ISSN 2063-5346

REVIEW ON THERMOLUMINESCENCE PHOSPHOR MATERIALS: SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS

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Article History: Received: 02.04.2023 **Revised:** 20.05.2023 **Accepted:** 22.06.2023

Abstract

Thermoluminescence (TL) phosphor materials have gained significant attention in various fields, including radiation dosimetry, dating techniques, and medical imaging. This review paper aims to provide a comprehensive overview of the synthesis methods for phosphor preparation and applications of TL phosphor materials. It covers both traditional and emerging TL phosphor materials, highlighting their unique properties and potential applications.

Key words: Thermoluminescence, Phosphor, Dosimeter, Solid state reaction.

Introduction

Thermoluminescence (TL) is a phenomenon exhibited by certain materials that emit light when heated after being exposed to ionizing radiation. The principle of thermoluminescence involves the trapping and subsequent release of charge carriers (electrons and holes) within the crystal lattice of the material. When a TL phosphor material is exposed to ionizing radiation (such as X-rays, gamma rays, or beta particles), the incident radiation transfers energy to the electrons present in the material. Some of these electrons get excited to higher energy levels and become trapped in localized energy states or "traps" within the crystal lattice[1]. Over time, these trapped electrons undergo a process called "thermally stimulated release." When the TL phosphor material is heated, either gradually or rapidly, the trapped electrons absorb thermal energy and are thermally excited to higher energy levels. As the electrons return to their original energy levels, they release the excess energy in the form of light, resulting in luminescence[2].

The emitted light is detected and measured using a photomultiplier tube or other light-sensitive detectors. The intensity of the emitted light is proportional to the amount of radiation previously absorbed by the material. By analyzing the emitted light, it is possible to determine the amount of radiation exposure the TL phosphor material has received[3,4]. The thermoluminescence phenomenon relies on the properties of the crystal lattice and the specific energy levels of the traps within the material. Different TL phosphor materials have varying trap depths and characteristics, allowing them to be used in a range of applications such as radiation dosimetry, luminescence dating, and medical imaging. In summary, thermoluminescence is the emission of light by a material when it is heated after being exposed to ionizing radiation. The principle involves the trapping of electrons during radiation exposure and their subsequent release as luminescence when the material is heated[5,6].

Importance of TL phosphor materials in radiation dosimetry and dating techniques

TL phosphor materials play a crucial role in radiation dosimetry and dating techniques due to their unique properties and ability to accurately measure and record radiation exposure. Here are the key reasons for their importance:

Radiation Dosimetry: TL phosphor materials are widely used in radiation dosimetry to measure and quantify the amount of radiation absorbed by various materials or living tissues. They offer several advantages over other dosimetry techniques:

- **High sensitivity**: TL phosphor materials exhibit high sensitivity to ionizing radiation, allowing for accurate detection and measurement even at low radiation doses.
- **Wide dose range**: TL phosphor materials can detect a wide range of radiation doses, making them suitable for applications ranging from medical radiation therapy to occupational radiation monitoring.
- **Retrievable and reusable**: TL phosphor materials can be reused for multiple measurements as they retain the recorded radiation dose until they are thermally stimulated. This makes them cost-effective and environmentally friendly compared to some other dosimetry methods.
- **Stability and long-term storage**: TL phosphor materials can retain the recorded dose information for extended periods, making them suitable for long-term dose monitoring and retrospective analysis.

Luminescence Dating Techniques: TL phosphor materials are instrumental in luminescence dating techniques, which involve estimating the age of geological and archaeological samples by measuring the accumulated radiation dose. Key aspects of their importance include:

- Trapped charge dating: TL phosphor materials can trap and store electrons when exposed to natural ionizing radiation. By measuring the intensity of the thermoluminescent emission, it is possible to determine the accumulated radiation dose and calculate the age of the sample.
- Dating diverse materials: TL phosphor materials can be applied to various materials, including ceramics, minerals, sediments, and archaeological artifacts. This versatility enables the dating of a wide range of samples from different time periods and environments.
- Non-destructive analysis: Luminescence dating techniques using TL phosphor materials allow for non-destructive analysis of samples, preserving their integrity and allowing further analysis or display.
- Complementary dating methods: TL dating often complements other dating methods, such as radiocarbon dating, extending the range and accuracy of age determination.

Radiography: TL phosphor materials have been used as scintillators in radiographic imaging systems. In these systems, X-rays are absorbed by the TL phosphor material, which in turn emits light (luminescence) in response. This emitted light is then converted into an electrical signal for image formation. TL phosphors offer high sensitivity and wide dynamic range, allowing for the capture of detailed X-ray images with low radiation doses. Calcium tungstate (CaWO4) and rare earth-doped phosphors, such as gadolinium oxysulfide (Gd2O2S:Tb), are commonly used TL phosphors in radiography[7,8,9].

