Paper

Electron Spin Resonance Study on Local Structure of Manganese Ions Doped in Gamma-Aluminum Oxynitride Phosphors

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ABSTRACT

We have studied the local structure of manganese ion doped in gamma aluminum oxynitride phosphors (γ -AlON: Mn) using electron spin resonance (ESR) experiment. Six sharp peaks appear in ESR spectra of γ -AlON: Mn, together with five weak doublets. These structures are caused by the hyperfine interaction of 3d electrons with the ^{55}Mn nucleus of spin $I=5/2$. The six peaks are attributed to the allowed transitions ($\Delta M_I=0$) between hyperfine splitting states of $M_S=\pm 1/2$. The five doublets are interpreted as the forbidden transitions ($\Delta M_I=\pm 1$) between the hyperfine splitting states. The spectral feature of γ -AlON: Mn resembles with the ESR spectrum of Mn^{2+} doped MgAl_2O_4 spinel, in which Mn^{2+} ions are substituted for tetrahedral Mg^{2+} sites. Since γ -AlON is also of the spinel structure, it is suggested that Mn^{2+} ions occupy tetrahedral Al^{3+} sites. We further chased the effect of Mg^{2+} co-doping on ESR spectra of Mn^{2+} ions in γ -AlON, in order to elucidate the luminescence enhancement in γ -AlON: Mn, Mg. It turned out that the Mg^{2+} co-doping increases Mn^{2+} ions at tetrahedral Al^{3+} sites.

KEYWORDS: oxynitride phosphor, γ -AlON, Mn^{2+} ion, electron spin resonance

1. Introduction

Transition-metal ions with $(3d)^n$ electron configurations have been utilized as activators in many phosphor materials, as well as rare-earth ions with $(4f)^n$ electron configurations. Among the transition-metal ions, the Mn^{2+} ion with five 3d electrons is very attractive, because its luminescence shows high luminance and high chromatic purity. Actually, a few Mn^{2+} activated phosphors have been in practical use for display and solid state lightening¹⁾. The luminescence properties of such phosphors strongly depend on ligands surrounding Mn^{2+} ions, and the luminescence wavelength can be controlled over the whole of the visible range by adjusting the lattice parameters of host materials²⁾.

Recently, new types of inorganic phosphors have been developed using nitrides and oxynitrides as host materials. These phosphors have advantages of luminance, chromaticity and thermal quenching. The gamma aluminum oxynitride doped with Mn ions (γ -AlON: Mn) is also one of such phosphors. Xie et al. have reported that this phosphor produces a green luminescence band at 512 nm under excitation with photons at 445 nm³⁾. Furthermore, it has been also presented that the green luminescence band is enhanced by the addition of Mg^{2+} ions into γ -AlON: Mn. Since the Mg^{2+} co-doped γ -AlON: Mn phosphor exhibits a small thermal

quenching, high quantum efficiency and high color rendering, it has the potential to be a better green phosphor.

The host γ -AlON is the binary mixed compound of Al_2O_3 and AlN, and is formed within the AlN concentration of 27–40 mol%⁴⁾. This material has a cubic spinel structure of the $Fd3m$ space group, as same as MgAl_2O_4 . Aluminum vacancies are inevitably introduced owing to the charge inconsistency between two different anions. There are two cation sites in the cubic spinel structure. One is the tetrahedral site coordinated by four anions. The other is the octahedral site coordinated by six anions. The point symmetry of the former and latter is T_d and O_h , respectively. As generally known, a blue-green luminescence band appears when a Mn^{2+} ion is placed in the tetrahedral coordination, whereas an orange-red luminescence band appears when a Mn^{2+} ion is placed in the octahedral coordination¹⁾. Since a green luminescence band is strongly observed in γ -AlON: Mn, it is expected that Mn^{2+} ions occupy tetrahedral Al^{3+} sites. On the other hand, Takeda et al. have investigated the X-ray absorption fine structure (XAFS) measurement of Mn-K absorption in γ -AlON: Mn, Mg⁵⁾. From comparisons with the X-ray absorption near edge structure (XANES) of various manganese oxides, it was proved that the valence of the

Mn ions was +2. Furthermore, the curve fitting analysis of the extended X-ray absorption near edge structure (EXAFS) has revealed that Mn^{2+} and Mg^{2+} ions are predominantly placed at tetrahedral Al^{3+} sites. It was also pointed out that the point symmetry at the Mn^{2+} sites is lower than the T_d symmetry.

