Inorganic thermoluminescent phosphors in radiation dosimetry: An overview

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Abstract. Thermoluminescence (TL) materials display a wide scope of uses in various zones, for example, personnel dosimetry, natural dosimetry, medical research and so forth. Doping of various rare earth impurities in various hosts is liable for changing the properties of materials valuable for different applications in various fields. These materials can be lighted by various kinds of bars, for example, γ-rays, X-rays, electrons, neutrons and so on. Different radiation systems, just as their portion reaction range, assume a significant function in thermoluminescence dosimetry. In the proposed article, initially we momentarily illustrate several delegate families of TLD phosphors. Secondly, we suggest the plan system focused on revelation of novel phosphors with center around the crystal structural deliberation. Finally, we overlook the results of other researcher on the current progresses in innovation and structural design of TLD phosphors that demonstrate the accepted approaches, together with (1) investigation of emerging phosphors from the auxiliary models, (2) preparation of new emerging phosphor materials of crystalline properties by doping and (3) basic change of the known phosphors. The crystalline properties of new emerging phosphor shows interest in crystal chemistry analysis for the development of new thermoluminescent dosimetric phosphors with the different properties like co-substitution and single particle analytical advances are also described in this literature.

Keywords: Thermoluminescence; dosimetry; TLD phosphors; radiation dosimetry, inorganic phosphors.

1. Introduction

The phenomenon of re-emission of absorbed radiation by phosphor when sample is heated is referred as thermoluminescence (TL) or optically stimulated luminescence (OSL) [1]. The metastable state is where the electron traps were formed and electrons get returned to the ground state from excited by releasing energy. This energy gets released in the form of heat. Boltzmann equation will administrate the prospect per unit time that a trapped electron will escape from a metastable state to an excited state [2]. To start with, the intensity of thermoluminescent emission doesn't stay consistent at stable temperature, yet diminishes with time and in the long run stops by and large. The thermoluminescence phenomenon is primarily used in the solid state dosimetric application for ionization dosimetry[3]. So as to balance out the snare structure, toughening forms dependent on temperature and time design are utilized to create the least inborn foundation and to get the most elevated proficiency. Different type of thermal treatments like anneling of phosphor material and exposing it with the radiation exposure has been given to the thermoluminescet phosphor before
it has been used in the field of dosimetric applications [4,5]. The reason behind this thermal treatment is to fix the trap depths created during the irradiation process. The background depends upon the high voltage that applied to the photomultiplier tube, on the temperature reliability of TL pursuer and moreover reuse of TL material.

2. Method of synthesis

Different methods have been developed in the recent years for the synthesis of inorganic thermoluminescent phosphors for the radiation dosimetry. Details of few methods have been explained below [6–8];

2.1 Wet chemical method:

Wet chemical method is chemical based method which requires materials in the form of nitrates usually because they are easily dissolvable in water. Wet chemical method is also a method for material synthesis but under this name “Wet Chemical” there are few more methods are added like sol-gel method, co-precipitation method, combustion method etc. combustion method contain more sub methods therefore we describe this method separately in the end of this section. So, here we explain sol gel method, main wet chemical method separately [9,10].

2.1.1. Main wet Chemical method:

In this method we don’t need any type of fuel for synthesis like we used before in sol-gel technique. Here we require starting materials which can dissolve in minimum amount of water. Take all starting materials in stochiometric ratio and dissolve them separately in beaker in minimum amount of water with constant stirring on hotplate keeping it at 80 °C. After dissolving it completely, add them in one beaker one by one with constant stirring in one beaker and keep it on hotplate. After this, a white precipitate was found keep this precipitate for drying in hot air oven for over the night at 90 °C. after that collect the dried sample and annealed it for 2 hours for removing an impurity. By cooling it at room temperature collect the final product for further characterizations.

