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THERMAL CHANGE OF Alq_3, TRIS(8-HYDROXYQUINOLINATO) ALUMINUM(III) STUDIED BY TG AND XRD-DSC

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The thermal change of the tris(8-hydroxyquinolinato)aluminum (Alq_3) is currently investigated by XRD-DSC and TG. The phase transition of Alq_3 from α-phase to γ-phase takes place at 643–669 K. A very sharp peak with the peak temperature at approx. 709 K is ascribed to the melting of the Alq_3. The decomposition of the Alq_3 was observed accompanied with the melting and evaporation at >703 K. The effect of the atmospheres on the mass loss procedure was studied by TG. It was found that thermal process of Alq_3 was strongly influenced by the partial pressure of water vapor in the atmosphere instead of oxygen.

Keywords: *Alq_3, mass loss, phase change, TG, XRD-DSC*

Introduction

Organic light emitting devices (OLEDs) are presently under intense investigation as the next generation displays and illuminators of the high brightness, wide view angle and flexibility [1–4]. Tris(8-hydroxyquinolinato)aluminum(III) (Alq_3, $C_{27}H_{18}AlN_3O_3$) has shown to be one of the most promising material for the fabrication of OLEDs. It is used as electron-transporting layer, as emission layer where green light emission is generated by electron-hole recombination in Alq_3, and it also serves as host material for various dyes to tune the emission colour from green to red [5]. Many studies in this field have focused on the optimisation of device performance with respect to efficiency and long-term stability or on the understanding of charge transport properties of amorphous thin films [6–10]. However, thermal change of Alq_3 is few reported as far as we know. Clarification of thermal change of Alq_3 is necessary to understand the phase transition, the impurity and the degradation, and to control the purification (sublimation) and film deposition process. Various phases of Alq_3 were discovered by the research group of Cölle and Brütting [11, 12]. The thermal conductivity of Alq_3 was determined by measuring its thermal diffusivity and specific heat [13]. The thermal stability of Alq_3 was discussed with the use of gas chromatography/mass spectroscopy (GC/MS) at elevated temperatures and a chemical degradation mechanism for Alq_3 has been published [14, 15]. But the reports of thermal analyses of Alq_3 seem extremely insufficient in spite of the strong industrial importance. Present work reports thermal change of Alq_3 in inert gas atmospheres (helium or nitrogen with and without water vapour) using TG and XRD-DSC (simultaneous measurement of X-ray diffraction and DSC).

Experimental

Alq_3 sample

The light yellow Alq_3 powder was purchased from OHJEC Corporation, and used without further purification.

XRD-DSC analysis

The high temperature crystal structures of the specimen were confirmed by Rigaku XRD-DSC (DMAX (RINT)/ULTIMA$^+$ PC series and Thermo Plus DSC 8230). Approximately $1\cdot10^{-5}$ kg specimen was weighed into an open aluminum crucible ($7\cdot7\cdot0.25\cdot10^{-9}$ m^3), and was heated with the heating

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rate of 10 K min^{-1} in high-purity N_2 with a flow rate of $1\cdot10^{-4}$ m^3 min^{-1}. Alumina was used as the reference material for the DSC. A line shaped copper X-ray source was operated at 40 kV and 40 mA and the data were collected in the range of $2\theta=3$ to 39.5° and 3 to 8.5° with an interval of 0.01° and a scan speed of 10 and 5° min^{-1}, respectively.

TG and SCTG analysis

TG was performed by a Rigaku Thermo Plus 8120D system. The specimen approximately $1\cdot10^{-5}$ kg was weighed into an open aluminum pan, and was heated up to 773 K with heating rate of 10 K min^{-1} in He, He+20% O_2 and static air with a flow rate of $1\cdot10^{-4}$ m^3 min^{-1}. In the TG experiments, to ignore adsorptions of Alq_3 on the reference material such as α-Al_2O_3, only an empty aluminum pan was used as reference.

The special type of TG apparatus equipped with SCTG mode and coupled with a humidity generator (Model HUM-1, Rigaku) was used to investigate thermal process of Alq_3 in nitrogen atmospheres of various partial pressures of water vapor. The specimen mass of ca. $1\cdot10^{-5}$ kg was weighted into an aluminum crucible, and was heated up to 773 K in dry nitrogen of controlled humidity, with a flow rate of $3\cdot10^{-4}$ m^3 min^{-1}.

