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Brief Reports

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Luminescence of Sm^{2+} ions as a probe of pressure-induced phase transitions in SrF_2

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The luminescence of Sm^{2+} ions in SrF_2 is used to monitor the β (cubic) -to-α (orthorhombic) phase transition of SrF_2 at ~ 5 GPa and 300 K. In contrast to those in the β phase, the Sm^{2+} spectra in the α phase show a series of sharp $4f$-$4f$ transition bands, even at 300 K, originating from the ${}^5D_0$ to ${}^7F_J$ multiplets including a strong transition for $\Delta J = 0$. At low temperatures, these transitions are not observed; instead, the $4f^5 5d^1$ band of the Sm^{2+} ions in the β phase reversibly shifts below ${}^5D_0$ ($4f^6$) level at 4.5 GPa and 30 K. The α phase is metastable and can be recovered at 1 atm and 30 K.

The narrow bands observed in the absorption and luminescence spectra of trivalent lanthanide ions are usually due to forced electric-dipole transitions within a $4f^N$ ($N = 2-13$) configuration.[1,2] For the divalent lanthanide ions, the first excited configuration $4f^{N-1}5d^1$ is much lower in energy, and transitions to this configuration may be observed in the visible and/or the near-infrared regions as broad absorption bands. For some divalent lanthanide ions, sharp bands are also observed in absorption and luminescence when excited levels of the $4f^N$ configuration are lower in energy than the $4f^{N-1}5d^1$ configuration. In this Brief Report intensity and energy changes in the sharp bands within the $4f^6$ configuration are used to monitor the phase change from the β (cubic) -to-α (orthorhombic) form of SrF_2 at 300 K as a function of pressure. In addition, the relative shifts of the lowest levels of the $4f^6$ configuration and the $4f^5 5d^1$ configuration are reported as a function of temperature and pressure.

One of the most thoroughly studied systems is that of Sm^{2+} diluted into the alkaline-earth fluorides CaF_2, SrF_2, and BaF_2.[3-5] At low concentrations of the Sm^{2+} ion, the symmetry site of the Sm^{2+} is of O_h point-group symmetry and the observed sharp transitions are of magnetic dipole origin. The energies of the observed luminescence lines of Sm^{2+} in the alkaline-earth fluorides are not very sensitive to the host crystal for transitions within the $4f^6$ configuration, but transitions between the $4f^5 5d^1$ and $4f^6$ configurations are much more sensitive to the surrounding environment. For example, Wood and Kaiser[5] report the energy difference between the ${}^5D_0$ and ${}^7F_0$ levels of Sm^{2+} in SrF_2 and BaF_2 as 14 616 and 14 652 cm^{-1}, respectively, a shift of 36 cm^{-1} to the blue for the larger lattice. By contrast, they report a shift of approximately 760 cm^{-1} to the blue for the energy difference between the lowest level of the $4f^5 5d^1$ configuration and the ${}^7F_0$ level ($4f^6$ configuration) for the same systems.

Increasing the external pressure provides a greater crystal field. The primary driving force is densification, which can exceed 10% of the initial volume at 10 GPa in many soft materials including alkaline-earth halides.[6] The number and energies of intraconfigurational $4f^N f$ band transitions depend on the site symmetry of the lanthanide ion and, therefore, the crystal structure of the host material. Thus the spectral changes of impurities associated with compression may reflect structural phase changes of the host lattice occurring at high pressures.

In this Brief Report the pressure-induced luminescence changes of Sm^{2+} impurities which probe the structural phase transition in the SrF_2 host lattice [from the cubic β phase, space group $Fm3m$ (O_h^5), to the orthorhombic α phase, space group $Pnma$ (D_{2h}^{16})] are reported. This is a typical transition in AX_2-type fluorites.[7] Evidence is given also of a pressure-induced f- to d-band crossing in the β phase. Recovery experiments of the high-pressure α phase are described as well.

