

## Synthesis of broadband emission phosphor $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$ for white light emitting diodes

M. Maeda<sup>a</sup>, K. Uematsu<sup>b</sup>, S. Kamei<sup>c</sup>, T. Ishigaki<sup>c</sup>, K. Toda<sup>a,c,\*</sup> and M. Sato<sup>b,c</sup>

<sup>a</sup>Graduate School of Science and Technology, Niigata University, Japan

<sup>b</sup>Department of Chemistry and Chemical Engineering, Niigata University, Japan

<sup>c</sup>Center for Transdisciplinary Research, Niigata University, Japan

We report the increased emission intensity of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  by partially substituting the  $\text{V}^{5+}$  ion for the  $\text{P}^{5+}$  ion. The emission intensity of  $\text{Ca}_2\text{KMg}_2(\text{V}_{0.95}\text{P}_{0.05})_3\text{O}_{12}$  was approximately 1.3 times greater than that of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$ . The obtained phosphors were excited and emitted at 360 nm and 520 nm, respectively, and the emission obtained as a greenish white emission. The color coordinates of  $\text{Ca}_2\text{KMg}_2(\text{V}_{0.95}\text{P}_{0.05})_3\text{O}_{12}$  were  $x = 0.377$  and  $y = 0.463$ .

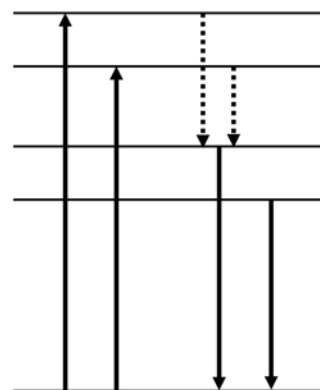
**Key words:** Host-sensitized luminescence,  $\text{VO}_4^{3-}$  tetrahedron, Vanadate, Phosphor.

### Introduction

Recently, the white LED (WLED) has been used as a new light source for replacing incandescent and fluorescent lamps. WLEDs consist of blue LED chips and yellow phosphor ( $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ) [1, 2] or ultraviolet LED (UVLED) chips and red-green-blue phosphors [3, 4]. These phosphors use rare earth elements as host materials and luminescent centers. For example,  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ ,  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ , and  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  phosphors show red, green, and blue emissions under near-UV light excitation, respectively [5 - 7]. However, rare earth elements are very expensive compared with alkaline metal and alkaline earth metal elements, because rare earth elements supply was limited all over the world. Therefore, it is necessary to develop new phosphors without rare earth elements.

The  $\text{VO}_4^{3-}$  tetrahedron is well known as the luminescent center of a host-sensitized luminescence phosphor. Host-sensitized luminescence is attributable to the charge transfer (CT) transition, which is due to the electron transition between the central metal ion ( $\text{V}^{5+}$ ) of the coordination polyhedron and the ligand ( $\text{O}^{2-}$ ). The emission mechanism of the  $\text{VO}_4^{3-}$  group is shown in Figure 1 [8]. The molecular orbital of the  $\text{V}^{5+}$  ion, which has  $T_d$  symmetry, is expressed as ground state  $^1\text{A}_1$  and as excited state levels  $^1\text{T}_1$ ,  $^1\text{T}_2$ ,  $^3\text{T}_1$ , and  $^3\text{T}_2$ . The absorption bands for  $\text{Ex}_1$  and  $\text{Ex}_2$  correspond to partly allowed spin-forbidden transitions from the ground state  $^1\text{A}_1$  to the excited state levels of  $^1\text{T}_2$  and  $^1\text{T}_1$ , respectively.

