

# Wavelength conversion film with glass coated Eu chelate for enhanced silicon photovoltaic cell performance

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## Abstract

In order to improve the conversion efficiency of a silicon-photovoltaic (PV) module, we investigated the combination with a wavelength conversion film (WCF), which consists of Eu chelate particles encapsulated by the sol-gel derived silica glass. The photoluminescence (PL) excitation spectrum of Eu chelate shows that the violet light below 400 nm is effectively converted to the red emission at 613 nm. Since the PV cell has higher sensitivity at the red wavelength region compared to the violet region, Eu chelate is one of the suitable material for a WCF. The diameter of fabricated sol-gel encapsulated Eu chelate was larger than the wavelength of irradiated sunlight, therefore, the transmittance of a WCF decreased with increasing the concentration of Eu chelate. The short circuit current ( $J_{SC}$ ) was increased by inserting the the WCF on the front side of Si-PV cell compared to the reference module (glass/ethylene vinyl acetate/WCF without Eu chelate/Si-PV cell/EVA/back-film), and the maximum increase of  $\Delta J_{SC}$  was 1.03 mA/cm<sup>2</sup> compared to the reference module. However, the maximum  $\Delta J_{SC}$  of fabricated module was almost same as the conventional Si-PV cell due to the refractive index mismatch of each layers.

*Key words:* Silicon-photovoltaic cell, Wavelength conversion film, Eu

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## 1. Introduction

A silicon (Si)-photovoltaic (PV) module efficiently converts a sunlight to an electrical output, and has been already in practical use in all over the world. This is because that Si has many advantages against other photoconductive materials for PV cells, such as abundance in earth, non-toxicity and ease to encapsulate. Generally, a Si-PV cell has lower sensitivity at violet and infrared wavelength regions compared to the visible region [1, 2, 3]. One of the key technique to improve the spectral mismatch between the photocurrent spectrum of a Si-PV cell and the spectrum of a sunlight is the wavelength conversion film (WCF), which consists of the up-conversion phosphors [4, 5, 6, 7]. The wavelength conversion efficiency of an up-conversion phosphor is not so high [8, 9], therefore, the enhancement effect to the conversion efficiency of a Si-PV module will be considered to be small. On the contrary, the photoluminescence (PL) at the visible light by the ultraviolet light excitation has high wavelength conversion efficiency compared to the up-conversion phosphor, and it enables to improve the Si-PV module performance.

Eu chelate has considerable promise as a light-emitting material for a WCF due to the high PL quantum efficiency by the ultraviolet excitation. Though the typical transition of trivalent Eu ion generates red emission [10, 11], a concentration quenching of Eu ion limits the available total emission intensity. Eu chelate, such as  $\text{Eu}(\text{TTA})_3\text{phen}$  [TTA: thenoyltrifluoronacetone, phen: 1,10-phenanthroline], improves the absorption coefficient per each Eu ion, and reduces the concentration quenching due to the inter-molecular interaction [12]. Therefore, Eu chelate has much attention for several applications such as white light-emitting diode and an organic light-emitting diode [13].

In comparison with conventional inorganic phosphors, on the other hand, the robustness of organic molecules is lower due to the bond strength of molecules fundamentally. In previous papers, organic-inorganic hybridized light-emitting devices were investigated to improve the device performance compared to the all organic device [14, 15, 16]. In addition, an encapsulation against ambient oxygen and water by sol-gel derived inorganic materials is one of crucial technological issues for practical applications [17, 18, 19, 20]. The sol-gel process is of great interest and has been considered as an excellent candidate for the preparation of inorganic-organic composite materials

in recent years due to its practical advantages including a low-temperature reaction, the ability to control the final composition and the convenience for the formation of various shapes. The conventional sol-gel method is based on hydrolysis and condensation of organoalkoxides as starting materials with the aid of catalyst, water and alcohol. Since the solution is homogeneous and the condition of such chemical synthesis is mild without the need for a high temperature process, it provides a versatile way to introduce  $\text{Eu}(\text{TTA})_3\text{phen}$ , thus fabricating inorganic-organic hybridized functional materials.

