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Application News

Spectrofluorophotometer RF-6000

Measurement of Photon Upconversion Luminescence Using RF-6000 Spectrofluorophotometer

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User Benefits

- The high-sensitivity detector of the RF-6000 enables measurement of weak upconversion.
- Measurement corresponding to long wavelength excitation is possible by installing any appropriate optical filter.

■ Introduction

Photon upconversion (UC) is a technique which makes it possible to convert long wavelength near-infrared light to short wavelength visible light. UC is expected to be used in medical applications such as photoimmunotherapy and drug delivery systems utilizing a method whereby near-infrared light, which has high biopermeability, is injected into the patient's body, and is then functionalized by conversion to visible light. Research on applications in the energy sector is also underway, for example in photovoltaic cells, by conversion of the wide range of wavelengths in sunlight to useful wavelengths.

In conventional photoluminescence by photon upconversion, it was necessary to irradiate molecules almost simultaneously with two photons, but for this reason, light with a high luminous flux density, such as laser light, was required in order to achieve an adequate emission intensity. However, in recent years UC materials with a long-lifetime excitation characteristic have been developed, and examples in which UC luminescence was confirmed even with luminous flux densities on the level of sunlight have also been reported.

This article introduces an example of measurement of the light emission obtained by UC with a weak exciting light source using Shimadzu RF-6000 spectrofluorophotometer. The RF-6000 is expected to be an important tool for research and development/quality control of next-generation UC materials.

■ Measurement Samples and Measurement Conditions

Table 1 and Fig. 1 show the measurement samples and their appearance, respectively. Materials were prepared by doping cerium oxide (CeO_2) with trace amounts of erbium (Er) and ytterbium (Yb) (Table 1: CeO_2-based UC material) and doping yttrium oxide (Y_2O_3) with trace amounts of Er and Yb (Table 1: Y_2O_3-based UC material). To confirm the effect of differences in the synthesis methods of these two materials on UC luminescence, test specimens were prepared by the two synthesis methods of solid-phase sintering or sintering after liquid-phase synthesis.

Table 1 Measurement Samples and Synthesis Methods

	Type of material	Synthesis method
Sample ①	CeO_2-based UC material	Solid-phase sintering
Sample ②	CeO_2-based UC material	Liquid-phase synthesis + Sintering
Sample ③	Y_2O_3-based UC material	Solid-phase sintering
Sample ④	Y_2O_3-based UC material	Liquid-phase synthesis + Sintering

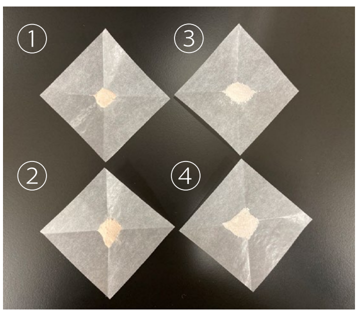

Fig. 1 Appearance of Measurement Samples

A solid (powder) sample holder was used in the measurements, as simple measurement is possible by packing the sample material in the powder dish.

An IR85N infrared transmitting filter manufactured by HOYA Corporation was used on the excitation side of the sample compartment. Fig. 2 shows the transmission spectrum of the IR85N filter. Light which is spectrally separated by a diffraction grating also includes weak light with wavelengths of 1/2 or 1/3 of the target wavelength. However, if the possible effect of these components on the measurement wavelength region is a concern, use of an optical filter to physically block higher-order light is an effective countermeasure. Since any desired optical filter can be set on both the excitation side and the fluorescence side of the RF-6000, as shown in Fig. 3, the optimum optical filters can be selected, even in special cases such as measurement of short wavelength luminescence excited by long wavelength light.

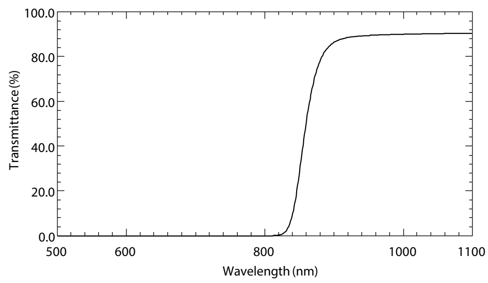

Fig. 2 Transmission Spectrum of IR85N Infrared Transmitting Filter

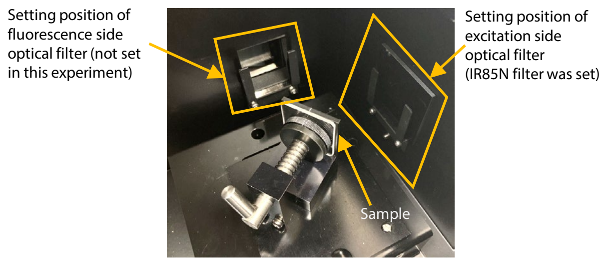

Fig. 3 Condition of Sample and Optical Filter Installation

The quantity of UC luminescence depends on the intensity of the exciting light. In conventional measurements, high intensity laser light was used as the exciting light source, but in this experiment, the UC luminescence emission spectrum when using exciting light with a small luminous flux density was measured by using the xenon (Xe) light source provided as the standard specification of the RF-6000. The detector sensitivity was set to High in order to detect UC luminescence, which is weaker than general fluorescence. Table 2 shows the other detailed measurement conditions.

