

PREPARATION AND CHARACTERIZATION OF Eu-MAGADIITE INTERCALATION COMPOUNDS

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Abstract—The intercalation of europium ions (Eu³⁺) into the interlayer space of a layered silicate, magadiite, was conducted by ion-exchange reactions between magadiite and europium(III) chloride. X-ray diffraction and elemental analysis results indicated that Eu³⁺ cations were intercalated into the interlayer space of magadiite. The ion exchange between Eu³⁺ and Na⁺ occurred preferentially so that the adsorbed Eu³⁺ amounts were controlled quantitatively. Thermal transformation of the original layered structure was suppressed by the intercalation of Eu³⁺. The resulting intercalation compounds exhibited photoluminescence arising from the intercalated Eu³⁺. The luminescence intensity varied in accordance with the amount of Eu³⁺ adsorbed, suggesting that the self-quenching occurred at higher loading levels. The luminescence intensity was also changed by the heat treatment, corresponding to the change in the surroundings of the Eu³⁺ adsorbed, induced by the removal of the adsorbed water molecules and the hydroxyl groups of the silicate.

Key Words—Europium, Intercalation, Luminescence, Magadiite, Nanocomposite.

INTRODUCTION

Intercalation is a method by which to synthesize hybrid materials with a wide range of chemical compositions and low dimensional nanostructures. The reaction can also be applied to the sequestration of toxic and/or noble materials from different environments. Magadiite (ideal formula Na₂Si₁₄O₂₉·nH₂O) is a layered silicate capable of incorporating guest species in the interlayer space to form intercalation compounds (Eugster, 1967; Lagaly, 1979). The cation-exchange properties of magadiite have been investigated and the nature of the cation exchange sites have been documented, though the quantitative evaluation is still controversial.

Magadiite possesses some unique properties for organizing guest species. (1) The surface silanol groups bear the cation exchange sites and the layer charge density is relatively high (~220 meq/100 g magadiite). (2) Magadiite can be conveniently prepared in a laboratory by hydrothermal synthesis as purely siliceous materials. Taking advantage of these characteristic features of magadiite, the introduction of functional species into magadiite has been reported together with fundamental studies on the intercalation reaction and the structures of intercalation compounds (Lagaly *et al.*, 1975a,b; Ruiz-Hitzky and Rojo, 1980; Ogawa *et al.*, 1998a,b; Isoda *et al.*, 2000; Kim *et al.*, 1997; Landis *et al.*, 1991; Dailey and Pinnavaia, 1992; Wang *et al.*, 1998). The organization of photoactive species on the surface of layered materials has been investigated to

construct photofunctional supramolecular systems (Ogawa and Kuroda, 1995). Along this line, the luminescence of the ruthenium tris(bipyridine) complex and the photochromism of cationic azobenzene derivatives have been reported previously (Ogawa and Maeda, 1998; Ogawa and Takizawa, 1999; Ogawa *et al.*, 2001a,b).

In this paper, we report the intercalation of Eu³⁺ ions into magadiite by ion-exchange reactions. Rare earth element-doped solids have been investigated extensively as possible advanced materials in applications such as luminescent, catalytic, sensing and possible optical recording materials (Bredol *et al.*, 1991). The immobilization of rare earth elements (*REE*) in various solid matrices including silica glasses (Zaitoun *et al.*, 2000), organosilicate gels (Nogami and Abe, 1997), zeolites (Arakawa *et al.*, 1979; Suib and Carrado, 1985; Bartlett *et al.*, 1988; Suib *et al.*, 1984), and organic polymers (Smirnov *et al.*, 1999) has been reported so far. Among possible solid matrices, crystalline inorganic solids are attractive due to the stability and well-defined microstructures. Accordingly, the introduction of *REE* into low-dimensional inorganic solids have been investigated in order to control the electronic properties of conducting oxides as well as to optimize optical properties of the doped solids (Kudo and Sakata, 1995; Honma *et al.*, 1998; Kudo, 1997).

