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LUMINESCENCE PROPERTIES OF RARE EARTH DOPED BORATE BASED PHOSPHORS

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Abstract

As a potential use in radiation dosimetry, this thesis investigates the production of borate-based phosphors that have been doped with rare-earth elements such as Ce, Dy, and Eu. The luminous properties of these phosphors are also investigated. Borate phosphors are ideal for the detection and measurement of ionizing radiation because of their outstanding temperature stability, chemical resistance, and powerful light properties for which they are renowned. In the course of the investigation, borate phosphor materials will be synthesized through the use of solid-state reaction techniques, and then their structural and optical properties will be characterized. X-ray diffraction, also known as XRD, was applied in order to validate the crystallinity and phase purity of the phosphors that were manufactured. In order to investigate the emission properties, photoluminescence (PL) tests were carried out. The results of these tests revealed that the Ce, Dy, and Eu dopants significantly enhance the luminous capabilities of the host material. In addition, thermoluminescence (TL) and chemiluminescence (ML) tests were carried out in order to evaluate the effectiveness of these materials in the detection of radiation. Upon being subjected to γ-irradiation, the phosphors exhibited notable TL glow peaks and consistent ML responses, which served as evidence of their efficiency as radiation dosimeters.

Keywords: Synthesis, Luminescence, chemiluminescence,

Introduction

The development of alternative sources of light, which was made possible by advances in scientific knowledge, has been of immense benefit to humankind. When viewed in the dark, a firefly and a blazing coal appear to be the same thing. It is important to keep in mind that you may repeatedly put a firefly on your palm, but it is not easy to touch a piece of coal that is burning. The existence of two separate types of light is demonstrated beyond a shadow of a doubt by this argument. Temperature can originate from a variety of sources, such as the sun, iron, tungsten filament, coal, and other similar materials. Incandescence contributes to the presence of continuous spectra and light emission, both of which are present in these situations. On the other side, cold light sources consist of things like fireflies, screens from oscilloscopes and televisions, light-emitting diodes and fluorescent lights, and a variety of other examples. It is not an incandescence phenomenon that causes the emission of light under these circumstances; rather, the light that is emitted can have either a band spectrum, a line spectrum, or both. The term "luminescence" was coined by the scientific community to describe the phenomena of cool light emission.

Luminescence

Wiedemann was the first person to use the term "luminescence" in the year 1888; however, it appears that the cold light that is emitted by certain insects, fish, plants, and minerals has been present in nature ever since the beginning of life. The extra light emission that occurred above and above the background thermal emission was assumed to be the cause, since incandescence and gaseous discharge were dismissed as possibilities. The luminescence spectra of a substance are found to be characterized by the predominance of intermediary processes in energy absorption and photon emission, as was discovered. When the system is not in a state of equilibrium, the transition from absorption to emission that causes the radiation to be emitted is referred to as luminescence. When the electronic states in a solid are stimulated by an external source of energy, the excited energy is released as light as a result of the relaxation of electronic charges through radiative transitions. As a form of radiation, luminescence, which is light that often occurs at low temperatures, is one of the types of radiation that cold bodies discharge. These phenomena can be brought about by a variety of factors, including chemical processes, electrical currents, subatomic pressures, and crystallographic stress. That is the distinction between luminescence and incandescence, which refers to the light that is created by extremely high temperatures being present. The process of luminescence takes place when an atomic electron is elevated from its lowest energy "ground" state to a higher energy "excited" state by an external energy source. The electron then releases this energy as light, which enables it to return to its lowest energy "ground" state.

Mechanism Of Luminescence

The process of luminescence can be broken down into at least two distinct phases: the first phase involves the excitation of an external energy source, and the second phase involves the emission of photons. It is possible to differentiate luminescence emission from thermal radiation due to the fact that it violates both Kirchhoff's and Wien's chemical laws. The incandescent emission has a continuous spectrum, in contrast to the luminescence spectra, which are either band or line spectra, or a combination of these two types of spectra. In contrast to Rayleigh scattering, Cerenkov emission, the Compton effect, and the Raman effect, luminescence is independent of these phenomena.

