Journal of Solid State Chemistry 184 (2011) 3247–3252

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Crystal structure of $Na_2MMgP_2O_8$ (*M*: Ba, Sr, Ca) orthophosphates and their luminescence properties activated by Eu^{2+}; analogous structural behaviors of glaserite-type phosphates and silicates

Yoshinori Yonesaki*, Chihiro Matsuda

Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Miyamae 7-32, Kofu 400-8511, Japan

A R T I C L E I N F O

Article history:
Received 9 August 2011
Received in revised form
7 October 2011
Accepted 8 October 2011
Available online 15 October 2011

Keywords:
Phosphor
Structure analysis
Phosphate
Glaserite
Blue emission

A B S T R A C T

Rietveld refinements of X-ray powder diffraction data and vibrational spectroscopy have confirmed the crystal structure of $Na_2MMgP_2O_8$ (*M*: Ba, Sr, Ca) prepared by a standard solid state reaction. They have glaserite-type layered structure. $Na_2MMgP_2O_8$ has a trigonal $P\bar{3}$ form for M=Ba, and monoclinic $P2_1/c$ forms for M=Sr and Ca. The observed structural transition is analogous to the corresponding layered orthosilicate $M_3MgSi_2O_8$.

Eu^{2+}-doped $Na_2MMgP_2O_8$ exhibits an intense blue to violet emission under ultraviolet excitation, based on 5*d*–4*f* electron transition of Eu^{2+} ions. The emission character is very sensitive to the structural transition induced by M^{2+} and the subsequent site symmetry changes.

1. Introduction

Phosphors are utilized for various purposes in our daily life, such as interior lamps, light sources for displays, paints for sign boards and so forth. Most of commercially available phosphors are obtained by doping transition metal or rare-earth metal ions into a host crystalline material. In particular, Eu^{2+} ion is a very important activator because of the intense emission and color controllability. Eu^{2+} emission originates in parity-allowed 5*d*→4*f* electron transition. Since energy band of the 5*d* orbitals is energetically affected by symmetry and strength of the crystal field, Eu^{2+} emission strongly depends on host material. For a few decades, Eu^{2+}-doped glaserite-type orthosilicates $M_3MgSi_2O_8$ (*M*: Ba, Sr, Ca) have been focused on as candidates for high performance phosphors, and there are many reports on their great potential for the intense blue emission [1–18]. Our group has also investigated their emission properties in terms of the crystal structure [7,13,16,18]. Fig. 1 shows a schematic illustration of the glaserite-type $BaCa_2MgSi_2O_8$ structure [7,17]. The layer is built up by corner-sharing of MgO_6 octahedra and SiO_4 tetrahedra, and Ba^{2+} and Ca^{2+} ions occupy interlayer sites. Larger alkaline-earth cations tend to occupy the interlayer A-site while smaller ones are prone to be at the layer-embedded B-site. It is noteworthy that in this type of silicates, interlayer A-site cations determine the crystal system. $M_3MgSi_2O_8$ crystallizes in trigonal system ($P\bar{3}$ or $P\bar{3}m1$) for larger A-site cations and in monoclinic system ($P2_1/c$) for smaller ones. Eu^{2+}-doped $M_3MgSi_2O_8$ shows an intense blue emission under UV excitation. The emission drastically changes in response to the crystal system; trigonal or monoclinic.

Recently, emission properties of Eu^{2+}-doped $Na_2CaMgP_2O_8$ have been reported by Lű et al. [19]. This phosphate exhibited blue emission under ultraviolet excitation. Interestingly, this compound has glaserite-type monoclinic layered structure (S.G., $P2_1/c$), in which interlayer A-site and layer-embedded B-site are occupied by Ca^{2+} and Na^+, respectively [20]. This report encourages us to find the presence of a highly ordered glaserite-type phosphates, in analogy with $M_3MgSi_2O_8$ orthosilicates. In the present study, the detail on the crystal structure of $Na_2MMgP_2O_8$ (*M*: Ba, Sr, Ca), in which interlayer A-site is occupied by M^{2+} ions, are described. Furthermore, the emission properties of the corresponding compounds doped with Eu^{2+} ions are discussed based on the solved structure.

