Radiation Measurements 80 (2015) 29–37

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Effect of annealing and impurity concentration on the TL characteristics of nanocrystalline Mn-doped CaF_2

P.D. Sahare [a, *], Manveer Singh [a], Pratik Kumar [b]

[a] Department of Physics and Astrophysics, University of Delhi, Delhi 110 007, India
[b] Medical Physics Unit, BRAIRCH, AIIMS, Ansari Nagar, New Delhi 110029, India

HIGHLIGHTS

- Nanocrystalline material CaF_2:Mn is prepared by simple coprecipitation method.
- The material is studied by XRD, TEM, ESR, TL and PL techniques.
- High impurity concentrations give rise to clusters causing material instability.
- Changes in ESR and PL and glow curve structures are studied and explained.
- Better characteristics than the bulk make the nanophosphor useful for dosimetry.

ARTICLE INFO

Article history:
Received 18 October 2013
Received in revised form
14 April 2015
Accepted 3 July 2015
Available online 6 July 2015

Keywords:
CaF_2:Mn nanoparticles
Thermoluminescence (TL)
Concentration effects
EPR
PL

ABSTRACT

Nanocrystalline samples of Mn-doped CaF_2 were synthesized by chemical coprecipitation method. The impurity concentration was varied in the range of 0.5–4.0 mol%. The structure of the synthesized material was confirmed using powder XRD analysis. TEM images of the nanoparticles show their size occurring mostly in the range of 35–40 nm, with clusters of some impurity phases formed on annealing of the material at higher temperatures. Detailed studies on TL showed that the structures of glow curves depend on Mn concentrations and annealing temperatures. Optimization of the concentration and annealing temperature showed that the sample (doped with 3.0 mol% and annealed at 673 K) has almost a single dosimetric glow peak appearing at around 492 K. EPR and PL spectra were further studied to understand the reasons for changes in the glow curve structures. All detailed studies on TL, PL and EPR showed that the changes in glow curve structures are caused not only by the stress connected with the difference in ionic radii of host Ca^{2+} and the guest impurity Mn^{3+}/Mn^{2+}, but are also governed by other reasons, like diffusion of atmospheric oxygen and formation of impurity aggregates, such as, MnO_2, Mn_3O_4, etc. This is true not only for nanocrystalline CaF_2:Mn but could also be so for the bulk CaF_2:Mn (TLD-400) and would thus help in understanding complex glow curve structure, high fading and the loss of reusability on annealing beyond 673 K.

1. Introduction

TLD phosphor CaF_2:Mn (TLD-400, microcrystalline powder or hot pressed chips) shows a high sensitivity and linear response over a wide range of radiation doses (0.5 mGy–1.0 kGy) (Thermscientific, TLD Materials, Features and Technical Specifications, 1981; Fehl et al., 1994). It is widely used for radiation dosimetry for last four decades. However, there are some drawbacks, such as, complicated glow curve structure, low stability and fast fading, loss of reusability, etc. (Danilkin et al., 2008). One of the main disadvantages of CaF_2:Mn is its low stability, on annealing and during repeated TL readouts, introducing inaccuracies in dose measurements. It is caused by a strong dependence of TL glow curve structures on the concentration of the impurity (Mn) and its related redox reactions during annealing. It is believed that low stability of the phosphor is caused by the oxidation of Mn^{2+} to higher charge states at higher temperatures (Danilkin et al., 2008; Planque, 1984). However, a well defined and simple high-temperature TL peak is observed when concentration of Mn ions

* Corresponding author.
E-mail addresses: pdsahare@yahoo.co.in, pdsahare@physics.du.ac.in (P.D. Sahare).

http://dx.doi.org/10.1016/j.radmeas.2015.07.003
1350-4487/

is very close to the threshold concentration (~3.0 mol%). But even at this concentration the sensitivity changes on annealing the sample beyond certain temperature (~673 K). In fact, incorporating such high concentration of the impurity forms aggregated solid solution. High concentration of impurity leads to aggregation and formation of impurity clusters introducing inhomogeneity in the material. The optical properties, in such solid solutions, not only depend on the inhomogeneity at molecular level but also on the starting materials, method of synthesis and heat treatments (Lust, 2007).