The luminescence of rare earth ions doped in crystalline inorganic solids has been reported (Bredol *et al.*, 1991). The concentration quenching of the luminescence caused by the excitation energy migration has already been observed in the systems of rare earth

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Table 1. Chemical composition of Eu^{3+} -magadiites.

Concentration of EuCl_3 solution mmol/L	Adsorbed Eu^{3+} /Added Eu^{3+} (%)	$\text{Eu}^{3+}/14\text{Si}$	Adsorbed $\text{Eu}^{3+}/\text{CEC}$ (%)
0.77	83	0.14	21
1.2	90	0.24	36
1.5	98	0.33	49
2.3	97	0.48	73
30		0.65	98
$30 \times 3^*$		0.68	100

* Ion exchange was repeated three times

ions-doped solids (Honma, *et al.*, 1998). It is vital for optimum performance to control the separation of adjacent rare earth ions. Although one can expect a wide range of chemical compositions and microstructures, studies on the introduction of *REE* into inorganic solids via soft chemical approach are limited (Bergaya and Van Damme, 1983; Constantino *et al.*, 1998). The ion exchange of rare earth ions into ion exchangeable crystalline inorganic solids is worth investigating from the viewpoints of spatial control of the rare earth ions as well as the recovery of rare elements from different environments (Miller *et al.*, 1982).

EXPERIMENTAL SECTION

Materials

Na-magadiite was synthesized hydrothermally from colloidal silica and NaOH, as described previously

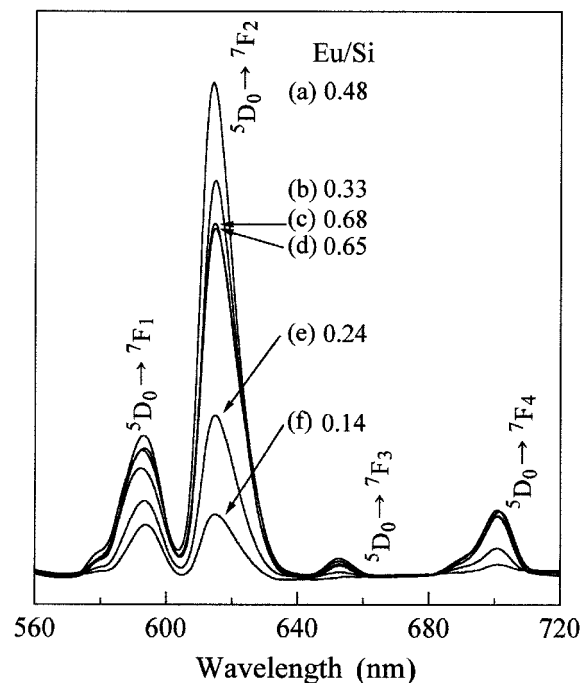


Figure 2. Luminescence spectra of Eu^{3+} -magadiites. Eu/Si = 0.48 (a), 0.33 (b), 0.68 (c), 0.65 (d), 0.24 (e) and 0.14 (f).

(Okutomo *et al.*, 1999). Europium(III) chloride was purchased from Tokyo Kasei Industries Co. and used without further purification.

Sample preparation

Intercalation of Eu^{3+} into magadiite was carried out by conventional ion-exchange reactions in which an

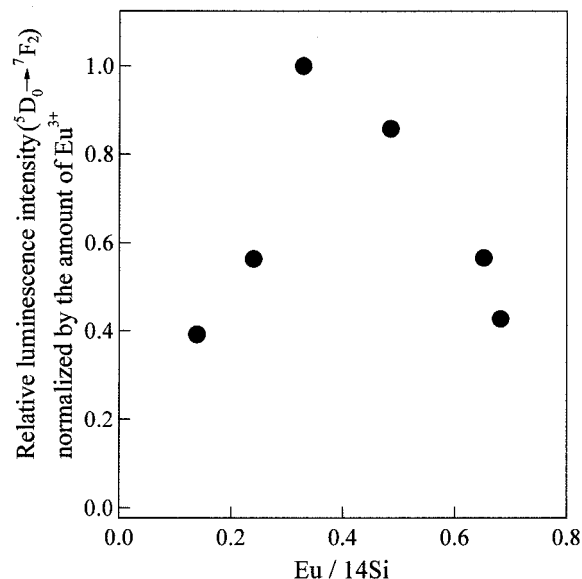


Figure 3. The relationship between the intensity of ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ luminescence band (at 614 nm) and the amount of Eu^{3+} adsorbed.

