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Preparation methods of thermoluminescent materials for dosimetric applications: An overview

Juan Azorin *

Autonoma Metropolitana-Iztapalapa Universidad Autónoma Metropolitana-Iztapalapa, México D.F. 09340, Mexico

HIGHLIGHTS

- A review of the main methods for preparing thermoluminescent materials is presented.
- Emphasis is placed on the methods to produce materials with suitable characteristics for ionizing radiation dosimetry.
- As a conclusion it can be said that chemical methods have advantages on physical methods to produce TL materials.

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ABSTRACT

Many different natural minerals and synthetic inorganic compounds present the phenomenon of thermoluminescence (TL); however, only a part of them satisfy the requirements to be used as TL dosimeters. The mechanism of excitation energy transformation into the output of light is one of the most important points in the TL materials designing. Both the threshold detection dose and accuracy of measurements depend on the efficiency of energy transformation.

The role of diverse mechanisms of energy transfer and energy losses is very different depending on the nature of the TL material and its composition including intrinsic defects and those induced by impurities. The structure of these defects can be controlled to a high extent by the preparation method. That is why the most important fact is to find the interrelations among the preparation methods, the structural defects and the TL properties of the material.

The aim of this paper is to give a selected review on the preparation methods of the most popular and commercially available phosphors as well as those less used or "homemade" for special studies.

1. Introduction

During the last four decades the application of thermoluminescence dosimetry (TLD) in radiation protection has grown steadily in parallel with the worldwide progress made in the development of solid thermoluminescent (TL) dosimeters.

Today, TLD is the dominant dosimetric method for the measurement of doses in medical physics personnel dosimetry and environmental monitoring. Different preparation methods and properties of several TL materials have been studied so far.

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Not all the numerous known TL materials are suitable to be used as radiation dosimeters. For dosimetric uses a TL material is expected to have the following characteristics.

Relatively simple glow curve with the main peak at about 200 °C, high sensitivity and stability (low fading), resistance to environmental factors, independence of the radiation energy, good linearity in the specific useful range of dose.

Only a few materials have been found so far to match all the above characteristics. However, research in this area is ongoing and is expected new appropriate TL materials to be developed in the near future.

2. Preparation methods

Preparation method of TL phosphors is critical because it generally controls the final properties of the materials, different

* Tel.: +52 55 58044600x1151; fax: +52 55 58044611.
E-mail address: azorin@xanum.uam.mx

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preparation techniques are generally based on powder processing with powder synthesis. However, TL materials processing has also to consider other techniques of synthesis and crystal growth, such as thin films and bulk with desirable microstructures and nanostructures architectures. Structural properties of the materials change their TL properties, as well as, thermal treatments for sintering process, by changing the crystallites size particles.

Typically the product of the synthesis of an inorganic material is a polycrystalline substance which is obtained in powder form. However, in many cases it is required that the material is obtained in special forms such as single crystals and thin films. The required form is logically determined by the use or application that will give the material.

Obtaining a single crystal is very important when it comes to structural characterization. Single crystals are also required for use in optics and electronics, as many times for certain properties are anisotropic. Single crystals for thermoluminescent dosimetry are not suitable because they usually do not have the dopant distributed homogeneously, so that to obtain a homogeneous material, the crystal must be ground.

The thin film, amorphous or both as mono or polycrystalline are very important in modern technology. They can be used to form protective covers on other materials and have played an essential role in the miniaturization of components of electronic devices, but also are useful in TLD dosimetry for low energy radiation. Another important feature is that their properties are often different from the properties of a bulk material, which is derived from the large area/volume ratio they possess.

The TL dosimetric materials currently available can be grouped into two main categories (Azorín, 1990):

(a) Tissue equivalent phosphors, which have an effective atomic number in the range from 7 to10 and generally show low sensitivity, such as alkali halides, alkali borates and alkaline earth metal oxides. For example: LiF, $Li_2B_4O_7$, BeO, etc.
(b) Phosphors with atomic numbers ranging from 15 to 18, with high sensitivity but no tissue equivalents such as salts of alkaline earth metals, and metallic oxides. For example: $CaSO_4$, CaF_2, Al_2O_3, ZrO_2, TiO_2, etc.

