QUANTUM EFFICIENCY OF YTTRIUM AND TERBIUM GARNETS

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Abstract

A measurement system and mathematical procedure are developed for determining the quantum efficiency of luminescent materials. This technique based on standard photoluminescence DARSA PSI 5100 system (Diode Array Rapid Scan Analysis, Professional Scientific Instrument Co, Korea) or any other that allows measure the emission and excitation spectra, is applied to conventional phosphor powders. The system described is tested for excitation in the near-UV and visible regions, but can be applied to higher energy excitation (UV), as well as lower energy excitation to near-IR, with the appropriate photodetectors and optical filters. The system was tested on standard phosphors and on the new compositions. The accuracy of this measurement technique is acceptable for express analysis of quantum efficiency of luminescent materials.

1. Introduction

There is a need for a simple and accurate method to determine the quantum efficiency of luminescent materials. Ideally, such a technique for express analysis should require minimal sample preparation and should be simple in application. In this paper we report a technique that satisfies these criteria. The quantum efficiency (QE) of a luminescent material is defined as the ratio of the number of photons emitted to the number of photons absorbed. This ratio is also termed quantum yield (QY). In contrast, the radiant efficiency (RE) is the ratio of the output power to the input power. Quantum efficiency has long been used as a criterion for the selection of luminescent materials for application in fluorescent lighting [1-3], at panel displays [4,5], and more recently, solid-state lighting. A problem with some QE measurement techniques described in the literature is the lack of an acceptable calibration standard. For example, QE measurements of powder samples are often made in a system that cannot accommodate liquid fluorescence standards. There are three predominant techniques in the literature for measuring QE: absolute optical; relative optical; and photocalorimetric. In optical approaches, a primary challenge is determining precisely the amount of incident light absorbed by the phosphor. The amount of incident light absorbed can be determined directly,

or calculated from the sample reflectance. Most of the QE values in the literature for powder phosphors use the latter method and the reflectivity of standards such as MgO or $BaSO_4$. Photocalorimetry and photoacoustic spectroscopy have been investigated as alternatives to optical methods for QE measurements [6–8]. In photoacoustic spectroscopy (PAS), a black absorbing standard is used. The method is based on the optoacoustic effect where modulated light incident on a sample will produce a temperature rise in the sample that manifests itself by a periodic pressure wave that can be measured with a microphone transducer. The magnitude of the temperature wave depends on the sample absorption and the efficiency of non-radiative transitions. In this technique, the thermal energy of the Stokes shift contributes to the PAS signal, as any other non-radiative processes do, but the luminescence energy does not. PAS and photocalorimetry are difficult because good thermal contact is critical, small temperature fluctuations (mK) are difficult to detect, and thermal isolation from the surroundings is a challenge.

The technique described herein is very simple and can be applied effectively to powder phosphors, all of which we are interested in characterizing.

2. Experimental

The luminescence spectrum is obtained by plotting the relationship between the wavelength and the intensity of the emitted light from a sample excited by an appropriate excitation source of constant energy. The excitation source can be light, an electron beam, heat, X-rays, or radiation from radioactive materials. The spectrum is obtained using a monochromator equipped with an appropriate light detector.

The apparatus for measuring the spectral characteristics of phosphors is shown in Fig.1