Computed Tomography (CT): TL phosphor materials have also been utilized in CT imaging systems, which provide cross-sectional images of the human body. In CT, TL phosphors serve as scintillators that convert the X-ray energy into visible light. This light is then detected by photodetectors, enabling the reconstruction of high-resolution images. TL phosphors used in CT imaging should possess high stopping power for X-rays and good temporal response. Materials like rare earth-doped yttrium aluminum garnet (Y3Al5O12:Ce) and lutetium oxyorthosilicate (Lu2SiO5:Ce) are commonly employed TL phosphors in CT scanners[10,11].

Positron Emission Tomography (PET): PET is a molecular imaging technique that uses radioactive tracers to visualize and quantify metabolic processes in the body. TL phosphor materials play a crucial role in PET detectors known as scintillation crystals. These crystals convert the gamma rays emitted by the positron-emitting radiotracers into visible light. This light is then detected by photomultiplier tubes or silicon photomultipliers for image reconstruction. TL phosphors used in PET imaging require high stopping power for gamma rays and excellent energy resolution. Bismuth germanate (BGO) and lutetium-yttrium oxyorthosilicate (LYSO) are widely employed TL phosphors in PET scanners

The advantages of TL phosphor materials in medical imaging include their high sensitivity, good linearity, and compatibility with different imaging modalities. They offer excellent image quality, enabling accurate diagnosis while minimizing patient radiation exposure. Additionally, TL phosphors can be tailored for specific applications by adjusting their composition and doping levels. In conclusion, TL phosphor materials have demonstrated significant potential in various medical imaging applications. Their unique luminescent properties make them valuable components in radiography, CT, and PET systems, contributing to improved diagnostic capabilities and patient care[12].

Synthesis Methods:

Solid-state synthesis: Solid-state synthesis is a widely used method for the preparation of thermoluminescent (TL) phosphor materials. It involves the direct reaction of solid-state precursors, typically powders or crystals, under controlled conditions to form the desired TL phosphor material. The process typically involves grinding, mixing, and heating the precursors to induce a solid-state reaction. The starting materials or precursors, which may be in the form of oxides, carbonates, or other compounds, are carefully weighed and mixed to obtain a homogeneous mixture. This mixture can be achieved by grinding the precursors in a mortar and pestle or using a ball milling technique. The powdered precursors are thoroughly mixed to ensure a uniform distribution of the chemical components. This step aims to promote the formation of a homogeneous solid solution during the subsequent heating process. The mixed precursor powder is subjected to controlled heating in a furnace or kiln. The heating is carried out at elevated temperatures, typically ranging from a few hundred to several hundred degrees Celsius, depending on the specific TL phosphor material being synthesized. The heating process induces chemical reactions between the precursors, resulting in the formation of the desired TL phosphor compound. After the reaction is completed, the synthesized material is cooled down slowly to room temperature to prevent the formation of undesired phases or crystal defects. In some cases, an annealing step is performed to optimize the crystal structure and enhance the TL properties of the phosphor material. Solid-state synthesis is a well-established method for the synthesis of TL phosphor materials and offers several advantages in terms of simplicity, cost-effectiveness, control over composition, scalability, and purity. It continues to be widely used in research and industrial settings for the production of high-quality TL phosphor materials[13,14]

Solution-based synthesis methods: Solution-based synthesis is a widely used approach for the fabrication of thermoluminescence (TL) phosphor materials. It offers several advantages, including the ability to control the composition, morphology, and crystalline structure of the materials. Within solution-based synthesis, there are several common methods, including precipitation, sol-gel, and hydrothermal methods[15].

Precipitation Method: The precipitation method involves the formation of TL phosphor materials through the precipitation of precursor compounds from a solution. The general process involves the following steps. Dissolving precursor salts or compounds in a solvent to form a solution. Addition of a precipitating agent or reactant to the solution, resulting in the formation of insoluble precipitates. Washing and drying of the precipitates, followed by thermal treatment to obtain the desired TL phosphor material[16].

Sol-Gel Method: The sol-gel method is based on the formation of a colloidal suspension or "sol" that undergoes gelation to form a solid network. The sol-gel process typically involves the following steps. Preparation of a precursor solution by dissolving metal alkoxides or other precursors in a suitable solvent. Hydrolysis and condensation reactions occur within the precursor solution, leading to the formation of a sol. Aging of the sol to promote further particle growth and gelation. Drying and calcination of the gel to obtain the final TL phosphor material[17].

