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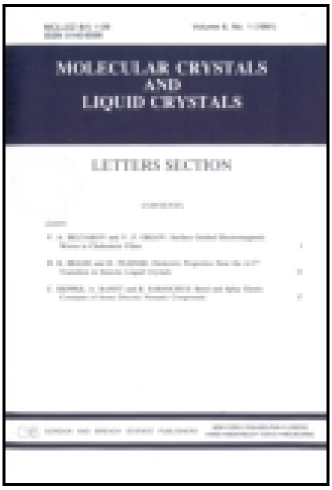

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Study on n-type Doped Electron-Transporting Layers in OLEDs by Electron Spin Resonance

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Study on n-type Doped Electron-Transporting Layers in OLEDs by Electron Spin Resonance

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We present an electron spin resonance (ESR) study of Cs_2CO_3 and LiF doped tris(8-hydroxyquinoline) aluminum (Alq_3) thin films. The g values of the Cs_2CO_3 and LiF doped Alq_3 thin films were obtained as 2.0040 and 2.0028, repectively. The g value of the LiF doped film was very close to a theoretically calculated one for an isolated Alq_3 radical anion, while Cs_2CO_3 doped film showed a large g shift. This feature can be explained by large spin-orbit interaction caused by heavy Cs atoms. While doping of Cs_2CO_3 did not showed cathode-metal (Al and Au) dependence, LiF doping required Al as cathode.

Keywords organic light-emitting diodes; electron spin resonance; doping; electron-transporting layer; charge transfer

Introduction

Electron injection is one of the key factors that determine the efficiency of organic light-emitting diodes (OLEDs). Using low work function metals such as Mg, Li, and Ca as cathode material can lower injection barrier at electron-transporting layers (ETLs). These metals are inappropriate for practical application because of their high reactivity in ambient air and alternative techniques have been introduced to obtain low injection barrier between cathodes and ETLs: insertion of a thin dopant layer between cathodes and ETLs [1,2] and coevaporation of ETL materials with dopants [3–9]. Among the dopants, alkali halides such as LiF and Cs_2CO_3 are the most frequently used materials because of their high stability in ambient air, which is an important factor for practical application. Furthermore, Cs_2CO_3 layer can be formed using solution process [10].

A photoemission spectroscopy study of the above-mentioned structures has suggested that a charge-transfer reaction between dopants and ETL materials is a main reason for the improved electron injection and transport properties [7]. The reaction results in forming radical anions of ETL materials. Electron spin resonance (ESR) spectroscopy can detect and quantify these radicals. Actually, we observed radical spins of tris(8-hydroxyquinoline) aluminum (Alq_3) in coevaporatied Alq_3:Mg samples [11,12]. In these studies, we showed

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that the actual doping concentration calculated using the number of spins obtained by ESR is not linearly correlated to coevaporation ratio in Alq$_3$:Mg system: the doping concentration tends to saturate in high Mg ratio region. Also, the analysis of the linewidth of the observed ESR spectra indicated that the observed radical species are mainly localized spins. Thus, ESR can both quantitatively and qualitatively evaluate doping effects through the spins of radicals. However, ESR investigations for various dopants except for Mg have not yet been reported, which will be extremely important for further understanding and improving the electron injection and transport properties.

In this paper, we investigate radical anions of Cs_2CO_3 and LiF doped Alq$_3$ thin films by ESR measurement in order to elucidate, via spins of radicals, what happens in doping process. Obtained ESR spectra show significantly different g values from that of Mg doped sample, which can be explained by the spin-orbit interaction of dopant atoms.

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Experimental

Doped Alq$_3$ films were prepared in a vacuum chamber under a pressure of lower than 2×10^{-4} Pa by thermally coevaporating Alq$_3$ and dopants (Cs_2CO_3, LiF) on quartz substrates. Molecular ratio (Alq$_3$:dopant) of the samples were 1:0.3 for Alq$_3$:Cs_2CO_3 and 1:10 for Alq$_3$:LiF, respectively. Subsequently, an additional metal (Al, Au) layer was deposited on the doped Alq$_3$ layer. The deposition of the metal layer was performed for the following two reasons: (i) to protect the radicals from oxygen and water, (ii) to investigate the effects of cathode metals. The thicknesses of the layers were 100 nm for the doped ETL layer and 70 nm for the metal layer, respectively. The thickness of the doped ETL layer was estimated based on the amount of Alq$_3$ that was vapor-deposited on the substrate using quartz thickness monitor. The areas of the layers were 0.84 cm^2. The fabricated samples were then placed in an ESR sample tube, and sealed under vacuum condition of approximately 6×10^{-5} Pa. ESR measurements were performed with a JEOL JES-FA200 X-band spectrometer. The absolute magnitudes of g value and ESR linewidth were calibrated using a Mn^{2+} standard marker sample.