2. Experimental

2.1. Synthesis

$Na_2MMgP_2O_8$ (*M*: Ba, Sr, Ca) crystalline powder samples were prepared from reagent grade Na_2CO_3, MCO_3 (*M*: Ba, Sr, Ca), magnesium carbonate hydroxide and $NH_4H_2PO_4$. A small amount

---

* Corresponding author. Fax: +81 55 254 3035.
E-mail address: yonesaki@yamanashi.ac.jp (Y. Yonesaki).

0022-4596/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2011.10.011

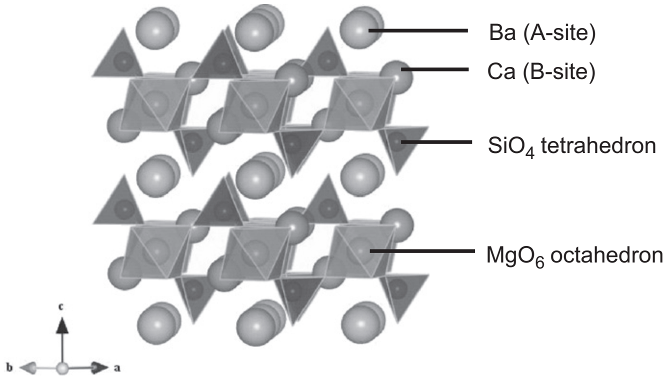

Fig. 1. Crystal structure of $BaCa_2MgSi_2O_8$, illustrated with MgO_6 octahedra and SiO_4 tetrahedra.

of NH_4Cl was used as a flux. Stoichiometric amounts of the reagents and the flux were ground and mixed by ball milling with zirconia beads in 2-propanol for 4 h. The mixed powder was heated at 1100 °C for 4 h in air with an intermittent re-grinding. The powder of $Na_2M_{0.98}Eu_{0.02}MgP_2O_8$ was prepared by heating stoichiometric mixture of the starting reagents and Eu_2O_3 at 1100 °C for 4 h in a flow of 2% H_2–98% N_2 gas with an intermittent re-grinding.

2.2. X-ray diffraction analysis

The prepared samples were investigated by X-ray powder diffraction (XRD) with a Rigaku RINT-2200HFV diffractometer using Cu*K*α radiation ($\lambda = 1.54058$ Å). The structural refinement was carried out with the XRD data collected at intervals of 0.02° from 10° to 120° 2θ at room temperature. Lattice parameters and structure parameters were refined by Rietveld method using a program RIETAN-FP [21]. Figures of crystal structure in this paper were drawn with VESTA [22].

2.3. Raman spectroscopy

Room-temperature Raman spectra were measured for the prepared samples in backscattering geometry by a 3000 grooves/mm grating monochromator and a charge-coupled device detector system (RENISHAW, inVia Reflex system). Samples were excited with the 488-nm laser line of a 50 mW Spectra-Physics Cyan™ Scientific CW laser. The laser beam was plain-polarized with a polarizer and focused on a sample with a 50 × lens. A spectral resolution was 0.5 cm^{-1}. The laser power was attenuated to 5 mW before sample irradiation.

2.4. Photoluminescence

Emission spectra were measured for the prepared samples at room temperature using a JASCO corporation FP-6500 spectrofluorometer.