The main aim of the present study is to obtain the information on the local structure of Mn^{2+} ions in $\gamma\text{-AlON}$ through the analysis of magnetic interaction. Electron spin resonance (ESR) experiment was performed at room temperature using powder samples of $\gamma\text{-AlON}$: Mn and Mg^{2+} co-doped $\gamma\text{-AlON}$: Mn with different concentration of Mn^{2+} and Mg^{2+} ions. ESR spectra were analyzed using a spin-Hamiltonian, in order to determine spin-Hamiltonian parameters. The local structures of Mn^{2+} ions in $\gamma\text{-AlON}$: Mn and $\gamma\text{-AlON}$: Mn, Mg are discussed in comparison with that in MgAl_2O_4 : Mn.

2. Experimental

Powder samples of $\gamma\text{-AlON}$: Mn and $\gamma\text{-AlON}$: Mn, Mg were prepared by sintering the powder mixture of $\alpha\text{-Al}_2\text{O}_3$, AlN, MgO, and MnCO_3 at 1800°C for 2 h in the nitrogen atmosphere of 0.5 MPa. The concentration of Mn and Mg ions was adjusted to be 0.05–0.5 mol% and 0.05–5 mol%, respectively, in the preparation. The concentration of Mn ions is rather low, compared to that in Ref. 3. This is because the spectral analysis makes it possible to investigate the local structure of Mn ions. Since ESR spectra exhibit only a single peak in high Mn concentration, it is hard to obtain fruitful information on the local structure of Mn ions.

Powder X-ray diffraction (XRD) experiment was carried out to investigate whether phosphor powders synthesized have the crystal structure of $\gamma\text{-AlON}$. The characteristic X-ray from a copper target was used in

Figure 1 XRD spectrum of $\gamma\text{-AlON}$: Mn (0.5 mol%) measured at room temperature. Solid circles correspond to XRD peaks of host $\gamma\text{-AlON}$ reported in Ref. 3. A number of weak peaks are also seen as indicated by cross. They are due to the corundum phase of Al_2O_3 .

the XRD experiment. The result of $\gamma\text{-AlON}$: Mn (0.5 mol%) is shown as an example in Figure 1. The peak positions indicated by solid circles are in good agreement with those of $\gamma\text{-AlON}$ in Ref. 3, indicating that the phosphor powders prepared have the $\gamma\text{-AlON}$ structure. Another peaks also appear in the XRD spectrum of Figure 1, as indicated by cross. These peaks are due to the corundum phase of Al_2O_3 .

ESR measurement was performed at room temperature using a X-band ESR spectrometer (Joel, FA-600). ESR spectra were measured under the magnetic field modulation of 100 kHz. The microwave power was adjusted to be 0.5 mW during measurement, so as not to saturate ESR signals.

3. Results and discussions

The first and second derivatives of the ESR spectrum of $\gamma\text{-AlON}$: Mn (0.5 mol%) are shown in the upper and lower parts of Figure 2, respectively. The positions of dips in the second derivative correspond to those of peaks in the original ESR spectrum which is not shown here. The original ESR spectrum consists of six prominent peaks and five weak doublets. The six peaks can be seen in inorganic phosphors doped with Mn^{2+} or Mn^{4+} ions. The possibility of Mn^{4+} ions excludes in $\gamma\text{-AlON}$: Mn, because this phosphor does not exhibit a red emission characteristic of Mn^{4+} ions¹⁾, similar to that of Cr^{3+} ions of ruby.

A free Mn^{2+} ion has the ground state of 6S in the high spin state of $S=5/2$. The 6S state splits into six levels of

Figure 2 First (upper) and second (lower) derivative ESR spectra of $\gamma\text{-AlON}$: Mn (0.5 mol%) measured at room temperature. Vertical bars indicate peak positions in the original ESR spectrum. The frequency of microwave was 9.438 GHz during measurement.