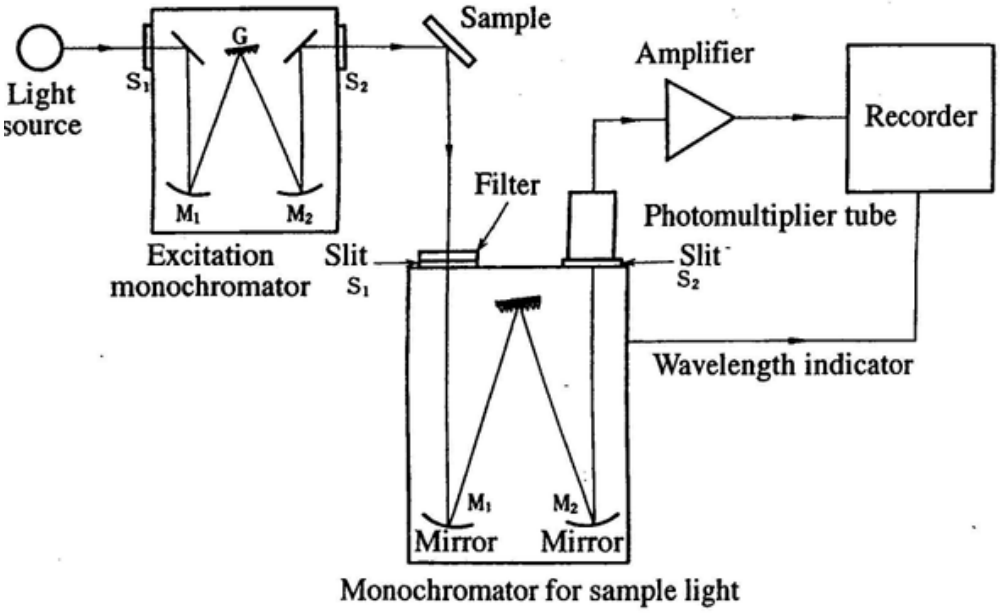

Fig.1. Spectroscopic measurement apparatus

The excitation source consists of the light source and a monochromator, which selects a specific wavelength range from the incoming light. The light emitted from the sample is analyzed by a monochromator equipped with a light detector.

Emission, excitation, and reflection spectra have to be measured for calculation of the quantum efficiency of phosphors. Two monochromators and Xe lamp as excitation source are necessary. $(YGd)_3Al_5O_{12}$:Ce (YAG) phosphor with known QE could be proposed as standard test sample.

Spectral photon irradiance is expressed as:

$$E_p(\lambda) = \frac{dE_p}{d\lambda}; \quad E_p = \int_0^\infty E_p(\lambda) d\lambda \tag{1}$$

For quantum efficiency of the investigated sample and the standard one we have:

$$\frac{\alpha_x q_x}{\alpha_{st} q_{st}} = \frac{E_{p_x}}{E_{p_{st}}}; \tag{2}$$

where q_x and q_{st} are the quantum efficiencies of the specimen investigated and the standard (commercial YAG material, for example), and α is an absorption coefficient

$$q_x = \frac{(1-R_{st}) \int_0^\infty E_{p_x}(\lambda) d\lambda}{(1-R_x) \int_0^\infty E_{p_{st}}(\lambda) d\lambda} q_{st} \tag{3}$$

The following formula is applied in the calculations:

$$q_X = \frac{(1-R_{ST})}{(1-R_X)} \frac{\Phi_X}{\Phi_{ST}} q_{ST} \tag{4}$$

R_X and R_{ST} are the reflectance of the specimen and the standard, and Φ_X and Φ_{ST} are the total measured luminescence efficiency (the integrated area under the emission spectrum) of the specimen and the standard, respectively.

The reflectance R_X and R_{ST}, respectively, of the investigated and standard samples are calculated from the formula

$$R_N = \frac{A_{RN}}{A_{RB}} 0.97 \quad , \tag{5}$$

where R_N stands for a sample reflectance (N = X and ST for investigated powders and the YAG standard, respectively), and A_{RN} and A_{RB} are total areas under the measured reflection spectra for the sample investigated and the MgO, respectively. In this formula the number 0.97 represents the reflectance of the MgO powder. (Instead of MgO, $BaSO_4$ with index 0.91 can be used).

3. Results and discussion

In figure 2 we show the scheme of experiment, which is realized with photoluminescent DARSA system for reflectance measurements:

