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^{151}Eu Mössbauer measurements of $CuLa_{1-x}Eu_xO_2$ with luminescent property

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Abstract An increase of the asymmetric ratio of photoluminescence lines from $CuLa_{1-x}Eu_xO_2$ was observed under 100 K, suggesting a lower site symmetry for the Eu cation. Mössbauer spectra of $CuLa_{0.8}Eu_{0.2}O_2$ measured at 77 K revealed that the valence of Eu is trivalent and that the crystal structure of $CuLa_{1-x}Eu_x$ O_2 might contain a EuO_6 octahedron with lower symmetry. The thermodynamic stability of the valence of Cu and Eu was calculated, showing agreement with Mössbauer spectra.

Keywords $CuLa_{1-x}Eu_xO_2$ · ^{151}Eu Mössbauer spectra · Photoluminescence · Thermodynamic calculation

1 Introduction

Polycrystalline $CuLa_{1-x}Eu_xO_2$ shows orange photoluminescence (PL) at room temperature, which is different from PL observed for usual Eu^{3+} or Eu^{2+} containing materials. The valence of Eu in $CuLa_{1-x}Eu_xO_2$ at room temperature has been clarified to be trivalent from Mössbauer spectroscopy and the origin of the orange PL has been identified as PL lines due to magnetic transitions ($^5D_0$ - $^7F_{0,1}$ transitions) of Eu^{3+} [1].

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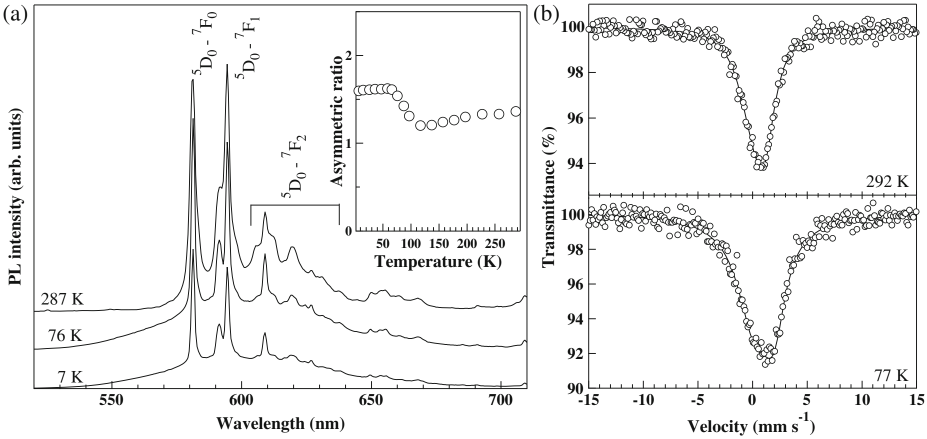


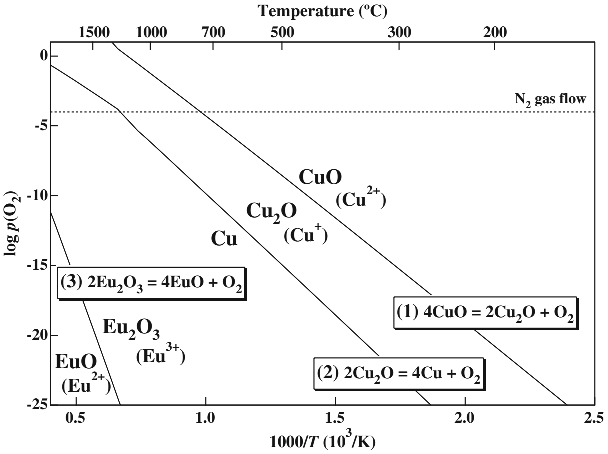
Fig. 1 **a** Photoluminescence spectra of $CuLa_{0.98}Eu_{0.02}O_2$ at 7 K, 76 K and 287 K. The asymmetric ratio is shown in the inset. **b** Mössbauer spectra of $CuLa_{0.8}Eu_{0.2}O_2$ at 292 K and 77 K

