PHOTOLUMINISCENCE METHOD AS A TOOL FOR INVESTIGATION OPTICAL PROPERTIES OF COORDINATION COMPOUNDS WITH Eu (III)

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METODA FOTOLUMINESCENȚEI CA INSTRUMENT DE INVESTIGARE A PROPRIETĂȚILOR OPTICE ALE COMPUȘILOR COORDONATIVI DOPAȚI CU Eu (III)

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Rezumat. Fotoluminescența (PL) reprezintă un instrument eficient pentru investigarea proprietăților de emisie ale compușilor coordinativi ai Eu(III). Este prezentat principiul de funcționare și instrumentarea de bază a tehnicii de fotoluminescență. Configurația este descrisă și este prezentat un exemplu de date experimentale privind compusul de coordonare [Eu(μ2-OC2H5)(btfa)(NO3)(phen)]2·phen. Sunt descrise avantajele și dezavantajele de bază, precum și domeniile de aplicație.

Cuvinte-cheie: Fotoluminiscență (PL), compus coordinativ, spectre de emisie, spectre de excitare, Eu(III).

Abstract. Photoluminescence (PL) method represents a powerful tool for investigation of emission properties of Eu(III) coordination compounds. Basic operating principle and instrumentation of photo-luminescence technique is presented. The set-up is described and example of experimental data on [Eu(μ2-OC2H5)(btfa)(NO3)(phen)]2·phen are presented. The basic advantages and drawbacks, as well as the applications domains are described.

Keywords: Photoluminescence, coordination compound, emission spectra, excitation spectra, Eu(III).

1. What is luminescence, types of luminescence

Luminescence is a physical phenomenon in which a body emits radiation of non-equilibrium that exceeds the amount of radiation expected for its temperature. The radiation occurs in a group of atoms or molecules that are in a non-equilibrium state. Compared to other types of light scattering, luminescence is characterized by a series of intermediate processes that occur between absorption and emission, and these processes have a duration that is longer than the period of the light wave[1].

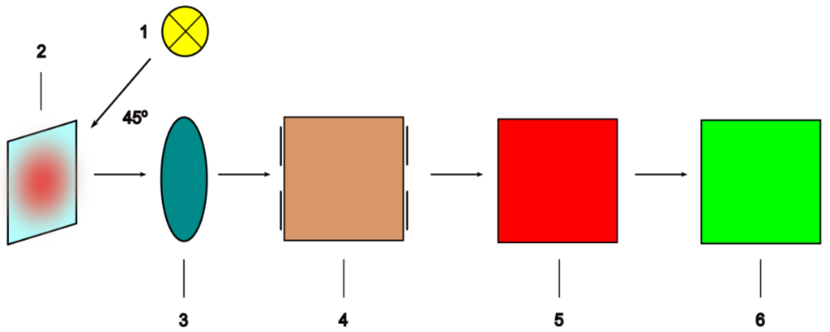
In all types of luminescence, the final stage is the spontaneous transition of a radiant microsystem from a higher energy state to a lower energy state. However, the methods of energy transfer to the luminescence centers and the subsequent elementary processes are different. The easiest excitation method is photoexcitation, in which light quanta transfer energy directly to the luminescence centers. Table 1 illustrates one of possible ways of classification of types of luminescence [2,3].

Table 1. Types of luminescence

Excitation	Types of Luminescence
Photoluminescence	is a glow excited by an electromagnetic optical frequency radiation
Cathodoluminescence	glow caused by cathode rays
Electroluminescence	is the glow produced by the action of electric field, it occurs in electroluminescent devices such as LEDs and OLED screens
Thermoluminescence	occurs when a material is heated and changes its energy state
Sonoluminescence	is the glow produced by acoustic cavitation
Radioluminescence	is the glow excited by radioactive isotopes (Radioisotope luminescence)
Triboluminescence	is the glow produced by mechanical impact/stress and by friction
Chemiluminescence	is a glow excited by energy chemical reactions
Bioluminescence	is a glow of living organisms, a special case of chemiluminescence.

2. Experimental setup and installation of samples

Figure 1.1. illustrates a typical setup for measuring photoluminescence emission spectra. The light source (1) provides excitation energy, which is directed towards the sample (2). The emitted light from the sample is then collected by the collimator (3) and passed through a monochromator (4), which separates the different wavelengths of light. The separated wavelengths are then detected by a photoreceptor (5), in our care we have an Photomultiplied Tube (PMT), and the resulting data are processed and analyzed by a computer (6). As an excitation light source we can use a Lased Diode at 405 nm.



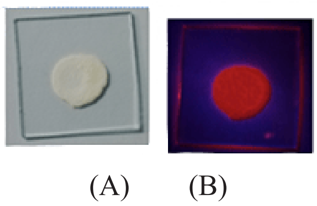


Fig. 1.1. PL emission spectra measurement setup (1 – Light source, 2 – Sample, 3– Collimator, 4 – Monochromator, 5 – Receptor, 6 – PC)

Fig. 1.2. Sample under : day light (A), under blue light (B)

Figure 1.2. illustrates a sample of Eu(III) coordination compound [Eu(μ2-OC2H5)(btfa)(NO3)(phen)]2·phen under day light illumination, and under blue light radiation 405 nm. [4].

