygroscopic all optical measurements were carried out in sealed quartz tubes.

Excitation spectra were recorded in a modified Cary 14 spectrophotometer equipped with an Oxford Instruments flow through cryostat, using the chopped radiation of either a tungsten-halogen (for visible/near-UV excitation) or a deuterium (for UV excitation) lamp as the excitation source with the emission detected by a red sensitive Hamamatsu R1477 photomultiplier tube (PMT) and appropriate narrow band interference filters. The signal was processed with a Stanford lock-in amplifier to increase the signal to noise ratio and suppress the PMT dark current. The excitation spectra were corrected for excitation photon flux using a calibrated Hamamatsu photodiode as a reference detector.

For the emission spectra the sample tubes were placed into an Oxford Instruments temperature variable cryostat. The samples were excited with the output of an LED source, the emission was recorded with a CCD camera attached to an Acton Research 0.25m spectrograph. The throughput of the detection system was calibrated with a NIST traceable tungsten lamp.

Time resolved measurements were obtained under LED excitation source filtered through a narrow band interference filter (10 nm width) driven by the amplified (Avantec) pulses of an Avtech AVP-C pulse generator. The emission was filtered through a 0.5 m McPherson monochromator and detected with a Hamamatsu R1477 PMT detector. The time resolved fluorescence was recorded through a photon counting system, consisting of an Ortec 567 time-to-amplitude converter in conjunction with an EG&G pulse height analyzer. The temporal response for this experimental setup was measuredto be 2 ns. The samples were mounted in a temperature variable Oxford Cryostat for measurements between 80 K and 300K, for the high temperature measurements the sample tubes were placed into a clam shell tube furnace.

Experimental Results and Discussion

The excitation spectra of divalent europium in $Rb_2CaP_2O_7$ and $Rb_2SrP_2O_7$ at T = 80 K are shown in Figure 1.a and 1.b respectively. Clearly evident is the splitting of the the Eu^{2+} $4f^6 5d^1$ electronic configuration into the lower t_{2g} and the upper e_g components.

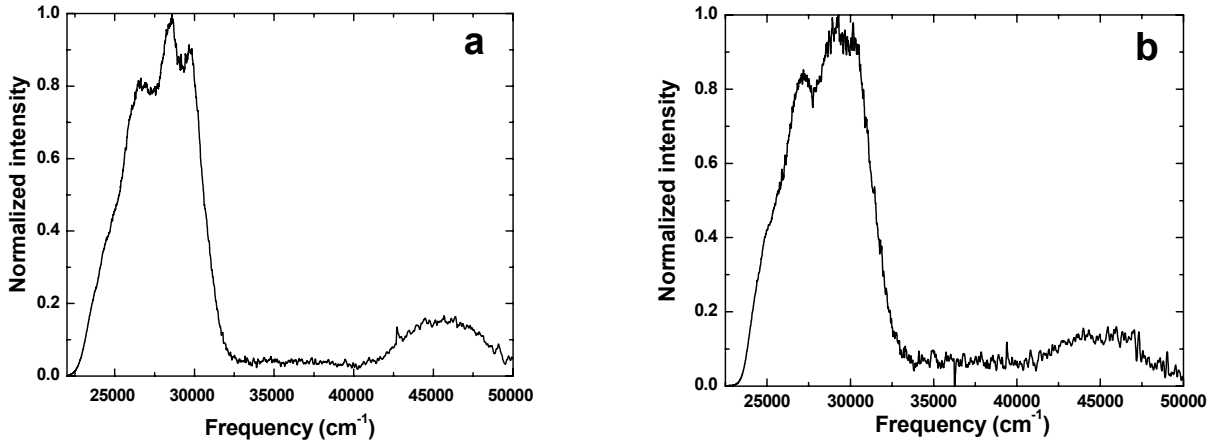


Fig. 1: Excitation spectra of Eu^{2+} in $Rb_2CaP_2O_7$ (a) and $Rb_2SrP_2O_7$ (b).

From our data we find a crystal field splitting of 10 Dq = 2.18 eV for $Rb_2CaP_2O_7$ and a splitting of 10 Dq = 2.02 eV for $Rb_2SrP_2O_7$. This finding is consistent with the expected reduction of the crystal field strength due to an increase of the lattice constant when the calcium ion is replaced by a strontium ion.