In general, the vanadate phosphors exhibit low emission efficiency [8]. The energy transfer tends to favor nonradiative transition process which is said thermal quenching, because the energy transfer between the  $\text{VO}_4^{3-}$  tetrahedron is likely to occur. In fact, luminescence of  $\text{YVO}_4$  is not observed at room temperature, however it is observed in  $\text{YPO}_4:\text{VO}_4^{3-}$  mixed crystals. The energy transfer between the  $\text{VO}_4^{3-}$  tetrahedron is inhibited, because the average distance between the  $\text{VO}_4^{3-}$  tetrahedron increased by substituting the  $\text{P}^{5+}$  ion for the  $\text{V}^{5+}$  ion in  $\text{YVO}_4$ . Therefore, the luminescent properties of vanadate phosphors are expected to enhance by partially substituting the  $\text{P}^{5+}$  ion for the  $\text{V}^{5+}$  ion. The  $\text{V}^{5+}$  ion can substitute for the  $\text{P}^{5+}$  ion because the ionic radius of the  $\text{V}^{5+}$  ion (coordination number (CN) = 4, 0.0495 nm) is close to that of the  $\text{P}^{5+}$  ion (CN = 4, 0.0310 nm) and has the same cation valence.



**Fig. 1.** Schematic model for the absorption and emission processes of the  $\text{VO}_4^{3-}$  tetrahedron having  $T_d$  symmetry [8]. The absorption bands for  $\text{Ex}_1$  and  $\text{Ex}_2$  correspond to partly allowed spin-forbidden transitions from the ground state  $^1\text{A}_1$  to excited state  $^1\text{T}_2$  and  $^1\text{T}_1$  levels, respectively. The emission band is attributed to  $\text{Em}_1$  and  $\text{Em}_2$  from the excited states  $^3\text{T}_2$  and  $^3\text{T}_1$  to the ground state  $^1\text{A}_1$ , respectively.

\*Corresponding author:

Tel :

Fax :

E-mail: ktoda@eng.niigata-u.ac.jp

In this study, we investigated the XRD patterns and luminescent properties of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  substituted with  $\text{P}^{5+}$  ion.

## Experimental

$\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  was synthesized by a conventional solid state reaction method. The starting materials were a stoichiometric mixture of  $\text{CaCO}_3$  (Kanto Chemical, Co., Inc 4N),  $\text{K}_2\text{CO}_3$  (Kanto Chemical, Co., Inc 4N),  $\text{MgO}$  (Kanto Chemical, Co., Inc 3N),  $\text{V}_2\text{O}_5$  (Kojundo Chemical Laboratory, Co., Ltd. 4N), and  $(\text{NH}_4)_2\text{HPO}_4$  (Kanto Chemical, Co., Inc 2N) powders. The mixture of the starting materials was fired in a platinum crucible at 973 K for 6 h in air. After grinding, the obtained samples were agitated in pure water for 24 h in order to remove the impurity phase of  $\text{KVO}_3$ . It was filtered and dried at 323 K. The obtained samples were characterized using powder X-ray diffraction and photoluminescence measurements.

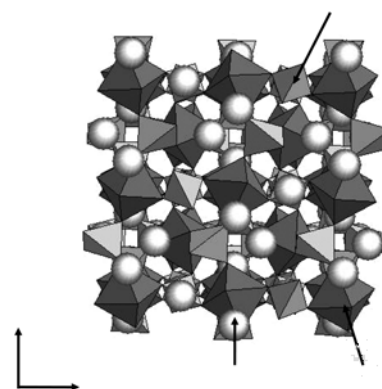
Powder XRD data was measured by using a diffractometer (MX-Labo with Cu  $\text{K}\alpha$  radiation; Mac Science Ltd.). Excitation and emission spectra of the powdered samples were measured using a spectrofluorometer (FP-6500/6600 with 150 W Xenon lamp; Jasco Inc.).