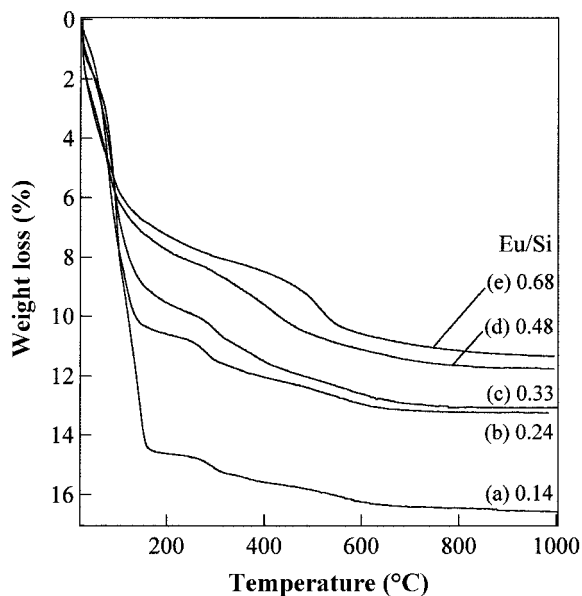


Figure 4. TG curves of Eu^{3+} -magadiites. $\text{Eu}/\text{Si} = 0.14$ (a), 0.24 (b), 0.33 (c), 0.48 (d) and 0.68 (e).

aqueous suspension of magadiite was mixed with an aqueous solution of europium(III) chloride ($\text{pH} \approx 5$) and the mixture was allowed to react for 1 day at room temperature. After centrifugation, the resulting solid was washed with ethanol and dried at 40°C for 2 days. The products were heat treated in air at $400\text{--}1500^\circ\text{C}$.

Characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Mac Science, MXP³ diffractometer using

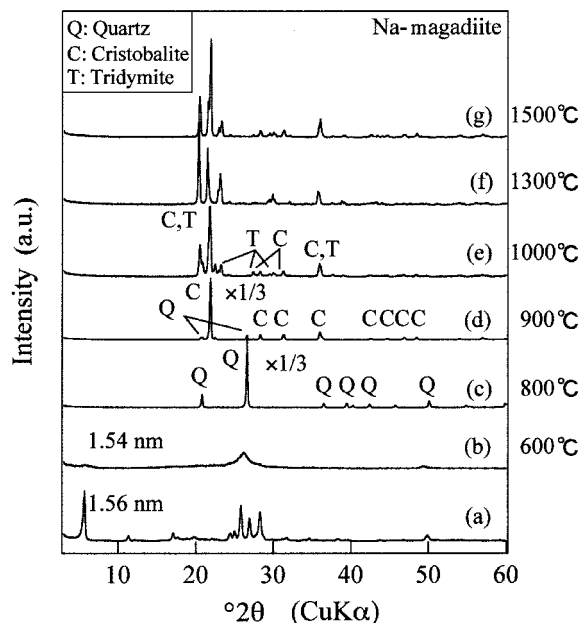


Figure 6. Powder XRD patterns of Na-magadiite before (a) and after the heat treatment at 600 (b), 800 (c), 900 (d), 1000 (e), 1300 (f) and 1500°C (g).

