Tb³⁺ and Ce³⁺ Intercalated Laponite Powder

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Tb³⁺ and Ce³⁺ Intercalated Laponite Powder: The Influence of Ce³⁺ Ions on Thermal Stability and Optical Properties of Tb³⁺ Intercalated Laponite

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Laponite samples intercalated with Tb³⁺ or Tb³⁺,Ce³⁺ ions were prepared by exchange of Na⁺ ions in interlayers with Tb³⁺ or Ce³⁺ ions. Strong green and weak blue emissions under vacuum ultraviolet (VUV) excitation (λ = 158 nm) were observed due to the $^5D_4 \to {}^7F_J$ and $^5D_3 \to {}^7F_J$ emission lines, respectively. Tb³⁺ ions in an interlayer of laponite mainly existed in ion pairs or clusters, as evidenced by the concentration-dependent luminescence of the Tb³⁺ ions on the relative intensities of the $^5D_3 \to {}^7F_J$ and the $^5D_4 \to {}^7F_J$ emission lines, due to the action of a cross-relaxation process. The addition of Ce³⁺ ions increased the thermal stability of Tb³⁺ intercalated laponite up to 650 ℃ and quenched the $^5D_3 \to {}^7F_J$ emission lines, probably by promoting the formation of Tb³⁺ ion pairs at relatively low Tb³⁺ concentrations.

Key Words : Amorphous materials, Thermal properties, X-ray powder diffraction, Luminescence, Laponite

Introduction

Smectite clay minerals have received considerable attention due to their unique swelling ability, intercalation, and ion exchange properties.[1-5] The alkali metal and alkaline earth ions in the interlayer space of the smectites can be replaced by ion exchange method with a variety of desired cations. The ability of smectite clay to adsorb both inorganic and organic materials gives novel functional organic/inorganic hybrid materials. For optical applications, laponite clay offers certain advantages over other smectite clays by providing homogeneous interlayer regions in which optically active ions can reside due to the absence of any tetrahedral substitution of Si by Al. The optical application of functionalized clays into useful devices necessitates the coating of the glass substrate, for which laponite is an excellent film forming material. Laponite is a synthetic polycrystalline similar in structure and composition to natural hectorite of the smectite group.[6] The empirical composition of laponite is $Na_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]$. Rare-earth-ion-doped inorganic compounds have been utilized in luminescent devices such as fluorescent lamps, cathode ray tubes, plasma display panels (PDPs), light emitting diodes, scintillators and amplifiers for fiber-optic communication.[7] There are few reports on laponite intercalated with rare-earth ions that show efficient luminescence. Recent studies have reported visible and near-infrared luminescence of Eu³⁺, Er³⁺ or Tb³⁺ inercalated laponite, along with thick films under UV excitation.[8,9] These reports suggest that laponite or laponite-annealed powder could be a promising host material for optical applications. The green emitting phosphor for many optical devices is based on Tb³⁺ ions. The present work describes the structural evolutions of Tb³⁺ and Tb³⁺, Ce³⁺ intercalated laponite powders at various temperatures and their luminescence, especially under vacuum ultraviolet (VUV) excitation.

Experimental

Materials. Analytically pure $Tb(NO_3)_3$ (Aldrich, 99.9%) and $Ce(NO_3)_3$ (Aldrich, 98%) were used as received. Water was distilled and further purified by a Millipore MilliQ system. Laponite RDS (Rockwood), containing 10% sodium phosphate ($Na_4P_2O_7$), was used without further purification.

Sample Preparation. Laponite RDS was considered an anionic material with a negative charge (cationic exchange capacity) of about 50 mmol/100 g. Laponite RDS (5.00 g, 2.50 mmol of negative charge) in 1000 ml of distilled water was vigorously stirred for an hour. When the laponite solution became transparent, terbium(III) nitrate (0.363 g, 0.83 mmol) was added and the resulting solution was stirred overnight. Cryogels of the resulting terbium ion-exchanged sample were obtained with a freeze-drying process using a Samwon deep freezer (SFDSM24L). The cryogels intercalated with Tb³⁺ or Ce³⁺ were named Lap-Tb or Lap-Ce, respectively. The degree of doping was expressed as the percent molar ratio ((moles of terbium ions × 3/cation exchange capacity) × 100). The cryogels were further annealed in air at 600, 650, 700, 900 and 1200 for 2 h.

