Optical Properties of Divalent Thulium in Crystalline Strontium Tetraborate[†]

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Absorption and luminescence spectra from $SrB_4O_7:Tm^{2+}$ prepared in air have been recorded at room temperature. Because thulium was introduced as Tm^{3+} from Tm_2O_3, a valence change from Tm^{3+} to Tm^{2+} was observed. Optimum production of Tm^{2+} ion occurs when the sample is heated in air at 650 °C. A broad emission band centered in the vicinity of 550 nm has been observed from the sample upon excitation at 457.9 nm. We suggest that it is due to Tm^{2+} ion emission from the 5d band into the ground-state 4f level ($^2F_{7/2}$). Several conditions promoting the reduction of Tm^{3+} ion in the sample are discussed. In addition, to aid the reduction of Tm^{3+} ion, we have also prepared $SrB_4O_7:Tm^{2+}$ in Ar/H_2 (4%) atmosphere and compared the optical characteristics of Tm^{2+} ion in these samples with those prepared in air.

Introduction

The luminescence of divalent lanthanide ions in crystals, powders, and glasses has attracted much attention over the past 15 years.[1-5] The amount of spectral data from these ions is very large. The luminescence from Eu^{2+},[6] Sm^{2+},[7] Yb^{2+},[8] and Tm^{2+} [9] ions in crystalline SrB_4O_7 prepared in N_2/H_2 atmosphere has been investigated. The spectra from these ions show that the $4f^{n-1}5d$ electronic configuration is at a relatively high energy in all four cases. High quantum efficiencies and vibrational structures indicate that nonradiative relaxation from their excited states is restricted.[10] This has been ascribed to the stiffness of the host lattice.[6,8] On the other hand, reduction of trivalent lanthanide ions to their divalent ones in solid-state compounds requires a reducing agent.[5] The most commonly used reducing agent is N_2/H_2 or H_2 atmosphere.[6-9]

Recently the observation of reduction of selected trivalent lanthanide ions to their divalent counterparts in SrB_4O_7 prepared in air has been reported.[11] It was found that Eu^{3+}, Sm^{3+}, and Yb^{3+} ions can be reduced to the corresponding divalent ions in air at high temperature in SrB_4O_7. No similar study with the next most easily reduced trivalent lanthanide ion, Tm^{3+}, was mentioned.[11] Whether these workers attempted and failed to reduce Tm^{3+} to Tm^{2+} in air in SrB_4O_7 or simply chose not to extend their studies to determine the lanthanide ion reducibility limit in air in SrB_4O_7 is unknown to the present authors. A more recent report discusses the preparation of Tm^{2+} in N_2/H_2 (25%) in SrB_4O_7 and its characterization via luminescence spectroscopy.[9] Because of our continuing interest in generating and characterizing unusual oxidation states of the f elements for particular application to the radioactive transuranium elements, we chose to repeat the reported work in SrB_4O_7 and to explore whether Tm^{2+} could be produced in air and/or in laboratory safer Ar/H_2 (4%) atmosphere.

This report is focused on the preparation of $SrB_4O_7:Tm^{2+}$ and the absorption and emission spectral characteristics recorded from divalent thulium ion. Preparations in air and in Ar/H_2 were carried out to determine the effect of this variable. In addition the extent of reduction from Tm^{3+} to Tm^{2+} ion as a function of the temperature of preparation was also investigated.

Experimental Details

Powder samples of $SrB_4O_7:Tm^{2+}$ were prepared as described in the literature[11] by solid-state reactions in air or Ar/H_2 (4%) atmosphere. Stoichiometric amounts of $SrCO_3$ and H_3BO_3 mixed together with a 3 mol % excess of H_3BO_3 to compensate for B_2O_3 evaporation, along with 1 mol % (based on Sr^{2+} mass) Tm_2O_3, were thoroughly ground together. Portions of this mixture were heated separately at 550, 600, 650, 700, and 800 °C in alumina crucibles for 5 h and then reground and heated at 650, 700, 750, 800, and 900 °C, respectively, for another 5 h.