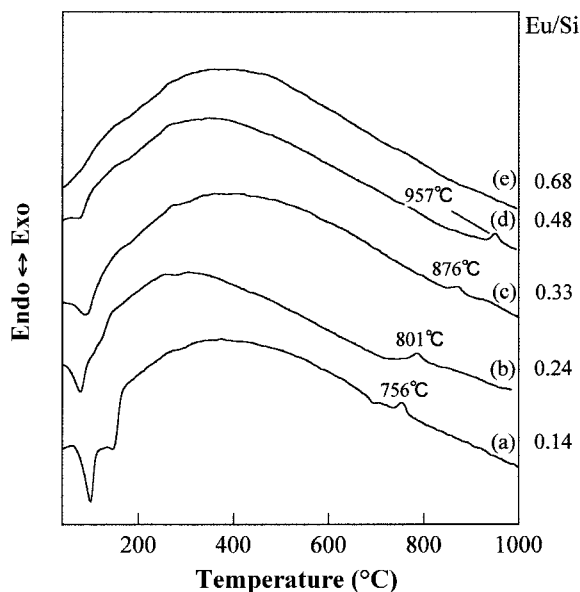


Figure 5. DTA curves of Eu^{3+} -magadiites. $\text{Eu}/\text{Si} = 0.14$ (a), 0.24 (b), 0.33 (c), 0.48 (d) and 0.68 (e).

monochromatic $\text{CuK}\alpha$ radiation. Steady-state luminescence spectra were recorded on a Hitachi F-4500 fluorospectrophotometer with the excitation wavelength of 394 nm. The chemical composition was determined by inductively coupled plasma (ICP) analysis (Seiko SPS7000A) after the samples were dissolved with HF , HNO_3 and H_2SO_4 . Scanning electron micrographs (SEM) were obtained using an HITACHI S-2500CX scanning electron microscope. Thermogravimetry-differential thermal analysis (TG-DTA) curves were recorded

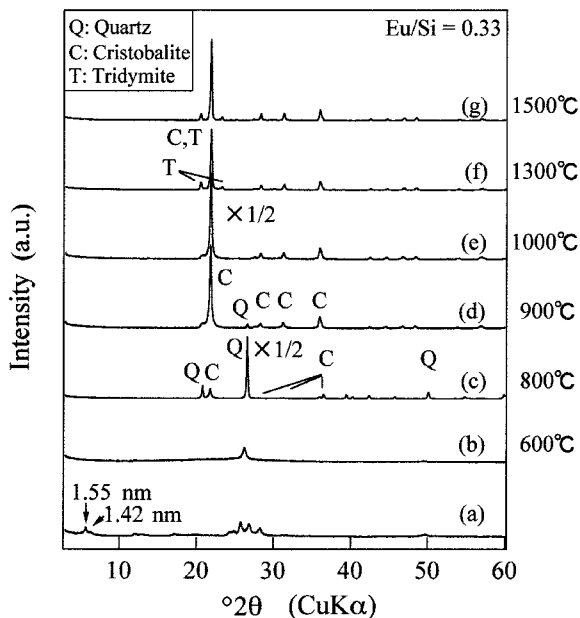


Figure 7. Powder XRD patterns of Eu^{3+} -magadiite ($\text{Eu}/\text{Si} = 0.33$) before (a) and after the heat treatment at 600 (b), 800 (c), 900 (d), 1000 (e), 1300 (f) and 1500°C (g).

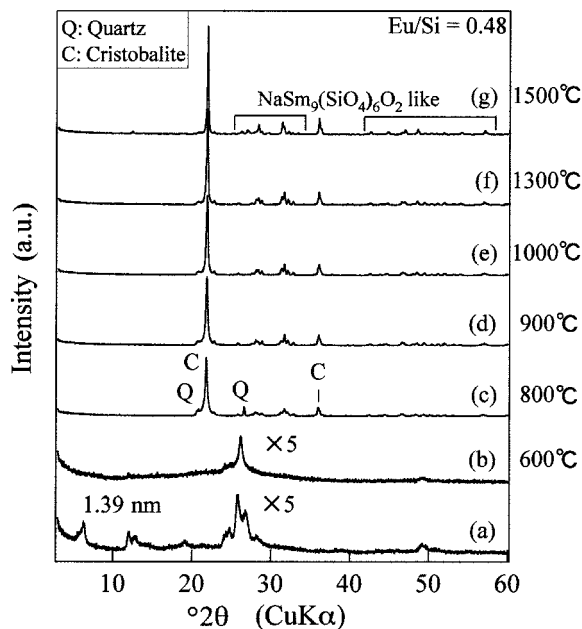


Figure 8. Powder XRD patterns of Eu^{3+} -magadiite ($\text{Eu}/\text{Si} = 0.48$) before (a) and after the heat treatment at 600 (b), 800 (c), 900 (d), 1000 (e), 1300 (f) and 1500°C (g).

