

Luminescent Characteristic of Organic Compound-Containing Inorganic Crystal at Room Temperature

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Abstract

The luminescent functional crystal was produced by the organic guest molecules conformation control in the inorganic host crystal matrix. Inorganic host-organic guest crystals were successfully prepared and luminescence spectra were investigated. These crystals had a phosphorescent property in room temperature by 254 nm UV irradiation. In this system, the potassium sulfate host matrix was effectively inhibited the molecular vibration of organic guest molecules by interaction between K^+ and π -electrons. In addition, control of the luminescence wavelength (both fluorescence and phosphorescence) was achieved by controlling the structure of organic molecules which were taken in anorganic compound-containing inorganic crystal. Specifically, theor-organic compound-containing inorganic crystals with 2-aminobenzenesulfonic acid and 2-naptylamine-1-sulfonic acid as a guest had a phosphorescence band of 455 nm and 510 nm, respectively.

Keywords

Phosphorescence, Potassium Sulfate, 2-Aminobenzenesulfonic Acid

1. Introduction

White organic light-emitting diodes are of current interest from practical points of view due to their potential applications in next generation full-color flat-panel displays and solid-state lighting sources [1] [2]. Recently, a series of studies revealed that high efficiency organic light-emitting diodes could be fabricated by employing phosphorescent iridium complexes [3]-[6]. In general, organic light-emitting diodes is composed by the combination of three colors (blue, green and red) or two colors (blue and orange). Till now, many high efficient green

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and red emitters have been developed, but blue emitters with comparable low efficient. Thus, the development of the efficient and stable blue color component is hoped for [7]-[9].

In this paper, we report a very simple phosphorescent emitter based on inorganic-organic crystal systems. And we have examined the control of emission wavelength by adjustment of structure of organic guest components.

2. Experimental Section

To crystallize the organic compound-containing inorganic crystals, the solution was prepared by dissolving solute (inorganic and organic materials) in water solvent. In this crystallization, we tried three combinations: 1) K_2SO_4 + ABSA (2-aminobenzenesulfonic acid), 2) K_2SO_4 + NS (2-naptylamine-1-sulfonic acid), 3) Rb_2SO_4 + ABSA [10]. Before crystallization, we examined the optimum ratio of inorganic and organic components. First, we dissolve K_2SO_4 or Rb_2SO_4 (16.23 g and 30.00 g, respectively.) in 60°C water solution by using stirrer for 3 h. Then, organic materials were introduced in solution where the inorganic matter had dissolved. Finally, the co-dissolved water was cooled from 60°C to 10°C by constant cooling ratio ($0.5^\circ\text{C}/\text{hour}$) for 100 h. After that, suspended solution was separated by the filtration for 2 h. These crystals were evaluated by X-ray diffraction and Emission spectrum. The composition of the obtained crystals is written as \times (molar ratio of guest-organic molecule G/host-inorganic molecule H).

3. Results and Discussion

1. Structure and luminescence properties of crystals

PXRD pattern of these crystals fabricated from different molar ratio solutions were demonstrated in **Figure 1**. From here, the crystals generated from the solution of a low molar ratio had the crystal frame of the potassium sulfate. On the other hand, the crystals generated from the solution of a high molar ratio had the crystal frame of ABSA.

Figure 2 showed the emission spectra of crystals fabricated from different molar ratio solution. The measurement conditions were 254 nm excitation and room temperature. As for the K_2SO_4 host crystals (molar ratio 0.01, and 0.05), it is understood that a new luminescence peak exists in the area of 370 nm and 450 nm that doesn't exist in former crystal. In contrast, the new luminescence peak was not able to be confirmed to ABSA host crystal (molar ratio 0.3).