In this study, we investigated the PL and PL excitation (PLE) spectroscopic characteristics of  $\text{Eu}(\text{TTA})_3\text{phen}$  encapsulated by sol-gel derived silica glasses. In order to estimate the dependence of sol-gel encapsulated Eu chelate on the device performance, we measured the particle size of sol-gel encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  and the transmittance of a WCF. We achieved the improvement in the short circuit current the Si-PV module by inserting the WCF with sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  particles.

## 2. Experimental

At first,  $\text{Eu}(\text{TTA})_3\text{phen}$  was dissolved into *N,N*-Dimethylformamide (DMF) with stirring for 30 minutes at room temperature. And then, tetraethoxysilane (TEOS), ethanol and distilled water were also mixed into another bottle. Both solutions were put together into a bottle and stirred for 30 minutes. The catalyst of  $\text{NH}_3$  was added into the bottle to start the sol-gel reaction. The mole ratio of TEOS:DMF:ethanol:distilled water: $\text{NH}_3$ : $\text{Eu}(\text{TTA})_3\text{phen}$  was 1:4:4:4:0.01:0.05. After stirring for more than 5 hours, flake-like precipitates were found, and then the reaction mixture was poured into Teflon tray to dry with 120 °C oven for more than 5 hours. The dried material was broken with an agate mortar.

The fabricated sol-gel encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  particles were mixed into the high refractive acryl resin as the WCF. The acryl polymer was synthesized as follows. At first, toluene was poured into the separable flask equipped reflux condenser at 70 °C. Fluorene based acryl monomer and an initiator, 2,2'-azobisisobutyronitrile, was dissolved into toluene, then the mixture was added drop-wise into the separable flask with taking for more than 30 minutes. The solution was stirred for 3-5 hours until increasing the viscosity. After cooling down to the room temperature, two-functional acryl oligomer, multi-functional monomer and an initiator, 2,5-dimethyl-2,5-

di(tert-butylperoxy)hexane, were added to the flask to obtain a thermosetting polymer solution mixture.

The mixture containing the sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  was dropped onto a transparent film, and was coated with an applicator adjusting the gap at 8 mil. And then, the coated film was dried at 120 °C for 10 minutes. The thickness of a fabricated film was typically 50  $\mu\text{m}$ . Above-mentioned sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  was added to the thermosetting polymer solution mixture with varying the amount from 0 to 2 wt%. The structure of PV module was cover glass/ethylene vinyl acetate (EVA)/WCF/Si-PV cell/EVA/back-film, as shown in Fig. 1. The lamination film was covered by a PV vacuum laminator on the top of a back-film. The lamination condition was 150 °C for 10 minutes in vacuum and 15 minutes in pressure of 0.1 MPa.

PL and PLE spectra of WCF were measured by a luminance spectrometer (FluoroMax-3, Horiba Jovin Yvon). The wavelength of monitoring in PLE and that of excitation in PL were 613 and 400 nm, respectively. To investigate the influence of the process condition on the optical characteristics of  $\text{Eu}(\text{TTA})_3\text{phen}$  encapsulated by sol-gel glass, the PL quantum yield of a WCF was measured by a luminance quantum yield measurement system (QEMS-2000, Systems Engineering Inc.), which consists of a calibrated integrated sphere and an exciting violet light source with the center wavelength of 365 nm. The PL quantum yield was determined as the photon number ratio of the PL to the absorption in the calibrated integrating system. In order to estimate the amount of scattering owing to  $\text{Eu}(\text{TTA})_3\text{phen}$  particles, the transmittance of the WCF was recorded by a haze meter (NDH-200, Nippon Denshoku). The diameter distribution of sol-gel encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  dissolved in toluene was measured by a dynamic light scattering method by a laser diffraction particle size analyzer (LS 13 320, Beckman Coulter Inc.). PV characteristics were measured by a solar simulator (WACOM, WXS-155S-10, AM1.5G) with AM1.5 (1000  $\text{mW}/\text{m}^2$ ) and the I-V curve tracer (EKO, MP-160).