2.1.2. Sol – Gel method:

In this method, all water dissolvable materials were used for the synthesis of phosphor. All precursors were liquefied in the beaker while keeping it on constant stirring at 80 °C. After dissolving all the reagents citric acid and polyethylene glycol (PEG) were added in the solution drop wise with the interval of 30 min. At this juncture citric acid is used as chilling agent and PEG is utilised as cross linking agent in the synthesis process. The ratio of citric acid and PEG is to be maintained 1:1 in the synthesis process. After mixing all the reagents, kept this solution on constant stirring with 80 °C temperature of hotplate. After some time a gel type solution is formed. This solution is then keep in oven for drying at 100 °C. after drying a black floppy sol was obtained. This black powder is due to chilling agent. This black powder is then annealed at above 500°C. After annealing a white fine powder is obtained this is further used for characterizations. Dy³⁺ activated Sr₅(PO₄)₃F phosphor is apatite type mineral phosphor [11].

2.1.3. Co-precipitation method:

This is another wet chemical based synthesis method which also required water dissolvable salts for synthesis. In this process, all the salts are dissolved into double distilled water solution and rare earths are also dissolved into water solution within the sight of ethanol. Ethanol is commonly utilized as a surfactant to: dodge agglomeration, control size of the particles, and keep up consistency in the particle size. The co-precipitation method without ethanol makes particles go through collection accordingly bringing about the non-consistency and expansion in particle size[12]. All solutions are mixed in the presence of ethanol. After mixing, the precipitate is then collect by centrifuging it. After getting final precipitate, wash it several times
by distilled water in order to remove impurity. This washed precipitate is then dried in oven at 100 °C for 24 hrs. This dried sample is then calcined for 2 hours and a final product is obtained after cooling it at room temperature[13,14].

2.1.4. Combustion synthesis:
Combustion synthesis is one of the main types of wet chemical based synthesis and further divided into two categories i.e. Simple combustion synthesis method and solution combustion synthesis method. In combustion synthesis method, type of synthesis technique is also differing by the fuel we are using for the synthesis. Different fuels are used for the preparation material by both solution and simple combustion methods like urea, citric acid, glycine, ethanol, DFH etc[5,15–18]. method for preparation of sample by both the methods are explained in subsequent part of this review.

2.1.4.1. Simple combustion method:
In simple combustion method, all the starting materials was weighed in stochiometric ratio and fuel which is used can be used in particular ratio and dissolve all the materials in a mortar pistel using distilled water. After dissolving all the samples in distilled water, transfer this solution in the china dish and fired this sample in open furnace at 500 to 550 °C. An enormous flame were analyze in the open furnace during the sample is burning. Once this sample is burned completely flame will damped in five minutes. Then takeout this sample from the oven and cooled it at room temperature. After cooling this sample can crushed for five minutes and keep it in furnace for annealing for 24 hrs in purpose of removing impurity. The sample is then cooled down at room temperature after 24 hrs and uses this sample for further studies.

2.1.4.2. Solution combustion method:
Solution combustion technique is another type of combustion technique using fuel. Same types of fuels were used in this method also like used in simple combustion technique. In this technique, all the starting materials were dissolved in a beaker by keeping it on constant stirring at constant temperature on magnetic stirrer. Once the starting materials and fuel get dissolved, transfer this solution into the china dish and repeat the same procedure as described in simple combustion method.

It is to be noted that when citric acid is used as fuel, the sample turns black after firing it in the open furnace in both the methods. Once it keep for annealing, it turns into white powder and useful for the studies.