From phosphorescence measurement, it has been understood that luminescence appears to 450 nm was a phosphorescence. From both figures, the emission characteristics of the organic compound-containing inorganic crystals seem to be expressed when organic molecules located in inorganic matrices. It is thought that the appearance of the new phosphorescence characteristic in this K_2SO_4 as an organic compound-containing inorganic crystal originates in the intermolecular interaction between an organic molecule and inorganic host matrix. These crystals efficiently reduce the non-radiative decay of emission center by an inorganic-organic interaction [11] [12]. **Figure 3** showed the phosphorescence spectrum of ABSA and crystal measured at different temperature. From this figure, crystal luminous intensity measured at 77 K is greater than the emission intensity of the crystal measured at 298 K. By contrast, there were significant differences in ABSA crystal. This shows that the non-radiative decay process of originating in the molecular motion in an organic compound-containing inorganic crystal has been reduced, and is thought that the molecular interaction formed between host and guest.

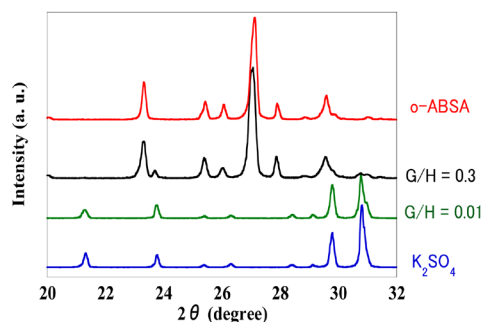


Figure 1. PXRD pattern of crystals fabricated from different molar ratio water solutions.

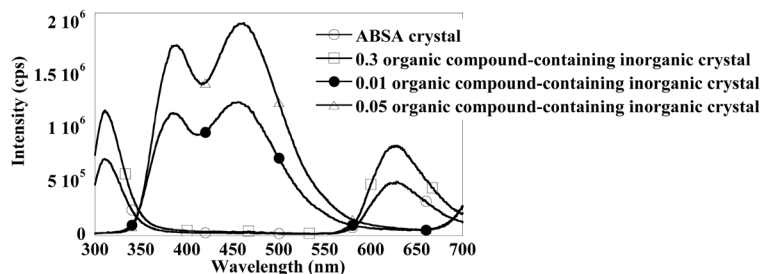


Figure 2. Emission spectra of crystals obtained and ABSA crystal by 254 nm excitation (molar ratio of guest molecule/host molecule).

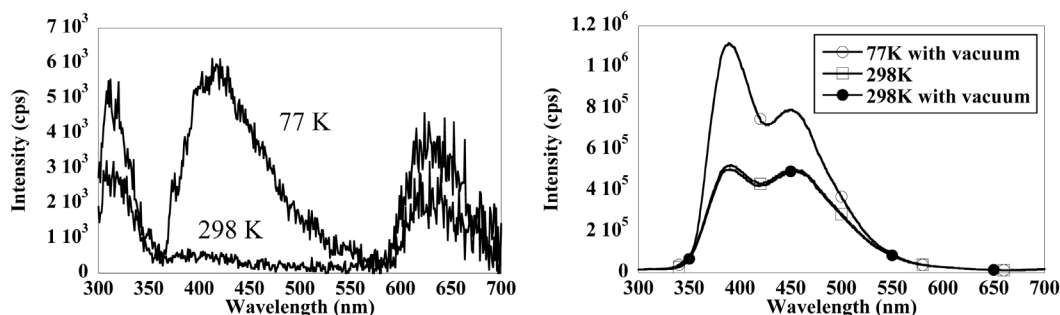


Figure 3. Phosphorescence spectra of crystals measured in different conditions (77 K and 298 K) with 254 nm excitation by delay time 50 m sec.

2. Relationship between quantum yield and crystal composition.

To optimize the crystal composition of organic compound-containing inorganic crystals, the quantum yields were measured and relationship between quantum yield and crystal composition were demonstrated in **Figure 4**. It can be seen that, maximum quantum yield was 32.1% (observed at crystal composition = 7.51×10^{-3}), and it gradually decreased as the distance from crystal composition = 7.51×10^{-3} both low and high area. Decrement of quantum yield in the low crystal composition area was caused because the density of the taken organic molecule in organic compound-containing inorganic crystals were low, and an appropriate organic compound-containing inorganic structure was not able to be formed. On the other hand, the decrement of quantum yield in high crystal composition area was caused by triplet-triplet annihilation [13]. So, it indicated that crystal composition had considerable effect on quantum yields. Therefore, to fabricate an organic compound-containing inorganic crystal of high quantum yield, it was shown to have to control the crystal composition highly.

