1 Introduction

The term “*luminescence*” was used for the first time by the physicist Eilhardt Wiedemann in 1888 to describe all phenomena of light, which are not driven by a rise in temperature.[1] Thus, thermal radiation is different from luminescence. The term “*luminescent material*” or “*phosphor*” was defined by G. Blasse as: “A luminescent material, also called a phosphor, is a solid, which converts certain types of energy into electromagnetic radiation over and above thermal radiation.”[2,3] This emitted radiation is usually in the visible range, but can also be in other spectral regions, such as ultraviolet (UV) or infrared (IR).[4] Luminescence can occur as a result of different kinds of excitation, and their influence on the resulting phenomena has been vividly described by H. A. Klaassens “Ultraviolet excitation compares to striking one key of the piano; cathode-ray or X-ray excitation compares to throwing the piano down the stairs.”[3]

Luminescent materials are highly requested for various applications, such as lamps, displays, X-ray intensifiers and scintillators.[2,5-10] A breakthrough in the field of luminescence is related to Nakamura’s invention of (In,Ga)N-based, blue-light-emitting diodes (LED) in 1994.[11] The need for new phosphors increased with the development of novel imaging techniques in medicine, such as computed tomography (CT), positron emission tomography (PET), and single-photon emission CT. Optical materials doped with rare-earth elements are of great interest in science and technology. Lanthanide ions are famous for their unique luminescence properties when incorporated into organic and inorganic compounds.[3,5] Their most prominent advantages are the large Stokes shift, the multiple narrow emission lines and the long emission lifetimes.[3] The motivation for using rare-earth ions is that they can absorb and emit over a wide range of wavelengths from near-infrared (NIR) through the visible to ultraviolet.

In general, fluorescent nanoparticles can be of interest for any kind of application, for which bulk phosphors are relevant, too.[4] Compared to bulk phosphors, the main advantages of fluorescent nanoparticles are especially related to their small size (below 100 nm), which makes them suitable for coating/incorporation on/in glass, paper, or polymers in terms of marking (e.g., advertising, emergency lighting) or security (e.g., banknotes, identification documents) and in medicine and molecular biology (e.g., optical imaging, targeting).[4,12-17] Key factors to all these purposes are, next to the small size, a huge number of fluorescent centers that guarantee for very intense and bright spotlight emission of each single nanoparticle, and the possibility of using different analytical tools to detect and localize the fluorescent nanoparticles.[3,4]

Nowadays, there is a great demand for red-emitting phosphor nanomaterials that can be excited with near-UV to blue light ($\lambda_{exc} > 350$ nm) instead of high-energy UV-excitation (e.g., mercury discharge excitation with $\lambda_{exc} < 330$ nm) for fluorescent thin-films (e.g., marking, advertisement, thin-film illumination or displays) as well as for medical applications (e.g., optical imaging, theranostics).[14-17] Besides red emission and nanoscale size, additional aspects such as quantum yield, physical/chemical stability, reproducible synthesis, etc., are of major relevance. Transferring well-known red-emitting bulk phosphors (e.g., $Y_2O_3:Eu^{3+}$, $YBO_3:Eu^{3+}$, $YVO_4:Eu^{3+}$ [5]) to the nanoscale shows low quantum yields (< 20%) and UV excitability ($\lambda < 330$ nm) only. Thus, there is still a strong need for inorganic nanomaterials showing efficient emission of red light.

Another specific area in the field of luminescence that has emerged is the search for efficient and stable phosphors for the conversion of vacuum ultraviolet (VUV) radiation into visible light (for Xenon-based fluorescent tubes and plasma display panels).[18] The high VUV energy allows for the generation of two visible photons for each VUV photon absorbed. This so-called quantum cutting process is possible using the energy level structure of lanthanide ions. The search for a VUV phosphor with 200% quantum efficiency is an exciting challenge in the field of luminescence research.[19,20]

