I O U R N A L O F

Ceramic Processing Research

Eu²⁺-luminescence in alkali metal magnesium monophosphates

Hyo Jin Seo*

Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea

Eu²⁺-luminescence was investigated in alkali metal magnesium monophosphates AMgPO₄ (A = Li, Na, and K). The samples were synthesized by solid-state reaction and emission and excitation spectra were measured at 18 K and room temperature. Unusual line emission due to the intraconfigurational $4f^7(^6P_{7/2}) \rightarrow 4f^7(^8S_{7/2})$ transition (f-f transition) and the anomalous broadband emission at low energy side are observed together with the normal band emission due to the $4f^65d^1 \rightarrow 4f^7(^8S_{7/2})$ transition (d-f transition). The anomalous band emission is attributed to the recombination of Eu²⁺-trapped exciton (Eu-TE). In the sequence of increasing ionic radius Li, Na, and K in AMgPO₄ the relative intensity of the f-f line is reduced and the d-f band shifts to red. The changes in spectral features are explained by the crystal-field strength acting on Eu²⁺ ion and substitutional sites for Eu²⁺ in AMgPO₄ (A = Li, Na, and K). The thermal activation between the lowest excited $4f^65d$ state and the Eu-TE state is responsible for the quenching of the d-f emission or the Eu-TE emission at room temperature.

Key words: 4f-4f transition, 5d-4f transition, Eu²⁺, Impurity trapped exciton, Crystal field strength.

Introduction

The excited Eu²⁺ ions produce usually the broad band emission due to the parity allowed $5f^6d^1 \rightarrow 4f^7$ transition (d-f transition) in a host lattice. The spectral feature of the d-f band depends on the crystalline environment around the Eu²⁺ ion in which the crystalfield strength experienced by the Eu²⁺ ion is one of the most important factors. The emission band varies from ultraviolet to red which is mostly determined by location of the lowest 4f⁶5d¹ level and the degree of coupling of Eu²⁺ with lattice vibrations. However, anomalous band broadening and bandshift of Eu²⁺ are often observed in a variety of host lattices [1-4]. It was suggested that the Eu²⁺-trapped exciton (Eu-TE) can be formed in a Eu-doped lattice and the recombination of Eu-TE causes the Eu²⁺-emission anomalously broadened and red-shifted [3-4]. When the lowest $4f^{6}5d^{1}$ level is located in or near the conduction band the Eu²⁺ ions can be trapped a hole from the valence band and an electron from the conduction band forming Eu-TE. However, it is sometimes hard to understand the origin of Eu²⁺-emission because so many factors can be involved in the relaxation processes.

In addition to the normal d-f emission and anomalous Eu-TE emission, the narrow line emission of Eu^{2+} is observed due to the $4f^{7}(^{6}P_{7/2}) \rightarrow 4f^{7}(^{8}S_{7/2})$ transition (f-f transition) in some host lattices. The energy of the $4f^{7}$ levels of Eu^{2+} are nearly independent on the crystal-

field strength experienced by the Eu²⁺ ion in host lattices compared to the 4f⁶5d states. The location of the lowest $4f^{6}5d$ state relative to the $4f^{7}({}^{6}P_{7/2})$ level is determined by splitting of the 4f⁶5d configuration into the $4f^{6}5d(t_{2g})$ state and the $4f^{6}5d(e_{g})$ state due to the crystal-field. The f-f line is observed at around 359 nm in the emission spectrum at low temperature for the case that the lowest 4f⁶5d state is located higher than the $4f^{7}(^{6}P_{7/2})$ level. Usually the crystalfield at the site for Eu^{2+} is stronger in oxides than that in fluorides and chlorides. The strong crystal-field pushes the lowest $4f^{6}5d$ state below the $4f^{7}(^{6}P_{7/2})$ level of Eu^{2+} in most oxides. Thus the f-f line is rarely observed in most oxides even at low temperature differently from that in fluorides and chlorides [4]. The f-f line emissions have been reported in many types of fluorides [4, 5], in some sulfates and in a few exceptional oxides [4]. Recently luminescence spectra of Eu^{2+} have been reported in many phosphates [6, 7] and monophosphates ABPO₄ (A = alkali metal, B = alkaline earth), for example, $ABPO_4:Eu^{2+}$ (A = K, Na, B = Ba, Sr) [8, 9]. However, no f-f line has been observed in the monophosphates except for LiMgPO₄ [10] and NaMgPO₄ [11].

In this paper, the normal d-f emission, anomalous Eu-TE emission, and the f-f line emission of Eu^{2+} are investigated in alkali metal magnesium monophosphates, AMgPO₄ (A = Li, Na and K) and the systematic analysis is performed for the relative intensity of the f-f line, redshift of the d-f band, quenching of the band emission in these three monophosphates. It is shown that the spectral changes are associated with the substitutional sites and crystal-field strength in AMgPO₄ Eu²⁺ (A = Li, Na and K).