In usual Eu^{3+} containing materials, Eu^{3+} is substituted into a site without inversion symmetry due to its large ionic radius, showing a red luminescence due to an electric dipole transition ($^5D_0$ - $^7F_2$ transition). However, for $CuLa_{1-x}Eu_xO_2$, since the Eu^{3+} substitution site is the La^{3+} site in the LaO_6 octahedron with inversion symmetry, which forbids the $^5D_0$ - $^7F_2$ transition, orange PL due to the $^5D_0$ - $^7F_{0,1}$ transition was observed to be more dominant than that due to the $^5D_0$ - $^7F_2$ transition [1]. Therefore, the relative PL intensity of the $^5D_0$ - $^7F_2$ transition to the $^5D_0$ - $^7F_1$ one, which is called the asymmetric ratio, gives a measure of the degree of distortion from the inversion symmetry of the local environment of Eu^{3+} in the matrix [2]. Sharp PL lines due to the dipole transitions of $CuLa_{0.98}Eu_{0.02}O_2$ with little variation as a function of temperature between 7 K and room temperature have been observed, except for an asymmetric ratio enhancement with decreasing temperature below 100 K. This suggests that the valence of Eu would be maintained at this temperature range but that the local environment of the Eu cation might be changed. In this study, in order to analyse the valence and the local environment of the Eu cation by temperature directly, Mössbauer spectroscopy at 77 K and 292 K has been measured on $CuLa_{1-x}Eu_xO_2$. Also a thermodynamic calculation of the valence of Cu and Eu cations was performed to confirm the valence of Eu in $CuLa_{1-x}Eu_xO_2$ evaluated with Mössbauer spectroscopy.

2 Experimental

Single phase $CuLa_{1-x}Eu_xO_2$ was prepared by the solid state reaction method with sintering 1273 K for 12 h under N_2 gas flow [1]. ^{151}Eu Mössbauer spectra were measured at 77 and 292 K using γ-rays from a $^{151}Sm/SmF_3$ light source. The isomer shift was calculated with respect to that of EuF_3 as a standard. PL spectra were measured with excitation laser light of the UV line from a continuous wave He-Cd laser (325 nm) at temperatures between 7 K and 287 K.

Fig. 2 Ellingham diagram for copper oxides and eurpium oxide. The *dotted line* represents log $p(O_2)$ under N_2 gas flow



3 Results and discussion

Figure 1a shows PL spectra of CuLa$_{0.98}$Eu$_{0.02}$O$_2$ at 7 K, 76 K and 287 K. As shown in the inset, the asymmetry ratio increased abruptly at 100 K with decreasing temperature, suggesting that the octahedron in which the Eu cation was substituting for La would distort in this temperature range.

Mössbauer spectra of CuLa$_{0.8}$Eu$_{0.2}$O$_2$ at 292 K and 77 K are shown in Fig. 1b. Isomer shifts are 0.62 mm s^{-1} at 292 K and 0.68 mm s^{-1} at 77 K, which can be indexed as absorption for trivalent Eu [3]. The absorption of Eu^{2+} that should be observed around 13 mm s^{-1} [4] was not observed, indicating that the valence of Eu cation was trivalent both at 292 K and 77 K. Although it is difficult to determine the accurate quadrupole coupling constants (e^2qQ) and asymmetric parameter (η) due to rather large linewidth for the $I = 5/2$ to 7/2 transitions of ^{151}Eu, the e^2qQ and η values at 292 K are estimated to be 7.5 mm s^{-1} and 0.47, respectively. At 77 K, these values increased to 8.7 mm s^{-1} and 0.54, suggesting that the crystal structure of CuLa$_{1-x}$Eu$_x$O$_2$ might contain a distorted octahedron at low temperature, in agreement with the increase of the asymmetric ratio of the PL spectra.

Trivalent Eu in CuLa$_{1-x}$Eu$_x$O$_2$ detected with Mössbauer spectroscopy and suggested in the PL spectra also showed correspondence with a thermodynamic calculation. Figure 2 shows coexistence lines of Cu_2O/CuO [5], Cu/Cu_2O and EuO/Eu_2O_3 calculated using program MALT-2 [6]. For the preparation of CuLa$_{1-x}$Eu$_x$O$_2$, sintering was performed at 1273 K under N_2 gas flow with oxygen partial pressure, $p(O_2)$, of about 10^{-4} atm. It has been revealed that monovalent Cu and trivalent Eu were thermodynamically stable in sintering conditions, which corresponds to the observed Mössbauer spectroscopy results.

4 Conclusion

Mössbauer spectra of CuLa$_{0.8}$Eu$_{0.2}$O$_2$ at 77 K revealed that the valence of Eu is trivalent and suggested that the crystal structure of CuLa$_{1-x}$Eu$_x$O$_2$ might contain a lower symmetry site for Eu^{3+} in the octahedron, which accounts for the increase of the asymmetric ratio of PL spectra. A thermodynamic calculation elucidated the stability of Cu^+ and Eu^{3+} under the preparation conditions, in agreement with the Mössbauer spectroscopy results.

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