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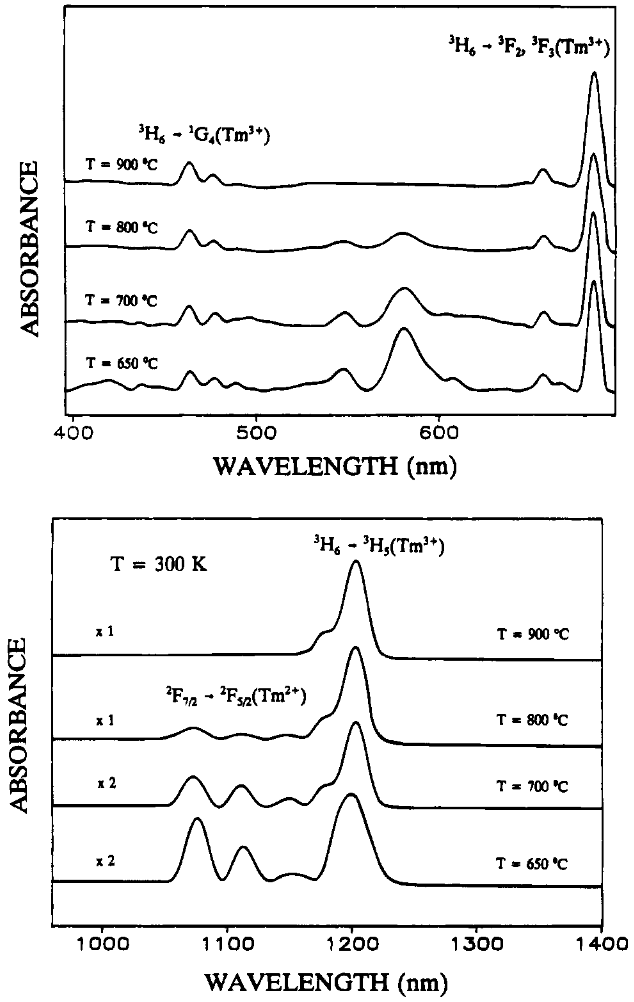

Figure 1. (a, top) Room-temperature absorption spectra in the wavelength region 385–720 nm from SrB_4O_7:Tm^{2+} samples prepared in air at different temperatures. (b, bottom) Room-temperature absorption spectra in the wavelength region 950–1400 nm from SrB_4O_7:Tm^{2+} samples prepared in air at different temperatures.

Visible and near-infrared absorption spectra (diffuse reflectance method)[12] from the various samples were recorded with a Cary Model 14H scanning spectrophotometer converted by On-Line Instrument Systems (OLIS) for data acquisition and analysis by an IBM-compatible computer. The 457.9 nm line from a Coherent Model 300 argon ion laser was used as the excitation source. Luminescence spectra were recorded with a Ramanor Model HG.2S spectrophotometer (Jobin-Yvon Instruments SA), having a resolution of 0.5 cm^{-1} at 514 nm. The collected light was detected by a photon-counting system, which employed a cooled photomultiplier tube (Hamamatsu R636) and a multichannel analyzer (Nicolet 1170) interfaced with an AT personal computer using "Spectra Calc" software (Galactic Industries Corp.).

Results and Discussion

The room-temperature absorption spectrum in the wavelength region 385–720 nm from SrB_4O_7:Tm^{2+} prepared in air at 650 °C is shown in Figure 1a. Bands centered at 463, 650, and 689 nm correspond respectively to absorption from the $^3H_6$ ground state to the $^1G_4$, $^3F_2$, and $^3F_3$ excited states of Tm^{3+} ion.[13,14] The energy levels of Tm^{2+} ion in CaF_2 and BaF_2 single crystals have been determined by others.[15–17] According to their energy level diagrams for Tm^{2+} ion, the three absorption bands centered at 420, 547, and 580 nm in Figure 1a are due to allowed 4f–5d transitions in Tm^{2+} ion.