^{*}Corresponding author:

Tel : +82-51-629-5568

Fax: +82-51-629-5549

E-mail: hjseo@pknu.ac.kr



Fig. 1. Excitation spectra of AMgPO₄: Eu^{2+} (A = Li, Na, and K) at room temperature. The monitoring wavelength was 390 nm. The dotted arrow means that the band shifts to high energy side in the sequence LiMgPO₄: Eu^{2+} , NaMgPO₄: Eu^{2+} , KMgPO₄: Eu^{2+} .

Results

The preparation of AMgPO₄:Eu²⁺ (A = Li, Na, and K) were carried out by solid state reaction. The syntheses of the samples and spectroscopic measurements are described in detail in Refs. [10-12]. Fig. 1 shows excitation spectra of Eu²⁺ in AMgPO₄ (A = Li, Na, and K) at room temperature. The two main bands due to the transitions from $4f^7(^8S_{7/2})$ to the excited e_g and t_{2g} states of the $4f^65d^1$ configuration are observed in the wavelength region 220-420 nm. The main bands seem to consist of some more bands due to the additional splitting of the e_g and t_{2g} states into two and three states, respectively, which occurs in a lower crystal-field symmetry than cubic. We note that the band maximum at lower energy side shifts to shorter wavelength in the sequence Li, Na, and K as shown in Fig. 1.

The emission spectra of the Eu²⁺ ions in AMgPO₄ (A = Li, Na and K) at 18 K and room temperature are shown in Figs. 2(a), (b), and (c), respectively. The spectra at 15 K are composed of two main bands for all three samples in the wavelength regions 350-420 and 420-600 nm. It is interesting to note that the bands at low energy side are much broader than those at high energy side. The band emission at high energy side is due to the $4f^{6}5d$ (e_g) $\rightarrow 4f^{7}$ (⁸S_{7/2}) transition (the d-f transition), while the band at low energy side with broad bandwidth is attributed to the recombination of Eu²⁺-trapped exciton (Eu-TE) which will be discussed below. The d-f band shifts to low energy in the sequence Li, Na, K in $AMgPO_4$ (A = Li, Na, and K) with a band maximum at 383, 390, and 405 nm, respectively. The f-f line is observed at 359 nm for LiMgPO₄ (Fig. 2(a)) and NaMgPO₄ (Fig. 2(b)) at 18 K. One observes the strong f-f line for LiMgPO₄ (Fig. 2(a)), while the line is so weak for NaMgPO₄ (Fig. 2(b)) and disappears in KMgPO₄ (Fig. 2(c)) even at 18 K. Three more sharp lines at 369, 379, and 393 nm in



Fig. 2. Emission spectra of AMgPO₄: Eu^{2+} (A = Li, Na, and K) at 18 K and room temperature. The excitation wavelength was 355 nm. The band maxima are normalized to 1. The spectra at room temperature and 18 K are indicated by solid lines and dotted lines, respectively.

the emission spectrum of LiMgPO₄: Eu^{2+} (Fig. 2(a)) are associated with the modes related to the one-phonon repetition of the zero-phonon line of the f-f line at 359 nm [5]. The peak intensity of the f-f line has a tendency to decrease in the sequence Li, Na, K. This is the same tendencies of the d-f band to shift to red and of the f-d excitation band to shift to blue in going from Li, Na to K.

As the temperature rises to room temperature the spectral features of Eu^{2+} -emission are significantly modified for all three samples. The total emission of Eu^{2+} is reduced in intensity with increasing temperature as is a general phenomenon of thermal quenching of

luminescence. The f-f line is quenched for all three samples at room temperature. The d-f band is significantly reduced in intensity and therefore the Eu-TE band dominates the emission spectrum in LiMgPO₄ (Fig. 2(a)) and KMgPO₄ (Fig. 2(c)) at room temperature. But for NaMgPO₄ (Fig. 2(b)), the spectrum shows the strong d-f band with maximum at 390 nm and a new band at 440 nm. The Eu-TE band of NaMgPO₄:Eu²⁺ is quenched at room temperature dissimilarly to those of AMgPO₄:Eu²⁺ (A = Li, K).