### 3. Results and discussion

Figure 2 shows PL and PLE spectra of  $\text{Eu}(\text{TTA})_3\text{phen}$  encapsulated by the sol-gel derived silica glass. The luminous transition of  $\text{Eu}(\text{TTA})_3\text{phen}$  originates from  $^5\text{D}_0$ - $^7\text{F}_J$  ( $J=0, 1, 2, 3$ ) in  $\text{Eu}^{3+}$  [10, 11]. The experimental result in Fig. 2 showed a distinct peak of  $^5\text{D}_0$ - $^7\text{F}_2$  transition of 613 nm

in the PL spectrum, resulting in the high color-purity as a red wavelength region. In addition, the PLE spectrum rapidly increased less than 400 nm region, and this result indicates that only the violet light is converted to the red emission. As a result, the visible light passes through the WCF with  $\text{Eu}(\text{TTA})_3\text{phen}$  particles, and it reaches the Si-PV cell without the optical loss. The Si-PV cell has little sensitivity at the violet wavelength region less than 400 nm [1], therefore, the red emission due to the  $\text{Eu}(\text{TTA})_3\text{phen}$  suggests the assumption of the increase the device performance.

In Fig. 3, we show the PL quantum yield of the WCF with sol-gel derived silica glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  particles as a function of the concentration in the high refractive acryl resin. The PL quantum yield increased with increasing the concentration of sol-gel encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ , and the maximum PL quantum yield of 64 % was achieved at the concentration of 15 %. This result indicates that the acryl resin has absorption at the excitation wavelength of 365 nm, resulting in the high PL quantum yield at the high concentration. In all the concentrations, the PL quantum yield was over 20 %, and the violet light is efficiently converted to the red emission. It is noted that the concentration quenching of  $\text{Eu}(\text{TTA})_3\text{phen}$  was not observed less than the concentration less than 16 wt%, implying a high total emission intensity from the WCF utilizing the large amount of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  in the WCF, as shown in Fig. 3. In addition, the WCF became clouded at the concentration over 16 wt%.

Figure 4 shows the straight and integrated transmittance of WCFs with different concentrations of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ . A halogen lamp was used as a light source to measure the transmittance. Both straight and integrated transmittance decreased with increasing the concentration due to the Rayleigh scattering. In addition, we show the diameter distribution of sol-gel encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  measured by a dynamic light scattering method in Fig. 5. As is evident from Fig. 5, the typical diameter of sol-gel encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  was 48  $\mu\text{m}$ , which is larger than the wavelength of incident light. Such a large particle size is considered to cause the decrease in the transmittance of a WCF with increasing the concentration of  $\text{Eu}(\text{TTA})_3\text{phen}$  particles. The long reaction time of sol-gel process more than 5 hours caused the large particle size in our experiment, therefore, the optimization of reaction time is necessary for further improvement in the transmittance against the visible light.

Figure 6 shows the improvement in the short circuit current ( $\Delta J_{SC}$ ) of a Si-PV module in combination with the WCF including different concen-

trations of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  particles. Here,  $\Delta J_{SC}$  was calculated as the difference between  $J_{SC}$  of Si-PV module with the WCF and  $J_{SC}$  of Si-PV cell before encapsulating as the module structure. In addition,  $\Delta J_{SC}$  of reference module at the concentration of 0 % was defined as 0, and the concentration dependence of  $\Delta J_{SC}$  was calculated as the difference in  $\Delta J_{SC}$  between 0 and each concentrations to compare the reference module without sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  particles. It is noted that  $\Delta J_{SC}$  increased with increasing the concentration of sol-gel encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  up to 2 %, and the maximum increase of  $\Delta J_{SC}$  was  $1.03 \text{ mA/cm}^2$  compared to the reference module. Since the PL quantum yield increased with increasing the concentration, as shown in Fig. 3, the total emission intensity of the WCF linearly increases with increasing the concentration of  $\text{Eu}(\text{TTA})_3\text{phen}$ . Therefore, the experimental result in Fig. 6 offers evidence that the improvement of  $\Delta J_{SC}$  was caused by the increase in the total emission intensity from the  $\text{Eu}(\text{TTA})_3\text{phen}$  particles. On the contrary,  $\Delta J_{SC}$  tended to decrease at the high concentration region. The transmittance of the WCF decreased with increasing the concentration of Eu chelate, as shown in Fig. 4, owing to the large particle size. In a viewpoint of the transmittance of a WCF, the high transmittance due to the low concentration is required, however, the high concentration in  $\text{Eu}(\text{TTA})_3\text{phen}$  generates strong red emission, resulting in the high module performance.