3. Emission wavelength control by changing structure of organic molecules inserted in same host structure.

It is well known that π -conjugate length of organic molecules significantly affects emission wavelength. So, we try to control the emission wavelength by regulate the π -conjugate length of organic molecules incorporated in inorganic host crystals. We fabricated and evaluated the crystal that used ABSA and NS as a guest molecule, respectively. Two kinds of guest molecules that had been used this time were thought that a basic frame was the difference (benzene and the naphthalene), and was the best for the evaluation of the control of wavelength by the change in the structure. **Figure 5** shows the emission spectra of organic compound-containing inorganic crystals fabricated by changing organic molecules. It shows that ABSA compound-containing inorganic crystal has a fluorescence and phosphorescence band about 385 nm and 455 nm, respectively. On the other hand, NS compound-containing inorganic crystal has a fluorescence and phosphorescence band about 405 nm and 510 nm, respectively. As a result, it was shown to be able to control the luminescence wavelength of an organic compound-containing inorganic crystal by controlling the structure. However, a further research is necessary to use this organic compound-containing inorganic crystal as an illuminant for the single luminescence layer because it is difficult for achieving the red color emission from the viewpoint of the water solubility of the organic molecule in similar structure.

4. Influence of the host structure to the emission characteristic of organic compound-containing inorganic crystals.

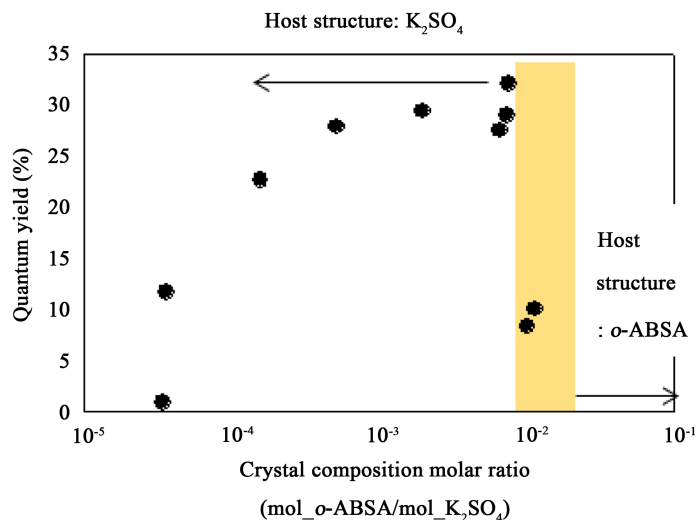


Figure 4. Relationship between quantum yield and crystal composition (molar ratio of guest molecule/host molecule) on crystals obtained.

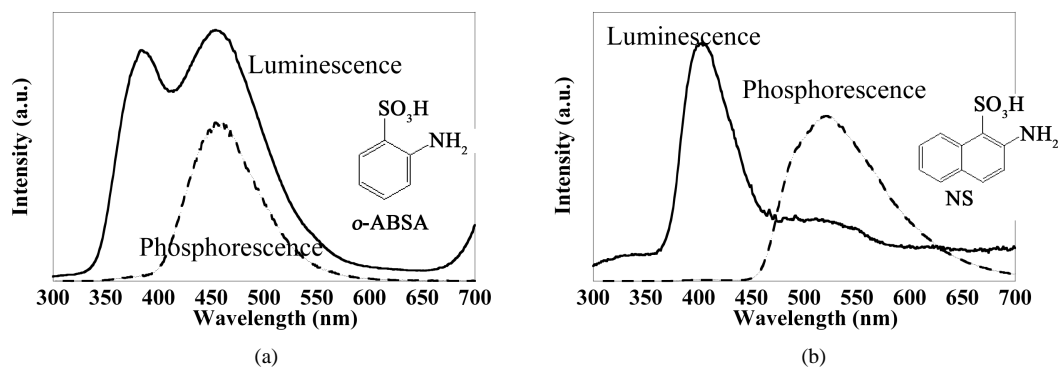


Figure 5. Normalized luminescence and phosphorescence spectra of organic compound-containing inorganic crystals crystallized from different organic molecules at 254 nm excitation (Phosphorescence spectra were measured at 50 m sec after excitation.). (a) ABSA as a guest, and crystal composition is 1.99×10^{-3} ; (b) NS as a guest, and crystal composition is 3.61×10^{-5} .