Hydrothermal Method: The hydrothermal method involves the synthesis of TL phosphor materials under high-pressure and high-temperature conditions within an aqueous solution. The key steps of the hydrothermal method include. Preparation of a reactant solution containing precursor salts or compounds dissolved in water. Sealing the reactant solution in a high-pressure vessel and heating it to the desired temperature. Allowing the materials to undergo nucleation and crystal growth in the high-temperature and high-pressure environment. Cooling, washing, and drying of the obtained TL phosphor material.

These solution-based synthesis methods offer several advantages, including precise control over composition, particle size, and crystallinity of the TL phosphor materials. Additionally, these methods allow for the incorporation of dopants or modifiers to tailor the luminescent properties of the materials. However, each method has its specific requirements and considerations regarding reaction conditions, precursor selection, and post-treatment processes. The choice of the synthesis method depends on the specific TL phosphor material desired, the targeted properties, and the intended applications. Researchers select the most suitable method based on factors such as ease of implementation, scalability, and the ability to achieve the desired material characteristics[18].

Review of Commercially Used Phosphor Materials

Calcium sulfate: Dysprosium (CaSO4:Dy) is commonly used as an activator dopant in calcium sulfate phosphors. It acts as a luminescent center by capturing the energy of ionizing radiation and releasing it as light during thermoluminescence. CaSO4:Dy exhibits a broad thermoluminescent glow curve with a peak temperature around 200-300°C, making it suitable for radiation dosimetry applications[19].

Calcium sulfate: Terbium (CaSO4:Tb) is another activator dopant used in calcium sulfate phosphors. It enhances the thermoluminescent properties and sensitivity of the material. Calcium sulfate doped with terbium exhibits a thermoluminescent glow curve with a peak temperature around 125-175°C. This type of phosphor is commonly used in medical dosimetry and radiation therapy applications[20].

Lithium fluoride-based phosphors(LiF:Mn): (Mn) is a commonly used activator dopant in lithium fluoride phosphors. It acts as a luminescent center, capturing the energy of ionizing radiation and releasing it as light during thermoluminescence. Lithium fluoride doped with manganese exhibits a thermoluminescent glow curve with a peak temperature around 200-300°C. This type of phosphor is widely used in radiation dosimetry applications, including medical, environmental, and personal dosimetry[21].

(LiF:Mg,Ti): LiF:Mg,Ti exhibits a thermoluminescent glow curve with a peak temperature around 120-200°C. This type of phosphor is commonly used in medical imaging applications, including radiography and computed tomography (CT). Overall, lithium fluoride-based phosphors, doped with activators such as manganese or co-dopants like magnesium and titanium, offer excellent thermoluminescent properties, making them valuable materials in various radiation-related applications[22].

Alkali halide phosphors: Alkali halide phosphors are a class of thermoluminescent materials composed of alkali halide compounds doped with impurities or activators. Alkali halides refer to ionic compounds composed of alkali metals (e.g., sodium, potassium) and halogens (e.g., chloride, bromide, iodide). These phosphors exhibit thermoluminescent properties, meaning they emit light when heated after exposure to ionizing radiation. Sodium iodide (NaI): Sodium iodide doped with impurities or activators, such as thallium (NaI:Tl), is widely used in radiation detection and imaging systems. NaI:Tl phosphors offer high sensitivity and excellent energy resolution, making them suitable for applications in gamma-ray spectroscopy and scintillation detectors[23].

Emerging Thermoluminescence Phosphor Materials

Transition metal-doped phosphors

(Mn)-doped phosphors: Mn-doped TL phosphors are widely studied and used in various applications. (Mn2+) act as activator centers, capturing ionizing radiation energy and emitting light during thermoluminescence. TL phosphors often exhibit broad TL glow curves with peak temperatures in the range of 150-250°C. These phosphors are employed in radiation dosimetry, luminescence dating, and medical imaging applications[24].

(Cu)-doped phosphors: Cu-doped TL phosphors possess unique luminescent properties and are used in TL dosimetry and imaging applications. (Cu+) as activators exhibit specific energy levels that facilitate efficient energy trapping and release during thermoluminescence. These TL phosphors typically exhibit TL glow curves with peak temperatures in the range of 200-400°C [(25)].

(Ni)-doped phosphors: Ni-doped TL phosphors are used in TL dosimetry and imaging applications. Ni^{2+}act as activators, capturing energy from ionizing radiation and emitting light during thermoluminescence. TL phosphors often exhibit TL glow curves with peak temperatures in the range of 200-400°C[26].

(Cr)-doped phosphors: Cr-doped TL phosphors are utilized in TL dosimetry and imaging applications. Cr ions (Cr^{3+}) as activators have energy levels suitable for efficient energy trapping and light emission during thermoluminescence. Cr^{3+}-doped TL phosphors typically exhibit TL glow curves with peak temperatures in the range of 150-250°C.