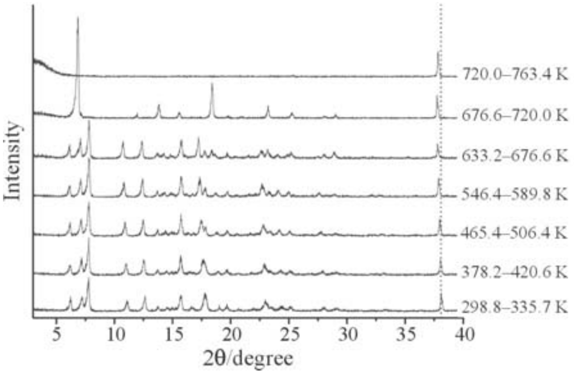

Fig. 1 XRD spectroscopy of Alq_3 from room temperature to 773 K

Results and discussion

Phase transition

Temperature has a strong influence on the formation of phases of Alq_3 and it is important to learn more about the thermal properties of Alq_3. Therefore the formation of the different phases of Alq_3 was investigated using simultaneous XRD-DSC. Figure 1 shows X-ray powder diffraction spectra of Alq_3 under different temperature. The specimen as received was confirmed to be the mainly well known α-Alq_3 [16] at the room temperature. However, the positions of the peaks shift a little with the temperature because of the thermal expansion. A phase transition from α to γ-Alq_3 takes place at high temperature, which is in agreement with our previous work [17]. After the phase transition a broad peak appears at low angle are due to the amorphous residue in the specimen pan. The diffraction peak at around 38.16° for 2θ is attributed to the aluminum used as a sample container.

In the XRD data the phase transition process is not clear because the temperature increases about 40 K during one scan. From the DSC curve in the Fig. 2, a sharp endothermic peak (peak temperature; 709.3 K) was observed in the temperature range from 703.8 to 715.4 K, which is assigned to the melting of Alq_3. But no any indication shows on the XRD spectroscopy. Cölle *et al.* [11] reported that increasing the temperature above 703 K results in decomposition of the Alq_3. In order to investigate the phase transition,

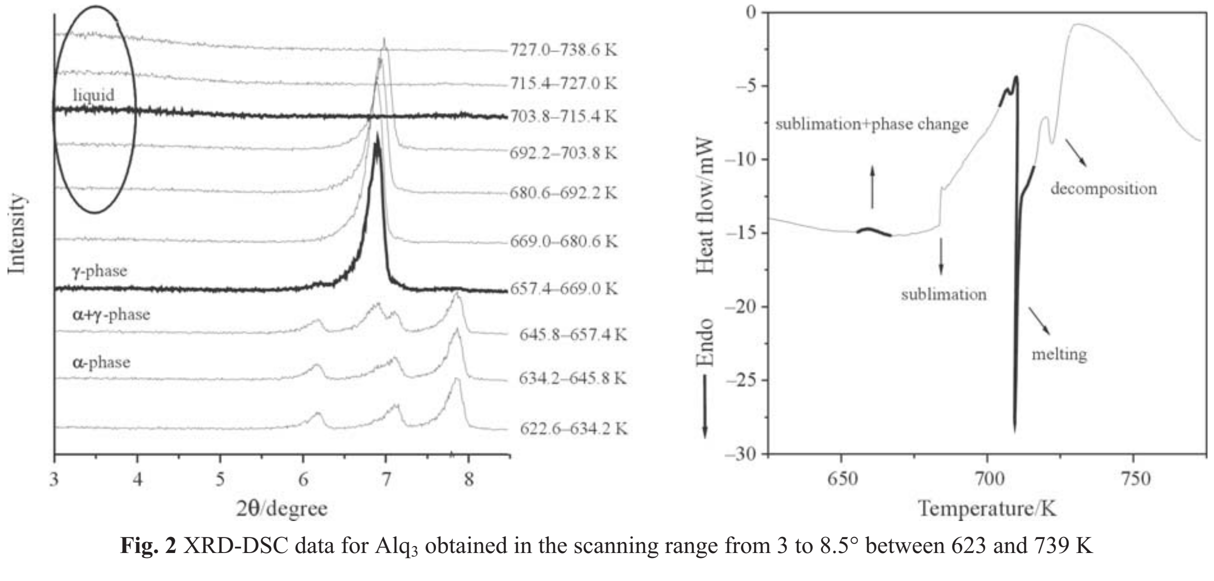

Fig. 2 XRD-DSC data for Alq_3 obtained in the scanning range from 3 to 8.5° between 623 and 739 K