## Results

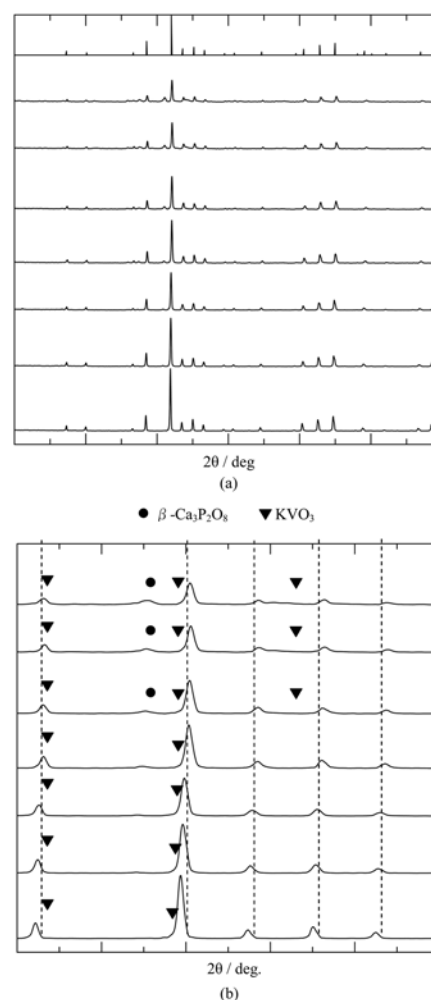
Figure 2 shows the crystal structure of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  [9]. This compound has a cubic structure ( $a = b = c = 12.50031 \text{ nm}$ ) with an  $\text{Ia}\bar{3}\text{d}$  space group. The  $(\text{Ca}^{2+}/\text{K}^+)\text{O}_8$  dodecahedron and the  $\text{VO}_4^{3-}$  tetrahedron are linked to each other in the lattice, which form three dimensional chains. Each  $\text{VO}_4^{3-}$  tetrahedron is isolated within the lattice such as in  $\text{Ba}_3\text{V}_2\text{O}_8$  and  $\text{ScVO}_4$  [10-11].

Figure 3(a) shows XRD patterns of  $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$  ( $x = 0 - 0.5$ ). When the concentration of the  $\text{P}^{5+}$  ion was  $x = 0 - 0.5$ ,  $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$  were obtained as a main phase. To identify the impurity phases and the shift in the XRD patterns more clearly, a part of Figure 3(a) ( $2\theta = 28^\circ - 38^\circ$ ) is presented in Figure 3(b). The peaks of the impurity phase were observed at  $2\theta = 28.5^\circ$ ,  $34.4^\circ$ , and  $31.0^\circ$ . The peaks of  $2\theta = 28.5^\circ$  and  $34.4^\circ$  were (121) and (200) of the  $\text{KVO}_3$  phase. The peak of  $2\theta = 31.0^\circ$  was (2010) of the  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$  phase. The solid solubility limit of the  $\text{P}^{5+}$  ion in  $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$  was approximately  $x = 0.2$ , because the diffraction peaks of the samples were not shifted on the high angle side and the  $\beta\text{-Ca}_3\text{P}_2\text{O}_8$  phase appeared up to  $x = 0.2$ .

Figure 4 shows the XRD patterns of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  before and after washing in pure water for 24 h at room temperature. According to the results, we obtained the single phase  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  by washing in pure water because  $\text{KVO}_3$  dissolved in pure water at room temperature. Moreover,  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  was very stable



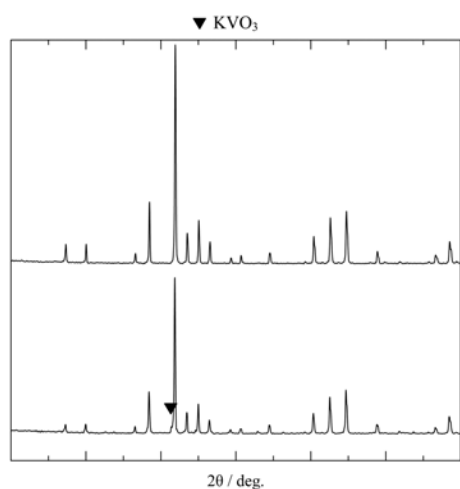
**Fig. 2.** Crystal structure of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$ . Tetrahedrons are  $\text{VO}_4$ , octahedrons are  $\text{MgO}_6$ , and spheres are  $\text{Ca}^{2+}$  or  $\text{K}^+$ .