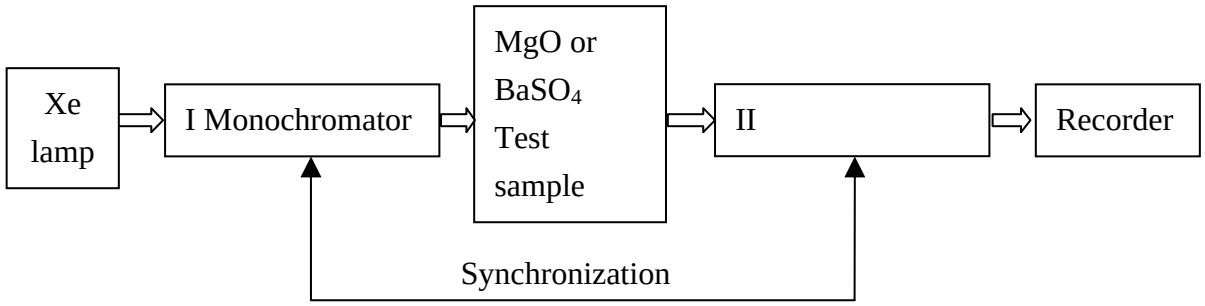

Fig.2 The scheme of QE measurement with DARSA system

If the spectroscopic system doesn't have a special integrated sphere (ISO40-SF/IG, for example), and does not allow to measure the guantum efficiency directly, the reflectance spectra measurements have to be carried out. Two monochromators are need to be synchronized at the excitation wavelength. At the fixed excitation wavelength of the first monochromator the emission spectra around this wavelength are measured by the second monochromator for the reference sample (MgO) and examined phosphors. Because of the Stock's shift (phosphors emit the light at the other wavelength that excite) the measured spectra are the reflectance spectra. The emission and excitation spectra of examined and standard samples are also registered.

Figure 3 compares excitation and emission spectra of investigated samples $Tb_3Al_5O_{12}:Ce^{3+}$ (TAG) and a double activated $Tb_3Al_5O_{12}:Ce^{3+},Eu^{2+}$ with commercial $(YGd)_3Al_5O_{12}:Ce^{3+}$ (YAG)

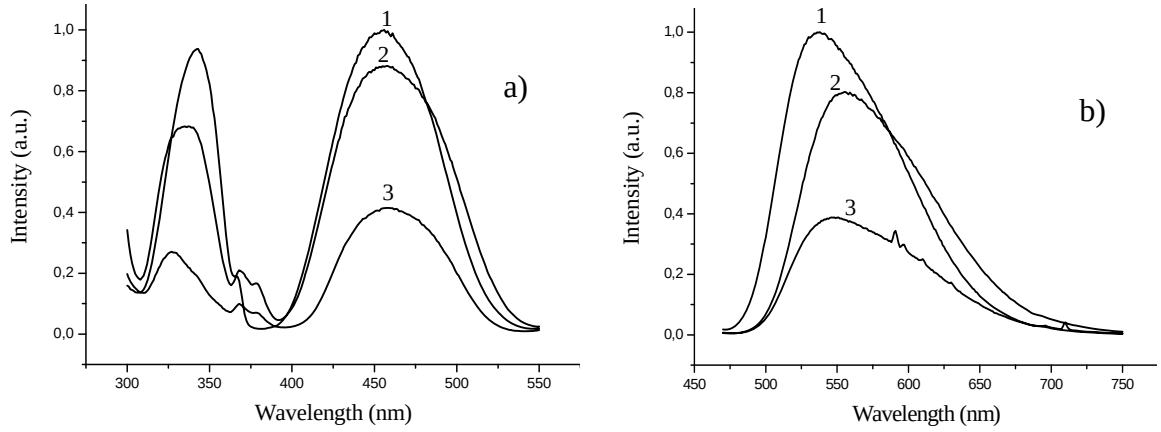

Fig.3. Excitation (a) and emission (b) spectra of investigated samples $Tb_3Al_5O_{12}:Ce^{3+}$(2) and double activated $Tb_3Al_5O_{12}:Ce^{3+},Eu^{2+}$(3) with commercial $(YGd)_3Al_5O_{12}:Ce^{3+}$ (1)

It is seen from Fig.3 that the luminescence spectra of specimens are very similar in the

shape and vary in intensities. The 2 broad bands from 310 to 380 nm in the long-wavelength UV region and from 400 to 520 nm in the blue spectral region correspond to the 4f-5d transitions of Ce^{3+} in YAG. The comparison of the luminescence spectra of the TAG -based phosphors with the emission of the commercial YAG convinces us that the latter can serve as a very convenient reference material against which the emission efficiency of our phosphors can be judged. Since the emissions of all materials investigated fall within exactly the same spectral region, there is no need to correct the emission spectra for the photomultiplier response to make a reasonable calculation of the quantum efficiencies of the emissions of the various TAG powders. Reliable judgment of the real efficiencies of the emissions from the various specimens requires an accurate determination of the amount of light absorbed by each of the phosphors investigated. This is especially important in our case, since the various specimens are characterized by different microstructures and the activator concentration. To compare the amount of light absorbed by an actual specimen, we measured reflection spectra for each of them and related them to the reflectivity of our standard commercial YAG phosphor and to the reflectivity of MgO. Equation (5) shows the relationship between the reflectance of the specimen investigated and the reflectance of the standard powder MgO.