melting and decomposition of the specimen precisely, we choose some diagnostic peaks in a narrow range from 3 to 8.5° as the scanning object with the scanning speed of 5° min^{-1}. This means the change of sample temperature during each XRD scan corresponds to approx. 10 K. The XRD pattern and DSC curve of Alq_3 during heating at a rate of 10 K min^{-1} from 623 to 739 K are shown in Fig. 2. From the XRD pattern, a weak peak of γ phase was observed together with the α phase peaks at 645.8 to 657 K and then the intensity of γ-Alq_3 becomes gradually stronger until the 669 K. A very small exothermic peak appears between 655 and 667 K on the DSC curve can be detected, which is corresponding to the phase transition. Due to the phase transition process accompanied with the sublimation of the specimen, the exothermic phenomenon is not obvious. The intensity of γ-Alq_3 decreases gradually with the sublimation of the specimen and disappears at 703 K. Almost no diffraction peak is observed in the temperature of 703.8~715.4 K and at the same time a very sharp peak with the peak temperature of 709.3 K shows on the DSC curve. Those two evidences make us confirm that the specimen is melted. Another endothermic peak appears with the peak temperature of 721.8 K that is caused by the decomposition of specimen according to the report of Cölle. Due to the intensity of the amorphous residue is low; we enlarge the elliptical part of Fig. 2 and represent it in the Fig. 3. It can be seen that the amorphous residue appears from 703.8 K during the melting of the specimen and its intensity increases with the temperature and reaches to a constant value at 738.6 K.

Thermal process in various atmospheres

Figure 4 is the TG curves of Alq_3 in He, He+20% O_2, static air, dry N_2+9.9·10^3 Pa H_2O and dry N_2 atmospheres. The thermal process was strongly influenced by the atmospheres. Monotonous single mass loss curve was observed and the sample was almost eliminated completely in dry nitrogen atmosphere. The TG curves are similar in He, He+20% O_2, static air, and dry N_2 atmosphere except for the mass loss. The total mass loss decreases in the order of static air >He +20% O_2>He>dry N_2, which suggests that the water vapor and the oxygen have effect on the thermal process of Alq_3. However, the beginning mass loss temperature (~513 K) in the dry N_2+9.9·10^3 Pa H_2O atmosphere is 60 K lower than that (~573 K) in other atmospheres. Two-step mass loss curve was observed, which the mass losses were 80 and 7%, respectively. The TG results in various atmospheres suggest the thermal process of Alq_3 was changed mainly by the partial pressure of water vapor, but not influenced by oxygen atmosphere. This conclusion is in agreement with the degradation mechanism of Alq_3 [14, 15].

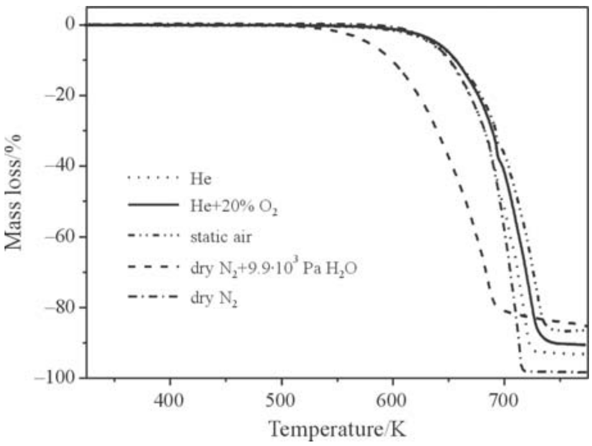

Fig. 4 TG curves of Alq_3 in different atmospheres

Figure 5 shows a comparison of the TG curves for Alq_3 at 10 K min^{-1} in nitrogen atmosphere of various partial pressures of water vapor (P_{H_2O}≤0.9, 2.4, 3.7 and 9.9·10^3 Pa). The thermal process was strongly influenced by the partial pressure of water vapor in the atmosphere. With increasing the partial pressure of water vapor, the total mass loss decreased and the