To investigate the effect of the crystallographic structure of host matrices for emission properties of the organic compound-containing inorganic crystals, we fabricated and compared the organic compound-containing inorganic crystals by using Potassium sulfate and Rubidium sulfate as a host. 3D Emission spectra of organic compound-containing inorganic crystals fabricated by changing host matrices were shown in **Figure 6**. From this figure, it shows that K₂SO₄ host organic compound-containing inorganic crystal has two emission peaks located at 385 nm and 455 nm. From phosphorescence measurement, emission located at 385 nm and 455 nm were identified as fluorescence and phosphorescence, respectively. On the other hand, Rb₂SO₄ host organic compound-containing inorganic crystal have only phosphorescence peak located at 450 nm. In addition, compared with potassium sulfate organic compound-containing inorganic crystal, the phosphorescent intensity of the rubidium sulfate organic compound-containing inorganic crystal was very strong. Rb₂SO₄ used as a host, achieved a high quantum yield around 60% by optimizing the crystal composition. This results indicate the potential to create a more efficient emitter for Rb₂SO₄ as a host

4. Conclusion

The luminescent functional crystal was produced by taking the organic molecules in the inorganic crystal matrices. The organic compound-containing inorganic crystals had a phosphorescent property in room temperature. It is suggested that the phosphorescence characteristic appears since the host matrix effectively controls the

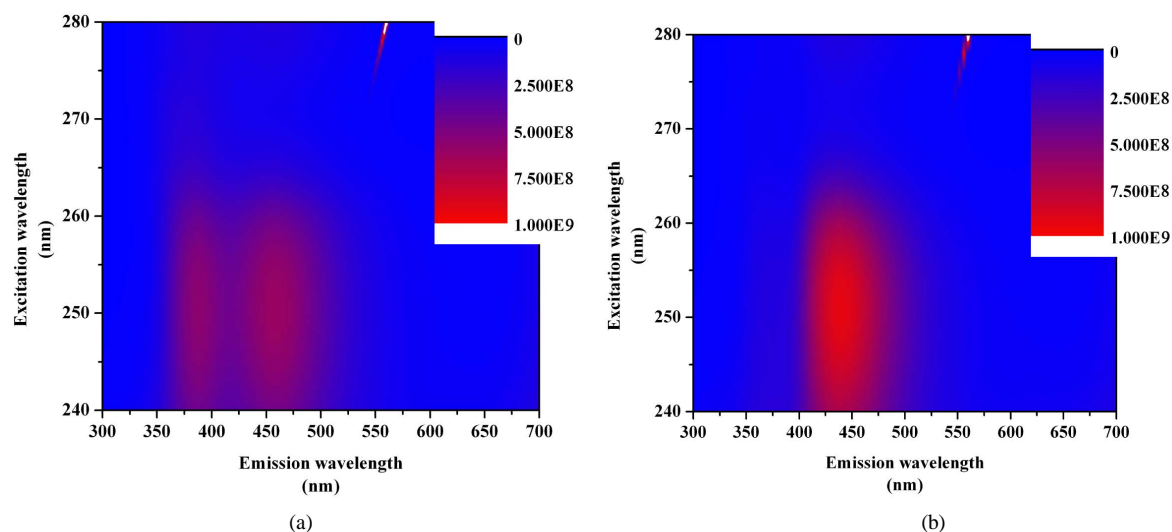


Figure 6. 3D spectra of organic compound-containing inorganic crystals crystallized by changing host molecules. (a) K_2SO_4 as a host; (b) Rb_2SO_4 as a host.

thermal motion of the guest organic molecules. The phosphorescence wavelength was able to be controlled by controlling the molecular configuration of the organic molecules in the same host frame. Therefore, there is a possibility that an organic compound-containing inorganic crystal can be applied to the illuminant.

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