Table 2 Measurement Conditions

Instrument	: RF-6000
Excitation (Ex) wavelength	: 900 nm
Fluorescence (Em) wavelength region	: 500 - 700 nm
Data interval	: Em 0.5 nm
Scanning speed	: 60 nm/min
Spectrum bandwidth	: Ex 20.0 nm, Em 5.0 nm
Sensitivity	: High

■ Difference of Synthesis Methods and Emission Spectra

Fig. 4 and Fig. 5 show the UC luminescence emission spectra of the CeO_2-based UC material and the Y_2O_3-based UC material, respectively. As a result of setting the exciting wavelength to 900 nm and measurement of the light emission in the range of 500 to 700 nm as shown in Table 2, it was possible to obtain an emission spectrum with a shape similar to that in measurements using a laser as the exciting light source, which has been reported in the reference literature [1]. Differences in the emission intensity and shape of the emission spectrum depending on the synthesis method were also confirmed.

Regarding emission intensity, emission spectra with higher intensities were obtained from the samples prepared by solid-phase sintering with both the CeO_2-based UC material and the Y_2O_3-based material. Although the spectra of the samples prepared by sintering after liquid-phase synthesis were weak, it was also possible to obtain emission spectra from those samples.

As for the emission spectrum shape, differences could be seen in the emission intensity ratio of the long wavelength side (around 670 nm) and short wavelength side (around 560 nm). Table 3 and Table 4 summarize the peak height ratios of the long wavelength side and short wavelength side of the CeO_2-based UC material and the Y_2O_3-based material, respectively. The emission on the short wavelength side appeared relatively strongly in the samples prepared by liquid-phase synthesis, and limited to the Y_2O_3-based UC material prepared by sintering after liquid-phase synthesis, it can be understood that the emission intensities of the long wavelength side and short wavelength side are reversed. This suggests the possibility that luminous efficiency and emission wavelength characteristics may differ depending on the synthesis method.

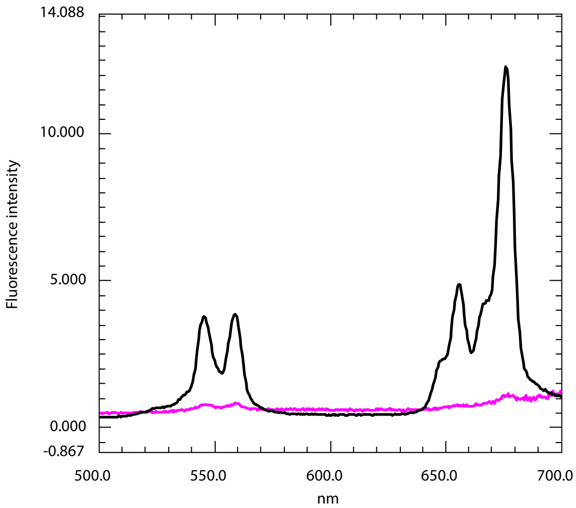

Fig. 4 UC Luminescence Emission Spectra of CeO_2-Based UC Material (Black: Solid-Phase Sintering, Pink: Liquid-Phase Synthesis + Sintering)

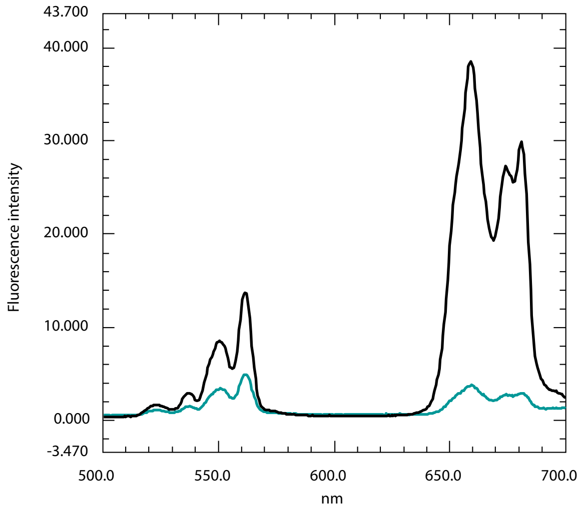

Fig. 5 UC Luminescence Emission Spectra of Y_2O_3-Based UC Material (Black: Solid-Phase Sintering, Blue: Liquid-Phase Synthesis + Sintering)

Table 3 Height Ratio of Representative Peaks of Emission Spectra of CeO_2-Based UC Material

CeO_2-based UC material	$I_{559\,nm}$	$I_{676\,nm}$	$I_{676\,nm}/I_{559\,nm}$
Solid-phase sintering	3.419	11.865	3.470
Liquid-phase synthesis + Sintering	0.252	0.489	1.940

Table 4 Height Ratio of Representative Peaks of Emission Spectra of Y_2O_3-Based UC Material

Y_2O_3- based UC material	$I_{562\,nm}$	$I_{659\,nm}$	$I_{659\,nm}/I_{562\,nm}$
Solid-phase sintering	13.207	38.085	2.884
Liquid-phase synthesis + Sintering	4.340	3.119	0.719

■ Conclusion

The emission spectra of four UC materials prepared using different types of materials and synthesis methods were measured using a Shimadzu RF-6000 spectrofluorophotometer. Although the emission intensity of upconversion (UC) luminescence is weaker than that of general light emissions, detection was possible by setting the detector sensitivity to High. When UC materials prepared by different synthesis methods were compared, differences in the emission intensity and in the emission intensities on the long wavelength and short wavelength sides were confirmed.

Since the RF-6000 makes it possible to investigate the emission characteristics of UC materials without using a special exciting light source or spectroscope, this instrument is expected to be a useful tool for research and development/quality control of UC materials, which are expected to be utilized in various applications in the future.

<Reference>

1) Koji Tomita, Journal of the Ceramic Society of Japan, 121 [9] 841-846, 2013.

<Related Applications>

1. Emission Spectrum Measurement for LED Lamp by the UV-2600 UV-VIS Spectrophotometer [Application News No.A444](#)
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01-00693-EN First Edition: Mar. 2024