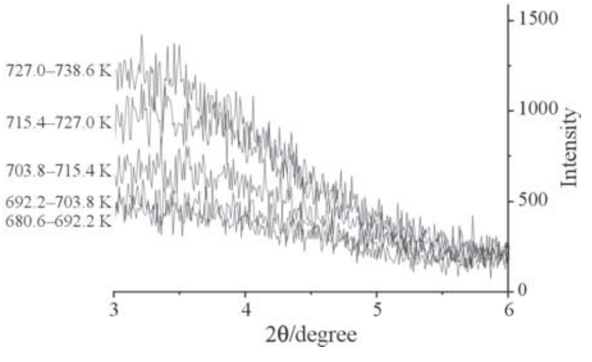

Fig. 3 Enlarged XRD spectroscopy of Alq_3 in lower diffraction angle with the temperature

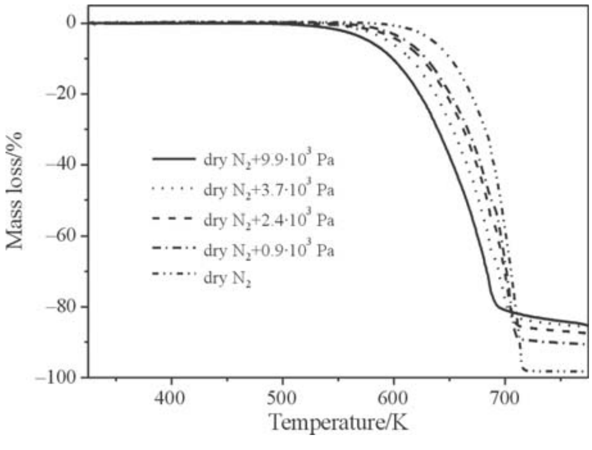

Fig. 5 TG curves for Alq_3 in nitrogen atmospheres of various partial pressures of water vapor

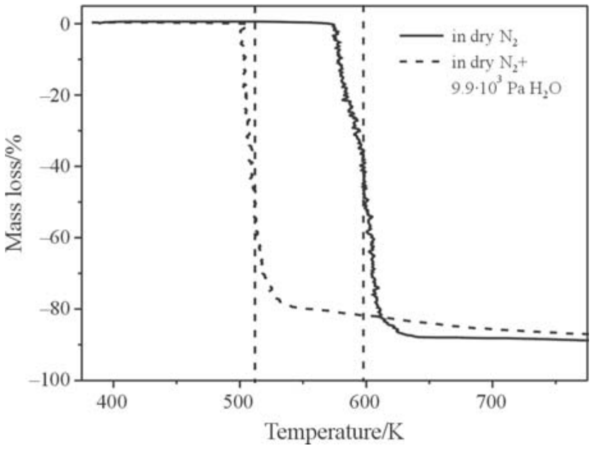

Fig. 6 Mass loss curves of Alq$_3$ by SCTG of 0.06% min^{-1} between dry nitrogen and nitrogen atmosphere of controlled humidity (P_{H_2O}=9.9·10^3 Pa)

apparent mass loss curves shifted gradually toward lower temperature region.

To elucidate the reaction of water vapor with Alq$_3$, SCTG is useful because the high-temperature sublimation is inhibited by controlling the mass loss rate. Figure 6 illustrates a comparison of both the SCTG curves by a constant mass loss rate of 0.06% min^{-1} in the different heating atmospheres of dry nitrogen and in nitrogen of controlled humidity (P_{H_2O}=9.9·10^3 Pa). Two-step mass loss curve was observed in SCTG in dry nitrogen atmosphere; 1st and 2nd stages were 28 and 62%, respectively. The mass loss was attributed to the sublimation of the Alq$_3$ and the discontinuous of the SCTG was tentatively ascribed to the phase transition from α to γ phase caused by temperature increase during the long time heating process. On the other hand, the SCTG in the atmosphere of controlled humidity was shown a continuous mass loss step. The curve was markedly shifted to lower temperature sides around 513 K, which indicates the mass loss was caused by the reaction of Alq$_3$ with water vapor instead of the sublimation. The reaction process will be investigated by SCTG-MS in the near future.

Conclusions

Using TG and XRD-DSC measurements the thermal change of Alq$_3$ was investigated. The specimen composes of mainly α-Alq$_3$ at the room temperature and has a phase change from α to γ-Alq$_3$ at about 663 K. The α- and γ-Alq$_3$ co-exist in the temperature range of 643~669 K. From the XRD spectroscopy and DSC curve, the melting of the Alq$_3$ can be observed. The evaporation, melting and the decomposition of the Alq$_3$ happened at the same time at temperature >703 K. The thermal process of Alq$_3$ in different atmospheres indicates that partial pressure of water vapor was the main reason caused the change of Alq$_3$ instead of oxygen.

Acknowledgements

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