on a Mac Science TG-DTA 2000S instrument at a heating rate of $10^\circ\text{C min}^{-1}$ under a dry air atmosphere using α -alumina ($\alpha\text{-Al}_2\text{O}_3$) as the standard material. Transmission electron micrographs (TEM) were obtained on an HITACHI H8100 transmission electron microscope with accelerating voltage 200 kV.

RESULTS AND DISCUSSION

The chemical compositions of the products are summarized in Table 1. The loaded Eu^{3+} cations were almost quantitatively adsorbed on magadiite. Hereafter, the products were denoted as Eu^{3+} -magadiite (n), where n indicates the molar ratio of Eu^{3+} to the $\text{Si}_{14}\text{O}_{29}$ unit of magadiite. The XRD patterns of the products are shown in Figure 1, together with that of original Na-magadiite. The basal spacing decreased from 1.56 nm to 1.42 nm after reaction with europium(III) chloride, suggesting the change in the hydration of the interlayer space from the highly hydrophilic Na-form to Eu-form. When the amount of Eu^{3+} loaded was small, two diffraction peaks were observed; one corresponds to the hydrated Na-magadiite (1.56 nm) and the other is ascribable to the Eu^{3+} -exchanged phase (~ 1.4 nm). Since the thickness of the silicate layer is 1.12 nm, as estimated from the basal spacing of the dehydrated H-magadiite (Rojo *et al.*, 1988), the gallery height of the Eu^{3+} -magadiites was estimated, from the observed basal spacing, to be 0.3 nm. The value is large enough to accommodate hydrated Eu^{3+} ions.

The luminescence spectra of the Eu^{3+} -magadiites (0.65) are shown in Figure 2. In the spectra, the

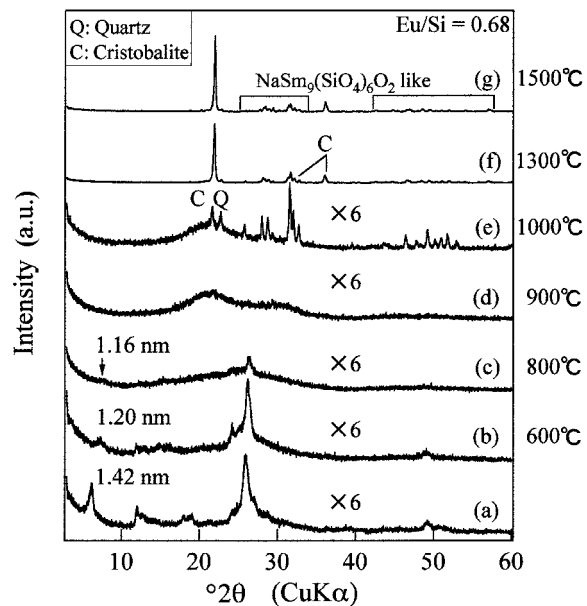


Figure 9. Powder XRD patterns of Eu^{3+} -magadiite ($\text{Eu}/\text{Si} = 0.68$) before (a) and after the heat treatment at 600 (b), 800 (c), 900 (d), 1000 (e), 1300 (f) and 1500°C (g).

luminescence bands ascribable to the ${}^5\text{D}_0\text{-}{}^7\text{F}_1$, ${}^5\text{D}_0\text{-}{}^7\text{F}_2$, ${}^5\text{D}_0\text{-}{}^7\text{F}_3$ and ${}^5\text{D}_0\text{-}{}^7\text{F}_4$ transitions of Eu^{3+} were observed at 592, 614, 655 and 702 nm, respectively. The relative luminescence intensity depends on the strength and symmetry of the electric field around the Eu^{3+} ions. The relative intensity ratio of each transition changed only slightly depending on the amounts Eu^{3+} adsorbed in the present system, showing that the Eu^{3+} ions adsorbed in a similar manner. The small difference in the relative luminescence intensity was thought to be caused by such parameters as water content and Eu^{3+} - Eu^{3+} interactions.