Additionally, the interest in the development of luminescent nanomaterials for conversion of IR to visible radiation is increasing (especially as fluorescent markers for biological imaging). This process can be obtained by up-conversion mechanisms, where several NIR photons can be absorbed by the material doped with rare-earth ions. Thus, up-conversion normally involves *f*-levels of the lanthanide ions, due to their precisely defined energy levels with low energy distribution and long lifetime. Many lanthanide-doped host materials are able to emit visible light under NIR excitation, but a highly efficient up-conversion process requires a good tuning between the host lattice, dopant ion and dopant concentration.[3,21]

This thesis reports on the research results concerning the rare-earth doping effects on structural, chemical, optical and photoluminescence properties of different host lattice materials. The main objective of the present work was to develop highly luminescent nanoparticles via incorporation of various lanthanide ions into the host lattice. In order to achieve bright emission and a high efficiency, any phosphor has to show high crystallinity to avoid any lattice defects or grain boundaries, as well as to obtain homogeneous incorporation of all dopants (e.g., activator/sensitizer or donor/acceptor). Non-radiative loss processes could be avoided by using high-purity starting materials, including dopants and absence of molecular functional groups with high-energy vibronic levels. Effective control of particle nucleation, growth, and agglomeration is essential to obtain high-quality nanoparticles. On the one hand, the synthesis has to be performed at a temperature as high as possible in order to increase the crystallinity and to avoid lattice defects; on the other hand, the synthesis has to be conducted at a temperature as low as possible in order to avoid uncontrolled particle growth and agglomeration. Coordinating solvents or stabilizers are necessary to control the particle size and the degree of agglomeration and to protect the particle surfaces. A modification of the resulting surface conditioning requires additional process steps and bears the risks of agglomeration and surface damage. The often complicated and time-consuming synthesis of luminescent nanocrystals is a challenge, but it offers the outlook to new and important applications.

In order to meet above mentioned criteria, ionic liquids (ILs) might be considered for the nanocrystals' synthesis. The properties of ILs can be tuned by different sets of cations and anions, what permits a design in properties that is difficult to achieve with conventional solvents. The importance of ionic liquids in the field of inorganic materials synthesis has been realized in terms of their excellent properties such as high thermal stability, low vapor pressure, wide temperature range for the liquid state, low interfacial tension, high ionic conductivity and broad electrochemical window.[22-25]

In this work, different luminescent phosphates, molybdates, fluorides, etc. based on the use of ILs as a reaction medium will be presented. The strategy to avoid agglomeration and achieve high crystallinity is a rapid heating over a short time interval, which can be accomplished by microwave irradiation in the case of highly polar ILs.[26,27] The combination of microwave heating and ionic liquids provides superior benefits for the rapid synthesis of materials over the conventional heating methods, especially in terms of reaction time and energy saving, resulting in small particle size, narrow particle size distribution and high purity. The structural, morphological and photoluminescence characterizations of the prepared samples and the results are presented in this work.

2 Analytical Methods

2.1 Spectroscopy

In general, spectroscopy is a scientific term related to interactions of various types of radiation with matter.[28-31] Spectroscopic methods refer to the measurement of the optical properties of radiation with photoelectric or other type of electronic devices. These methods are based on the electromagnetic spectrum that includes radiation varying from low-energy radiowaves and microwaves, infrared (IR), visible (VIS) and ultraviolet (UV) light, to high-energy gamma- and X-rays. Spectrochemical methods employing not only visible but also ultraviolet and infrared radiation are often called optical methods despite the human eye's inability to sense either of the latter two types of radiation.

When a sample is stimulated by application of an external electromagnetic radiation source, several processes are possible: reflection, scattering and absorption.[29] When some of the radiation hitting the surface is absorbed, it promotes an analyzed sample to an excited state. In absorption spectroscopy, the amount of light absorbed as a function of wavelength is measured. This can give both qualitative and quantitative information about the sample. In photoluminescence spectroscopy, the emission of photons is measured after absorption. The most important forms of photoluminescence for analytical purposes are fluorescence and phosphorescence spectroscopy. The analyzed sample is stimulated either by electromagnetic radiation or electrical energy or by a chemical reaction. Emission spectroscopy usually involves methods, in which the stimulus is electromagnetic radiation or electrical energy, and chemiluminescence spectroscopy refers to excitation by a chemical reaction. In both cases, measurement of the radiant power emitted as the analyte returns to the ground state can give information about its identity and concentration. The results of such a measurement are often expressed graphically by a plot of the emitted radiation intensity as a function of frequency or wavelength, which is called a spectrum.