3. Inorganic phosphors for radiation dosimetry
3.1. Silicate phosphors
Silicate phosphors are one of the most common phosphor considered in the field of luminescence due to his energy storage capacity. In this manner, among all the different types of silicate phosphors, choosing a correct host and activators for the synthesis is the major concern in thermoluminescence. The correct combination of dopant host material helps in the ideal doping level for dopants and it assumes to be help in the development of novel TLD phosphors. For the most part, rare-earths are chosen as dopant alluded to as activators. Among all the rare earths (REs), Dy³⁺ particle is a significant rare earth. As a dopant to the host as a result of their luminescence conduct like advanced and optical characters emerging from their non-full 4f configuration, narrow emission spectra, the exceptional narrowband emission and intricacy in strength levels assorted advances are likely, Dy³⁺ particles are engaged with electron trapping, and in light of this the persistent emission is more grounded when Dy³⁺ is conveyed into the host. The very reality that Dy³⁺ particles can refresh the three particles of the host, the Dy³⁺ particles may sell the development of deformities that go about as electron traps, as practical oxygen opportunities. In most recent couple of years, different silicate materials have been found by the researchers such as Ba₂MgSi₂O₇:Eu²⁺, Dy³⁺[19] Sr₂SiO₄: Dy³⁺ [20], Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ [21], Sr₃MgSi₂O₈[22]. Ba₂SiO₄: Dy³⁺ [23], Sr₃MgSi₂O₈ [23] and many more. TL material shows afterglow properties, which is understood as persistent luminescence and that they are especially functional in several applications like glow within the darkness road, bio-imaging and emergency
signs. As of now, the improvement of emerging phosphor presents to a substitution and rapid developing utilization of investigation in physical science, prescription field further as humanities dating, forensic science and radiation dosimetry. The chief vital use of thermoluminescent phosphor for radiation dosimetry. The uses of the novel radiant materials are upheld the data of the instrument. TL dosimetry discovers significance inside the space of wellbeing material science, radiation protection and private observance. As a rule, the character of materials is very delicate; it's low reliance on energy of light, low blurring and limit portion and with synthetic compounds naturally consequently, it's important to look out the novel mineral based phosphors for thermoluminescence dosimetry.

3.2. Sulfate phosphors
Few of the novel sulfate based mineral phosphors has been reported by the researchers as BaCa(SO₄):[24], K₂Ca₂(SO₄)₃:Eu [25], CaSO₄[26]. All of them, CaSO₄ phosphor is used as a commercial TLD phosphor for radiation dosimetry. This phosphor has been synthesized by different methods and reported by so many researchers yet. But very few sulfate based mineral phosphors are reported till the time. It’s essential to discover the novel mineral based sulfate phosphors for thermoluminescence dosimetry.

3.3. Phosphate phosphors
Recently, Phosphate materials make an emerging impact in the field of biomedical applications due to their noel properties like biocompatibility and bioresobality. Na₂Sr₂Al₂PO₄Cl₉ phosphate based chloroaapatite mineral phosphor is reported by the researchers [27] and it is further comprehensive by means of doping of mono, di and trivalent ionized ions. Thermoluminescence studies of synthesized phosphor were completed on exposing all phosphors by ⁶⁰Co-γ (gamma) source. The proposed phosphor shows TL glow curve with high intensity in the range of 180 °C to 250 °C. Few mono, di and trivalent activated ions in Na₂Sr₂Al₂PO₄Cl₉:Eu³⁺ phosphors, thermoluminescence intensity diminishes and peak get shifted in some extent which is might be due to change in local crystal structure. Enthrallingly, on doping of Y³⁺ ion in phosphor, TL intensity amplify in petite amount. Thus, the presence of mono, di and trivalent ionized ions in the Na₂Sr₂Al₂PO₄Cl₉: Eu³⁺ phosphor may perhaps endow with confirmation of its significance in the thermoluminescence dosimetric applications. Thermoluminescence glow curve of optimum TL intenisty with concentration quenching and linearity is as displayed in figure 1.
3.4. Titanate phosphors