Figure 3 shows the relationship between the intensity of the ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ luminescence band (at 614 nm) and the amount of Eu^{3+} adsorbed. The intensity was normalized by the amount of Eu^{3+} , as in the equation $I_n = I_m/m$; where I_n , I_m and m denote normalized luminescence intensity, observed luminescence intensity, and the amount of Eu^{3+} adsorbed, respectively. With the increase in the amount of Eu^{3+} , the luminescence was intensified and the maximum intensity was recorded for the Eu^{3+} -magadiite (0.33). Further increase in the amount of Eu^{3+} resulted in a weakening of the luminescence. This observation is explained by the concentration quenching at the higher Eu^{3+} loadings. Similar phenomena have been observed for the other Eu^{3+} -doped low dimensional oxide systems (Kudo and Sakata, 1995; Honma *et al.*, 1998; Kudo, 1997).

Water molecules and hydroxyl groups deactivate the excited states of Eu^{3+} to cause quenching of the luminescence. In the present system, Eu^{3+} cations are located in the interlayer space where adsorbed water molecules and hydroxyl groups (silanol groups) are present. In order to observe the effect of the interlayer

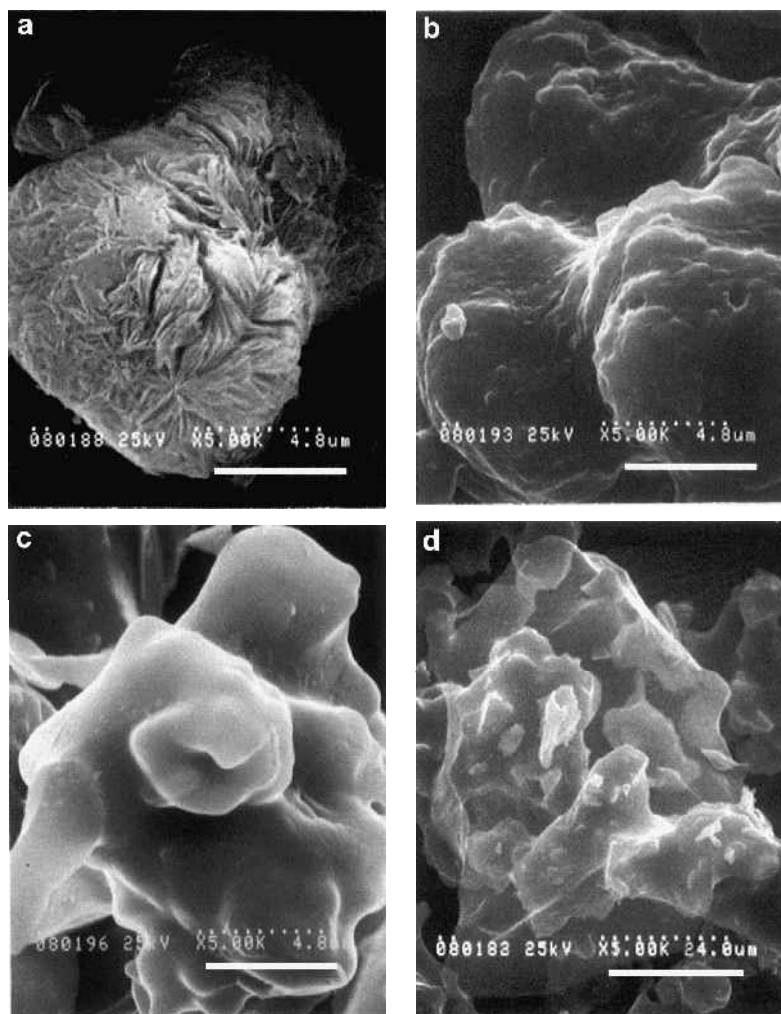


Figure 10. SEM images of Na-magadiite before (a) and after the heat treatment at 900 (b), 1200 (c) and 1500°C (d). Scale bars in a, b and c = 5 μm ; in d, scale bar = 25 μm .