The luminescence of solids is considerable and structurally sensitive, making it one of the most important features of solids. The energy level of the electrons in the solid, which are organized into bands, is what has the most influence on it. Impurities cause the crystal's perfect periodicity to be disrupted, which leads to the introduction of more localized levels in the forbidden gap. This occurs when impurities are made into the crystal. In these kinds of materials, luminescence occurs in an effective manner at molecular regions where electron transitions can optically reemit the energy that has been absorbed. Solids are said to have luminescence centers when they are found in certain specific regions. In order to determine the centers of recombination for electrons and holes, their respective effective cross sections are utilized. These cross sections are represented by the symbols σe for electron capture and σh for hole capture, respectively. It is possible for a center to be classified as a luminescence center if the probability of radiative emission (Pr) is much higher than the likelihood of non-radiative emission. If this is not the case, the center is referred to as a "killer" center. The recombination center is the factor that determines how long the free electrons and holes in the material will remain in existence.

Objectives

1. To prepare the optimum thermoluminescence, immunoluminescence and photoluminescence materials by doping rare earth impurities in borate based phosphors.
2. To understand the mechanism of luminescence excitation in borate-based phosphors using TL, ML studies.

Synthesis, X-Ray Diffraction

Synthesis is the process of creating a new substance by combining chemical components, groups, or simpler compounds, or by breaking down an existing complex molecule. Synthesis can also be utilized to create a new substance by breaking down an existing complex compound. In order to successfully synthesize phosphors, it is necessary to possess cutting-edge capabilities in the areas of high-temperature chemistry, precursor handling and preparation, and starting material purity. The manufacturing of devices necessitates the use of additional scientific disciplines, such as thin film technology and suspension chemistry.

Despite the fact that there are already over 10,000 phosphors available for purchase, researchers are still looking for phosphors that have low processing temperatures and affordable prices. One of the most important factors that determines their characteristics is the synthesis process. A number of different approaches can be taken in order to successfully synthesize luminous materials. Given that the chemical formula of the majority of phosphors is already known, it would appear that the manufacture of the light materials would be a straightforward process. This is because the host materials are already known. Nevertheless, in actual practice, the synthesis of phosphors that possess the requisite characteristics can prove to be a significant challenge. Challenges arise as a result of the huge number of elements that need to be taken into consideration. These aspects include, but are not limited to, activator integration at target locations, impurity removal, application-specific grain size and shape, manufacturing cost, batch homogeneity and repeatability, and many more.

Photoluminescence

A substance is said to exhibit photoluminescence (PL) when it absorbs photons and then emits them once the absorption process is complete. In a theoretical sense, this is analogous to the emission of a photon when the system is excited to a higher energy level and then dropped back down to a lower energy state thereafter. The utilization of photo excitation is one of the primary ways in which this particular type of luminescence is distinguished from others. In most cases, the amount of time that passes between an emission and an absorption is on the order of ten nanoseconds that is considered to be extremely brief. Under certain circumstances, however, it is feasible to extend this time period into the minutes or even the hours by a significant amount. Research on photoluminescence has a wide range of applications, some of which include estimating the concentration of semiconductors, finding particular faults, and determining the band gap energy of semiconductors. Through the examination of photoluminescence, one can gain a deeper comprehension of the physical mechanism that underlies recombination. Within the scope of this chapter, the synthesis of luminars that are based on borate and have been doped with rare earth elements happens. The generation of compounds was validated by XRD data, and the presence of rare earth impurities in the host materials was validated by PL measurements. Both of these findings were confirmed successfully.

- **Experimental**

In this investigation, phosphors doped with rare-earth impurities were synthesized using the procedures described in previous research (Lavat et al., 2004; Yang et al., 2006). The phosphors that were produced were MB4O7:RE (M = Ba, Ca, Sr) and LnCa4O(BO3)3:RE (Ln = Gd, La, Y). According to the findings of XRD analysis, one of the disadvantages of the precipitation and melt method is that it results in the production of samples that have a polycrystalline multiphase composition that contains a number of M-polyborates components. For an extended period of time, reheating and regrinding the sample would not result in the production of a material that consists of only one phase inside it. In light of this, the Solid-State Diffusion technique was the primary focus of our attention. A list of the samples that were prepared for this investigation may be seen in Table 2.1.