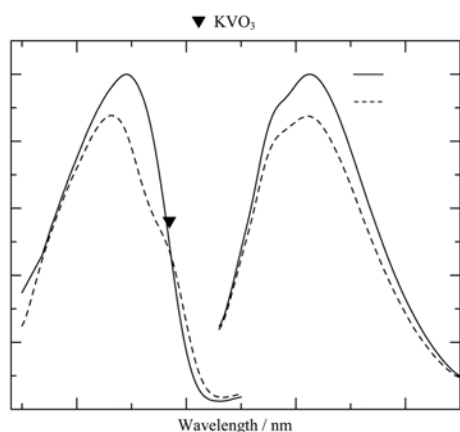
**Fig. 3.** (a) XRD patterns of  $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$  ( $x = 0 - 0.5$ ). The standard patterns of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  (JCPDS No.24-1044) are attached. (b) Part of the XRD patterns of  $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$  ( $x = 0 - 0.5$ ) ( $2\theta = 28^\circ - 38^\circ$ ).

for pure water.

Figure 5 shows the excitation and emission spectra of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  before and after washing in pure water. In the samples after washing, the excitation spectra of  $\text{KVO}_3$  were not observed because  $\text{KVO}_3$  dissolved in pure water as described in Figure 3(b). The samples



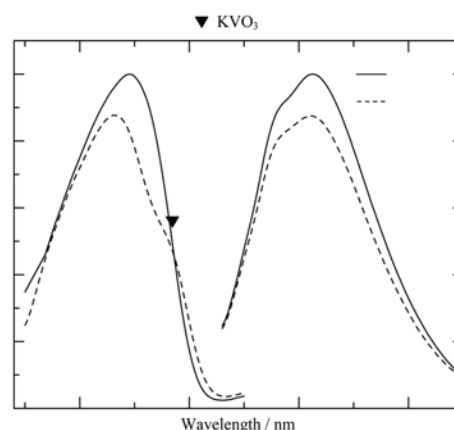
**Fig. 4.** XRD patterns of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  before and after washing in pure water.



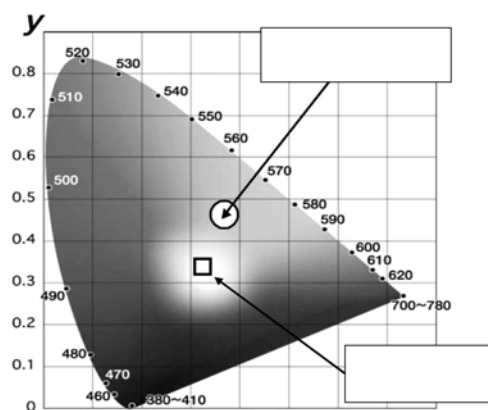
**Fig. 5.** Excitation and emission spectra of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  before and after washing in pure water.

exhibited broadband excitation spectra ranging over 200 - 450 nm; the main peak was at 350 nm with a weak shoulder peak at 280 nm. The main and shoulder peaks corresponded to  $\text{Ex}_1$  and  $\text{Ex}_2$ , respectively. On the other hand, the broadband emission spectra between 400 nm and 700 nm consisted of double peaks with maxima at 510 nm and 560 nm. The peaks at 510 nm and 560 nm corresponded to  $\text{Em}_1$  and  $\text{Em}_2$ , respectively. Moreover, the emission intensity of the sample after washing was greater than that before washing. This phenomenon was explained by the fact that the sample was able to absorb excitation energy efficiently by removing  $\text{KVO}_3$ .

Figure 6 shows the concentration dependence of the emission intensity of  $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$  ( $x = 0 - 0.5$ ). The optimum concentration of  $\text{P}^{5+}$  ion was  $x = 0.05$ . The emission intensity of  $\text{Ca}_2\text{KMg}_2(\text{V}_{0.95}\text{P}_{0.05})_3\text{O}_{12}$  was 1.3 times greater than that of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$ . This phenomenon was explained that the energy transfer between the  $\text{VO}_4^{3-}$  tetrahedron was inhibited by substituting the  $\text{P}^{5+}$  ion for the  $\text{V}^{5+}$  ion same as the  $\text{YPO}_4:\text{VO}_4^{3-}$  phosphor [12]. As described in introduction,  $\text{YVO}_4$  do



**Fig. 6.** Concentration dependence of the emission intensity of  $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$  ( $x = 0 - 0.5$ ).