The maximum  $\Delta J_{SC}$  of fabricated module was almost same as the conventional Si-PV cell. The possible reason of this experimental result is that the refractive index mismatch of each layers, and the incident light is reflected at the interface between the high and low refractive index layers. As a result, a part of incident light cannot reach the Si-PV cell. The WCF was consisted of the acryl layer on a polyethylene terephthalate (PET) film with a high refractive-index of 1.6. The decrease of  $\Delta J_{SC}$  of reference module by inserting only the acryl layer on the PET film was approximately  $1 \text{ mA}^2$ . This result indicates that 4 % of the incident light was not used for the optical-electrical conversion in the Si-PV cell due to the reflection at the interface of each layer.

If the scattering loss owing to the Eu chelate is ignored,  $\Delta J_{SC}$  is considered to increase with increasing the concentration of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ . We can achieve the increase in  $\Delta J_{SC}$  of  $5 \text{ mA/cm}^2$  at the concentration of 10 wt.%. However, it is difficult to realize due to the aggregation of Eu chelate.

#### 4. Conclusion

We demonstrated the Si-PV module in combination with the WCF including the sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ , which has the high luminance red emission with the near violet excitation. The  $\Delta J_{SC}$  increased constantly with increasing  $\text{Eu}(\text{TTA})_3\text{phen}$ , and it decreased over 2 wt% owing to the scattering of  $\text{Eu}(\text{TTA})_3\text{phen}$  particles. Since the physical size of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  was approximately 48  $\mu\text{m}$ , the large scattering loss caused the decrease in  $\Delta J_{SC}$  at the high concentration region. However, the  $\Delta J_{SC}$  of all the modules were lower than the conventional module owing to the refractive index mismatch of each layers. The use of acryl resin with low absorption coefficient at the excited light and the optimized device structure is one of the useful way for further improvement in the efficiency of the Si-PV module.

#### References

- [1] C. Strümpel, M. McCann, G. Beaucarne, V. Arkhipov, A. Slaoui, V. Švrček, C. del Cañizo, I. Tobias, *Solar Ener. Mater. Solar Cells* 91 (2007) 238-249.
- [2] M. Kondo, T. Matsui, Y. Nasuno, H. Sonobe, S. Shimizu, *Thin Solid Films* 501 (2006) 243-246.
- [3] T.V. Torchynska, A.V. Hernandez, G. Polupan, S.J. Sandoval, M.E. Cueto, R.P. Sierra, G.R.P. Rubio, *Thin Solid Films* 492 (2005) 327-331.
- [4] T. Trupke, A. Shalav, B.S. Richards, P. Würfel, M.A. Green, *Solar Ener. Mater. Solar Cells* 90 (2006) 3327-3338.
- [5] A. Shalav, B.S. Richards, M.A. Green, *Solar Ener. Mater. Solar Cells* 91 (2007) 829-842.
- [6] S.T. Bailey, G.E. Lokey, M.S.Hanes, J.D.M. Shearer, J.B.McLafferty, G.T. Beaumont, T.T. Baseler, J.M. Layhue, D.R. Broussard, Y.-Z. Zhang, B.P. Wittmershaus, *Solar Ener. Mater. Solar Cells* 91 (2007) 67-75.
- [7] E.K. Klampaftis, D. Ross, B.S. Richards, *Solar Ener. Mater. Solar Cells* (in press doi:10.1016/j.solmat.2009.02.020).

