Electrochemical Luminescence of Rare Earth Doped $Mg_xCa_{1-x}In_2O_4$ Solid Solutions

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Introduction

The electrochemical luminescence (ECL) under the cathodic polarization has been studied by many researchers using various semiconductors. However, there are few reports on the ECL under the anodic polarization and the relationship between the structure of materials and the ECL property is not clear. In this paper, we have synthesized $MgIn_2O_4$:Ln, that shows no photo luminescence, and $Mg_xCa_{1-x}In_2O_4$:Ln and refined the structure to investigate the relationship between the structure of $Mg_xCa_{1-x}In_2O_4$:Ln and the ECL property.

Experimental

$Ca_xMg_{1-x}In_2O_4$ and $Ca_xMg_{1-x}In_2O_4$:Ln were synthesized by conventional solid-state reaction. The stoichiometric constituent components were obtained by coprecipitation method. The mixture was sintered at 800 ˚C for 10h under air. The pellets were crushed and sintered at 1400 ˚C for 12h under air again. The obtained samples were examined by X-ray diffraction (Rigaku Rotaflex 12 kW). Structural parameters were refined by Rietveld analysis with RIETAN-2000. Measurements of ECL were carried out under potentiostatic control, unless otherwise noted, in a conventional cell with a platinum counter electrode and a Ag/AgCl reference electrode in 0.5 M Na_2SO_4 solution. .

Results and discussion

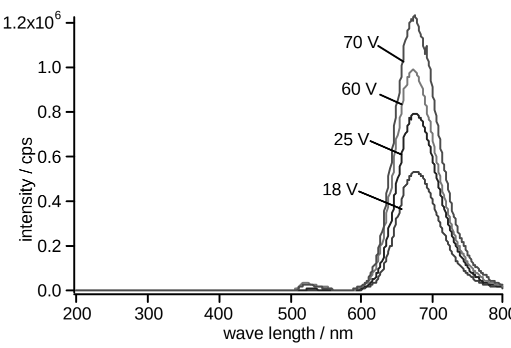
ECL of non dope $MgIn_2O_4$ was measured. Under the anodic polarization, very low current was observed because of n-type semiconductor rectifying action. A broad ECL was observed at the region from 600 nm to 800 nm over 18V (Fig. 1). The intensity of this ECL increased with the increase in the potential imposed on the semiconductor electrode. $MgIn_2O_4$:Ln (Ln: Dy^{3+}, Sm^{3+}, Ho^{3+}, Er^{3+}, Eu^{3+}, and Eu^{2+}) showed ECL spectra that are assignable to emission from rare earth metals. The lattice parameter of $MgIn_2O_4$:Er, refined by Rietveld analysis, increased in proportion to the dopant concentration. The distance between 16*d*(Mg, In)-32*e*(O) also increased with the increase in the Er^{3+} ion concentration. These results suggest that Er^{3+} ion makes solid solutions with $MgIn_2O_4$ and locates at 16*d* site of $MgIn_2O_4$.

In spite of these bright ECL at $MgIn_2O_4$:Ln electrode, $MgIn_2O_4$: Ln hardly shows photo luminescence (PL). On the other hand, ECL was not observed at $CaIn_2O_4$:Ln, that shows bright PL. To rise the ECL intensity by improving the PL host property, we have synthesized a serious of $Ca_xMg_{1-x}In_2O_4$: Er and investigated its ECL property.

$Ca_xMg_{1-x}In_2O_4$ solid solutions were obtained in the range of 0<x<0.4. ECL intensity was improved by adding Ca and indicated a peak at x=0.25, whereas the PL intensity increased with the increase in x (Fig. 2). This difference in the dependence on the Ca ratio would indicate the ECL intensity is concerned with some other properties of the host than the PL property.

References

T. Ohtake, N. Sonoyama, T. Sakata, *Chem. Phys. Lett.* , 1998, **298**, 395-399



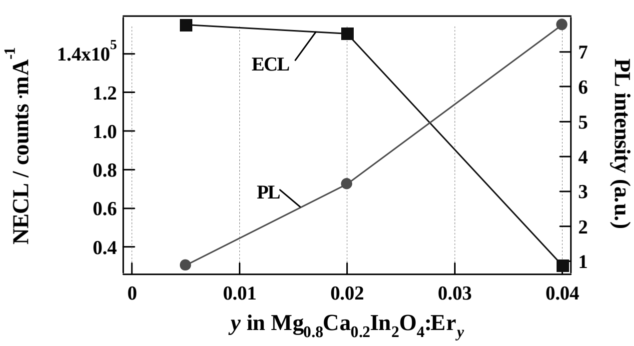


Fig.2 Er ion concentration dependence of ECL and PL intensity for $Mg_{0.8}Ca_{0.2}In_2O_4:Er_y$