Lattice Deformation and Lattice Strain of BaMgAl_{10}O_{17}: Eu^{2+} Induced by Thermal Treatment

H. YAMADA, H. KUSABA, W. S. SHI, K. NISHIKUBO and C. N. XU

1. Introduction

Since some efficient phosphors with the magnetoplumbite and the \( \beta \)-alumina type structure were developed for three-color fluorescent lamps in 1974,\(^1\) considerable research of these phosphors has been carried out to improve their luminescent properties.\(^2\)

Barium magnesium aluminate, \( \text{BaMgAl}_{10}\text{O}_{17} \), doped with \( \text{Eu}^{2+} \) (BAM) is one such blue-emitting phosphor and shows high luminescence efficiency under vacuum ultraviolet (VUV) rays. Though recently it is commercially applied to plasma display panels (PDP) as a blue emitting component,\(^2\)\(^5\) some problems still exist with regard to its luminous stability. One of the problems is the luminous decrease, which takes place during the baking process in the PDP manufacture and the VUV irradiation in PDP works.\(^5\)\(^,\)\(^7\) The former problem is called thermal degradation and is more serious for the BAM phosphor because its degradation is larger than that of other color components such as \( \text{ZnSiO}_3\text{Mn}^{2+}, \text{LaPO}_4\text{Ce}^{3+}, \text{ Tb}^{3+}, \) and \( \text{Y}_2\text{O}_3\text{Eu}^{2+} \) phosphors.\(^5\) Much research on the thermal degradation in BAM has been carried out to improve the luminescent performance. Oshio \textit{et al.} first made a systematic investigation of the thermal degradation of BAM using photoluminescence (PL), electron spin resonance (ESR), X-ray absorption near-edge structure (XANES) and powder X-ray diffraction (XRD) measurements. They concluded that the thermal degradation resulted in the formation of a new phase, \( \text{EuMgAl}_{10}\text{O}_{16} \), in which the valence state of the Eu ion changes from a divalent to trivalent state.\(^8\) Recently, some studies suggest that the origin of the thermal degradation was not due to the change of the valency, but due to the structural change, for example, the change of the local atomic configuration surrounding the \( \text{Eu}^{2+} \) ions,\(^9\) the intercalation of water in the conduction layers,\(^10\) or the displacement of the \( \text{Eu}^{2+} \) ion from the original position.\(^11\) However, the structural evidence was not clarified in these studies.

In the current work, we firstly demonstrate that the effects of the thermal degradation appear in the lattice parameters and the lattice strains using the Rietveld analysis with precise powder X-ray diffraction data. On the other hand, change in the lattice does not occur for the non-doped BAM. We compared the lattice parameters and the lattice strains in doped BAM with those of the non-doped one.

2. Experimental details

2.1 Sample preparation

\( \text{Ba}_{0.90}\text{Eu}_{0.10}\text{MgAl}_{10}\text{O}_{17} \) (BAM) phosphor samples were prepared using three kinds of synthetic methods: an amorphous citric acid precursor (ACP) method, an amorphous malic acid precursor (AMP) method, and a spray pyrolysis (SP) method. The particles were then calcined at 900°C in air by thermally deteriorating the samples. The lattice parameters for the Eu doped BAM clearly showed the deformation of the unit-cell, whereas the non-doped BAM showed no deformation. Together with the lattice deformation, the anisotropic lattice strains were also induced in the doped BAM. These results suggest that any defects are generated in the lattice by the thermal treatement and therefore the thermal degradation in BAM is possibly attributed to the defects.\(^\text{[Received August 5, 2003; Accepted December 24, 2003]}\)

\textbf{Key-words}: Barium magnesium aluminate, BAM, Thermal degradation, Structural characterization, lattice strain, Rietveld refinement

\textbf{Paper}
divergent and scattering slits were controlled to keep the same
width of incident X-rays on the sample holder in all 2θ ranges
by using a programmable slit system.

2.3 Refinement
The crystal structure of BAM, as shown in Fig. 1, is related
to the β-alumina structure with a hexagonal form, and it con-
sists of the conduction layers and the spinel blocks, stacking
them alternatively along the c direction.

We have already proposed a newly crystal structure model
of BAM, which is called the split-atom model.12) In this
model, a cation site splits from a 2d site (1/3 2/3 3/4) into a
12j site (x y z/4: x = 0.3604, y = 0.687) and therefore Ba and
Eu ions are randomly distributed at these splitting positions.