**Fig. 7.** Chromaticity diagram of  $\text{Ca}_2\text{KMg}_2(\text{V}_{0.95}\text{P}_{0.05})_3\text{O}_{12}$ .

not emit at room temperature owing to the thermal quenching. However  $\text{YPO}_4:\text{VO}_4^{3-}$  mixed crystals is improved the thermal quenching and show the luminescence of  $\text{VO}_4^{3-}$  at room temperature, because the average distance between the  $\text{VO}_4^{3-}$  tetrahedron increased by substituting the  $\text{P}^{5+}$  ion for the  $\text{V}^{5+}$  ion.

Figure 7 shows the chromaticity diagram of  $\text{Ca}_2\text{KMg}_2(\text{V}_{0.95}\text{P}_{0.05})_3\text{O}_{12}$ . The sample was expressed using the color coordinates of the CIE (Commission Internationale de l'Eclairage) chromaticity diagram at  $x = 0.377$  and  $y = 0.463$ . It indicated that the location of the color coordinates of  $\text{Ca}_2\text{KMg}_2(\text{V}_{0.95}\text{P}_{0.05})_3\text{O}_{12}$  was near the white region and closed to the pure white point at  $x = 0.333$  and  $y = 0.333$ .

## Conclusion

In conclusion, we obtained the sample as  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  in a main phase by using a solid state reaction. After agitating in pure water at room temperature,  $\text{Ca}_2\text{KMg}_2(\text{V}_{1-x}\text{P}_x)_3\text{O}_{12}$  ( $x = 0 - 0.2$ ) was obtained as  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$  in a single phase, because  $\text{KVO}_3$  was dissolved in pure water. The main excitation band of this greenish white phosphor was at 360 nm, and the dominant emission peak was at 520 nm. The emission intensity of

$\text{Ca}_2\text{KMg}_2(\text{V}_{0.95}\text{P}_{0.05})_3\text{O}_{12}$  was approximately 1.3 times greater than that of  $\text{Ca}_2\text{KMg}_2\text{V}_3\text{O}_{12}$ . The energy transfer between the  $\text{VO}_4^3$  tetrahedron was inhibited, because the average distance between the  $\text{VO}_4^3$  tetrahedron increased by substituting the  $\text{P}^{5+}$  ion for  $\text{V}^{5+}$  ion. Therefore, we expect this material to be useful in applications for WLEDs without rare earth elements.

### Acknowledgements

This work was supported by a project from the Center for Transdisciplinary Research, Niigata University.

### References

1. R.J. Xie, M. Mitomo, K. Uheda, F.F. Xu, and Y.J. Akimune, *Am. Ceram. Soc.* 85 [2] (2002) 1229-1245.
2. O.A. Lopez, J. McKittrick, and L.E. Shea, *J. Lumin.* 71 [1] (1997) 1-11.
3. C.-K. Chang, and T.-M. Chen, *Appl. Phys. Lett.* 90 [16] (2007) 161901.
4. G. Webster, and H.G. Drickamer, *J. Chem. Phys.* 72 (1980) 3740-3748.
5. T.W. Choua, S. Mylswamy, R.S. Liua, and S.Z. Chuang, *Solid State Communications* 136 (2005) 205-209.
6. L.-T. Chena, C.-S. Hwang, I.-G. Chena, and S.-J. Chang, *J. Alloys Compd.* 426 (2006) 395-399.
7. C. Shen, Y. Yang, S. Jin, and J. Ming, *Physica B* 405 (2010) 1045-1049.
8. T. Nakajima, M. Isobe, T. Tsuchiya, Y. Ueda, and T. Kumagai, *J. Lumin.* 129 (2009) 1598-1601.
9. J. Li, K. Qiu, J. Li, W. Li, Q. Yang, and J. Li, *Mater. Res. Bull.* 45 (2010) 598-602.
10. K.-C. Park, and S.-I. Mho, *J. Lumin.* 122-123 (2007) 95-98.
11. B.C. Chanoumakos, M.M. Abraham, and L.A. Boatner, *J. Solid State Chem.* 109 (1994) 197-202.
12. S. Shionoya, W.M. Yen and T. Hase, in "Phosphor handbook / edited under the auspices of the Phosphor Research Society; editorial committee co-chairs" (CRC press, Newyork, 1999).