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Excited State Absorption Measurements of Sm^{2+} in CaF_2, SrF_2, and $SrCl_2$

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Abstract

We measured the pump-probe spectrum of the Sm^{2+} ion in three materials: CaF_2, SrF_2, and $SrCl_2$. The onset of the observed prominent excited-state absorption band is consistent with an electrostatic model for impurity levels in a solid-state material.

1. Introduction

While the vast majority of rare-earth laser ions exploit the 4f-4f electronic transition, several lasers based on a 5d-4f transition exist. Divalent samarium in calcium fluoride (early recognized as a solid-state laser system, discovered not long after ruby) is based on a 5d-4f transition[1]. Similarly, cerium has gain on a 5d-4f transition in at least two hosts[2,3]. Finally, neodymium in lanthanum trifluoride has shown gain on a high lying 5d-4f transition[4]. Since 5d-4f transitions are very different in nature than the familiar 4f-4f transitions, they represent a entirely distinct class of laser systems. However, the overall value of 5d-4f transitions as laser transitions has not yet been adequately addressed.

The major problem apparent from existing work on these systems, especially for the case of divalent rare earth ions, is the presence of an extremely strong excited-state absorption (ESA) band. The ESA is due to a 5d→conduction band transition (Fig. 1). This type of transition was first observed for Eu^{2+} in CaF_2[5] and has since been seen in several other Eu^{2+} doped materials: i.e., KCl[6,7], KBr[6], NaCl[6], and NaF[8]. We have also observed the 5d→conduction band transition in $CaF_2:Sm^{2+}$[9].

Here, we expand on our measurements of $CaF_2:Sm^{2+}$ to include pump-probe measurements of $SrF_2:Sm^{2+}$ and $SrCl_2:Sm^{2+}$. Additionally, we have adapted the electrostatic model developed by Pedrini, Rogemond and McClure [10] for placing the energy levels of the impurity ion in the band gap of the host in order to predict the onset of this type of ESA.

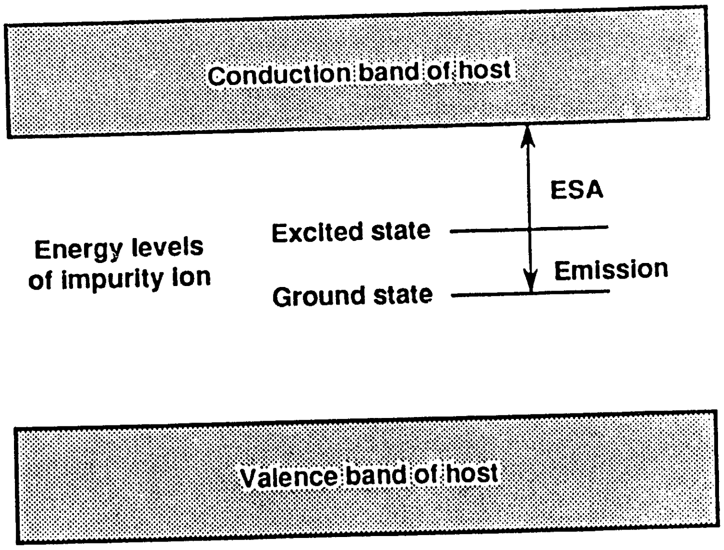

Figure 1. The energy levels of the impurity ion reside in the band gap of the host. ESA occurs if the conduction band is accessible from the excited state.

2. Theory

The onset of the 5d→conduction band transition may be calculated as follows,

$$E_{esa}= I_p-(E_m+E_p)-E_{ex} \,. \qquad (1)$$

The electrostatic model[10] which gauges the depth of the impurity ion's energy levels in the band gap begins with the ionization potential of the free ion (I_p). This energy is corrected for the stabilization afforded the ion by the crystalline host, namely the Madelung energy (E_m) and the polarization energy (E_p). The Madelung energy is corrected for the difference between the impurity-ion distance and the lattice distance. The polarization stabilization is based on the difference in energy between the impurity ionization states arising from the polarizability of the anions. Since this gives us the depth of the ground state from the conduction band, we then subtract zero phonon energy of the excited state (E_{ex}) to calculate the predicted onset of the ESA band(E_{esa}).

One difficulty with this model is that it requires the subtraction of large numbers from one another and results in values with a large relative error. Using $CaF_2:Sm^{2+}$ as an example, we note that the ionization potential is 23.4 eV, while the Madelung and polarization energy collectively are 19.8 eV. This places the ground state of Sm^{2+} 3.6 eV below the conduction band within an uncertainty of approximately 0.5 eV. Since the excited $4f^55d$ state lies 1.8 eV above the ground state, E_{esa} is 1.8 eV. Since the uncertainty is on the order of 0.5 eV, this results in over a 25% uncertainty. Thus, the trends predicted by this model may prove more useful than quantitative calculations.