With this structure model, each structural parameter with
isotropic atomic-displacement parameter was refined using
the Rietveld method with the computer program RIETAN-
2000.13) It should be emphasized that all XRD data showed no
change to another phase such as a structural phase transition.

Therefore, the structural model was commonly adopted in all
Rietveld refinements. As for a profile function, the pseudo-
Voigt function of Thompson, Cox and Hastings (TCH)14) was
used and its profile made in asymmetric form according to
the procedure of Finger et al.15) We would like to emphasize
that TCH’s function is best suited to characterize the crystal-
line, such as the microstrain and the crystallite size. The back-
ground was represented by a 6th-order Legendre polynomial.

The final results of each refinement are listed in Table 1.

2.4 Microstrain and crystallite size
A microstrain and a finite crystallite-size are usually
attributed to the profile broadening in a powder diffraction
pattern. The two effects show the different 2θ dependences of
the full-width-at-half-maximum (FWHM) Hk, of which the
deprivation is expressed by

$$
\Delta H_k = \frac{\lambda \sec \theta_k}{L} + 2e \tan \theta_k,
$$

where K is the diffraction index, and the λ and the L in the
first term indicate an incident X-ray wavelength and crystallite
size, the ε in the second term is the lattice strain, and the θk is
the peak position.16) When using the TCH’s pseudo-Voigt
function, it is possible to estimate the crystallite-size and the
lattice strain from the profile parameters refined using the
Rietveld analysis because terms of sec θk and tan θk exist in
the formula. According to Larson and Von Dreelle,17) the crys-

tallite size and the lattice strain involving the anisotropic peak
broadening can be extracted from the following formula,

![Fig. 1. Crystal structure of BaMgAl₆O₁₄: Eu. It consists of alternative stacks of a spinel block that contains some Al( or Mg)O₄ tetra-
hedra, AlO₆ octahedra, and a mirror plane which includes an oxygen
ion and a barium or a europium ion. Notice that this figure was
drawn with VENUS developed by Dilanian and Izumi using atomic positions in
Ref. 12.](image)

| Table 1. Lattice Parameters, Crystallite Sizes, and Refinement Results for BaₓEuₓMgAl₆O₁₄ Prepared by a Spray Pyrolysis (SP) Method, an
| Amorphous Citric Acid Precursor (ACP) Method, and an Amorphous Malic Acid Precursor (AMP) Method, and BaMgAl₆O₁₄ Prepared by a
| SP Method. "Before" and "After" Indicate the Pre- and Post Calcinning Samples in Air at 900°C, Respectively
| Sample names | ACP | AMP | SP | SP without Eu
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Nm)</td>
<td>0.562668(3)</td>
<td>0.562570(4)</td>
<td>0.562664(3)</td>
<td>0.562577(3)</td>
</tr>
<tr>
<td>c (Nm)</td>
<td>2.26289(1)</td>
<td>2.26363(1)</td>
<td>2.262700(9)</td>
<td>2.26343(1)</td>
</tr>
<tr>
<td>V (Nm³)</td>
<td>0.620438(5)</td>
<td>0.620425(7)</td>
<td>0.620377(5)</td>
<td>0.620386(5)</td>
</tr>
<tr>
<td>Crystallite size</td>
<td>210(30)</td>
<td>210(10)</td>
<td>150(9)</td>
<td>173(2)</td>
</tr>
<tr>
<td>Lₐ₀₀₁ (Nm)</td>
<td>600(200)</td>
<td>520(70)</td>
<td>320(40)</td>
<td>333(4)</td>
</tr>
<tr>
<td>Crystallite size</td>
<td>4.95</td>
<td>4.76</td>
<td>4.94</td>
<td>3.94</td>
</tr>
<tr>
<td>Rₑp(%)</td>
<td>1.41</td>
<td>1.67</td>
<td>1.93</td>
<td>1.28</td>
</tr>
<tr>
<td>S</td>
<td>2.014</td>
<td>1.9488</td>
<td>2.022</td>
<td>2.5582</td>
</tr>
</tbody>
</table>

*S=Rₑp/Rₑ

\[ L_\perp = \frac{180K_\perp}{\pi X}, \quad L_{//} = \frac{180K_{//}}{\pi(X + X_e)}, \]

\[ \varepsilon_\perp = \frac{\pi}{180} (Y - Y_e) \times 100, \]

\[ \varepsilon_{//}} = \frac{\pi}{180} (Y + Y_e - Y_e) \times 100, \tag{2} \]

where \( K \) is the Scherrer constant, and \( X, X_e, Y, Y_e \) are the anisotropic Lorentzian profile coefficients, respectively. \( Y_e \) is a characteristic value depending on the diffractometer used, and its value was estimated from the Rietveld refinement of the standard powder sample, \( \text{CeO}_2 \) (NIST SRM 674a). For further information for the profile broadening relating to the lattice strain and the crystallite size, refer to Ref. 16.