1 Synthesis of MB4O7:RE (M= Ba, Ca, Sr; RE= Ce, Dy, Eu) Phosphors

MB4O7 (M = Ba, Ca, Sr) phosphors were synthesized using the solid-state diffusion approach. These phosphors were both undoped and doped with rare earth elements (RE = Ce, Dy, Eu). For the purpose of this method, the necessary quantity of carbonates (BaCO3, CaCO3, SrCO3), boric acid, and rare earth oxides (Ce2O3, Dy2O3, Eu2O3) were thoroughly crushed in a pestle and mortar. After that, the mixture was heated at 725 degrees Celsius for a period of twelve hours, and then it was gradually cooled. The obtained sample was milled once more, then burned at 750 degrees Celsius for a further twelve hours, and finally allowed to gradually cool down to room temperature.

Table 3.1: Samples collected for this study

Host	Dopant	Concentration of Dopant (mol%)						
BaB_4O_7	Ce	0.05	0.1	0.2	0.5	1	2	3
BaB_4O_7	Dy	0.05	0.1	0.2	0.5	1	2	3
BaB_4O_7	Eu	0.05	0.1	0.2	0.5	1	2	3
CaB_4O_7	Ce	0.05	0.1	0.2	0.5	1	2	3

CaB_4O_7	Dy	0.05	0.1	0.2	0.5	1	2	3
CaB_4O_7	Eu	0.05	0.1	0.2	0.5	1	2	3
SrB_4O_7	Ce	0.05	0.1	0.2	0.5	1	2	3
SrB_4O_7	Dy	0.05	0.1	0.2	0.5	1	2	3
SrB_4O_7	Eu	0.05	0.1	0.2	0.5	1	2	3

XRD Characterization

Phosphors that were created for the current experiment were analyzed using an X-ray diffractometer manufactured by Philips called the PANalytical X'pert Pro. The technical details of this instrument are presented in table 2.2 below. For the purpose of confirming that the sample was formed, the XRD pattern that was produced from the sample is compared with the data that corresponds to it in the JCPDS system.

Table 3.2: Specifications of the Philips PANalytical X'pert Pro X-ray diffractometer in terms of its technical specifications

Parameter	Specification
Target-anode Material	Cu
K-alpha radiation [^{0}A]	1.54060
Generator setting	40mA,45kV
Measurement temperature [^{0}C]	25.00
Specimen Length [mm]	10.00
Scan Type	Continuous
Scan speed/Scan Step Time[s]	13.5665
Step Size[degree-2theata]	0.0170
Start position[degree-2theata]	5.0044
End position[degree-2theata]	99.9834

3 Photoluminescence Characterization

The Spectro fluorophotometer was used to record the PL of the samples in order to verify the presence of rare earth ions in borate-based phosphors and to determine the role that these ions play in the samples. An excitation light is used to irradiate a sample, and then the Spectro fluorophotometer analyzes the fluorescence that is emitted from the sample after it has been irradiated. This allows the measurement of either qualitative or quantitative analysis. The following diagram (Fig 3.1) provides a schematic representation of a typical configuration of the Spectro fluorophotometer Simadzu RF-5301PC.