Earlier, several workers have investigated the material (CaF_2:Mn) and tried to understand TL processes and defects (Danilkin et al., 2008; Planque, 1984; Lust, 2007; Horowitz, 1984; McKeever, 1985; McMasters et al., 1987; Danilkin et al., 2006; McKeever et al., 1986). But the lack of clear knowledge about the TL mechanism, defects formation and their instability at high temperatures showed that the system (CaF_2:Mn) is yet to be fully understood. For example, Danilkin et al. (2006) have studied the effect of Mn impurity concentration on TL and argued that the changes observed in TL glow peaks could be attributed to the stress generated in the crystal lattice because of the difference in ionic radii of Ca^{2+} and Mn^{2+}, i.e., on replacing Ca^{2+} (ionic radius 1.26 Å) by Mn^{2+} (ionic radius 1.10 Å), at lower concentrations but could be compensated by incorporation of more Mn^{2+} at higher concentrations. They further concluded that these distortions would affect the structure of the TL glow curve by affecting the activation energies (due to changes in the stress). They suggested the role of self-trapped excitons (STE) in the energy storage mechanism. But they could not explain satisfactorily the changes in the glow curve structures and loss of reusability on annealing the material beyond ~673 K based on their model. This interaction model also does not seem to be tenable as most of the defects might get annealed out and also the stress may be reduced considerably on annealing. Another important observation made by them was that the radiation had no effect on the amount of Mn^{2+} after irradiating the samples with doses up to 400 Gy as observed from the EPR studies. If it is the case, indeed, then the phosphor should be very stable but it has been found to be otherwise. The same group further tried to explain the changes in the glow curve structures due to *'jumps'* of the fluorine ions into interstitials and forming the neutral F_2 molecules storing the energy and releasing it on their dissociations again changing the activation energies and the glow curve structure (Danilkin et al., 2008). But, it seems it is not the stress or the fluorine ions only but *'something else'* that might also be contributing to it. These were some of the issues that prompted us to revisit the Mn-doped CaF_2 TLD phosphor material. The material is studied in nanocrystalline form as the changes in optical and other characteristics of these materials get enhanced by any small change(s) in the matrix due to its tiny size (Sahare et al., 2012).

In the present work, we have investigated Mn-doped CaF_2 in its nanocrystalline form using XRD, TEM. EPR and PL studies have been done to see redox reactions of impurity ions on annealing and irradiation. TL characteristics, dose response and fading have also been studied to find its suitability for radiation dosimetry. TL glow curves were also theoretically fitted into different glow peaks using Kitis' formulae (Kitis et al., 1998) to determine trapping parameters.

2. Experimental

2.1. Method of synthesis

Chemical coprecipitation method was used to synthesize nanocrystalline CaF_2. The starting materials $CaCl_2$ (99.9%, Merck India), NH_4F (98.0%, Merck India) and $MnCl_2$ (99.0%, CDH India) of analytical (AR) grade were used as received without further purification. The samples were prepared taking into consideration the following chemical reaction:

$$CaCl_2 + 2NH_4F + MnCl_2(0.0 - 4.0\ \text{mol\%}) \xrightarrow{H_2O+EtOH} CaF_2 : Mn + 2NH_4Cl.$$

Aqueous solution of NH_4F (0.1 N) was added into the aqueous solution of $CaCl_2$ (0.1 N) drop-wise through a burette at the rate of 0.25 ml/min in the presence of ethanol (EtOH) while stirring continuously for 2 h at room temperature for completion of the reaction. The appropriate amount of impurity salt ($MnCl_2$) was also added into the $CaCl_2$ solution for doping. All the utensils, such as, beakers, burettes, pipettes, funnels, etc. used were made up of Teflon (PTFE) to avoid any contamination due to the formation of reactive fluoride ions. White precipitate, formed on completion of the reaction, was separated from the solution by centrifugation at 5000 rpm and washed several times with triply distilled deionized water and EtOH to remove traces of any unreacted ingredients. The collected precipitates were dried at 400 K for 12 h in an inert atmosphere and annealed at different temperatures in air for further studies.

2.2. Characterization and measurements

The Powder X-Ray Diffraction (XRD) patterns were recorded at room temperature using a high-resolution D8 Discover X-ray diffractometer (Bruker, Germany) equipped with a point detector (scintillation counter). Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å) monochromatized with a pair of Göbel mirrors was used to obtain the XRD patterns. XRD was recorded at the scan rate of 1.0 s/step with the step of 0.013°. The high-resolution images of nanoparticles were taken using Philips Tecnai G2 F30 TEM with 300 kV accelerating voltage.

Thermoluminescence (TL) was recorded at a constant heating rate of 5 Ks^{-1} using Harshaw TLD Reader 3500HT with the upper temperature limit of 873 K. A ^{137}Cs γ-radiation was used to irradiate the samples before TL recording. TL of the samples was taken immediately after the irradiation (0.1 Gy–100 kGy) except for the samples used for studying fading. Almost equal amount of sample (~5 mg) was taken for each experiment. At least three glow curves were recorded for any sample to check reproducibility.

PL measurements of the powder samples were taken on Varian Cary Eclipse Fluorescence Spectrophotometer using a Xenon flash lamp as a source and a wide band PMT as a detector. Both emission and excitation spectra were recorded with slit width at 2.5 nm. The EPR measurements were taken at room temperature on the JOEL JES-FE3XG X-band EPR spectrometer operating at ~9.4 GHz with a 100 kHz magnetic field modulation. The diphenyl-picryl-hydrazyl (DPPH, g = 2.0037) was used as a standard sample for calibration.

3. Results and discussion

3.1. XRD

The XRD has been checked for the samples with different impurity concentrations in the range 0.5–4.0 mol% and annealed at 673 K. The XRD pattern of CaF_2:Mn (3.0 mol%) nanoparticles is shown in Fig. 1. All the peaks observed in the diffraction pattern are indexed to the cubic structure (JCPDS file # 87-0971) with space group Fm3m (225). The crystalline size of the nanocrystalline particles, determined from the broadenings of the XRD peaks and using Debye-Scherer's formula, was found to be about ~38 nm. The slight relative shift of the XRD peaks due to decrease of lattice constant is observed at increasing Mn concentration (Fig. S1, Supplementary Material). These results are similar to those