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Structural and luminescence responses of $CaMoO_4$ nano phosphors synthesized by hydrothermal route to swift heavy ion irradiation: Elemental and spectral stability

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ABSTRACT

The present paper reports on the swift heavy ion (SHI) induced modifications in the structural, optical and luminescence properties of Dy^{3+} doped $CaMoO_4$ phosphors synthesized via hydrothermal route. The material is irradiated by 30 MeV Li^{3+}, 75 MeV C^{6+} and 100 MeV Ag^{7+} ions in the fluence range varying from 1×10^{11} to 1×10^{13} ion/cm^2. The ion induced modified properties were investigated by using X-ray diffractometer (XRD), Field Emission Scanning Electron microscopy (FESEM) with energy dispersive x-ray spectroscopy (EDS), X-Ray photoelectron spectroscopy (XPS), diffuse reflectance (DR) and photoluminescence (PL) spectroscopy. The XRD and the FESEM results confirm the loss of crystallinity and reduction of the particle size after SHI irradiations. The change in elemental behavior before and after SHI irradiation is described via EDS assisted elemental mapping and XPS spectroscopy. DR spectra exhibit a red shift in the absorption band, resulting in a decrease in the band gap after ion irradiation. The change in the intensity of the PL peaks without any change in the band positions was noticed after ion irradiation. The variation in structural and optical properties and colour characteristics with ion fluence is discussed in details on the basis of the variation of defect concentration, elemental behavior and the linear energy transfer with ion irradiation.

1. Introduction

Current research trends show a sheer interest towards modifications of materials induced by heavy ions since this offers a unique tool to engineer and modify the materials in a controlled fashion such as physical, chemical, structural, and optical properties [1–7]. Electronic excitations are produced by the energetic swift heavy ion irradiation on materials, thus changing their properties [8–12]. When bombarded with ions with energy in the MeV range, the electron phonon coupling around the path of the ions causes an instant sudden upward spike in temperature. The impulses occurred by the ionized atoms are coherent in space and time, so that a feasible coupling of the excitation with the low frequency phonons can take place. This temperature spike creates ‘shock waves’ which causes radial diffusion of heat in the target which in turn may increase the volume of the target. It leads to swellings in the materials and fragmentation of the grains due to the sudden explosion of ionized matter. In case of phosphors, this energy deposition and heat diffusion may produce new colour centres, point defects and sometimes the reorganization of the trapping and luminescent centres are observed which results in the modification of luminescence properties. Investigations are carried out at large on the effect of swift heavy ions on the luminescence and other characteristics of phosphors with nanoscale dimensions [1–19].

Calcium molybdate is a widely studied phosphor which has diverse applications in light emitting diodes (w-LED), solid state

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lasers, scintillators, fluorescent lamps, solar cell, electrolyte material for solid oxide fuel cells and catalysis [20–24]. When doped with rare earth ions the phosphor shows better luminance efficiency and thus has been a focus of study for use in the lighting industry. In the current study $CaMoO_4$:Dy^{3+} nanophosphors are the subject of investigation, which have earlier been synthesized and investigated for photoluminescence [20–27]. Till date, no studies have been carried out in the literature on the changes imparted due to the bombardment of heavy ions on $CaMoO_4$: Dy^{3+} phosphor which prompted to study the structure, optical and photoluminescence changes of the Dy^{3+} doped $CaMoO_4$ nanophosphors due to the effect of swift heavy ions. The ions used for irradiation in the current study were 30 MeV Li^{3+}, 75 MeV C^{6+} and 100 MeVAg^{7+} ions. The main focus for the selection of the above mentioned ions for irradiation was to observe the effect of ions with lower mass and energy to higher mass and energy in the periodic table. Therefore the Li ion with 30 MeV energy has been taken as lower energetic element and, 75 MeV C ions as intermidiate energetic element and finally 100 MeV Ag ion for the higher range and thus it is possible to get the idea about the effect of different ions in the whole periodic table. The ion induced structural, optical and colour characteristics is discussed on the basis of the variation of defect concentration, elemental behavior and the linear energy transfer with ion irradiation for the first time. The 15-UD Pelletron facility of the Inter-University Accelerator Center (IUAC), New Delhi, has been employed for ion irradiation. The ion fluences chosen in the present work were 1×10^{11} to 1×10^{13} ion/cm^2 [3,9,11]. The phosphors have been characterized by X-ray diffraction (XRD), Field emission scanning Electron Microscopy (FESEM), X-ray Photoelectron Spectroscopy (XPS) and Photoluminescence (PL) spectroscopy.