The sample, nominally 0.3% weight of Sm^{2+} doped into a single crystal of SrF_2, was obtained from Optovac Inc. A small piece of the crystal was placed in an Inconel gasket hole, typically 200 μm in diameter, of a diamond anvil cell of the Merrill-Bassett design.[8] The sample was then pressurized with liquid N_2 as the pressure medium, which provided good hydrostatic conditions at high pressures and low temperatures. The Raman lines of N_2 were also used as a pressure calibrant,[9] since the strong ruby R lines (the conventional pressure calibrant) obscured details of the sample luminescence. In this way the uncertainty in pressure measurements is estimated to be near

0.2 GPa. A closed-cycle liquid-He cryostat from CTI Inc. was modified to hold the diamond anvil cell and to control pressure isothermally down to 30 K. Typically, 50 mW of an Ar$^+$-ion laser at 514.5 nm excited the sample, and a conventional detection system using a diode array detector coupled to a spectrograph monitored the luminescence from the sample. The spectral resolution of the Sm^{2+} luminescence spectra reported here is typically 0.15 nm ($\sim$3 cm^{-1}).

The experiments were performed along various (P,T) pathways including isothermal compression, isobaric cooling, and their reverse processes. These pathways were chosen because the nature of the Sm^{2+} spectrum strongly depended on the loading history of the sample as a result of an extremely large kinetic barrier accompanying the transition. This will be discussed below.

Figure 1 illustrates the luminescence spectra of Sm^{2+} ions that are characteristic of the pressures, temperatures, and crystal phases of SrF$_2$. The spectrum at ambient pressure shown in Fig. 1(a) is composed of a few sharp lines associated with f-f transitions and broad vibronic bands. The sharp features at 14 353 and 13 140 cm^{-1} correspond to the transitions within the $4f^6$ configuration from $^5D_0$ (A_{1g}) to the $^7F_1$ (T_{1g}) and to $^7F_3$ (T_{1g}) levels, respectively, which are magnetic dipole allowed. The other sharp, but weak features at 14 605, 13 953, and 13 580 cm^{-1} are the $^5D_0$ to $^7F_0$ (A_{1g}), $^7F_2$ (T_{2g}), and $^7F_2$ (E_g) transitions, respectively. The weak features are strictly forbidden in the O_h symmetry and likely arise from the ions at the perturbed sites. The broad vibronic bands are spaced by average frequencies of 93, 150, 217, 289, and 349 cm^{-1}, all of which are in agreement (within 10 cm^{-1}) with earlier measurements.[5] As the temperature increases, the sharp features diminish because of broadening of the vibronic bands and the formation of a broad background. This results in a broad, structureless, weak band from 12 000 to 15 000 cm^{-1}, which peaks at 14 250 cm^{-1} at ambient temperature.