2.1.1 Fluorescence Spectroscopy

Electromagnetic radiation is produced when excited atoms, ions or molecules relax to lower energy levels by releasing energy as radiation. Excitation can be achieved in many ways: (a) exposure to high-energy electrons, which generally leads to the emission of

X-radiation, (b) exposure to an electric current producing ultraviolet, visible or infrared radiation, (c) irradiation with a beam of electromagnetic waves, which produces fluorescence or phosphorescence radiation, and (d) an exothermic chemical reaction that produces chemiluminescence.[31] Radiation from an excited sample is characterized by an emission spectrum, showing the wavelength distribution of the emitted radiation, measured at a fixed excitation wavelength. Furthermore, recording an excitation spectrum is a converse procedure. An excitation spectrum shows the dependence of emission intensity on the excitation wavelength, measured at a fixed emission wavelength, usually at the emission maximum.

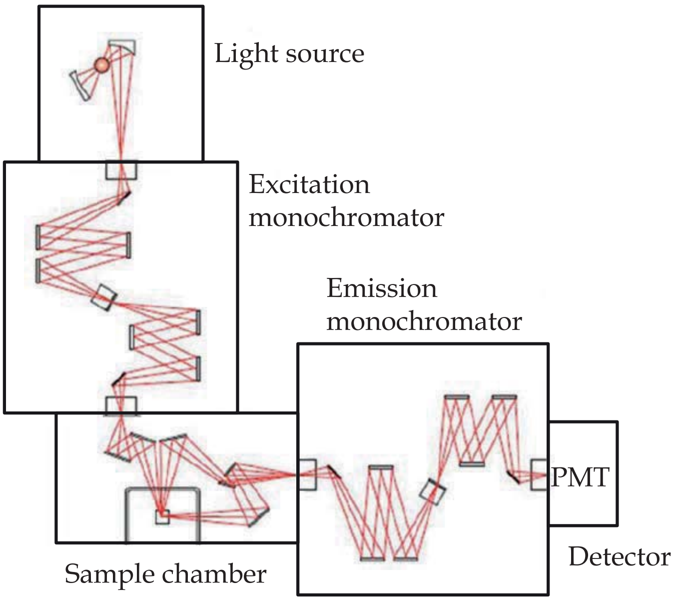

Figure 2.1: *A schematic diagram of a fluorescence spectroscope showing a light source, a sample chamber, a double grating excitation and emission monochromator and a detector (modified from reference [32]).*

The photoluminescence spectrometer used in this work (Figure 2.1) is equipped with two monochromators, to select both the excitation and emission wavelengths. The dual grating monochromator suppresses light with wavelengths different from the chosen one. The beam of light emitted by the light source is filtered by an excitation monochromator that allows the selection of a single wavelength of light to reach the sample. After exciting the sample, the resulting radiation is filtered by an emission monochromator and the intensity is measured using photomultiplier tube (PMT). By plotting the intensity signal against the wavelength, an emission spectrum is obtained.