microenvironments on the luminescence characteristics, the products were heated in air. The TG and DTA curves of the products are shown in Figures 4 and 5, respectively. The desorption of adsorbed water occurred below 200°C and the dehydroxylation of silanol groups occurred at higher temperatures (250–800°C) as shown in the TG curves. As reported previously by Muraishi (1999), the phase transformation of Na-magadiite into quartz, cristobalite and tridymite occurred above 700°C. The thermal behavior of the products changed after the introduction of Eu^{3+} . With the increase in the Eu^{3+} content, the exothermic peaks ascribable to the phase transition (in the temperature range 750–950°C) appeared at higher temperatures (Figure 5).

The variation in the XRD patterns, after heat treatment, is shown in Figures 6–9 for Na-magadiite and Eu^{3+} -magadiites. The phase transition temperature increased with the increase in the Eu^{3+} content as shown in Figure 6. For the Eu^{3+} -magadiite (0.68), the diffraction peaks ascribable to the layered structure remained at

900°C, while Na-magadiite and Eu^{3+} -magadiites with lower Eu^{3+} contents transformed into cristobalite and tridymite at lower temperatures.

Scanning electron micrographs of magadiite and Eu^{3+} -magadiite (0.68) are shown in Figures 10a and 11a, respectively. The rosette morphology composed of platelet particles of original magadiite was retained during the ion exchange with Eu^{3+} . After the heat treatments, the morphology changed, as shown in Figures 11b–d and 12b–d. The original morphology of magadiite was lost below 900°C for magadiite while the morphology of Eu^{3+} -magadiite (0.68) remained up to 1200°C. These observations were consistent with the XRD results, confirming that the transformation of the silicate layers was suppressed by the presence of Eu^{3+} ions in the interlayer space.

When Eu^{3+} -magadiite (0.68) was heated above 900°C, new diffraction peaks appeared in addition to those ascribable to cristobalite. These diffraction peaks appeared at positions close to those of $\text{NaSm}_9(\text{SiO}_4)_6\text{O}_2$