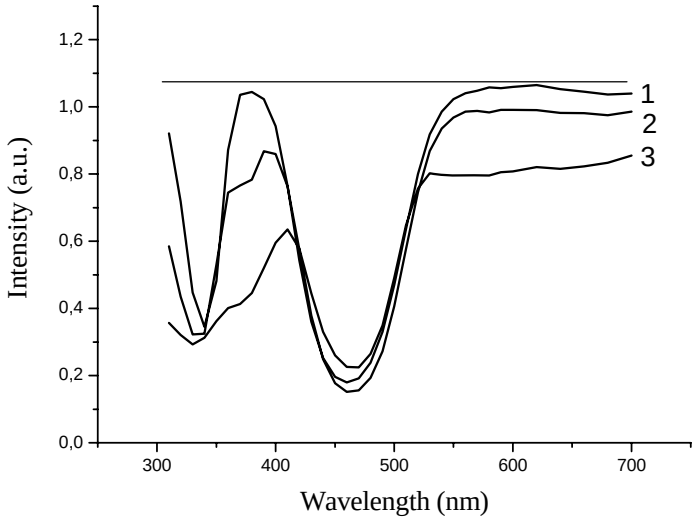

Fig.4. Diffuse reflection spectra of the $Tb_3Al_5O_{12}:Ce^{3+}$(2), double activated $Tb_3Al_5O_{12}:Ce^{3+},Eu^{2+}$(3) and commercial $(YGd)_3Al_5O_{12}:Ce^{3+}$ (1) in comparison with MgO.

In figure 4 we show reflection spectra for the commercial YAG and all the TAG samples (one of them (2) is doped with 6 mol % of Ce^{3+} and the other (3) with 3 mol % of Ce^{3+} and 3 mol % of Eu^{2+}), together with the spectrum of MgO. The results leave no doubt that, for reliable estimation of the quantum efficiency of an emission, it is definitely not enough to compare just the luminescence efficiency - it is also necessary to take into account the variations in the amounts of light absorbed by each of the samples. Despite the fact that all TAG specimens presented in figure 4 have the same host lattice, their capabilities for

reflecting the incident light vary strongly. It can be explained by the different Ce^{3+} activator concentration in the samples (2) and (3), as well as influence of Eu^{2+} on the luminescence properties of the sample (3). Thus the amount of light accessible for absorption by the Ce^{3+} ions (able to excite the phosphor) must also alter. Generally, as expected, with rising Ce content (6 mol % in the sample 2 and 3 mol % in the sample 3) less and less light is being reflected, what means that a still increasing amount of the light is being absorbed by the phosphor.

On the basis of the excitation (Fig. 3) and reflection (Fig.4) spectra, we decided that for the measurements of the quantum efficiencies of our phosphors, the most convenient excitation wavelength would be 460 nm. The diffuse reflection spectra at this wavelength are presented in Fig.5.

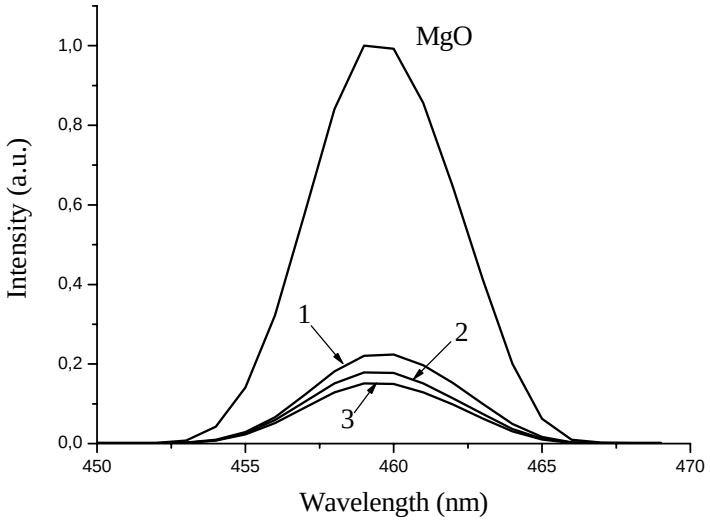

Fig.5. Diffuse reflection spectra of the $Tb_3Al_5O_{12}:Ce^{3+}$(2), double activated $Tb_3Al_5O_{12}:Ce^{3+},Eu^{2+}$(3) and commercial $(YGd)_3Al_5O_{12}:Ce^{3+}$ (1) in comparison with MgO at 460 nm excitation.