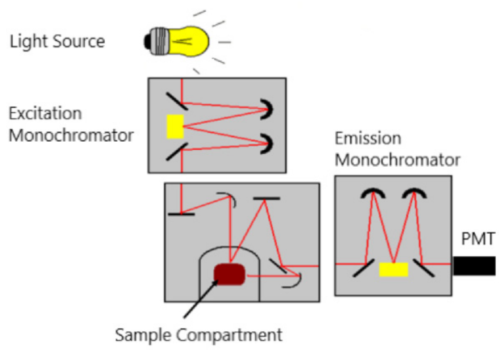


Figure 1.3. PL excitation measurement setup with 2 monochromators

Figure 1.3. illustrates the setup for registration of PL excitation spectra, the light produced by an excitation source is focused on the entrance slit of the excitation monochromator. The monochromator disperses it, producing monochromatic light. The emission from the sample is focused on the entrance slit of the emission monochromator, which disperses it, and then this light passes through the exit slit, finally reaching the photomultiplier tube [5].

3. Characteristics of a luminescent solid: emission spectra, quantum yield, and luminescence relaxation kinetics.

The most important characteristics of a luminescent solid are: **The emission spectra** (luminescence) represent the distribution of the light energies emitted by the material during the luminescence process. They can be used to determine the colors and intensities of light emissions from the material. **The excitation** spectra describe the energy needed to excite electrons in the material in the luminescent state, and these can be used to evaluate the effectiveness of the luminescence process. **Absorption spectra** are the distribution of light energies absorbed by the material and can be used to assess the absorption efficiency and the material's ability to absorb energy. **Quantum yield** and the **kinetics** of luminescence relaxation are the parameters used to measure the efficiency of the luminescence process and the rate of loss of luminescence over time [6].

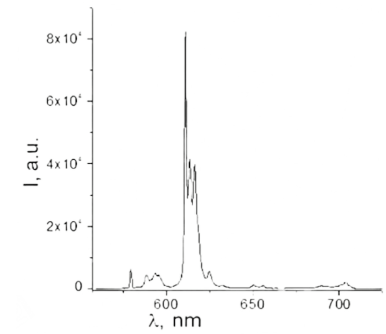


Figure 1.4. PL emission spectrum of Eu(III) complex

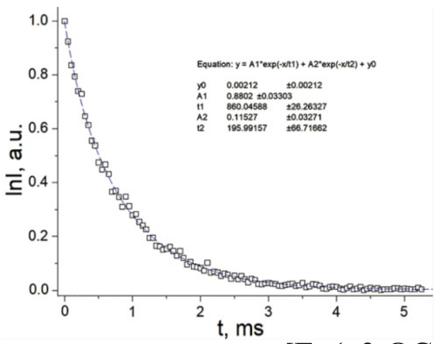


Figure 1.5. PL time decay of [Eu(μ2-OC2H5)(btfa)(NO3)(phen)]2·phen

Figure 1.4 illustrates the PL emission spectrum of the Eu(III) compound under blue light excitation 405 nm. In figure 1.5. is showed PL decay profile in powder sample at 300 K measured at 612 nm under pulsed excitation at 337 nm. The measured luminescence decay of the Eu(III) 5D0→7F2 transition is bi-exponential, suggesting the existence of two nonequivalent, nearly identical coordination environments of Eu3+ in the matrix.

We observe the relaxation in the time scale of milliseconds which is very important for medical applications, since it's more suitable for observing the luminescence when the relaxation time is pretty long [7]. The quantum yield of luminescence is the ratio of the total number of emitted photons $N_{emitted}$ to the number of absorbed photons of excitation radiation $N_{absorbed}$.

4. Advantages and Drawbacks of PL technique

Advantages of PL method : PL is a highly sensitive technique that can detect even small amounts of luminescent materials, making it useful for detecting trace amounts of materials in various samples. Unlike some other analytical techniques, PL does not require extensive sample preparation, which can save time and reduce the risk of introducing errors. PL is a non-destructive technique, which means that the sample can be reused for further analysis, reducing the amount of sample needed for analysis and making it a cost-effective method. Compared to some other analytical techniques, PL instruments are generally more affordable, which can make them more accessible to researchers with limited budgets [8,9].

The main disadvantage of PL technique is the sample's surface defects that could affect the signal, and latter complicate the interpretation of the results [10].

Conclusion

In conclusion, PL spectroscopy is a versatile and powerful analytical tool with applications in various fields such as semiconductor industry, forensic science, chemical industry, sensor industry, biological imaging, and environmental monitoring. Its high sensitivity and ability to measure light emitted from a sample after excitation make it a valuable technique for analyzing properties of nanomaterials, identifying compounds, detecting pollutants, and tracking chemical reactions. PL spectroscopy has a wide range of potential applications, and its use is likely to continue to grow in the future.

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