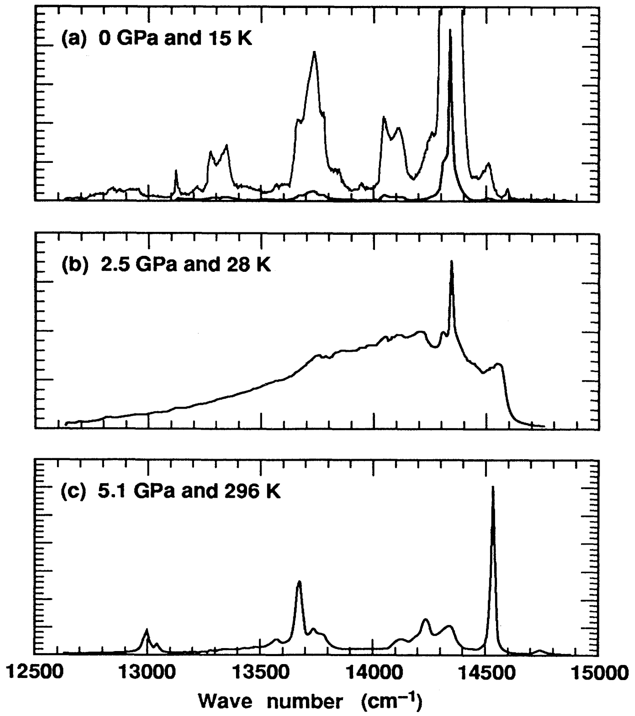

FIG. 1. Luminescence spectra of Sm^{2+} ions doped in SrF$_2$ crystals: (a) $4f$-$4f$ transitions in the β-SrF$_2$ at the ambient pressure and 15 K, (b) $4f$-$4f$ and $5d$-$4f$ transitions in the β-SrF$_2$ at 2.5 GPa and 28 K, and (c) $4f$-$4f$ transitions in the α-SrF$_2$ at 5.1 GPa and 296 K.

Similar spectral changes are associated with increasing pressure. In fact, the spectrum at 2.5 GPa and 28 K shown in Fig. 1(b) is strikingly similar to the spectrum observed at 1 atm and 77 K. The sharp feature near 14 350 cm^{-1} in Fig. 1(b) is obviously the f-f transition band from the $^5D_0$ (A_{1g}) to the $^7F_1$ (T_{1g}) level, but the band intensity is substantially reduced with respect to the vibronic band intensity (for example, the shoulder at 14 300 cm^{-1}). A broad emission is evident also in the region from 13 000 to 14 700 cm^{-1}. As the pressure increases, the sharp feature decreases in intensity and eventually disappears at 4 GPa, whereas the broadband continues to increase in intensity. Although a quantitative analysis of the intensity changes has not been made, the relative enhancement of the broadband continues to at least 9 GPa, at which point the band edge becomes very broadened. At higher pressures the intensity changes are not clear, partly because a major part of the spectrum is shifted to the near-infrared region and outside the experimental spectral range. The peak positions of both the broad and narrow bands shift toward the red as pressure increases; however, the broadband shifts substantially greater than the sharp one. At the pressures above 4 GPa, the high-energy edge of the broadband is actually shifted below the peak position of the sharp feature. These spectral changes in intensity and energy are reversible up to 12 GPa at low temperature, after which no additional changes are evident. Further details including the nature of the broadband will be discussed below.

The luminescence spectrum of the Sm^{2+} ions is broad and structureless at room temperature; however, a series of sharp lines appear at pressures higher than 5 GPa. This is shown in Fig. 1(c). The transition pressure 5 GPa is in agreement with the structural phase-transition pressure of pure SrF$_2$ crystals; that is, the transition from the cubic β phase to the orthorhombic α phase.[6] No additional changes were observed up to 12 GPa at room temperature.

Upon cooling of the sample at 5 GPa, a broad feature appears and overlaps with the sharp features. The intensity of the broadband with respect to the sharp one is substantially enhanced as temperature decreases. the characteristics of the broadband are similar to those seen in Fig. 1(b), suggesting that the α phase transforms back to the β phase. It also implies that the phase boundary between the β and α phases has a negative dP/dT slope as previously seen in BaF$_2$ crystals.[10]

The spectral changes at 5 GPa are reversible in pressure and temperature, but are associated with a large hysteresis, particularly in pressure. This is shown in Fig. 2, which plots the pressure dependences of the 14 353-cm^{-1}

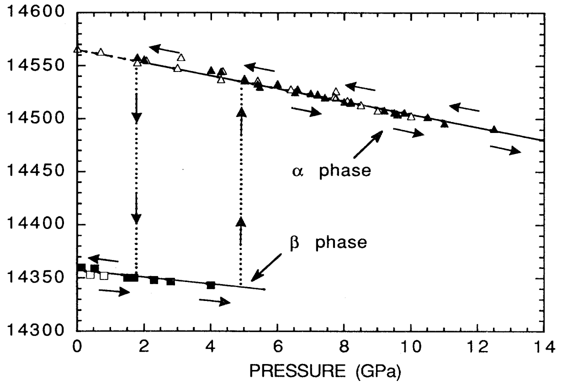

FIG. 2. Peak positions of the 14 353-cm^{-1} band in the β phase and 14 565-cm^{-1} band in the α phase as a function of pressure, showing the α- to β-phase transition in SrF_2 and a large pressure hysteresis associated with the transition. Solid and open symbols indicate the up and down strokes in pressure, respectively. The dashed line and the peak positions below 1.6 GPa in the α phase are from the samples recovered at low temperatures.