3. Results

3.1. Crystal structure of $Na_2MMgP_2O_8$

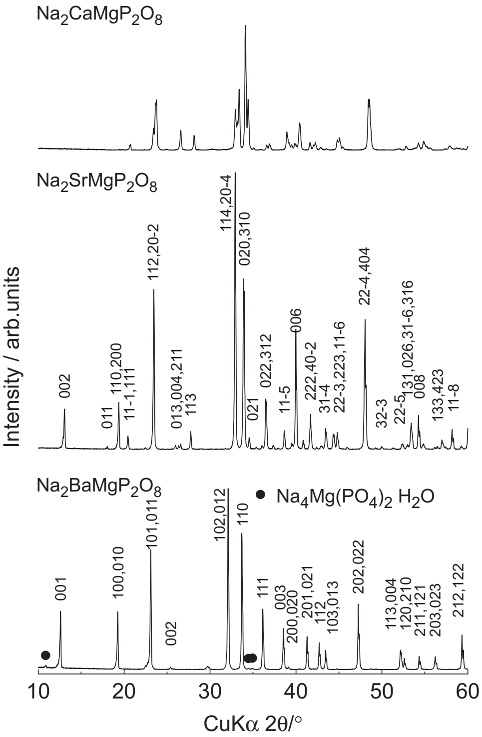

Fig. 2. X-ray powder diffraction patterns for the prepared samples. For the samples of M=Sr and Ba, diffraction peaks from the $Na_2MMgP_2O_8$ phase are indexed.

Table 1
Crystallographic data for $Na_2MMgP_2O_8$ (M: Ba, Sr).

M	Ba	Sr
Empirical formula	$Na_2BaMgP_2O_8$	$Na_2SrMgP_2O_8$
Formula weight	397.55	347.85
Crystal system, space group	Trigonal, $P\bar{3}$ (no. 147)	Monoclinic, $P2_1/c$ (no. 14)
Unit cell parameters	$a = 5.3043(9)$ Å	$a = 9.124(3)$
	$c = 6.9915(8)$ Å	$b = 5.279(15)$
		$c = 13.499(4)$
		$\beta = 90.013(5)$
Volume (Å^3)	170.36(4)	650.3(3)
Z	1	4
Calculated density (g cm^{-3})	3.88	3.55
R_p (%)	9.86	12.25
WR_p (%)	14.13	16.18
R_I (%)	3.87	6.44
R_F (%)	1.75	3.83

Fig. 2 shows the XRD patterns for the $Na_2MMgP_2O_8$ samples. The $Na_2CaMgP_2O_8$ pattern agrees well with the previous data [19]. Although a small amount of impurity phase can be seen in the sample of $Na_2BaMgP_2O_8$, the main reflections are indexed with a hexagonal unit cell with $a = 5.3043(9)$ Å and $c = 6.9915(8)$ Å for $Na_2BaMgP_2O_8$, and with a monoclinic unit cell with $a = 9.124(3)$ Å, $b = 5.279(15)$ Å, $c = 13.499(4)$ Å and $\beta = 90.013(5)°$ for $Na_2SrMgP_2O_8$. Using glaserite-type families as initial structure model, the crystal structure of $Na_2BaMgP_2O_8$ and $Na_2SrMgP_2O_8$ has been successfully refined (the final profile fits are attached as supplementary materials). The crystal data and atomic parameters are listed in Tables 1 and 2, respectively. Lattice constants for the trigonal $P\bar{3}$ cell can be converted to the corresponding monoclinic $P2_1/c$ cell with the relation that $a_m = \sqrt{3}a_t$, $b_m = b_t$ and $c_m = 2c_t$ (subscript "m" means monoclinic and "t" trigonal). To check the reasonability of the refined structure, vibrational spectroscopy was attempted for them. Fig. 3 shows the Raman spectra of the $Na_2MMgP_2O_8$ samples. Intense Raman peaks appear at about 1000, 440, 1120 and 590 cm^{-1}. Generally, Raman peaks at such high wavenumbers (> 400 cm^{-1}) are attributed to internal vibrations of certain atomic groups. In the present case, they are derived from the four normal modes of PO_4 tetrahedra; symmetric stretching vibration ν_1,