Characterization. The prepared samples were analyzed by X-ray powder diffraction (XRD) using Cu Kα radiation (λ = 0.1540 nm). The emission spectra in the wavelength range of 300-800 nm under VUV excitation (λ = 158 nm) were measured at room temperature by a homebuilt VUV spectrometer composed of a 30 W deuterium lamp (Hamamatsu), a vacuum monochromator (ARC VM502), a vacuum sample compartment, and a photomultiplier tube (PMT, ARC HP-300). A high vacuum of 1 × 10⁻⁵ Torr was maintained in the excitation monochromator and sample compartment by a molecular turbo pump.

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Results and Discussion

Influence of Tb^{3+} and Ce^{3+} Ion Concentration on Stability of Laponite Structure. The XRD patterns for the thermally treated samples of Lap-Tb(100%) shown in Figure 1(a) were similar to those published for Eu^{3+} or Er^{3+} intercalated laponite powder.[8,9] When the sample was heated to 600 °C, obvious sharpening of the $d_{(001)}$ peak located at 9.0^0 in Lap-Tb(100%) was observed. The basal spacing of Lap-Tb(100%) at 600 °C was 0.98 nm, which was shorter than that of a laponite intercalated with Na^+ ions (1.08 nm on the sample heated to 300 °C under vacuum).[10] This is due to the smaller ionic radius of Tb^{3+} (92 pm) compared to that of Na^+ (95 pm).[11] The major new peaks observed at $2\theta = 28.12, 31.18, 35.52$ and 43.26^0 from 700 to 900 were attributed to the formation of enstatite polymorphs ($MgSiO_3$).[12,13] Three polymorphs of enstatite are found in the XRD patterns. The low temperature polymorph is orthoenstatite (JCPDS file 19-0768) and the high temperature polymorphs are protoenstatite (JCPDS file 11-0273) and clinoenstatite (JCPDS file 35-0610). To investigate the effect of Tb^{3+} and Ce^{3+} ion concentration on the stability of the laponite layer structure, XRD study was conducted for different concentrations of Tb^{3+} and Ce^{3+} ions heated to 650 °C, as shown in Figure
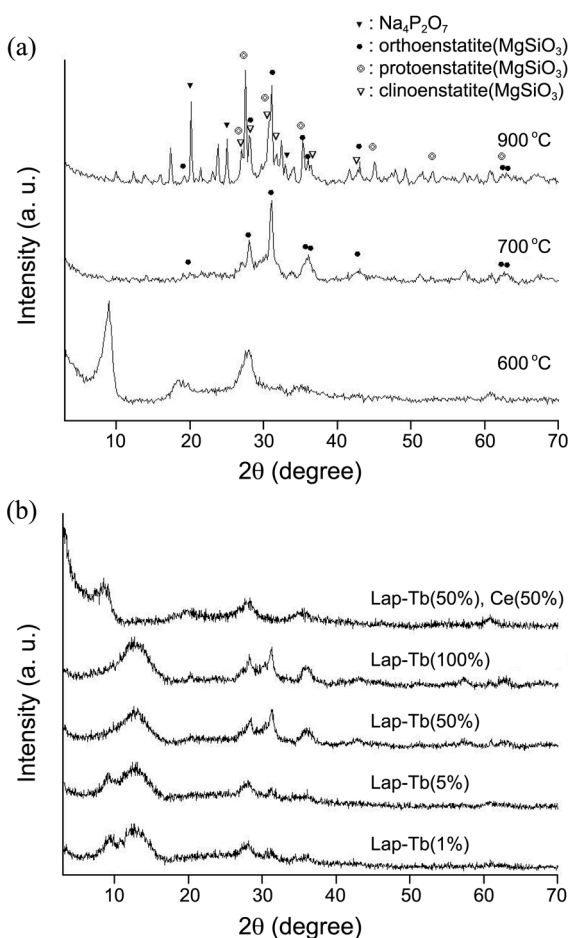
1(b). At low Tb^{3+} concentrations in Lap-Tb(1%), Na(99%) and Lap-Tb(5%), Na(95%), $d_{(001)}$ peaks were still observed around 9.0^0. These $d_{(001)}$ peaks were attributed to the characteristic $d_{(001)}$ peak of laponite containing Na^+ ions. At high Tb^{3+} concentrations (50 and 100%), however, no $d_{(001)}$ peaks were observed and a significant amount of enstatite polymorphs appeared. This suggests that Tb^{3+} ions, rather than Na^+ ions, migrate more easily into the silicate layer, thereby collapsing the laponite layer. Interestingly, the broad peak around 12.50^0 has not been previously reported in the literature and might be due to the continued presence of amorphous silicates after the formation of enstatite polymorphs. The substitution of Ce^{3+} ions for Na^+ ions in the presence of Tb^{3+} (50%) prevented the migration of Tb^{3+} ions into the silicate layer, as shown in Figure 1(b), which was attributed to the high coordination numbers of Ce^{3+} ions and the limited number of non-network oxygen atoms in laponite. Added Ce^{3+} ions coordinate with many non-network oxygen atoms and induce the Tb^{3+} ions to form ion-pairs or agglomerated clusters between the laponite layers. This stabilizes the whole structure by preventing the migration of Tb^{3+} ions. The clustering behavior of rare-earth ions has been attributed in the literature to the limited number of non-network oxygen atoms in the glass matrix.[14]