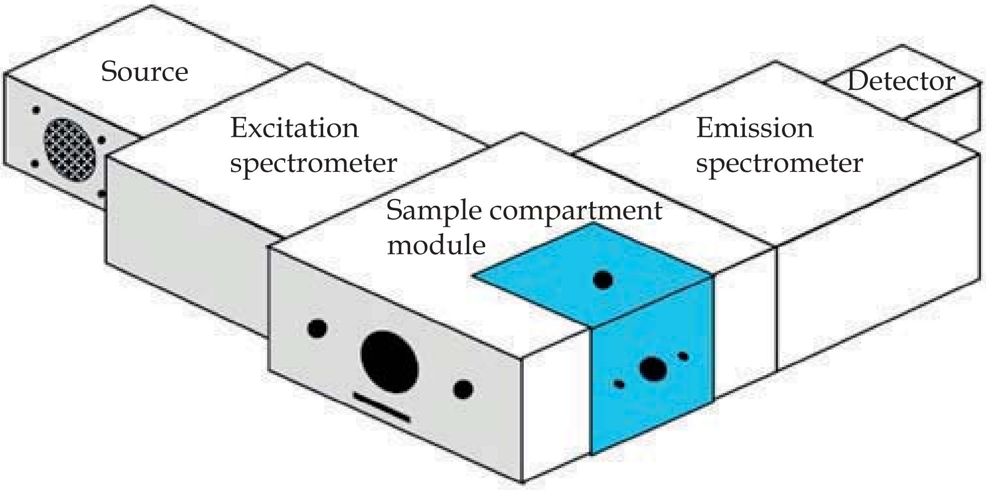

Figure 2.2: *The model of a Spex-Fluorolog 3.2.2 (modified from reference [32]).*

In this work, all photoluminescence measurements performed at room temperature were recorded using a Spex-Fluorolog 3.2.2 from HORIBA Jobin Yvon (Munich, Germany) (Figure 2.2). This spectrometer is equipped with a 450 W Xenon Arc Lamp as a source of excitation light, which provides a continuous spectrum from 250 to 650 nm, and a 975 nm laser diode (L975P1WJ) from Thorlabs (Munich, Germany) integrated on the side of the sample compartment module. The 9 mm package laser diode, placed inside the temperature controlled laser diode mount (TCLDM9) operates with a maximal current of 2 A and the optical output power of 1 W.[33] It is connected to the laser diode controller (LDC 210C) as well as to the thermoelectric temperature controller (TED 200C). Solutions and suspensions were measured in quartz cuvettes of quality 6Q from STARNA (Pfungstadt, Germany), whereas solid samples were pressed and placed as thin films directly in the solid-sample holder.

2.1.1.1 Determination of Quantum Yields

The fluorescence quantum yield is the ratio of photons emitted to photons absorbed through fluorescence:

$$QY = \frac{N(emitted)}{N(absorbed)} * 100\% \tag{2.1}$$

There are two different methods for recording the quantum yield: relative and absolute. The relative method is the comparative method established by Williams *et al.*, which involves the use of the well characterized standard samples with known values.[34] It is important that the standard and test samples are excited at the same wavelength, meaning that they absorb the same number of photons. Hence, a simple ratio of the integrated fluorescence intensities of the two samples (recorded under identical conditions) will yield the ratio of the quantum yield values:

$$QY = \frac{E_S * A_R}{E_R * A_S} * Q_R \tag{2.2}$$

QY: quantum yield of the specimen; Q_R: quantum yield of the reference; E_S and E_R: measured emission intensities of the specimen and the reference; A_S and A_R: measured absorption of the specimen and the reference

The second method used for the quantum yield measurements is called the absolute method. The major advantage of this method, described by Friend *et al.*, is that it provides a means of determining quantum yields for highly scattering samples by comparing them with an empty quartz cuvette.[35] As in the relative method, the use of identical conditions while performing emission and scattering measurements of the sample and the empty cuvette is very important, too. Photoluminescence (PL) efficiency measurements in solutions are relatively simple because it is usually easy to assume an isotropic angular distribution for emission. However, in the case of samples with a high refractive index, it is difficult to determine the angular distribution of emission, refractivity and absorption. A standard technique for measuring quantum yield of solid samples involves the use of an integrating sphere (also known as an Ulbricht sphere). An integrating sphere is a hollow sphere, which has its inner surface coated with a reflecting material. The interior of the used integrating sphere is made from a material known as Spectralon, which has a very wide, flat reflectance of over 95%, from the UV through the IR range. When a light source is placed inside the sphere, the angular dependence of emission influences the light. Hence, if the number of detected photons over a solid-angle Ω is N_Ω, the total number of emitted photons N is shown in the following equation:

$$N = N_\Omega \frac{4\pi}{\Omega} \tag{2.3}$$

Between the wall of the sphere and the grating spectrometer, there is an optical fiber. Immediately in front of the fiber, there is a baffle to prevent direct illumination of the optical fiber. The laser illumination of specified wavelength is directed to the sample through a small entrance. A fraction of the incident laser light is reflected by the sample, the other part is transmitted and the remaining light is absorbed. The unabsorbed light strikes the surface of the sphere from which it is scattered. A fraction of this scattered light is then absorbed by the sample. In this model, it is assumed that later light scattered from different locations on the sphere interior contributes identically to the measured spectrum.