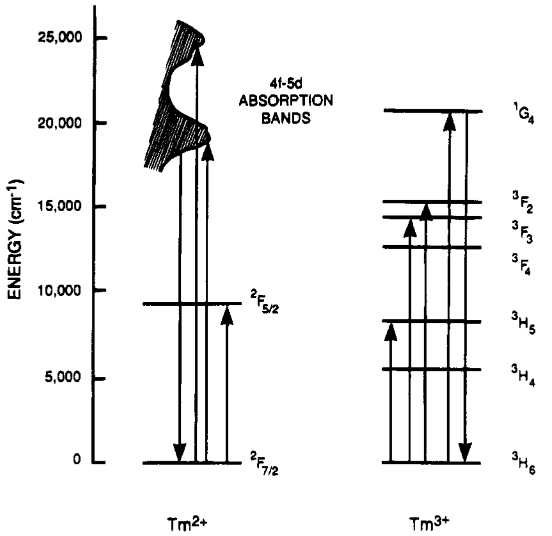

Figure 2. Schematic energy level diagrams for Tm^{2+} and Tm^{3+} ions with some indicated absorption and emission processes.

The room-temperature absorption spectra in the wavelength region 950–1400 nm from SrB_4O_7:Tm^{2+} prepared in air at different temperatures are shown in Figure 1b. Here we find three main absorption bands, centered at 1073, 1110, and 1200 nm. In accord with the energy level diagrams of Tm^{2+} ion,[15–17] the bands at 1073 and 1110 nm correspond to transitions from the $^2F_{7/2}$ ground state to the $^2F_{5/2}$ excited state in Tm^{2+} ion. The most intense absorption band at 1200 nm is due to the Tm^{3+} ion transition from the $^3H_6$ ground state to the $^3H_5$ level (see Figure 2). Also very evident from the data shown in Figure 1b is the decrease in concentration of Tm^{2+} ion with increasing temperature of preparation. Clearly the concentration of Tm^{3+} ion increases with increasing temperature of preparation. With the change in preparation temperature from 650 to 850 °C (Tm^{2+} absorbance from samples prepared in air at 900 °C was unmeasurable), the absorbance of Tm^{2+} ion decreased by a factor of 3, while that of Tm^{3+} ion increased by a factor of 2. To determine the optimum heating temperature for generation of Tm^{2+} ion in the SrB_4O_7 host compound, the ratio of the absorbance of Tm^{2+} and Tm^{3+} ions (based on integrated intensities: 547 and 580 nm bands for Tm^{2+}; 689 nm band for Tm^{3+}) was measured as a function of the preparation temperature between 650 and 900 °C. The results of this study showed that the most favorable preparation temperature for Tm^{2+} production was 650 °C.

The emission spectra recorded at room temperature from samples prepared in air at various temperatures under 457.9 nm light excitation in the range 460–730 nm are shown in Figure 3. Two main emission bands, centered at 476 and about 560 nm, are observed. In

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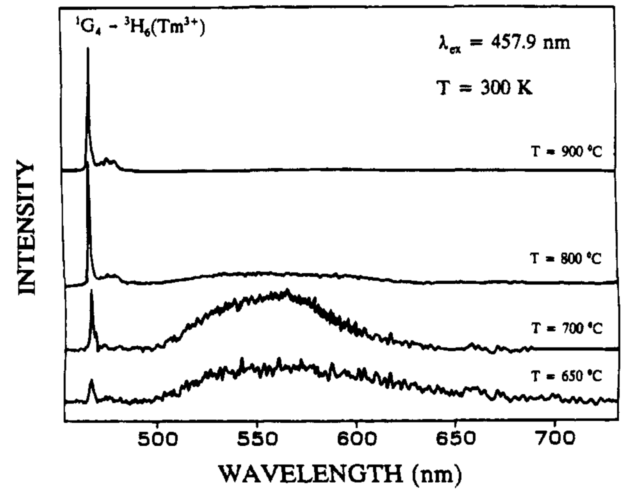

Figure 3. Room-temperature emission spectra from SrB_4O_7:Tm^{2+} samples prepared in air at different temperatures under 457.9 nm light excitation.

accord with the energy level diagrams of Tm^{3+} ion,[13,14,18] the sharp emission band at 476 nm is attributed to the $^1G_4 \rightarrow {}^3H_6$ transition. The shape and position of the broad emission band are consistent with the corresponding 4f−5d absorption band in Tm^{2+} ion (see Figure 1a). We have also measured the absorption spectrum of the SrB_4O_7 host. One end of a broad absorption band is at 330 nm, with the center wavelength of this band being about 270 nm. This observation agrees with that of others.[5,11] Therefore it is not likely that one would observe emission through a charge-transfer band of Tm^{3+} ion by 457.9 nm light excitation of the SrB_4O_7 host. We assume then that the broad emission centered at about 560 nm in Figure 3 stems from 5d → 4f transitions in Tm^{2+} ion. Our luminescence spectra recorded at room temperature are consistent with, although not as highly resolved as, the luminescence spectrum recorded at liquid helium temperature by Schipper et al.[9]