Results and Discussion

Figure 1 shows respective ESR spectra of the Alq$_3$:Cs_2CO_3, Alq$_3$:Mg (from Ref. 10, the ratio is 1:0.5), and Alq$_3$:LiF samples when Al is used as cathode metal. We have successfully observed ESR spectra of the Cs_2CO_3 and LiF doped Alq$_3$ thin films; such ESR spectra have not yet been reported. The detection of the radical spins directly indicates the charge transfer between Alq$_3$ and the dopants. Although this charge transfer has been suggested in the Alq$_3$:Cs_2CO_3 system by other group [7], we demonstrate it from a microscopic viewpoint. Respective g value and peak-to-peak ESR linewidth ΔH_{pp} of the spectra are 2.0040 and 2.49 mT for Alq$_3$:Cs_2CO_3 sample, 2.0030 and 2.19 mT for Alq$_3$:Mg sample, 2.0028 and 1.49 mT for Alq$_3$:LiF sample.

First, we discuss the g shifts in the three samples. The g shift increases as the atomic number of the reactive metal atom in dopant increases. This tendency of the g shift can be explained by considering the spin-orbit interaction as follows: The effect of the spin-orbit interaction on the g shift is known to be proportional to a spin-orbit coupling constant λ which is again proportional to the atomic number of constituent atoms. Here, we compared the observed g values with a calculated g tensor of an isolated Alq$_3$ radical anion. The principal values of g tensor were calculated as 2.0024, 2.0029, and 2.0032 using a density functional theory [11]. In amorphous state as in the Alq$_3$ films, an apparent g value is most

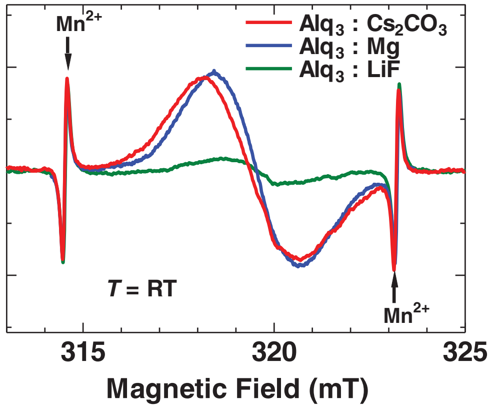

Figure 1. ESR spectra of Alq$_3$:Cs$_2$CO$_3$ (red line), Alq$_3$:Mg (blue line, from Ref. 10), and Alq$_3$:LiF (green line) samples at room temperature. The spectra include those from a Mn^{2+} standard marker. Coevaporation ratio (molecular ratio) for each sample is 1:0.3, 1:0.5, and 1:10, respectively.

likely to be the average of the three principal *g* values, ca. 2.0028. The observed *g* value of the Alq$_3$:LiF sample is close to this theoretical value. On the other hand, the *g* value of Alq$_3$:Cs$_2$CO$_3$ sample shows a significant *g* shift from the theoretical value, which is caused by heavy Cs atoms. The influence of the spin-orbit interaction of dopant atoms suggests that the wave function of an unpaired electron spreads out to the dopant molecules to some extent. The previous research based on photoemission spectroscopy also pointed out the existence of a substantial chemical reaction between Alq$_3$ and Cs$_2$CO$_3$ [7].

Next, we discuss the effect of the cathode metals. The ESR spectrum of Alq$_3$:LiF sample was disappeared when Au was used as cathode metal. Note that pure Alq$_3$ thin films with cathode metal of Al and Au do not show any significant ESR signal. Previous works have shown that LiF can be decomposed into Li atoms through a reaction $3\text{LiF} + \text{Al} = \text{AlF}_3 + \text{Li}$, and that the formation of n-doped Alq$_3$ by released Li atoms is the main mechanism of the doping process [13,14]. Ref. 14 also shows that LiF does not react with Au. Therefore, we reasonably conclude that the LiF doping occurs only when Al is adjacent to LiF and Alq$_3$. This is probably the reason why the ESR spectrum of the Alq$_3$:LiF sample is small compared to other samples because the doping only occurs at interface between Alq$_3$:LiF and Al layer. On the other hand, the ESR spectra of Alq$_3$:Cs$_2$CO$_3$ remain unchanged when cathode metal was changed from Al to Au. Thus, we conclude that Cs$_2$CO$_3$ itself can react with Alq$_3$ molecule without cathode metals.

Summary

We have investigated radical anion states of n-doped Alq$_3$ thin films using ESR spectroscopy. We have successfully observed ESR spectra of Cs$_2$CO$_3$ and LiF doped Alq$_3$ thin films. The detection of radical spins is a direct evidence for the charge-transfer reactions between Alq$_3$ and dopants. The observed *g* shifts depend on the dopants, which can be explained by the spin-orbit interaction introduced by dopant atoms. The ESR spectrum of the LiF doped sample was disappeared by changing the cathode metal from Al to Au, whereas the Cs$_2$CO$_3$ doped sample did not show the cathode-metal dependence. Thus, ESR spectroscopy can offer the information of doping process in detail from a microscopic viewpoint.

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