Several luminescence phenomena are accessible and thermoluminescence is one of them. In general, thermoluminescence studies are performed on a phosphor or material in the view to use it for radiation dosimetric application. On the other hand, in the proposed work, thermoluminescence studies were performed to check the superiority of phosphor and its use in radiation dosimetry. Here thermoluminescence studies of Eu\textsuperscript{3+} and Dy\textsuperscript{3+} doped CaTiO\textsubscript{3} phosphors were performed by irradiating both the samples with γ -rays using 60Co open source with dose rate of 6.2 KGy/hour[28]. Fig. 2 displays the TL glow curve for different concentration of Eu\textsuperscript{3+} ion. On enhancing concentration of Eu\textsuperscript{3+}, TL glow curve intensity has been enhanced upto 0.5 mol % concentration and further than that TL glow curve intensity has been reduced on more increasing concentration. TL glow curve of Dy\textsuperscript{3+} activated CaTiO\textsubscript{3} phosphor for different concentration of Dy\textsuperscript{3+} are as shown in Fig. 3. This series of CaTiO\textsubscript{3}: X mol % Dy\textsuperscript{3+} are irradiated at 1.03 K Gy by γ -rays using 60Co irradiation source having dose rate of 6.2 K Gy/hour. It is observed that CaTiO\textsubscript{3}: 0.5 mol % Dy\textsuperscript{3+} phosphor shows maximum TL intensity and beyond that intensity goes on decreasing with increasing concentration of Dy\textsuperscript{3+}, known as concentration quenching. It is to be noted that both samples show high intensity peaks centered at 260 to 270 °C range which is one of the important characteristics of TL glow curve peak used for TLD applications. Moreover, CaTiO\textsubscript{3}: Dy\textsuperscript{3+} shows more intensity at low dose (3.1 K Gy) as compared to CaTiO\textsubscript{3}: Eu\textsuperscript{3+} (6.2 K Gy). Thus this all results show their potential that RE\textsuperscript{3+} activated CaTiO\textsubscript{3} phosphors demonstrate potential application in thermoluminescence dosimetric applications[28].
Figure 2. TL glow curve of Eu$^{3+}$ activated CaTiO$_3$ phosphor. (Reproduced with the permission from the ref. [28] ©2020 Elsevier publications).

Figure 3. TL glow curve of Dy$^{3+}$ activated CaTiO$_3$ phosphor (Reproduced with the permission from the ref. [28] ©2020 Elsevier publications).
4. Future trends in development in TLD materials

Mineral based TLD materials have attracted much more attention in the past few years. Consequently, thermoluminescence parameters like activation energy, order of kinetics, frequency factor are strongly depends on the thermoluminescence glow curve, source of irradiation and the phosphor we choose. In this review, firstly we described the art of structural design in the TLD phosphor especially in the mineral based TLD phosphor and their mathematical calculations to find-out trapping parameters of the TL glow curve. We also summarized some standard mineral phosphor types which show interesting properties in the thermoluminescence dosimetry and their structural design which is very important in the view of crystal chemistry. It is discovered that crystal-site engineering methodology include the shift of the occupied sites normally required for a high doping level, and afterward it for the most part forfeits the emission intensity and thermal stability of phosphors.

Here we describe some mineral based phosphors which are already reported in thermoluminescence dosimetry application. From these entire mineral based phosphors, apatite type mineral phosphors shows more potential towards the improvement in thermoluminescence dosimetry. From all the above report it is clear that very less work has been done in the other types of mineral phosphors which could also show potential application towards thermoluminescence dosimetry. There are a lot of minerals which can be useful in the thermoluminescence dosimetry which can be used in the environmental as well as personnel dosimetry.

5. Summary

This review summarized initially momentarily illustrates several delegate families of TLD phosphors. Secondly, we suggest the design methodology meant at innovation of novel phosphors with concentrate on the crystal structural deliberation. Finally, we took outlook of the results of the results of other researcher on the modern advances in innovation and structural design of TLD phosphors that demonstrate the accepted approaches, together with (1) investigation of emerging phosphors from the auxiliary models, (2) preparation of new emerging phosphor materials of crystalline properties by doping and (3) basic change of the known phosphors. The crystalline properties of new emerging phosphor shows interest in crystal chemistry analysis for the development of new thermoluminescent dosimetric phosphors with the different properties like co-substitution and single particle analytical advances are also described in this literature.

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