a

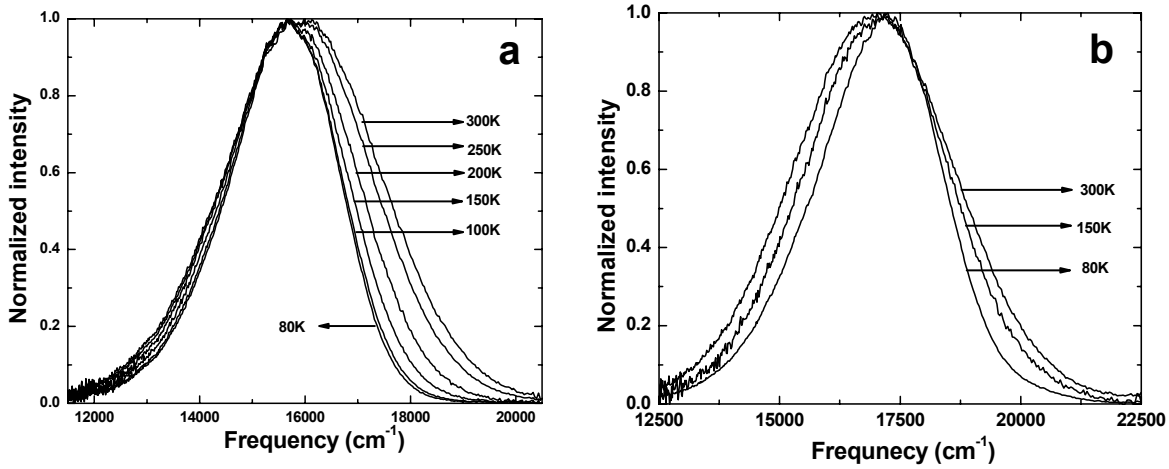
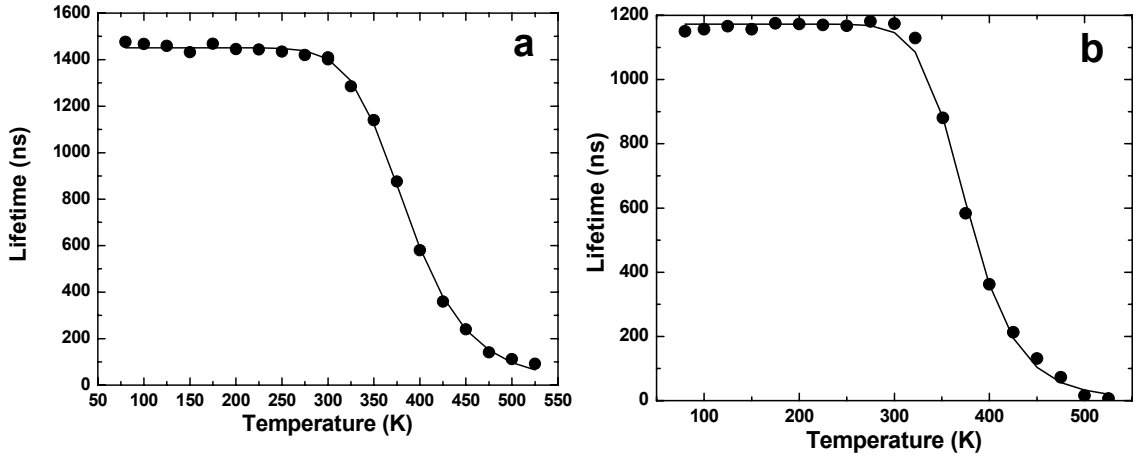


Fig. 2: Emission spectra of Eu^{2+} in $Rb_2CaP_2O_7$ (a) and $Rb_2SrP_2O_7$ (b).

Figure 2 shows the emission spectra of the two samples under 400 nm excitation. The $Rb_2CaP_2O_7$ sample (Fig. 2.a) exhibits an emission peak around 640 nm at T = 80K, and we estimate the Stokes shift to be 1.06 eV. For the $Rb_2SrP_2O_7$ sample (Fig. 2.b) the emission peak is located at 580 nm, with a Stokes shift of approximately 0.88 eV. Interesting is the temperature dependence of the Eu^{2+} emission band: while the $Rb_2SrP_2O_7$ sample shows merely a broadening with increasing temperature, the $Rb_2CaP_2O_7$ sample exhibits a distinctive shift towards higher frequencies with rising



temperatures. We attribute this behavior tentatively to a splitting of the t_{2g} component

Fig. 3: Relaxation time of Eu^{2+} in $Rb_2CaP_2O_7$ (a) and $Rb_2SrP_2O_7$ (b) as a function of temperature (solid dots). Solid line: Arrhenius fit.

due to a distortion of the octahedral symmetry, either because of the non-ideal octahedral site symmetry (the Ca/Sr octahedral site is slightly distorted (3)) or to spontaneous symmetry reduction due to a Jahn Teller distortion.

Figure 3 shows the dependence of the relaxation time on the sample temperature. For both samples, the low temperature relaxation times of 1.16 μsec ($Rb_2SrP_2O_7$) and 1.44 μsec ($Rb_2CaP_2O_7$) are within the typical range found for divalent europium, with the relaxation time increasing as expected with increasing emission wavelength. Also shown in Figure 3 are curves that represent an Arrhenius fits of our lifetime data. From these fits we obtain an activation energy of 0.39 eV for $Rb_2CaP_2O_7$ and 0.47 e for $Rb_2SrP_2O_7$. We tentatively ascribe the quenching to a metal-to-metal charge transfer process, however, for a conclusive distinction from quenching via level crossing, photoionization studies are being conducted in our laboratory.

Photoionization studies will also help to identify the nature of the Eu^{2+} emission in our systems, because very large Stokes shift (about 1 eV in our systems) is often interpreted as a signature of an excitonic emission.

Summary

In conclusion, we have studied the optical transition of divalent europium ions in $Rb_2M^{2+}P_2O_7$, with $M^{2+} = Ca^{2+}$ and Sr^{2+}. In both hosts, the Stokes shift is extremely high, leading to an extreme red-shifted Eu^{2+} emission. In the case of $Rb_2CaP_2O_7$ the observed emission peak wavelength is the longest ever reported for a phosphate based host material. We tentatively ascribe the observed luminescence to an intra-ionic d-f transition, however, photoionization studies are under way to further investigate these intriguing systems.

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