We used the model to calculate the onset on the ESA in three fluorite hosts: CaF_2, SrF_2 and $SrCl_2$ (Table 1). We found that the ESA should occur in SrF_2 at longer wavelengths than in CaF_2, while the ESA in $SrCl_2$ should be shifted strongly towards the blue (see Table 1). Measuring the actual position of the ESA in these hosts provides us a test of the model and these predictions.

Table 1

Calculated and observed onset of the Sm^{2+} 5d-conduction band transition

host	predicted(eV)	observed(eV)
CaF_2	1.8	2.0
SrF_2	1.1	1.6
$SrCl_2$	2.8	>2.5

3. Experimental setup

The technique we used to measure the ESA spectrum involved a conventional pump-probe geometry. However, characterizing the 5d→conduction band transition of Sm^{2+} in SrF_2 and $SrCl_2$ requires special consideration of the lifetime of the $4f^55d$ state in these materials. While the $4f^55d$ manifold gives rise to the lowest excited state in CaF_2, an excited $4f^6$ level ($^5D_0$) is the lowest excited state in both SrF_2 and $SrCl_2$ (Fig. 2). The population of the $4f^55d$ state in $SrF_2:Sm^{2+}$ has been measured to relax to the $^5D_0$ ($4f^6$) level on a time scale of approximately 2 ns[11]. We measured the 5d→4f transient emission in $SrCl_2:Sm^{2+}$ and obtained a similar lifetime, 2.3ns. Previous ESA measurements of $SrF_2:Sm^{2+}$ and $SrCl_2:Sm^{2+}$[12] conducted on a long timescale studied the behavior of the $^5D_0$ ($4f^6$) level and demonstrated that comparable transitions do not occur between the $4f^6$ and conduction band states. Therefore, the short lifetime of the $4f^55d$ state in these two materials requires that we record the pump-probe spectrum on a time scale shorter than 1ns in order to see the ESA band of interest.

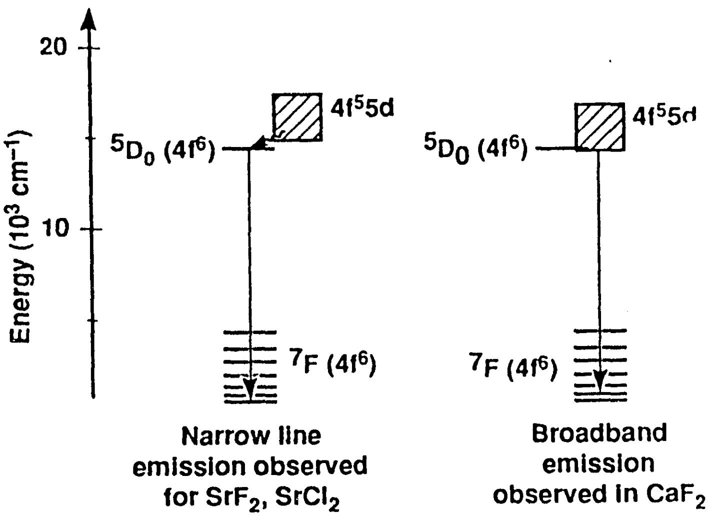

Figure 2. Energy level ordering of the Sm^{2+} ion in the three hosts. While the lowest excited state of $CaF_2:Sm^{2+}$ is the $4f^55d$ state, the lowest excited state in $SrF_2:Sm^{2+}$ and $SrCl_2:Sm^{2+}$ belongs to the $4f^6$ configuration. The relaxation from the $4f^55d$ state to the $^5D_0$ ($4f^6$) occurs in these materials with a timescale on the order of a nanosecond.

In order to do this we used an amplified picosecond dye laser with a pulse length of 0.5 ps tuned to 640 nm to both pump the sample and to generate a probe beam. We produced a broadband continuum by focusing a portion of the dye beam into a cell filled with D_2O (Fig. 3). The transmission of the continuum probe through the sample was monitored in the presence and absence of the pump by collecting it into a spectrograph and recording the spectrum using an optical multichannel analyzer.

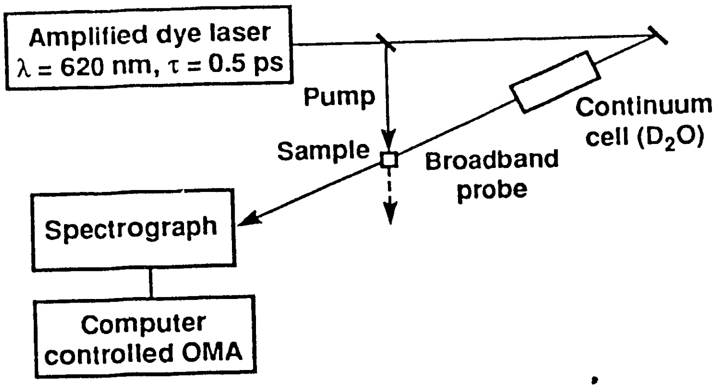

Figure 3. Schematic description of the pump-probe experiment (OMA = optical multichannel analyzer)

