Reversible Valence Change of the Europium Ion Doped in Alkaline-earth Tetraborates

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Valence state of the europium (Eu) ion doped in MB_4O_7 (M=Sr and Ba) was reversibly changed between the trivalent and divalent state by repeating the crystallization and vitrification cycle of the host lattices by heating even in air at 973-1273 K and such valence change was discussed on the basis of their structural connection manner for the BO_3 and/or BO_4 units in the networks of crystalline and vitreous forms.

Trivalent lanthanide ions are very common but, even under a condition of γ-ray irradiation or evacuation, they are partially or completely reduced to the divalent ones without using any reductant, which possess the unique luminescence property as differs from those of the trivalent counterparts considerably.[1-3] Among them, Sm^{2+}, Eu^{2+}, Tm^{2+}, and Yb^{2+} ions are well known to be stabilized owing to the parallel or antiparallel configuration characteristics of 4f electrons: $4f^6$ for Sm^{2+}, $4f^7$ for Eu^{2+}, $4f^{13}$ for Tm^{2+}, and $4f^{14}$ for Yb^{2+}, and some Eu^{2+}-activated alkaline-earth borates such as $SrB_4O_7{:}Eu^{2+}$ and δ–$SrB_2O_4{:}Eu^{2+}$ (high-pressure phase) provide strong blue band emissions.[4,5] Particularly, their crystal structures consist of a $(B_4O_7)_\infty$ or $(B_3O_6)_\infty$ network of the BO_4 units by which each Eu^{2+} ion is effectively surrounded and isolated from the neighboring Eu^{2+} ones, so that the concentration quenching effect on the luminescence of $SrB_4O_7{:}Eu^{2+}$ and δ–$SrB_2O_4{:}Eu^{2+}$ is lowered and one can observe still the intense blue band emissions even on EuB_4O_7 and δ–EuB_2O_4.[4,5] Furthermore, these europium(II) compounds show good oxidation resistance compared with the other borates in the system EuO-B_2O_3, and the temperature to start the oxidation of EuB_4O_7 has been evaluated to be 757 K.[6] Meanwhile, a series of Ln^{2+}-doped SrB_4O_7 materials (Ln=Sm, Eu, and Yb) are also produced only by heating the starting material mixtures of $SrCO_3$, Ln_2O_3, and H_3BO_3 without any reduction treatment,[7] and the same work has been followed on $SrB_4O_7{:}Tm^{2+}$.[8] However, no answer has been given to the question why the reduction of Ln^{3+} ions takes place during the formation of the SrB_4O_7 host lattice.

In this work, the valence change characteristics for the Eu^{n+} (n=2 or 3) ions incorporated in the alkaline-earth borates, $MB_4O_7{:}Eu^{n+}$ (M=Sr and Ba), were studied by taking into account the luminescence and structural property for their crystalline and vitreous phases.

Crystalline and vitreous tetraborates $MB_4O_7{:}Eu^{n+}$ (1 at%) as activated by 1 at% of Eu^{n+} ions were prepared by heating the intimate mixtures of $MCO_3{:}Eu^{3+}$ and H_3BO_3 or B_2O_3 at 973-1273 K for 2×5 h (two times), where $MCO_3{:}Eu^{3+}$ were coprecipitated from the solutions of $M(NO_3)_2$ containing 1 at% of $Eu(NO_3)_3$ by adding a NH_4CO_3 solution and dried in vacuo at 373 K for 5 h. Structural characterization for the resulting materials was made by XRD and IR spectrum measurements.

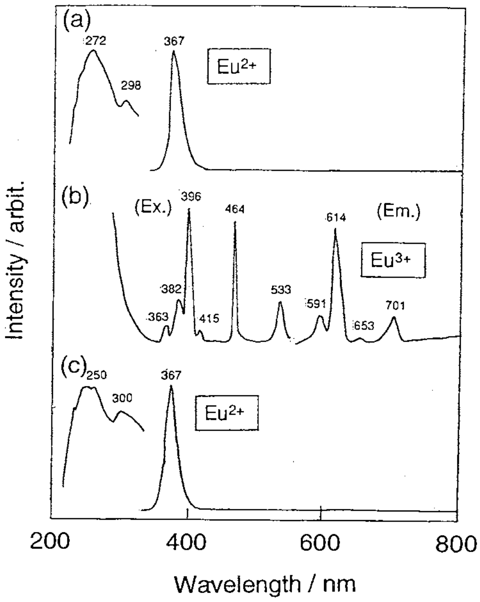

Figure 1. Luminescence spectra of (a) crystalline, (b) vitreous, and (c) recrystallized $SrB_4O_7{:}Eu^{n+}$ materials at room temperature.