Discussion

The alkali metal magnesium monophosphates, $AMgPO_4$ (A = Li, Na, and K), are a family with slightly different types of structure depending on the relative size of Li, Na, and K [13-16]. We note that Mg^{2+} is the smallest ion in size among the divalent alkaline earth ions and it forms the MgO₆ octahedron in AMgPO₄ (A = Li, Na, and K). The MgO₆ octahedron is surrounded by the PO₄ tetrahedra in which the structure of Mg- $(PO_4)_n$ depends strongly the size of alkali metal ion A⁺. For example, the MgO₆ octahedron in KMgPO₄ is considerably distorted because of large ionic radius of the K^+ ion. The monovalent ion in AMgPO₄ (A = Li, Na, and K) has coordination number of 6, 8, and 10, respectively, in the sequence of increasing ionic radius. The larger ionic radius of the A⁺ ion could lead to shrink and distort the MgO₆ octahedron and the Mg- $(PO_4)_n$ frame in AMgPO₄.

There are two possible cations (A⁺ and Mg²⁺) for the substitutional Eu^{2+} ions in AMgPO₄ (A = Li, Na, and K) lattices. Considering the ionic radii of Eu^{2+} (1.31, 1.39, and 1.49 Å for CN = 6, 8, and 10, respectively) and Li^+ (0.90 Å, CN = 6), Na^+ (1.32 Å, CN = 8), and K^+ (1.73 Å, CN = 10) ions, the Eu^{2+} ion substitutes for the monovalent sites in $AMgPO_4$ (A = Li, Na, and K). However, the incorporation of Eu^{2+} at the A⁺ site requires charge-compensating defects in the host lattices. The substitution of Eu²⁺ at the Mg²⁺ sites can form the chemically stable AMgPO₄ lattices without charge compensation although the Mg^{2+} ion (0.86 Å, CN = 6) is smaller than the Eu²⁺ ion. If the Eu²⁺ ions occupy the monovalent sites in $AMgPO_4$ (A = Li, Na, and K), it is expected that the Eu²⁺ ion experiences stronger crystal-field strength in the sequence at Li, Na, K because the Eu^{2+} ions are surrounded by oxygen ions with the coordination number 6, 8, 10, respectively. However, the changes in spectral features indicate that the crystal-field strength on Eu²⁺ is stronger in the reversed sequence LiMgPO₄, NaMgPO₄, KMgPO₄. This means that the Eu²⁺ ions occupy the Mg²⁺ sites in $AMgPO_4$ (A = Li, Na, and K). This is because the MgO₆ octahedron is remarkably distorted in the reversed sequence Li, Na, K with increasing ionic radius giving rise to the stronger crystal-field strength. However, the substitution of Eu²⁺ should not be totally negligible for



Fig. 3. Configuration coordinate diagram of Eu^{2+} in AMgPO₄ (A = Li, Na, and K). The parabola at bottom is the ground $4f^7(^8S_{7/2})$ state. The excited states of $4f^7(^6P_{7/2})$ and $4f^65d(e_g)$ and Eu^{2+} -trapped exciton (Eu-TE) state are indicated. a, b, and c are the excited $4f^65d$ states in AMgPO₄ (A = Li, Na, and K), respectively. The $4f^7(^6P_{7/2}) - 4f^7(^8S_{7/2})$ transition (1), the $4f^65d(e_g) - 4f^7(^8S_{7/2})$ transition (2), and the recombination of Eu^{2+} -trapped exciton (3).

the A^+ sites in AMgPO₄. The unusual Eu²⁺-emission band at 440 nm (Fig. 2(b)) can be attributed to the Eu²⁺ ions at the Na⁺ sites in NaMgPO₄ which will be discussed elsewhere.

The anomalous luminescence in relation to impuritytrapped exciton (ITE) of Eu^{2+} and Yb^{2+} was reported in a number of oxide and fluorides [4]. The red-shifted broad-emission bands (Figs. 2(a), (b), and (c)) in AMgPO₄: Eu^{2+} (A = Li, Na, and K) are attributed to the Eu^{2+} -trapped excitons (Eu-TEs). The lowest excited 4f⁶5d state of Eu^{2+} could be situated near the conduction band edge of AMgPO₄ (A = Li, Na, and K) and the excited 5d electron is trapped close to the Eu ion and the nearest-neighbor Mg²⁺ and A⁺ ions forming the Eu-TE state. The recombination of Eu-TE gives rise to the Eu^{2+} -emission which is broader and red-shifted compared to the normal d-f emission.