In the end, quantum yield is obtained by comparing the measured scattering and emission spectra of the sample and the empty cuvette, using the FluorEssence Software Version 3.5.8.63 from HORIBA Yvon Jobin GmbH.

2.1.2 Ultraviolet-Visible (UV-VIS) Spectroscopy

When radiation passes through a layer of solid, liquid or gas, certain frequencies may be selectively removed by absorption, a process in which electromagnetic energy is transferred to the atoms, ions or molecules composing the sample.[28-31,36]

Ultraviolet-visible (UV-VIS) light refers to electromagnetic radiation with a wavelength interval of 10-780 nm. Ultraviolet-visible spectroscopy applies UV-VIS radiation to identify different types of electronic transitions: (a) transitions of electrons in high energy orbitals of one atom, (b) transitions of electrons in a molecule from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO), (c) transitions of electrons in a complex compound between the ligand and the central atom, and (d) transitions of electrons in a semiconductor from the valence band to the conduction band.

The energy difference for the electron transition from the valence band to the conduction band is referred to as the band gap energy (E_g). In the UV-VIS range, the band gap energy of semiconductors is low enough for electron transitions. For these materials, there are generally two types of band gaps: (a) the direct band gap, where electrons and holes have the same momentum in valence and conduction band, (b) the indirect band gap, where the electrons have to pass through an intermediate state and transfer momentum to the crystal lattice. In the case of a direct band gap, the energy E_g can be calculated using equation 2.4 given by Tauc:[37-39]

$$\alpha h\nu = C\sqrt{(h\nu - E_g)} \tag{2.4}$$

α: absorption coefficient; hv: energy of incident radiation; E_g: band gap energy; C: constant relative to the material

When a specimen is exposed to UV-VIS radiation that matches the energy difference of possible electron transitions, part of the radiant energy will be absorbed and the electrons will reach an excited state. An UV-VIS spectroscope records the absorption at different wavelengths and a spectrum of absorbance (A) versus wavelength (λ) can be plotted. This spectrum shows one or more absorption peaks, where the wavelength at which the specimen absorbs the maximum amount of energy, is known as λ_{max}.

In this work, optical spectra in UV-VIS region of powder samples were collected in a wavelength interval of 250-900 nm with a Cary 100 spectrometer from VARIAN (Palo Alto, USA). The spectrometer was equipped with an integrating sphere from LABSPHERE (North Sutton, USA). A deuterium lamp was used as UV-light source; a quartz halogen lamp was used as visible light source. To eliminate background noise (for calibration of the baseline), barium sulfate was applied as reference for powder samples.

2.1.3 Fourier Transform Infrared (FT-IR) Spectroscopy

Infrared (IR) radiation refers to the electromagnetic radiation between the visible and microwave range. With wavelength in the range of 780 nm- 30 µm, IR can be divided in three regions: near (780 nm – 1.4 µm), middle (1.4 – 8 µm) and far IR (8 – 30 µm). The method used to identify the functional groups in organic and inorganic molecules is known as IR spectroscopy.[40,41] Herein, by exposing a molecule with functional group to infrared radiation, different kinds of vibrations are excited by the interaction of their dipole moments with this type of radiation. When the radiant energy matches the energy of a specific molecular vibrations associated with a change in dipole moment, absorption occurs. Vibrational frequencies of a particular group of atoms in molecules tend to behave mostly independent from those belonging to other groups of atoms in a molecule. Hence, the absorption frequencies for a particular chemical group are essentially constant and the IR absorption appears approximately in the same region of each spectrum.

A typical IR spectrum shows the energy expressed in wavenumber (cm^{-1}) plotted on X-axis and the transmittance on Y-axis. The absorbed energy can be described with following equation:

$$E = h\nu = h\frac{c}{\lambda} \tag{2.5}$$

E: absorbed energy; h: Planck's constant; ν: frequency; c: speed of light; λ: wavelength