4. Results

The results of our measurements are displayed in Fig. 4. The spectrum recorded for CaF$_2$:Sm^{2+} agrees with the spectrum we previously observed in which a 3 microsecond flashlamp probe was employed. The agreement between the spectra acquired from two entirely different experimental apparatuses provides strong evidence that our methodology is viable. The data in Fig. 4 also shows that a strong ESA band is observed for . Although it is similar in appearance to the ESA spectrum of CaF$_2$:Sm^{2+}, the ESA spectrum of SrF$_2$:Sm^{2+} begins at much longer wavelength. On the other hand, we did not observe comparable excited state absorption in SrCl$_2$:Sm^{2+}. These results are consistent with the calculated onset of the ESA band in the different materials based on the electrostatic model (Table 1).

The recent publication of the photoionization threshold of SrF$_2$:Sm^{2+} [13] provides an additional confirmation of our model. Photoionization thresholds directly correspond to the depth of the ground state of the impurity from the conduction band. Unfortunately, photoconductivity measurements of CaF$_2$:Sm^{2+} [14] resulted in thresholds much smaller than predicted by the electrostatic model, possibly due to the presence of a compensated Sm^{2+} ion [15] which possesses a smaller threshold than that of Sm^{2+}. By measuring the charge-transfer of a co-doped Eu^{2+}-Sm^{2+} system, Fuller and McClure inferred the photoionization threshold for SrF$_2$:Sm^{2+} to be 3.4 eV, fairly close to 3.06 eV, the value predicted by the electrostatic model. On the basis of the photoconductivity data, the ESA band is predicted to occur near 825 nm (i.e., 1.5 eV) in good agreement with our observations (1.6 eV).

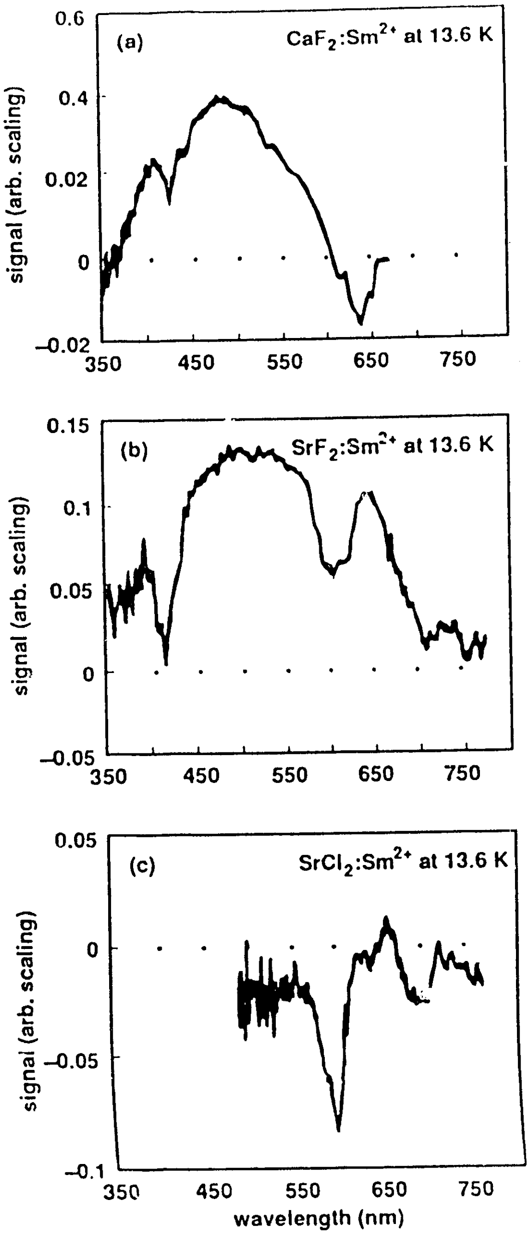

Figure 4. The pump-probe spectrum of Sm^{2+} in (a) CaF$_2$, (b) SrF$_2$ and (c) SrCl$_2$ recorded within 100 ps of the excitation pulse.

5. Discussion

The strong ESA present in Sm^{2+}doped materials can be explained as arising from a 5d→conduction band transition. We believe the unusual strength of this transition to be due to the mixing of the impurity and ligand orbitals which leads to intensity borrowing from valence band to conduction band transitions[9]. This type of transition may limit the usefulness of 5d-4f transitions in all of the divalent rare-earth ions and may be an issue in trivalent rare-earth ions as well. The electrostatic model described here allows us to predict trends in the onset of the ESA band for different hosts. Since the depth of the impurity ion energy levels from the conduction band is much more sensitive to the host than is the spacing between the impurity energy levels, it may be possible to select laser materials for other divalent rare-earth ions such as Eu^{2+} in which the ESA does not overlap the emission region.

6. Acknowledgments

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