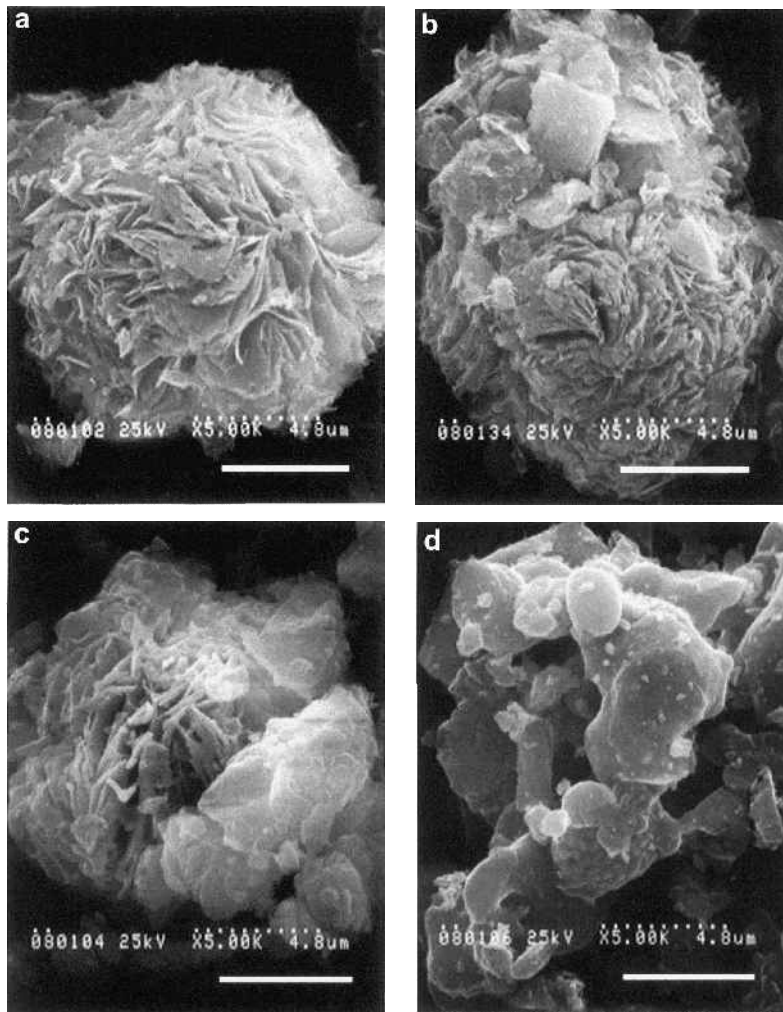


Figure 11. SEM images of Eu^{3+} -magadiite (0.65) before (a) and after the heat treatment at 900 (b), 1200 (c) and 1500°C (d). All scale bars = 5 μm .

(JCPDS 32-1147). Similar diffraction peaks appeared after the heat treatment above 1200°C for the Eu^{3+} -magadiites with lower Eu^{3+} content, and the diffraction intensity was in accordance with the Eu^{3+} content. Consequently, the diffraction peaks were thought to be due to a crystalline phase ($\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$) of the structure similar to $\text{NaSm}_9(\text{SiO}_4)_6\text{O}_2$.

The luminescence intensity of the heated products is summarized in Figure 12. The luminescence was intensified up to 500°C irrespective of the Eu^{3+} contents, showing that the removal of the adsorbed water and hydroxyl groups located close to the interlayer Eu^{3+} ions. Heat treatment at higher temperatures (>700°C) results in weakened luminescence. This observation might account for the aggregation of Eu^{3+} . During the transformation of the silicate layers, Eu^{3+} ions are separated to form a Eu^{3+} -rich phase while the silica layers form a purely siliceous crystalline phase such as quartz and cristobalite as shown in Figures 6–9. As a

result of the phase separation, concentration quenching occurred leading to a weakening of the luminescence intensity.

CONCLUSIONS

The intercalation of Eu^{3+} ions into the interlayer space of magadiite has been conducted by ion-exchange reactions in aqueous media. The luminescence of the adsorbed Eu^{3+} ions was observed for the intercalation compounds. The luminescence intensity varied depending on the loaded Eu amounts as well as the heat treatment, indicating the concentration quenching and the quenching by the adsorbed water and hydroxyl groups in the system. Thus, the present Eu-magadiite intercalation compounds can be regarded as novel types of Eu-doped silicas. The layered structure of magadiite was stabilized by the introduction of Eu ions in the interlayer space.

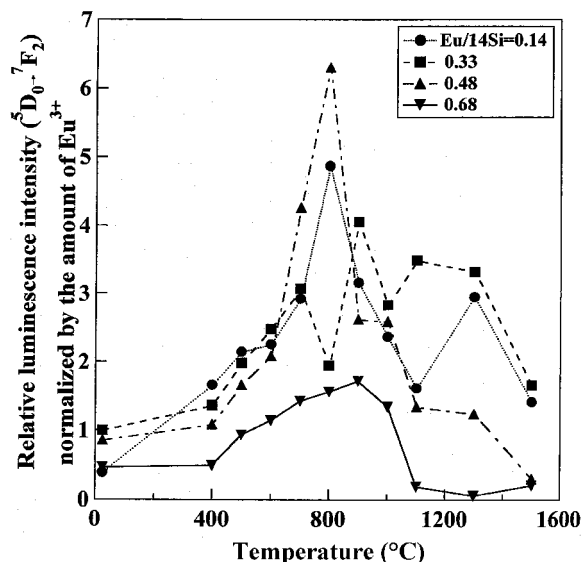


Figure 12. Variation of normalized luminescence intensity of Eu^{3+} -magadiites as a function of the heat treatment temperature.

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