$M_S=\pm 5/2, \pm 3/2, \pm 1/2$ by Zeeman splitting. In powder samples, the transition between $M_S=\pm 1/2$ is only observable, because the peaks are remarkably enhanced by the superposition of ESR spectra from randomly oriented single crystallites with respect to an external magnetic field. The other transitions of $M_S=\pm 5/2 \leftrightarrow \pm 3/2$ and $M_S=\pm 3/2 \leftrightarrow \pm 1/2$ are not very conspicuous owing to the angular variation of their peaks. Each level of $M_S=\pm 1/2$ further splits into six sublevels by the hyperfine interaction with the ^{55}Mn nucleus of spin $I=5/2$. The ESR transitions are allowed when the conditions of $\Delta M_S=\pm 1$ and $\Delta M_I=0$ are satisfied between initial and final states. Therefore, the six peaks are attributed to the transitions of $\Delta M_I=0$ between the hyperfine splitting states of $M_S=\pm 1/2$.

In order to determine the spin-Hamiltonian parameters, the spin-Hamiltonian of an axial symmetry is introduced by considering the symmetry lowering at Mn^{2+} sites pointed out in Ref. 5. The formula is given by

$$\mathcal{H} = g\mu_B \mathbf{S} \cdot \mathbf{H} + D\{S_D^2 - S(S+1)/3\} + A\mathbf{S} \cdot \mathbf{I}, \quad (1)$$

where g is the spectroscopic factor, μ_B the Bohr magneton, D the zero-field splitting parameter of an axial symmetry, and A the hyperfine structure coupling constant. The z axis was chosen to be along the principal axis of symmetry. The parameter D was set to be zero, because there was no fine structure due to the zero-field splitting term in Figure 2. The values of g and A were assumed to be isotropic. The energy eigenvalues were calculated up to the second order in perturbation⁷. From the peak fit analysis of the six peaks, the values of g and A were determined to be 2.002 and 8.3 mT, respectively.

The ESR spectrum in the upper part of Figure 2 resembles that of $\text{MgAl}_2\text{O}_4:\text{Mn}$ ^{8,9}. As listed in Table 1, the values of g and A of $\gamma\text{-AlON}:\text{Mn}$ are also in good agreement with those of $\text{MgAl}_2\text{O}_4:\text{Mn}$ ¹⁰. Especially, the agreement of the A value suggests that there are similarities on the local structure of Mn^{2+} ions between these materials, because the spatial extension of $\text{Mn-}3d$ orbitals is reflected on the A value. In $\text{MgAl}_2\text{O}_4:\text{Mn}$, it was reported that Mn^{2+} ions occupy tetrahedral Mg^{2+} sites. We suppose that, in $\gamma\text{-AlON}:\text{Mn}$, Mn^{2+} ions are placed at tetrahedral Al^{3+} sites. This supposition is supported by the fact that a green luminescence band is predominantly observed in $\gamma\text{-AlON}:\text{Mn}$.

In the lower part of Figure 2, one can see the five doublets, together with the six dips. Assuming that the doublets are caused by the transitions of $\Delta M_S=\pm 1$ and $\Delta M_I=\pm 1$, the positions are easily calculated using the spin-Hamiltonian parameters. The calculated result reproduces the positions of five doublets, as indicated by vertical bars. Therefore, it is reasonable to attribute the five doublets to the transitions of $\Delta M_I=\pm 1$ between the

Table 1 Comparison of the spin-Hamiltonian parameters g and A between $\gamma\text{-AlON}:\text{Mn}$ and $\text{MgAl}_2\text{O}_4:\text{Mn}$

	g	A (mT)
$\gamma\text{-AlON}:\text{Mn}$	2.003	8.3
$\text{MgAl}_2\text{O}_4:\text{Mn}$	1.998 ^a , 2.003 ^b	8.2 ^a , 8.3 ^b

^a Reference 8.