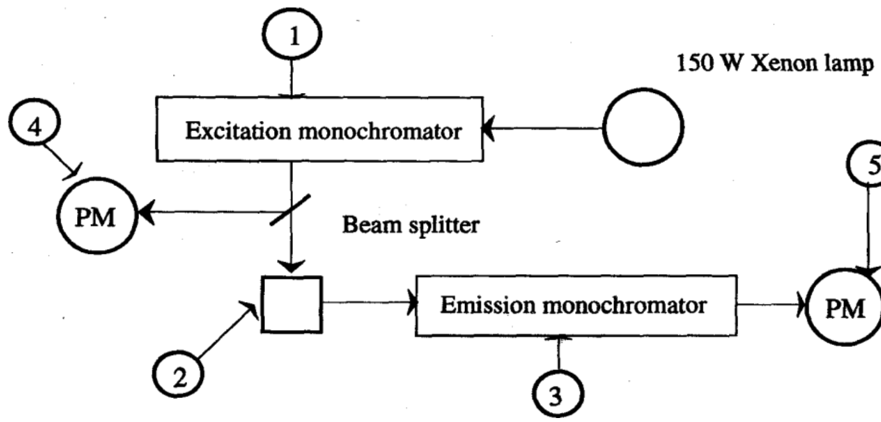

Fig 1 Constitution of RF-5301PC

In order to obtain excitation light, the excitation monochromator (1) separates a band of a specific wavelength from the light that is emitted by the Xenon lamp. The excitation monochromator comprises a diffraction grating with a bigger aperture in order to capture the most amount of light possible. This is due to the fact that brighter excitation light will contribute to a higher sensitivity of the Spectro fluorophotometer. A cell that is full of sample is accommodated within the cell holder (2). Fluorescence that is emitted from the sample is selectively received by the emission monochromator (3), and the intensity of the fluorescence is measured by the photomultiplier tube that is contained within the monochromator. This particular monochromator is equipped with a diffraction grating that is of the same size as the one found in the excitation monochromator. This makes it possible to gather the maximum quantity of light and maintain an uninterrupted radiation spectrum. In the absence of any countermeasures, however, their propensity to emit light in an unstable manner will lead to an increase in the amount of output signal noise. For the purpose of monitoring, the photomultiplier tube (4) is used. When it comes to spectro-fluorophotometers, the Xenon lamps that are utilized are typically distinguished by their very high emission intensity and Additionally, the distortion in the spectrum is caused by the non-uniformity in the radiation spectrum of the Xenon lamp as well as in the spectral sensitivity characteristics of the photomultiplier tube. These criteria are commonly referred to as instrument functions. A portion of the excitation light is monitored by the photomultiplier tube (4), and the resultant signal is then fed back to the photomultiplier tube (5) for fluorescence scanning. This allows the photomultiplier tube to overcome the factors specified above. (The light-source compensation system is the name given to this particular scheme).

Mechanoluminescence

Mechanoluminescence (ML) is the term used to describe the phenomenon of light emission that occurs as a consequence of the deformation and fracture of materials. This phenomenon was found a very long time ago. In order to characterize the wide range of processes that result in the emission of light as a result of the application of mechanical energy to solids, the term "mechanoluminescence" is now being utilized. The ML approach provides a number of intriguing opportunities, such as the identification of cracks in solids and the mechanical activation of a variety of traps that are present in the solids. A technique that is ideal for the clarification of the mechanical, optical, structural, and electrical properties of solids has arisen as a result of the emergence of ML as a solid-state physical phenomenon. Due to the fact that ML emission is connected with stress, fracture, and damage of solids, this inherent behavior of ML material has been utilized in order to manufacture mechanoluminescent stress, fracture, and damage sensors (Chandra, 2008). This is despite the fact that there is still a correlation between ML intensity and mechanical deformation.

Research on machine learning has evolved into an interdisciplinary field of study. In the fields of physics, chemistry, geology, and material science, it is generally accepted. The study of the association between ML and the physical properties of the substance is being done in the field of Physics. The function that molecular behavior and structure play in the process of molecular ligand excitation is something that chemists are interested in studying. For the purpose of geological research, the association between ML and cleavage and crystal structure is investigated. Studies are conducted in the field of material science to investigate the relationship between ML and the deformation, fracture, and hardness of the crystal. In spite of the fact that there are differences in the field of machine learning research, the primary purpose of the majority of researchers up to this point is to comprehend the mechanism of ML's excitation and to investigate the ways in which this phenomenon may be utilized to improve the well-being of human beings. The phenomena known as ML is observed in about half of all inorganic solids and between one-fourth and one-third of all organic solids, regardless of whether they are crystalline or nanocrystalline compounds. In addition to being detected in conductors, it has also been observed in insulators and semiconductors (Chandra, 1998).