Luminescence of Tb^{3+} Ions at Various Temperatures and a Cross-Relaxation Process Involving Two Tb^{3+} Ions. The room-temperature luminescence spectra resulting from 158 nm excitation of Tb^{3+} in the Lap-Tb(100%) samples heated to various temperatures are shown in Figure 2. The wavelength was set at 158 nm, rather than 147 nm, at which the phosphor for PDP was excited, because higher intensities of emission lines were obtained under this wavelength. The figure shows a typical Tb^{3+} luminescence due to the transitions of $^5D_4 \rightarrow {}^7F_J$ ($J = 3 \rightarrow 6$) and $^5D_3 \rightarrow {}^7F_J$ ($J = 3 \rightarrow 5$). The energy level diagram of Tb^{3+}, with labeled transitions that correspond to the observed emission lines between 379 and 622 nm, is shown in Scheme 1. The $^5D_4 \rightarrow {}^7F_J$ ($J = 3 \rightarrow 6$) emission lines in Lap-Tb (100%) heated to 600 °C dominated the spectrum, as shown in Figure 2, which suggest that the
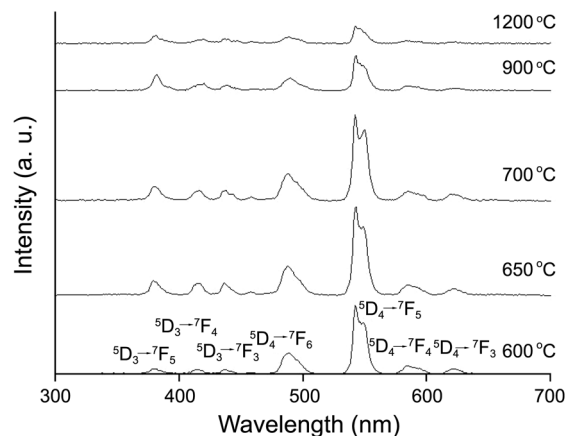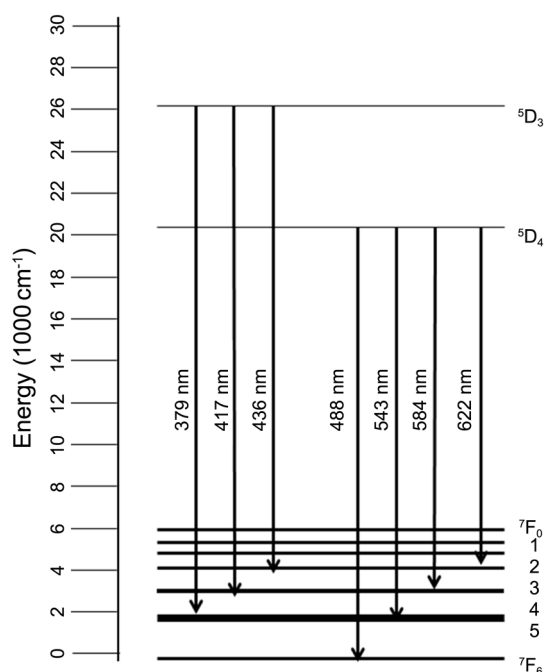

Figure 1. XRD patterns for (a) the thermally treated samples of Lap-Tb(100%), and (b) samples with different concentrations of Tb^{3+} and Ce^{3+} heated to 650 °C.