- [8] J. Méndez-Ramos, V.K. Tikhomirov, V.D. Rodríguez, D. Furniss, J. Alloys Compd.440 (2007) 328.
- [9] D. Matsuura, T. Ikeuchi, K. Soga, J. Lumin. 128 (2008) 1267-1271.
- [10] K. Binnemans, P. Lenaerts, K. Driesen, C. Görller-Walrand, J. Mater. Chem. 14 (2004) 191-195.
- [11] R. Reifeld, J. Electrochem. Soc. 131 (1984) 1360-1364.
- [12] H. Li, S. Inoue, K. Machida, G. Adachi, Chem. Mater. 11 (1999) 3171-3176.
- [13] C. Adachi, M.A. Baldo, S.R. Forrest, J. Appl. Phys. 87 (2000) 8049-8055.
- [14] L.D. Carlos, R.A.S. Ferreira, V.Z. Bermudez, and S.J.L. Ribeiro , Adv. Mater. 21 (2009) 509-534.
- [15] T. Fukuda, B. Wei, E. Suto, M. Ichikawa, Y. Taniguchi, Phys. Stat. Sol. (RRL) 2 (2008) 290-292.
- [16] K. Morii, M. Ishida, T. Takashima, T. Shimada, Q. Wang, M.K. Nazeeruddin, M. Grätzel, Appl. Phys. Lett. 89 (2006) 183510.
- [17] W. Streck, J. Sokolnicki, J. Legendziewicz, K. Maruszewski, R. Reifeld, T. Pavich, Opt. Mater. 13 (1999) 41-46.
- [18] L.C. Cides da Silva, T.S. Martins, M.S. Filho, E.E.S. Teotônio, P.C. Isolani, H.F. Brito, M.H. Tabacniks, M.C.A. Fantini, J.R. Matos, Micro. Meso. Mater. 92 (2006) 94-100.
- [19] V. Bekiari, G. Pistolis, P. Lianos, Chem. Mater. 11 (1999) 3189-3195.
- [20] H. Peng, C. Wu, Y. Jiang, S. Huang, J. McNeill, Langmuir 23 (2007) 1591-1595.

## Figure captions

Figure 1 The schematic configuration of the PV cell in combination with the WCF. The sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$  was mixed into the WCF.

Figure 2 PL and PLE spectra of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ . The wavelength of monitoring in PLE and that of excitation in PL were 613 and 400 nm, respectively.

Figure 3 The PL quantum yield of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ . The wavelength of excited light was 365 nm.

Figure 4 The straight and integrated transmittance of WCFs with different concentrations of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ .

Figure 5 The diameter distribution of  $\text{Eu}(\text{TTA})_3\text{phen}$  encapsulated by the sol-gel glass measured by a dynamic light scattering method.

Figure 6 The relationship between the concentration of  $\text{Eu}(\text{TTA})_3\text{phen}$  encapsulated by the sol-gel glass and  $\Delta J_{SC}$  of the PV cell.

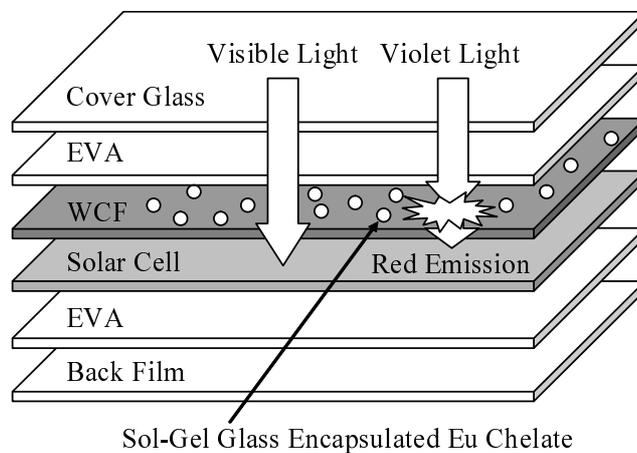


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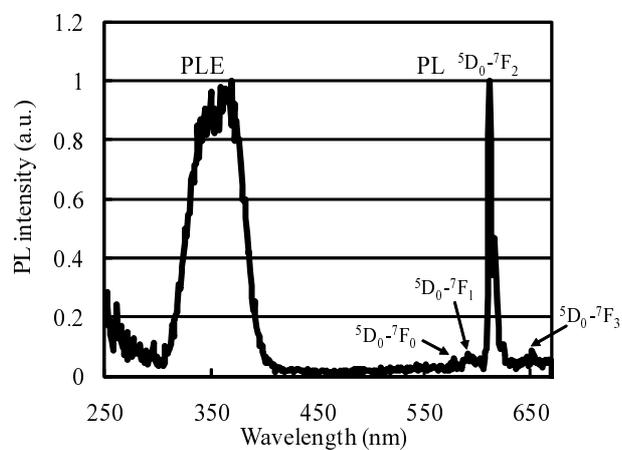