The quantum efficiency of phosphors calculated according to equations 4 and 5 and by using the experimental data from Fig.5, gives us the 76% for $Tb_3Al_5O_{12}:Ce^{3+}$ (6 mol % Ce) and 40% for $Tb_3Al_5O_{12}:Ce^{3+}$, Eu^{2+} (3 mol % Ce and 3 mol % Eu) relatively 90% $(YGd)_3Al_5O_{12}:Ce^{3+}$. It is not astonishing, because the main reason for a low intensity of the last sample is a lack of Ce activator and weak emission intensity in comparison with standard sample. The quantum efficiency practically does not depend on excitation wavelength in the large excitation area. It is good seen from Fig.6 for our samples and could be explained by the same processes of energy absorption, energy transfer and emission at different excitations. The quantum efficiency strongly depends on the sample structure and activator concentration.

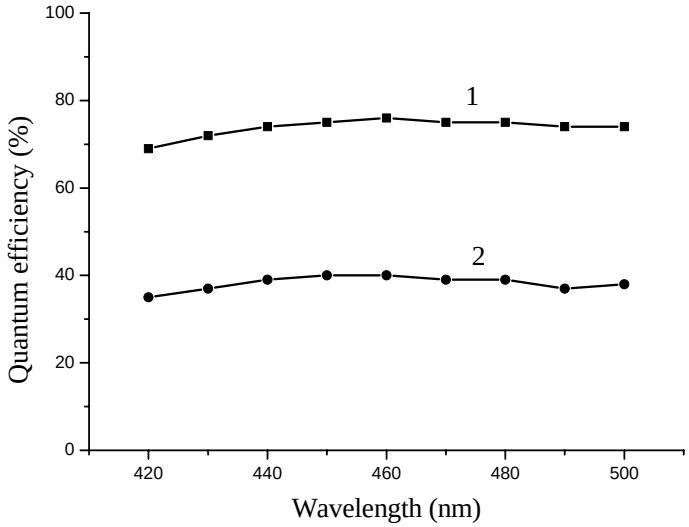

Fig.6. The quantum efficiency of (1) $Tb_3Al_5O_{12}:Ce^{3+}$ (6 mol % Ce^{3+}) and (2) $Tb_3Al_5O_{12}:Ce^{3+},Eu^{2+}$(3 mol % Ce^{3+} and 3 mol % Eu^{2+}) in dependence on excitation wavelength.

Energy absorption does not necessarily take place at the activator ion itself but can occur at a random place in the lattice. This implies that energy transfer of the absorbed energy to the luminescent center takes place before emission can occur. The migration of the energy absorbed by the lattice can take place through one of the following processes:

- migration of electric charge (electrons, holes),
- migration of excitons,
- resonance between atoms with sufficient overlap integrals,
- reabsorption of photons emitted by another activator ion or sensitizer

The occurrence of energy transfer within a luminescent material has far-reaching consequences for its properties as a phosphor. On the one hand the absorbed energy can migrate to the crystal surface or to lattice defects where it is lost by radiationless deactivation. As a consequence the phosphor energy yield, that is the quotient of emitted light energy to initially absorbed energy, drops. In the same phosphor structure with the same defect concentration the energy loss is also the same and emission is determined by the activator concentration.

4. Conclusion

Simple express method of quantum efficiency measurement and calculation using PL spectroscopy system is proposed and the experimental scheme compatible with DARSA system is suggested.

The methodology of calculation of quantum efficiency from reflection spectra is discussed. The obtained results show that it is definitely not enough to compare just the

luminescence efficiency - it is also necessary to take into account the variations in the amounts of light absorbed by each of the samples.

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