Figure 2. Room temperature luminescence spectra of Tb^{3+} in Lap-Tb(100%) heated to various temperatures under excitation at 158 nm.

Scheme 1. Energy level diagram of Tb^{3+}, with labeled transitions corresponding to the observed emission lines.

Tb^{3+} concentration between the laponite layers was sufficiently high to facilitate the well known, cross-relaxation process involving two Tb^{3+} ions.[7] In general, materials at low Tb^{3+} concentration, in which the Tb^{3+} ions are homogeneously distributed, exhibit a predominant $^5D_3 \rightarrow {}^7F_J$ ($J = 3\rightarrow5$) emission. At high Tb^{3+} concentration, Tb^{3+} ion-pairs or clusters are formed and $^5D_3 \rightarrow {}^7F_J$ ($J = 3\rightarrow5$) emission decays non-radiatively to the $^5D_4$ state *via* a cross-relaxation process. As a result, the major emission changes from $^5D_3 \rightarrow {}^7F_J$ ($J = 3\rightarrow5$) to $^5D_4 \rightarrow {}^7F_J$ ($J = 3\rightarrow6$) emission lines. As the temperature was increased up to 1200, the intensities of the $^5D_4 \rightarrow {}^7F_J$ ($J = 3\rightarrow6$) emission lines decreased and this result was consistent with the fact that the Tb^{3+} ions migrated into the hexagonal holes of the SiO_4 network in laponite above 600 °C and the resulting amorphous phase recrystallized to give the enstatite polymorphs observed by XRD experiment. Similarly, previous thermal analyses of laponite showed that enstatite polymorphous were formed above 750 °C.[15] The $^5D_3 \rightarrow {}^7F_J$ ($J = 3\rightarrow5$) and $^5D_4 \rightarrow {}^7F_J$ ($J = 3\rightarrow6$) emissions at 900 °C and 1200 °C, respectively, were attributed to the emissions due to the Tb^{3+} ions mainly in enstatite polymorph. The broad features of these emission lines suggest that the Tb^{3+} ions lie in an interlayer of laponite and that the amorphous enstatite polymorphs are distributed in many different sites.

Because the local coordination of Tb^{3+} in Lap-Tb(100%) heated to 650 °C was similar to that of Lap-Tb(100%) heated to 600 °C, and as the intensities of the $^5D_3 \rightarrow {}^7F_J$ ($J = 3\rightarrow5$) and $^5D_4 \rightarrow {}^7F_J$ ($J = 3\rightarrow6$) emissions lines were the highest among the prepared samples, the experiment for observing the cross-relaxation process was conducted with Lap-Tb (100%) heated to 650 °C. The intensity of the $^5D_4 \rightarrow {}^7F_J$ ($J =$
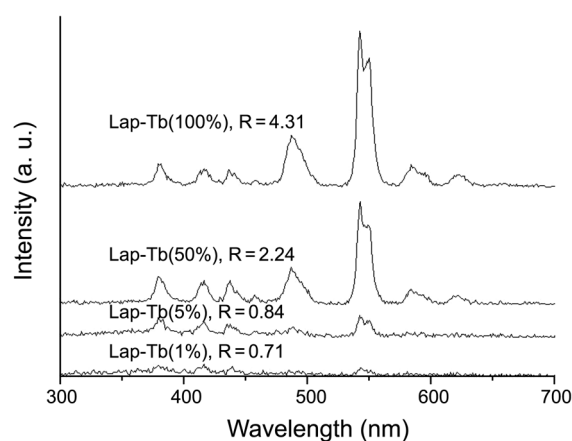

Figure 3. Room temperature luminescence spectra of samples with different concentrations of Tb^{3+} in Lap-Tb heated to 650 °C.