Organic-inorganic hybrid phosphors

Organic-inorganic hybrid thermoluminescence (TL) phosphors are a class of materials that combine organic and inorganic components to exhibit thermoluminescent properties. These hybrid phosphors offer unique advantages by leveraging the desirable properties of both organic and inorganic materials. In organic-inorganic hybrid TL phosphors, the organic component usually consists of an organic matrix or polymer, while the inorganic component includes luminescent centers or activators embedded within the organic matrix. The combination of these components leads to enhanced thermoluminescent properties and tailored luminescent behavior. Synthesis methods for organic-inorganic hybrid TL phosphors typically involve the incorporation of luminescent inorganic particles or nanoparticles into the organic matrix using techniques like sol-gel, polymerization, or blending methods. The choice of organic and inorganic components, their composition, and the doping concentration can be optimized to achieve the desired thermoluminescent properties. Applications of organic-inorganic hybrid TL phosphors include radiation dosimetry, medical imaging, and optoelectronic devices. Their tunable emission wavelengths and enhanced sensitivity make them suitable for various radiation detection systems, ranging from personal dosimeters to imaging devices used in medical diagnostics and industrial inspections

Nanomaterial-based phosphors

Nanomaterial-based phosphors are a promising class of materials that exhibit thermoluminescent properties at the nanoscale. These phosphors consist of nanosized particles or structures that have unique properties compared to their bulk counterparts, including enhanced luminescence efficiency, improved sensitivity, and tunable emission characteristics. Semiconductor nanocrystals (Quantum Dots) composed of semiconductor materials, such as cadmium selenide (CdSe) or lead sulfide (PbS). Quantum dots exhibit size-dependent luminescence properties, making them attractive for tunable thermoluminescent applications. Various types of nanoparticles, such as metal oxides (e.g., zinc oxide, titanium dioxide) and rare earth-doped nanoparticles, have been investigated for thermoluminescence. These nanoparticles offer unique luminescent properties and can be tailored for specific applications. Nanowires and nanotubes are one-dimensional nanostructures which have shown potential as thermoluminescent materials. The high aspect ratio of these structures provides efficient charge carrier trapping and release, leading to improved thermoluminescent performance.

Perovskite-based phosphors

Perovskite-based thermoluminescence (TL) phosphors are a class of materials that exhibit thermoluminescent properties and are composed of perovskite crystal structures. Perovskites are a group of materials with a specific crystal structure characterized by the general formula ABX3, where A and B represent cations, and X represents an anion. These phosphors have gained significant attention in recent years due to their excellent luminescent properties, including high TL sensitivity, wide TL temperature range, and tunable emission characteristics. Inorganic perovskite phosphors are composed of inorganic cations and anions in the perovskite crystal lattice. Common examples include metal halides and oxides. Inorganic perovskite phosphors exhibit excellent TL properties, such as high TL sensitivity and well-defined TL glow curves. They can be doped with various activators or impurities to enhance their luminescent properties. These phosphors find applications in TL dosimetry, radiation detection, and imaging systems. Hybrid organic-inorganic perovskites, also known as organometal halide perovskites, consist of both organic and inorganic components within the perovskite crystal structure. These materials have gained significant attention in the field of optoelectronics due to their exceptional photovoltaic and light-emitting properties.

Challenges and Future Perspectives:

The challenges and future perspectives in thermoluminescence phosphors involve improving TL efficiency and sensitivity, advancing synthesis methods, integrating with nanotechnology, exploring multifunctional properties, expanding applications in emerging fields, enhancing characterization techniques, and addressing environmental considerations. These efforts will contribute to the development of more efficient and versatile thermoluminescence phosphors for various applications. The development of TL phosphors with additional functionalities, such as optical sensing or photocatalysis, is also an area of future exploration.

Conclusion

This review paper aims to provide researchers, scientists, and engineers with a comprehensive understanding of thermo luminescence phosphor materials, their synthesis methods, characterization techniques, and potential applications. It also highlights the challenges and future directions for advancing the field. TL phosphor materials continue to find new applications and opportunities in emerging fields, such as radiation therapy, radiation shielding, and environmental monitoring. Integration of TL phosphors with nanomaterials, organic-inorganic hybrids, and perovskite structures opens up possibilities for advanced dosimetry systems and tailored luminescent materials with enhanced properties. Overall, TL phosphor materials have made significant contributions to radiation dosimetry, luminescence dating, and medical imaging. Their unique properties, dosimetric capabilities, and reliability have enabled precise dose measurements, accurate dating of materials, and improved imaging techniques, making them invaluable tools in various scientific and practical applications.

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