band in the β phase [Fig. 1(a)] and of the 14 530-cm^{-1} band in the α phase at 5 GPa [Fig. 1(c)]. The temperature-induced shifts of these bands are negligible, less than 0.03 cm^{-1}/K, when compared to the pressure-induced shifts, 3.6 cm^{-1}/GPa for the 14 353 band and 5.9 cm^{-1}/GPa for the 14 530 band. Note that the transition from the α to β phase occurs at about 1.6 GPa. The hysteresis in pressure between the forward and reverse transitions indicates a considerable activation energy is involved in the transition, which controls the kinetics of the transition.

The large activation energy involved in the transition enables the high-pressure α phase to be observed at 1 atm. The dashed line of the α phase in Fig. 2 was obtained from the sample recovered at low temperatures near 30 K. it is also possible to obtain a mixture of two phases whose composition depends on the quenching conditions of the sample. The spectrum obtained from a sample recovered from 7 GPa or above typically showed a pure α phase; yet the sample held at 6 GPa for several days resulted in a mixed phase after unloading at 30 K. Therefore, it is suggested that compression is the primary driving force accelerating the transition.

For very dilute crystals of Sm^{2+}/SrF_2, the Sm^{2+} ions substitute for the Sr^{2+} ions at sites of O_h symmetry. The crystals used in these experiments had a total Sm concentration of 0.3 wt. %, but the concentration of Sm^{2+} ions is unknown. From the β-phase spectrum shown in Fig. 1(a), the weak luminescence line at 14 605 cm^{-1} is assigned as the ${}^5D_0(A_{1g}\rightarrow{}^7F_0(A_{1g})$ transition. This assignment is slightly shifted from that of Wood and Kaiser[5] and may be due to the high Sm-ion concentration. McFarlane and Melzer[11] have reported the identification of some Sm^{2+} ions in a slightly perturbed O_h symmetry site in a 0.05% Sm/SrF_2 crystal, resulting in the C_{4v} symmetry site of the perturbed Sm ions at which the ${}^5D_0(A_1')\rightarrow{}^7F_0(A_1)$ transition becomes allowed.

The site symmetry at the Sm^{2+} (Sr^{2+}) site in the orthorhombic α-SrF_2 phase is C_i. In this symmetry no degeneracies remain for the J manifolds of the $4f^6$ configuration since all levels belong to the A_g representation, and transitions from ${}^5D_0(A_g)$ to all ${}^7F_J(A_g)$ levels are allowed. The strongest band in the α phase is at an energy of 14 530 cm^{-1} at 5 GPa [Fig. 1(c)] and is assigned to the ${}^5D_0(A_g)$ to ${}^7F_0(A_g)$ transition. This transition is found at 14 565 cm^{-1} in the metastable α phase at 1 atm pressure as shown in Fig. 1(c). With this assignment the difference between the ${}^5D_0$-${}^7F_0$ energies in the β and α phases is 40 cm^{-1}. The high-pressure α phase is 8% denser than the β phase[6] and the F coordination number increases by one to nine coordinates in this phase.[12] Thus $\Delta J = 0$ is redshifted in the denser phase and follows the trend found in the fluorite phases where this transition is redshifted by 36 cm^{-1} as the host material is changed from β-BaF_2 to β-SrF_2.