The spectral features and temperature dependence of the three different types of Eu²⁺-emissions observed in Eu²⁺-doped AMgPO₄ (A = Li, Na, and K) lattices are explained by the configuration coordinate model as shown in Fig. 3. In the configuration coordinate diagram the lowest parabola is the ground $4f^7(^8S_{7/2})$ state. The excited $4f^65d^1$ state of Eu²⁺ is shifted to the right by δ . The parabola of the Eu-TE state shifts to the right by Δ which is larger than δ because the electron (e + Eu³⁺) is weakly bound to the conduction band and strongly influenced by environment than those of the $4f^65d^1$ state to lower energy from a, b to c corresponding to LiMgPO₄, NaMgPO₄, KMgPO₄, respectively. The excited Eu²⁺ ion is relaxed to the

bottom of the $4f^7$ (${}^6P_{7/2}$) state followed by the f-f emission indicated by (1) in Fig. 3. The parabola of the $4f^65d^1(e_g)$ state moves down to c from a with increasing crystal-field strength. This is the reason why one observes the intense f-f line for LiMgPO₄:Eu²⁺ (Fig. 2(a)), the line becomes weaker for NaMgPO₄:Eu²⁺ (Fig. 2(b)), and no f-f transition occurs for the parabola c. The thermal activation of the Eu-TE state via the crossing point x is responsible for the quenching of the d-f emission at room temperature. It seems that the different behavior of the d-f and Eu-TE emissions in NaMgPO₄:Eu²⁺ (Fig. 2(b)) is ascribed to the complicated energy level structure of Eu²⁺, e.g. the $4f^65d^1$ state of Eu²⁺ at the Na site with different Eu-TE state.

Conclusions

The emission and excitation spectra of Eu²⁺ are investigated in Eu²⁺-doped AMgPO₄ (Li, Na, and K) phosphors. The line emission due to the $4f^{7}(^{6}P_{7/2})$ $\rightarrow 4f^{7}(^{8}S_{7/2})$ transition is strong in LiMgPO₄:Eu²⁺ and is weak in NaMgPO₄:Eu²⁺ at 18 K. For KMgPO₄:Eu²⁺ the f-f line was not detected even at 18 K. The emission band of the d-f transition shifts to red in the sequence Li, Na, K. The results mean that the crystalfield strength is stronger in the sequence Li, Na, K indicating that the excited 4f65d state is located at lower energy in the same sequence. The anomalous band emissions due to the recombination of Eu-trapped exciton (Eu-TE) are observed in all three AMgPO₄ (Li, Na, and K) phosphors. The d-f emissions in LiMgPO₄:Eu²⁴ and KMgPO₄:Eu²⁺ are quenched at room temperature, while that in NaMgPO₄: Eu^{2+} phosphor is rather stronger than the Eu-TE band. This is attributed to the relative positions of the excited 4f65d state and the EuTE state giving rise to thermal activation between the d-f state and the Eu-TE state.

Acknowledgement

This work was supported by the Pukyong National University Research fund (PK-2012-47).

References

- 1. D.S. McClue, and C. Pedrini, Phys. Rev. B. 32 (2007) 8465-8468.
- D.B. Gatch, D.M. Boye, Y.R. Shen, M. Grinberg, Y.M. Yen, and R.S. Meltzer, Phys. Rev. B 74 (2006) 195117.
- 3. P. Dorenbos, J. Phys.: Condens. Matter 15 (2003) 2645-2665.
- 4. P. Dorenbos, J. Lumin. 104 (2003) 239-260.
- S. Mahlik, M. Grinberg, L. Shi, and H.J. Seo, J. Phys.: Condens. Matter 21 (2009) 235603.
- N. Xie, Y. Huang, and H.J. Seo, J. Ceram. Process. Res. 11 (2010) 358-361.
- 7. H.J. Seo, J. Ceram. Process. Res. 11 (2011) s36-s38.
- S. Zhang, Y. Nakai, T. Tsuboi, Y. Huang, and H.J. Seo, Inorg. Chem. 50 (2010) 2897-2904.
- S. Zhang, Y. Nakai, T. Tsuboi, Y. Huang, and H.J. Seo, J. Am. Ceram. Soc. 94 (2011) 2987-2992.
- S. Zhang, Y. Huang, L. Shi, and H.J. Seo, J. Phys.: Condens. Matter 22 (2010) 235402-1-6.
- 11. Y. Huang, S. Zhang, S.I. Kim, Y.M. Yu, and H.J. Seo, J. Electrochem. Soc. 159 (2012) J23-J28.
- S. Zhang, Y. Huang, and H.J. Seo, Opt. Mater. 32 (2010) 1545-1548.
- M.B. Amara, M. Blasse, G.L. Flem, and P. Hagenmuller, Acta Crystallogr. C 39 (1983) 1483-1485.
- 14. F. Hanic, M. Handlovic, K. Burdova, and J. Majling, J. Crystallogr. Spectrosc. Res. 12 (1982) 99-127.
- 15. J. Alkemper, and H. Fuess, Z. Kristall. 213 (1998) 282-287.
- G. Wallez, C. Colbeau-Justin, T. Le Mercier, M. Quarton, and F. Robert, J. Solid State Chem. 136 (1998) 175-180.