In general, nominally pure compounds show weak TL signal, and are not considered efficient dosimetric materials. Much higher efficiency is obtained by doping such materials with proper impurities which act as activators of TL phenomenon. The impurity is normally chosen on the basis of the highest TL response, but other important dosimetric characteristics must be taken into account. Then, the search of good dosimetric TL materials, points to an optimized coupling of a suitable host material with a dopant of very high efficiency to be easily introduced into the desired TL phosphor.

The preparation method used depends on the physical form required for the TL material, either polycrystalline powder, single crystals or thin films (Azorín et al., 1993a). Most commonly used methods for obtaining polycrystalline powder are precipitation and evaporation; while for single crystals, most commonly used methods are those of Czochralski, zone melting and precipitation from solutions or molten phases (flow method). While for thin films, the most common methods are chemical vapor deposition, spray pyrolysis and sol–gel. Below is a brief description of the above mentioned methods:

2.1. Precipitation method

In this method, a solution of the precursor reactants is mixed with dopants in acid solution. Once the precipitate has the desired compound, the sample is centrifuged and washed repeatedly. The precipitate is treated at high temperature, then cooled to room temperature and dried in an inert atmosphere. Thereafter, the temperature is raised to higher temperature, holding for a time. Subsequently, the sample is moved slowly toward a zone of lower temperature to crystallize, then the sample is removed from the furnace by cooling rapidly to room temperature. Finally, the product is pulverized and sieved, selecting powder with desired grain size (Zumdahl, 2009). This method has been used by some authors for synthesizing diverse materials such as alkaline earths sulfides (Rao, 1986), metallic oxides (Kumar et al., 1994; Azorín-Vega et al., 2007), strontium aluminate (Chengkang et al.), calcium phosphate (Madhukumar et al., 2007), lithium fluoride (Vu Thi Thai Ha et al., 2007) or calcium sulfate (Rivera et al., 2010).

2.2. Evaporation method

This method consists in homogeneously mixing the reactants in acid solution by adding the dopants in the desired concentration.

The mixture is placed in a sealed system for evaporating at a high temperature for a given time, by carrying the acid with an air or nitrogen flow. Crystallization is controlled by varying both the temperature and the gas flow. After the evaporation, crystals whose dimensions depend on both the initial reagents and the type and concentration of the dopants are obtained. Crystals obtained are washed several times to remove the remaining acid and submitted to a thermal treatment at high temperature. Finally, the product is pulverized selecting powder with a desired grain size.

Evaporation is the well-known method most widely used to produce calcium sulfate singly doped or co-doped. Considerable work has been done on singly or co-doped $CaSO_4$ phosphors in the last few decades. Rare earths, especially Dy or Tm have been used as dopants (Yamashita et al., 1971; Prokic, 1978; Azorín et al., 1980; Azorín et al., 1984; Azorín and Gutiérrez, 1989). This method has been also applied by Furetta et al. (2000); by Ege et al. (2007), for producing lithium borates. The evaporation method has also been used to produce metallic oxide TL phosphors (Azorin et al., 2002; Rivera et al., 2002).

2.3. Czochralski method

In this method a single crystal is grown from a melt of the same composition. A crystal seed is brought into contact with the surface of the melt, whose temperature is maintained slightly above the melting. Withdrawing the seed slowly goes over to the surface and the melt solidifies in the same crystallographic orientation than the original seed. The growing crystal and the crucible with the molten usually rotate in opposite directions during extraction, so as to maintain a constant temperature. Usually employs an inert gas (argon or xenon) at a high pressure to prevent volatilization losses (Müller et al., 2004). Jiri Kvapil et al. (1980) have used this method to produce corundum single crystals to be used as TL materials. Rare earths phosphates have been also prepared as TL materials by using the Czochralski method (Bold et al., 1985). Kelemen et al., 2011 have prepared lithium tetraborates single crystals by the Czochralski method.

2.4. Zone melting

In this well-known method crystals are grown by slow cooling of the small molten zone. Under these conditions the atoms are arranged such that the crystal is formed with a preferential orientation (Pfann, 1966). Lithium fluoride has been produced by using this method by Watcher (1982).

2.5. Precipitation from solutions or molten phases. (Flow method)

In this method the crystal growth occurs from a liquid phase of different compositions to the crystal; for example,