The lowest level of the $4f^5 5d^1$ configuration of Sm^{2+} in β-SrF_2 (1 atm pressure) has been assigned as the A_{1u} level and is 450 cm^{-1} higher in energy than the ${}^5D_0$ of the $4f^6$ configuration. The energy of the $4f^5 5d^1$ of Sm^{2+} shifts continuously to lower energy relative to the $4f^6$ configuration as a function of pressure. This shift is shown in Fig. 3 where the beginning of the $4f^5 5d^1 \rightarrow 4f^6$ transitions (red edge) is plotted (circles) as a function of pressure. The squares show the peak position of the sharp band in the β phase (${}^5D_0 \rightarrow {}^7F_1$ transition) at temperatures below 30 K. The linear lines represent the least-squares fits to each set of data points. Note the rate of the redshift of the $5d \rightarrow 4f$ band, 149 cm^{-1}/GPa, is substantially greater than that of the $4f \rightarrow 4f$ band, 3.9 cm^{-1}/GPa. This causes the band crossing at approximately 4.5 GPa. The last observation of the narrow $4f \rightarrow 4f$ band was at ~4 GPa. After this crossing only the broad $5d \rightarrow 4f$ band is evident from the luminescence spectra. This result is consistent with the data on Sm^{2+}

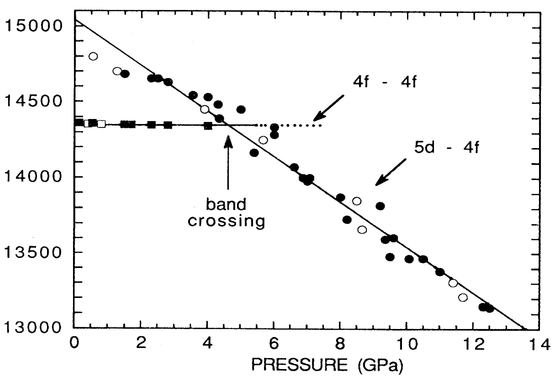

FIG. 3. Peak position of the $4f$-$4f$ band and the red edge position of the $4f$-$5d$ band in the β phase as a function of pressure, showing the band crossing at 4.5 GPa and 30 K. Solid and open circles represent the up and down strokes in pressure, respectively. A strong pressure shift of the $4f$-$5d$ band represents a strong crystal-field effect on the $4f^5 5d^1$ configuration.

in CaF_2 where the beginning of the $4f^55d^1$ configuration is below the $^5D_0$ of the $5f^6$ configuration and only $4f^55d^1 \rightarrow 4f^6$ transitions are apparent in luminescence spectra. Thus it appears the $4f^55d^1$ configuration of Sm^{2+} in β-SrF_2 crosses the $^5D_0$ level of the $4f^6$ configuration at a pressure slightly above 4 GPa. The linear extrapolation of the red absorption edge of $4f^55d^1$ configuration for Sm^{2+} in β-SrF_2 gives 15 032 cm^{-1} at 1 atm pressure. This energy at 1 atm agrees well with the data of Wood and Kaiser, 15 066 cm^{-1}.[5]

The spectrum of Sm^{2+} impurities monitor changes in the bulk SrF_2 crystals quite well and clarifies an ambiguity existing in earlier studies on SrF_2.[13,14] For example, the Raman study[13] shows that the β-to-α transition is reversible; whereas the x-ray work[14] claims that it is irreversible. The Sm^{2+} spectral changes associated with the β-to-α transition in SrF_2 agree with the Raman study. The irreversible nature of the x-ray result is likely due to the high temperature 200 °C at which the sample pressure was released.

In conclusion the electronic structure of the Sm^{2+} impurity ions is sensitive to the changes in the bulk SrF_2 crystal under high pressures. The β-phase SrF_2 transforms into the α phase at 5 GPa; however, at low temperatures and high pressure, the β phase is stable. The high-pressure α phase may be recovered at 1 atm and low temperature with the proper *P-T* pathway. At the quenching pressures between 5 and 7 GPa, a mixture of the α and β phases is obtained, whereas at the higher quenching pressures the pure α phase is obtained. The luminescence spectrum of the α phase is also presented. The ambiguity concerning the reversibility of the α-to-β transition previously observed in the studies on SrF_2 crystals is resolved.

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