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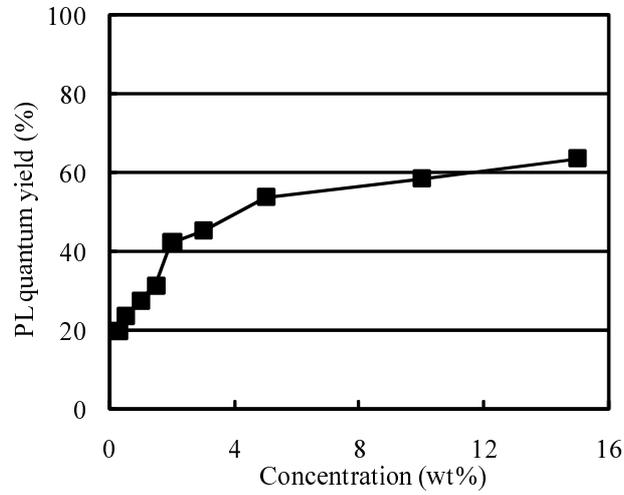


Figure 3: The PL quantum yield of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ . The wavelength of excited light was 365 nm.

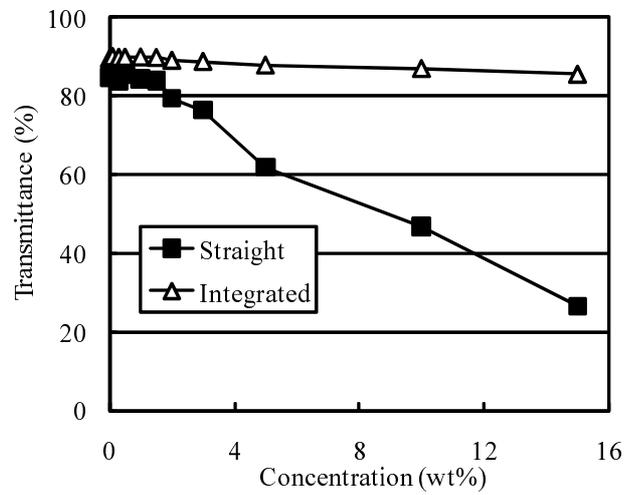


Figure 4: The straight and integrated transmittance of WCFs with different concentrations of sol-gel glass encapsulated  $\text{Eu}(\text{TTA})_3\text{phen}$ .

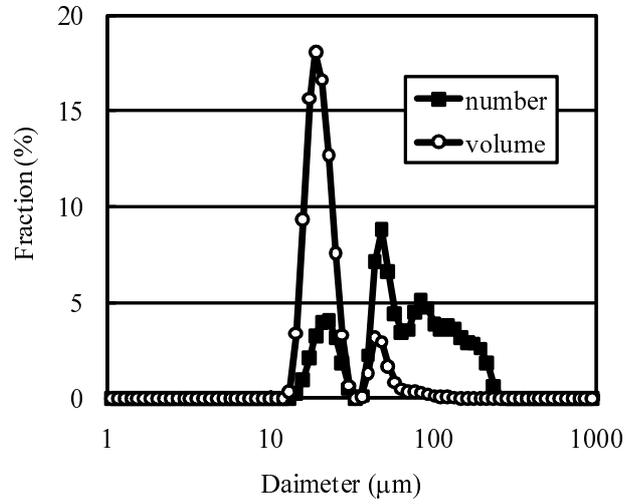


Figure 5: The diameter distribution of  $\text{Eu}(\text{TTA})_3\text{phen}$  encapsulated by the sol-gel glass measured by a dynamic light scattering method.

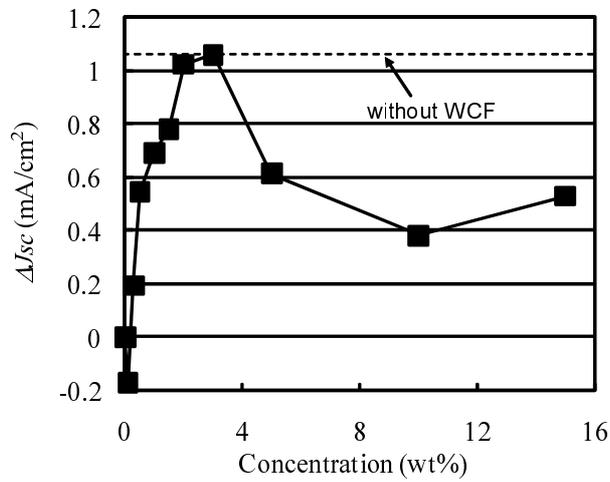


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