$3\rightarrow6$) emission lines relative to that of the $^5D_3 \rightarrow {}^7F_J$ ($J = 3\rightarrow5$) emission lines increased gradually with increasing Tb^{3+} concentration, as shown in Figure 3, indicating the action of the cross-relaxation mechanism. The ratio R of the intensities of the two luminescent bands

$$R = \Sigma_J I({}^5D_4 \rightarrow {}^7F_J)/\Sigma_J I({}^5D_3 \rightarrow {}^7F_J), (J = 0,1,2,3,4,5,6)$$

is measured by integrating the areas in the range 470 to 640 nm and 360 to 470 nm for the transitions $^5D_4 \rightarrow {}^7F_J$ and $^5D_3 \rightarrow {}^7F_J$, respectively, and is shown in Figure 3. Considering the extensive formation of enstatite polymorph in Lap-Tb(50%),Na(50%) and Lap-Tb(100%) at 650 °C, as shown in Figure 1(b), the increment of the $^5D_4 \rightarrow {}^7F_J$ ($J = 3 \rightarrow 6$) emission would be larger than that observed in Figure 3.

Effect of Ce³⁺ Concentration on Tb³⁺ Luminescence. Figure 4 shows the luminescence spectra of various concentrations of Tb^{3+} and Ce^{3+} ions in Lap-Tb,Ce heated to 600 °C. As expected, the intensities of spectra in these samples decreased with decreasing Tb^{3+} ion concentration. The emission spectra of these samples exhibited predominant $^5D_4$ emission lines, as shown in Figure 4. This result suggests that a cross-relaxation occurred even in high Ce^{3+}
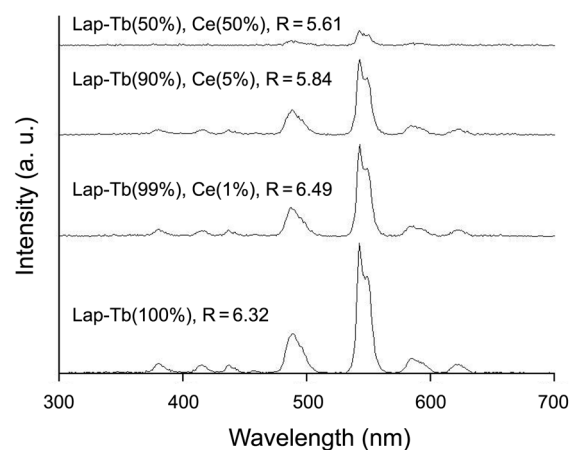

Figure 4. Room temperature luminescence spectra of samples with different concentrations of Tb^{3+} and Ce^{3+} in Lap-Tb,Ce heated to 600 °C.

concentration of these systems, which was attributed to the paired existence of the Tb^{3+} ions in the interlayer of laponite. The addition of Ce^{3+} ions promoted the formation of Tb^{3+} ion pairs rather than their dispersal. This result is consistent with the aforementioned observation of increased thermal stability of laponite upon addition of Ce^{3+} ions. Tb^{3+} has been reported to tend to form ion pairs or clusters in the one-dimensional structure of K_2YF_5, even at low Tb^{3+} concentration.[16]

Conclusion

Optically active rare-earth ions can be incorporated into layers of laponite. Our investigation into the spectroscopic behavior of Tb^{3+} ions has provided valuable information about the interaction between Tb^{3+} ions and the surrounding environment. Tb^{3+} ions in an interlayer of laponite or enstatite polymorphs mainly existed in ion pairs or clusters, as evidenced by the concentration-dependent luminescence of the Tb^{3+} ions. Addition of Ce^{3+} ions played an important role in increasing the thermal stability and affected the emission characteristics of laponite. These properties can be explained by the effect of Ce^{3+} ion addition in promoting the formation of Tb^{3+} ion pairs or clusters in preference to Tb^{3+} ion dispersal. Laponite is an excellent host material for phosphors and provides a unique interlayer environment in which optically active ions or compounds can be manipulated.

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