^b Reference 9.

hyperfine splitting states of $\Delta M_S=\pm 1/2$. The transitions are basically of ESR forbidden. The forbidden character is lifted through the admixture of hyperfine levels with the same M_S due to the third order perturbation terms containing the cross product of D and A ¹¹. Accordingly, the parameter D has to be a non-zero value, when the forbidden doublets appear in ESR spectra. In this case, many more peaks should be observed due to zero-field splitting. However, such peaks are not found in ESR spectra of Figure 2. This inconsistency would be explained by considering lattice distortions around Mn^{2+} ions. As we have already mentioned, the host $\gamma\text{-AlON}$ contains two kinds of anions and Al^{3+} vacancies. Because of their inhomogeneous distributions, electrostatic interactions do not uniformly work on each of Mn^{2+} ions. Thus, various types of lattice distortions will be induced around Mn^{2+} ions, when they are introduced into $\gamma\text{-AlON}$. The superposition of ESR spectra of such Mn^{2+} ions will smear out many peaks due to the zero-field splitting. Therefore, it is likely that the ununiformity of lattice distortions around Mn^{2+} sites is responsible for $D=0$. This idea is in line with the result in Ref. 5. Estimation of the zero-field splitting constant D has been performed using the ESR spectrum of a powder sample⁷. This work may not be very meaningful in $\gamma\text{-AlON}:\text{Mn}$, because each of Mn^{2+} ions has the different D value with each other.

To clarify the origin of the luminescence enhancement by the co-doping of Mg^{2+} ions, the relationship between the spin number and Mg^{2+} concentration was investigated. The result is shown in Figure 3. The spin number was estimated by integrating original ESR spectra. The value is proportional to the concentration of Mn^{2+} ions at tetrahedral Al^{3+} sites. In Figure 3, it is increased with the concentration of Mg^{2+} ions. Since the green luminescence band of $\gamma\text{-AlON}:\text{Mn}$ is also enhanced by the Mg^{2+} co-doping³, it is natural that the luminescence enhancement is connected with the increase of the Mn^{2+} ions. In Ref. 3, it was revealed that the Mg^{2+} co-doping stimulates the formation of $\gamma\text{-AlON}$ phase with a spinel structure of the MgAl_2O_4 type³. In addition, it was also found that the lattice constant of Mg^{2+} co-doped $\gamma\text{-AlON}:\text{Mn}$ is in good agreement with that of MgAl_2O_4 . Since the ionic radius of a Mn^{2+} ion is almost the same as that of a Mg^{2+} ion¹², more Mn^{2+} ions

Figure 3 Relationship between the spin number and Mg^{2+} concentration in $\gamma\text{-AlON: Mn, Mg}$. The spin number was estimated by integrating the original ESR spectra.

can be substituted for tetrahedral Al^{3+} sites by Mg^{2+} co-doping. Consequently, the increase of tetrahedral Mn^{2+} ions results in the luminescence enhancement of Mg^{2+} co-doped $\gamma\text{-AlON: Mn}$.

4. Summary

In the present study, we have measured ESR spectra of $\gamma\text{-AlON: Mn}$ and Mg^{2+} co-doped $\gamma\text{-AlON: Mn}$. The second derivatives of ESR spectra were composed of six prominent dips and five weak doublets. The former and latter were assigned to allowed transitions of $\Delta M_S = \pm 1$ and $\Delta M_I = 0$ and forbidden transitions of $\Delta M_S = \pm 1$ and $\Delta M_I = \pm 1$. From the peak fit analysis, the spin-Hamiltonian parameters g and A were determined to be 2.002 and 8.3 mT, respectively. The values of g and A were in good agreement with those of $\text{MgAl}_2\text{O}_4: \text{Mn}$. It was thus suggested that Mn^{2+} ions doped in $\gamma\text{-AlON}$ occupy tetrahedral Al^{3+} sites. An appearance of the five doublets was elucidated by the symmetry lowering at the Mn^{2+} sites. It was pointed out that the magnitude and/or direction of lattice distortions are not uniform at the Mn^{2+} sites. By adopting this idea, the absence of many peaks due to zero-field splitting was explained. Luminescence enhancement of Mg^{2+} co-doped $\gamma\text{-AlON: Mn}$ was connected to the increase of tetrahedral Mn^{2+} ions.

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