Figure 1 shows the luminescence spectra observed on the crystalline, vitreous, and recrystallized $SrB_4O_7{:}Eu^{n+}$ powders, where the respective heating conditions made in air are as follows: 973 K, 5 h and 1123 K, 5 h (solid-state reaction), 1273 K, 5 h (melting), and 1248→1198 K, 2.5 K h^{-1} (gradual cooling: recrystallization). The crystalline and recrystallized tetraborates showed the strong blue band emissions at 367 nm, which are characteristics of the crystalline $SrB_4O_7{:}Eu^{2+}$ material as prepared by the conventional solid-state reaction method as performed in an atmosphere containing H_2 as the reductant for the Eu^{3+} ions in the starting materials. However, the vitreous modification (glass) of $SrB_4O_7{:}Eu^{2+}$ only provided the red line emission based on the Eu^{3+} ions and one observed no longer any blue band emission of Eu^{2+} ions. These results mean that (1) the Eu^{2+} ions are never incorporate in the vitreous SrB_4O_7 host lattice prepared by melting in air and completely oxidized to the trivalent ones, even though it is derived from the crystalline $SrB_4O_7{:}Eu^{2+}$ material, and (2) the Eu^{3+} ions in the vitreous $SrB_4O_7{:}Eu^{3+}$ materials are reduced during the recrystallization of them, in a similar manner as the formation process for the crystalline $SrB_4O_7{:}Eu^{2+}$ ones as previously reported by Pei *et al.*[7]

From the structural analysis by the XRD and IR spectrum measurements, the crystalline or recrystallized $SrB_4O_7{:}Eu^{2+}$ materials prepared in this work were confirmed to be isostructural with SrB_4O_7 and EuB_4O_7, which consisted of the three-dimensional $(B_4O_7)_\infty$ network as connected by the BO_4 units together.[6,9] Contrary to this, the vitreous $SrB_4O_7{:}Eu^{2+}$ materials

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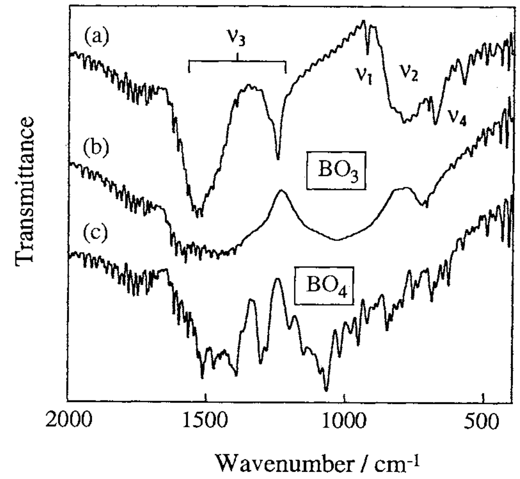
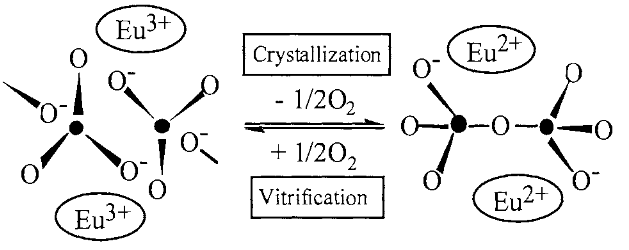


Figure 2. Infrared spectra of (a) vitreous B_2O_3, (b) vitreous SrB_4O_7:Eu^{n+}, and (c) recrystallized SrB_4O_7:Eu^{n+} materials at room temperature. Vibration modes of BO_3 unit: ν_1, the symmetrical stretch; ν_2, the out-of-plane bend; ν_3, the antisymmetrical stretch; ν_4, the in-plane bend.

which only possess flattened, broad XRD profiles provide IR spectrum patterns as assigned to the B-O stretching and bending modes of BO_3 triangles mainly as shown in Figure 2.[10] These structural characteristics of them allow us to propose the following valence change mechanism for the Eu^{n+} ions as,



When the terminal oxygens denoted as O^- in the BO_3 units were connected one another to form BO_4 units in the crystallization process of SrB_4O_7 host lattice, the Eu^{3+} ions were reduced by evolving the resulting free oxygens and the converted Eu^{2+} ions were stabilized by occupying the Sr^{2+} ion sites. Since the BO_3 triangles are generally the major borate units in the melt phase of metal borates, the Eu^{2+} ions in the crystalline host lattice should be oxidized in the vitreous one derived from the melt of SrB_4O_7.

From the above model, one can expect that the similar valence state modification of Eu^{n+} ions should be observed on the host lattice of BaB_4O_7 which consists of a three-dimensional network containing BO_4 tetrahedra. The crystalline BaB_4O_7:Eu^{2+} samples prepared in air gave a strong blue band emission at 376 nm, which was responsible for the Eu^{2+} ions in the crystalline host lattice of BaB_4O_7. On contrary to the crystalline materials, the vitreous BaB_4O_7:Eu^{2+} ones as prepared from the melt only provided the red line emission based on Eu^{3+} ions. The spectrum variety observed on these crystalline and vitreous barium tetraborates fairly supports the valence change mechanism as proposed above.

In conclusion, the structural change between the BO_3 and BO_4 units during the crystallization and vitrification process of the MB_4O_7 host lattices induces the redox between the trivalent and divalent states for the Eu^{n+} ions incorporated in them even in air. The mechanism as proposed above for the reversible valence change suggests that a series of metal borates with the networks containing of BO_4 units should induce the same redox behavior for the Eu^{n+} ions incorporated in them.

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