The ratio of integrated intensities of the 560 nm emission to the 476 nm emission versus sample preparation temperature over the 650−900 °C range was calculated. This ratio decreases rapidly (from 1.7 to 0.2) with increasing sample preparation temperature in the range 650 to 750 °C. Above about 800 °C, this broad emission band is almost nonobservable. These results, based on luminescence analysis, are quite similar to those we obtained based on absorption spectral analysis.

When a sample of SrB_4O_7:Tm^{2+} is prepared in an Ar/H_2 (4%) atmosphere, the absorption spectrum of the sample at room temperature (see Figure 4) exhibits much increased intensity in the Tm^{2+} absorption bands compared to that from an identically prepared sample in air. The spectral characteristics of Tm^{2+} (peak shape, position, and relative intensity) obtained from both preparation routes are the same.

There are several probable reasons for the reduction of Tm^{3+} ion to Tm^{2+} ion in SrB_4O_7. When Tm^{3+} ion replaces Sr^{2+} ion, some defects will occur in the solid to create a charge balance. It may be the transfer of an electron from such a defect to a Tm^{3+} ion that reduces it to Tm^{2+} ion. The temperature of sample preparation is also quite important, especially when the sample is

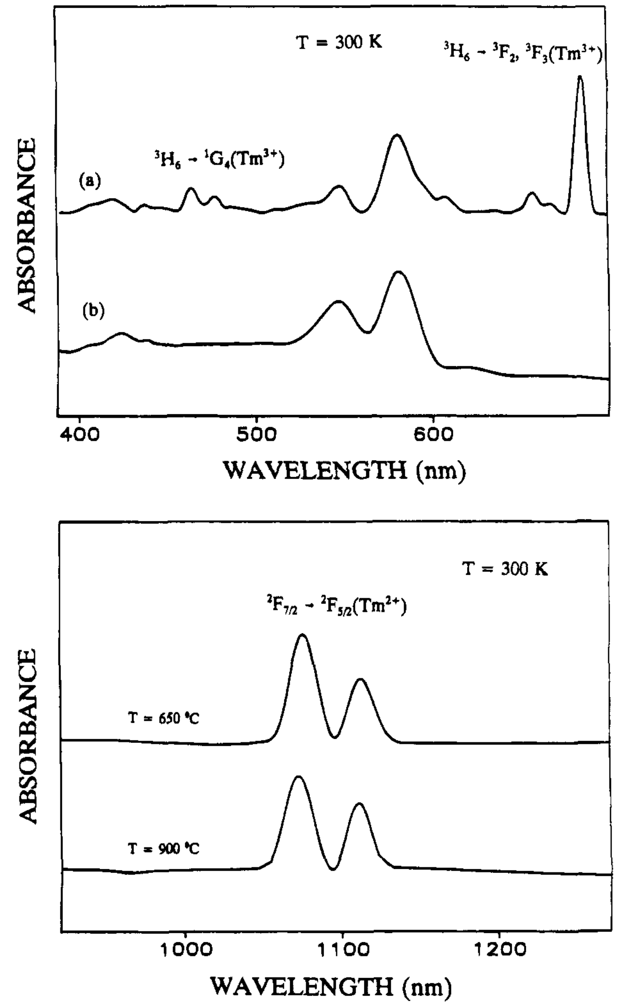

Figure 4. (a, top) Room-temperature absorption spectra in the wavelength region 390−700 nm from SrB_4O_7:Tm^{2+} samples prepared at 650 °C in (a) air and (b) Ar/H_2 (4%) atmosphere. (b, bottom) Room-temperature absorption spectra in the wavelength region 930−1270 nm from SrB_4O_7:Tm^{2+} samples prepared in Ar/H_2 (4%) atmosphere at 650 and 900 °C.

prepared in air. Divalent lanthanide ions are easily oxidized to trivalent ones at elevated temperatures in an oxidizing atmosphere.[19] It was confirmed in our experiments that the absorbance and emission intensities of Tm^{2+} ion decrease with increasing temperature of sample preparation in air, while those of Tm^{3+} ion increase with increasing temperature. When a sample is prepared in Ar/H_2 (4%), the absorption and emission bands observed are from Tm^{2+} ion regardless of the temperature of sample preparation. This implies that a reducing agent (H_2) is necessary for complete reduction to Tm^{2+} ion.