3. Results and discussion

The results of the Rietveld refinements are listed in Table 1. In this table, the crystallite size was calculated by formula (2) with the Scherrer constant \( K = 0.9 \) and therefore, the crystallite of all BAM samples exhibited a plate-like form with a size of sub-micron order, in which the normal to the plate corresponds with [001]. Furthermore, the crystallite size of ACP and AMP samples was larger than that of SP samples, and those sizes showed almost no change between pre- and post-annealing samples. These results indicate that the crystallite size was not affected by the thermal treatment.

To identify the appearance of an impurity phase in BAM samples, the XRD patterns of pre-annealing samples were compared with those of the post-annealing ones, as shown in Fig. 2. Some work reported that the impurity phase of \( \text{EuMgAl}_2\text{O}_4 \) appeared in BAM powders calcined in air at above 500–800°C,\(^{9,17}\) however none of our all samples exhibited any appearance of such a phase. The discrepancy suggests that the thermal degradation may be very sensitive to crystallinity and stoichiometry of the samples.\(^{7,8}\) Some impurity phases were observed in our three BAM powders calcined at temperatures higher than 1100°C. These facts suggest that our samples possess high crystallinity and stoichiometry and therefore are resistant to thermal degradation.

Figure 3 shows the relative changes in the lattice parameters \( a, c \), Volume in the SP, AMP, ACP, and non-doped SP samples. Notice that the lattice parameters were normalized with those of the pre-annealing samples. Up to now, some studies have been carried out by ascertaining a trace of the thermal degradation in the structure, however, they could not successfully detect such structural behaviors,\(^{9,17}\) concluding that the average structure in the thermally deteriorated BAM did not change. However, our results clearly showed systematic changes in the lattice parameters for the three Eu doped samples, that is, the unit-cell contracted in the \( c \)-axis direction and expanded in the \( c \)-direction, maintaining the volume. On the other hand, the non-doped BAM particles show no such deformation. In addition, our recent experiments revealed that the volume of doped BAM particle calcined at higher than 1100°C expanded abruptly and was consistent with that of the non-doped BAM particles.\(^{18}\) These results indicate that the lattice deformation is not caused by a separation of the impurity phase with the Eu ion, but by a displacement of the Eu ion or induced defects.

In connection with the lattice deformation, the peak broadening was observed in the XRD data of Eu-doped samples. Using the profile parameters refined by the Rietveld refinements, the anisotropic lattice strains were calculated using the formula (2) (Fig. 4). The lattice strains were anisotropically induced in the doped samples and not in the non-doped sample. Moreover, the lattice strain parallel to the \( c \)-axis was slightly larger than that normal to its axis. Normally the lattice strains are attributed to some lattice defects such as point defects and dislocations. Generally, some defects in a lattice involve the optical properties in materials and therefore interest in the defects has been shown in the thermally deteriorating BAM. If the lattice defects correspond to lattice vacancies, the Rietveld refinement makes it possible to roughly estimate the amount and the location of defects by refining the parameters of the occupancy ratio at each atomic position in principle. In our XRD data, however, it was difficult to obtain their reasonable values because of the strong correlation between occupancy ratios and atomic displacement. These difficulties will be overcome by high resolved XRD data or powder neutron diffraction data and we plan to perform this using high-resolved XRD measurements.

Fig. 2. Comparisons of XRD patterns between pre- and post-annealing samples prepared by the SP, ACP, and AMP methods. The "before" and the "after" in the figure refer to the caption in Table 1.

Fig. 3. Relative lattice parameters before and after calcining in air at 900°C. All parameters were normalized with the "before" parameters. The "SP without Eu" indicates BAM non-doped with an Eu ion.
with a synchrotron radiation.

4. Conclusions

The lattice deformation and the lattice strain induced by the thermal treatment have been firstly detected in Eu-doped BAM particles using the Rietveld refinements with XRD data, whereas BAM particles non-doped with the Eu ion exhibited no such lattice deformation. In addition, the lattice deformation involved the anisotropic lattice strains, which were possibly attributed to some defects generated by the thermal treatment. The results suggest that the lattice deformation is dependent on the presence of Eu ions in a lattice. It may be also suggested that the lattice defects play an important role in the thermal degradation in BAM phosphor.

References