Thermoluminescence

When a solid sample is heated after being excited by high-energy radiation, a phenomenon known as thermoluminescence (TL) or thermally induced luminescence occurs. Radiation (ionizing, UV, etc.) causes the TL material to absorb energy, which it then stores until heated. Thermoluminescence glow curves show the light intensity versus temperature. Since the heating rate is typically constant, the literature frequently depicts the glow curve as the TL intensity vs. the measurement cycle time or channel number rather than the temperature. Glasses, ceramics, polymers, and even certain organic substances display TL. The materials with the highest TL sensitivity are insulating solids that have been doped with activators, which are appropriate chemical impurities. Typically, this phenomenon is explained in terms of the band theory of solids. Irradiation creates holes and electrons in a material. A localized energy level within the forbidden gap is created by a fault in the solid. Trapped at these defect sites upon irradiation are electrons and holes. With enough heat applied to the material, the trapped electrons and holes are able to release themselves and enter the conduction band, also known as the valence band. From here, they can either recombine with trapped holes or electrons or be re-trapped. Recombination centers are spots where DNA recombination takes place. The term "luminescence center" describes this location when recombination is radiative.

Following is a list of the most important applications of TL:

- **Radiation dosimetry:** Nowadays, ionizing radiation is widely used in engineering, medicine, research, and technology for a variety of beneficial purposes. Accurate measurement of radiation energy absorption by the exposed material is crucial for achieving the intended outcomes in all applications. To estimate unknown radiations, TL dosimetry relies on the fundamental principle that the TL output is exactly proportional to the radiation dosage absorbed by the phosphors.

- **Archaeology:** Through the use of the thermo luminescence technique, it has been discovered that the dating of ancient ceramic pieces is quite successful.

- **Geology:** Geology was one of the first fields of study to embrace the TL approach for use in a wide range of applications. These applications include the dating of mineralization, the measurement of igneous activity, the appraisal of sedimentation, and the assessment of the rate of expansion of beaches and sand dunes. In situations where other conventional procedures are unsuccessful, the TL dating technique has been proven to be beneficial in dating specimens of geologically recent origin.

- **Forensic science:** Among the most important research topics in the field of forensic science is the development and standardization of methods for comparing evidential materials with other materials of known origin that are comparable to them but are only available in minute quantities and are required to be studied in a non-destructive manner for the goal of providing evidence. Thermoluminescence has the potential to provide appealing techniques in a variety of materials that are frequently encountered in crime investigations, such as glass, earth, safe insulation aerials, and other similar materials.

- **Biology and Biochemistry:** With regard to the investigation of hydroxy and aminobenzoic acids, proteins, nucleic acid, plant leaves, algae, and bacteria, the endeavors have been fruitful. It is possible that the results of the TL experiment will reveal that the Ortho form of benzoic acid is stable, as well as that radiation damage in nucleic acid is transferred intramolecularly. Protein and the components that make up proteins might have a correlation with the TL behavior of proteins.

- **Quality control:** The TL approach has the potential to be utilized in the quality control of a wide variety of products, including ceramics, glasses, and semiconductors. Recently, it has been demonstrated that the changes in the low temperature TL glow curve can be connected with structural differences and/or chemical tracer impurities in the case of textile fibers. This was demonstrated in some recent research.

Thermoluminescence (TL) is now extensively used in dosimetry of ionizing radiations. Rare earth doped sulphates, borates, tungstates, phosphates, vanadates, silicates and fluorides are good phosphors for application in thermo luminescence dosimetry. Though the use of thermo luminescence for radiation measurements had been stated to be made as early as in 1895 by Wiedmann and Schimidt, the work on the topic took momentum with report of Daniels et al (1953) based on the extensive work on the feasibility of using TL in dosimetry and other related applications.

Conclusion

In the recent past, a number of researchers have investigated the association between ML and other types of luminescence. Comparisons of various types of luminescence have been the subject of a number of experiments that have been carried out. the phosphors $MgSO_4$, $CaSO_4$, $SrSO_4$, and $BaSO_4$ that were activated with Tb^{3+} and found that they had PL and TL values. According to their findings, the conventional model of the TL emission mechanism is incompatible with the significant disparities that exist between the characteristics of the PL emission spectrum and the TL emission spectrum respectively. the connections between ML and TL in Dy activated $CaSO_4$ phosphors are quite strong. research on the ML of $ZnAl_2O_4$:Mn that was created by friction. They came to the conclusion that the ML is caused by triboelectricity induced electroluminescence. the ML and TL spectrum shift of γ-irradiated KBr and KCl crystal. They came to the conclusion that the spectral shift could be the result of a change in the lattice parameter as well as the energy of the band gap associated with changes in temperature and pressure. In order to provide evidence in favor of the proposed hypothesis, they do glow curve measurements.

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