The crystal structure of SrB_4O_7 is conducive to the stabilization of divalent lanthanide ions substituting for Sr^{2+} ion. Pei et al.[11] have found that when Eu^{3+} ion is doped into $Sr_3La_2(BO_3)_4$, it cannot be reduced to Eu^{2+} ion even by H_2, because the Eu^{3+} ion occupies the La^{3-} ion site created by the packing of the stable, triangular $(BO_3)^{3-}$ ions. In the $Sr_3B_2O_6$, $Sr_2B_2O_5$, and SrB_2O_4 compounds, in which the borate anions also consist of triangular $(BO_3)^{3-}$ groups, dopant Eu^{3+} ion replaces Sr^{2-} ion and in these matrices, it can be reduced to Eu^{2+} ion

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by H_2 reduction but not in air. In SrB_4O_7 tetrahedral BO_4 units build up a three-dimensional $[(B_4O_7)^{2-}]_\infty$ network structure,[19] in which it has been found in this work that even Tm^{3+} ion can be reduced to Tm^{2+} ion (partially in air; completely in Ar/H_2) and in the work of others,[11] that Eu^{3+}, Yb^{3+}, and Sm^{3+} ions are reduced to their divalent counterparts in air. The three-dimensional network structure of SrB_4O_7 provides a metal ion site completely surrounded by the tetrahedral BO_4 units of the $[(B_4O_7)^{2-}]_\infty$ network and of a size closely matched to the ionic radii of these divalent lanthanide ions. Thus, the ability of this matrix to stabilize the less easily reduced Sm^{3+} and Tm^{3+} ions can be attributed to its structural framework.

Machida et al.[20,21] have reported the oxidation temperatures for a series of Eu(II) borates. It is known that all compounds containing Eu^{2+} ion can be oxidized to Eu^{3+} by heating to some temperature (the oxidation temperature) in an oxidizing atmosphere. In $Eu_3B_2O_6$ with triangular $(BO_3)^{3-}$ groups, the oxidation temperature is 400 °C; in $Eu_2B_2O_5$ with two triangular $(BO_3)^{3-}$ groups sharing one oxygen, it is 410 °C. In EuB_2O_4 with its $(BO_2)_\infty$ network chain, the oxidation temperature rises to 480 °C; and in EuB_4O_7 with its three-dimensional $[(B_4O_7)^{2-}]_\infty$ network, it is 760 °C. It is obvious that the oxidation temperature of EuB_4O_7 is considerably higher than those of the other Eu(II) borates. This is a reflection of the increased stabilization of the divalent state by this tetraborate stoichiometry. Strontium borates exhibit structures similar to the corresponding europium(II) borates. In the present case where Sr^{2+} ion sites are occupied partially by Tm^{2+} ions, the Tm^{2+} ion is completely surrounded by tetrahedral BO_4 units of the $[(B_4O_7)^{2-}]_\infty$ network and therefore protected from attack by oxygen.

In summary we have observed divalent thulium in SrB_4O_7 prepared in air and in Ar/H_2 (4%) at elevated temperature and characterized it via absorption and emission spectroscopy. This both confirms the recent report of Tm^{2+} in SrB_4O_7 prepared in N_2/H_2 (25%)[9] and extends the conditions under which it can be prepared and its spectral characterization. Previously divalent thulium was usually obtained only in alkaline earth fluorides (CaF_2, BaF_2) by irradiating with γ-rays or by reactions of thulium metal with the thulium trihalides. It is of major importance that in the present work divalent thulium was obtained in a straightforward laboratory procedure in air. This reduction was facilitated in a laboratory-safe Ar/H_2 (4%) atmosphere. Future work will determine if there is a concentration limit to the Tm^{2+} ion stabilization in this matrix. Extension of this work to selected actinide ions is also of great interest in order to be able to characterize more fully their divalent oxidation states.

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