2. Materials and methods

2.1. Synthesis of Dy^{3+} doped $CaMoO_4$

Hydrothermal method was used for the synthesis of Dy^{3+} doped $CaMoO_4$ nanophosphors and the details are reported elsewhere [28]. The mol concentration of 2 mol % of Dy^{3+} which was optimized for PL was taken for ion irradiation [28]. The target nanophosphors used for irradiation was used in the form of pellets [11]. The complete information about the SHI irradiation is also reported elsewhere [3,9,11].

2.2. Characterization of Dy^{3+} doped $CaMoO_4$

All the studies were carried out at ambient temperature. The phase characterization of irradiated phosphors was carried out using a Bruker D8 Focus X Ray Diffractrometer with CuKα target radiation ($\lambda = 0.154056$ nm). The morphology of the phosphors was examined by using an Agilent make Supra 55 FESEM. The X-ray photoelectron spectroscopy was done using a PHI 5000 Versaprobe-Scanning ESCA microprobe. The measurements were done with a 100 μm, 25 W, 15 kV monochromatic Al Kα x-ray source with photon energy 1486.6 eV. Survey scans (binding energies ranging from 0 to 1400 eV) were performed using a 1 eV/step and 100 ms acquisition times while for higher resolution spectra the hemispherical analyser pass energy was maintained at 11.8 eV for 10 cycles using 0.5 eV/step. The pressure during acquisition was typically 2.8×10^{-9} Torr. MULTIPAK software was used for the deconvolution of the peaks. The Perkin Elmer make Lambda 35, UV–vis spectrophotometer fitted with an integrating sphere assembly in the wavelength range 190–800 nm was used to record the DR spectra. The PL studies were carried out on a Hitachi Fluorescence Spectrophotometer F-2500 in the range 220–650 nm.

3. Results and discussions

3.1. Phase identification and the solubility of Dy^{3+} in $CaMoO_4$ host with ion irradiation

Fig. 1(a–d) shows the comparative XRD patterns of the unirradiated and 30 MeV Li^{3+}, 75 MeV C^{6+} and 100 MeVAg^{7+} ion irradiated $CaMoO_4$: Dy phosphors for the ion fluence of 1×10^{13} ions/cm^2. The XRD pattern of the unirradiated $CaMoO_4$: Dy phosphors match well with JCPDS pdf no. 77-2244 and indexed properly indicating the formation of tetragonal $CaMoO_4$ structure with space group I41/a as shown in Fig. 1(a). No peak corresponding to the Dy ion was observed even though the long term XRD scan for the regions where XRD peaks from Dy_2O_3 are expected to occur were carried out. The fact indicates that the Dy^{3+} ions were substituted properly into the $CaMoO_4$ structure. To get an idea about the effect of the ion irradiation on the phase and the structure of the phosphor, the XRD pattern of 30 MeV Li^{3+}, 75 MeV C^{6+} and 100 MeVAg^{7+} ion irradiated phosphors were recorded for the ion fluence of 1×10^{13} ions/cm^2 and is shown in Fig. 1(b–d) respectively.

The patterns are analogous to that of the unirradiated sample. It shows that C, Li and Ag SHI irradiation of the specific energy is not enough to change the phase of the phosphors. The right inset of Fig. 1 shows the main XRD peak after the different type of ion irradiation. The main XRD peak has shifted towards the lower angle side. It may be owing to the loss of crystallinity after ion irradiation as explained later. Fig. 1(e) presents the refinement results of the unirradiated $CaMoO_4$: Dy^{3+} phosphors. The solid black curve indicates the observed experimental diffraction data and the " × " marks represent the simulated diffraction data. The straight green bars show the positions of simulated diffraction patterns, and the blue zigzag line denotes the variation among the simulated and experimental values. The calculated R_p and wR_p parameters were connected to consistent values of 5.32% and 7.21%, respectively. The refinement results showed that 2 mol% Dy^{3+} doped $CaMoO_4$ phosphor possessed tetragonal structure with space group I41/a [29]. From the refinement parameter the crystal structure was drawn via the VESTA software [30] and shown in Fig. 1(f). From the crystal structure, it is clear that both the Ca and Mo sites have S4 point symmetry and its crystal structure has two building blocks of CaO_8 clusters and MoO_4 tetrahedra as is clear from Fig. 1(f). Each O atom links with two Ca atoms and one Mo atom. There are two different Ca–O bond lengths in CaO_8 and one Mo–O bond length in MoO_4. The comparative refinement parameters of unirradiated and different ion irradiated phosphors are summarized in Table S1. It is evident from Table S1 that the lattice parameter increased with ion irradiation. In general, the deposition of high electronic energy by swift heavy ions into the system increases the energy inside the crystal which expanded the bond length leading to the expansion of the lattice volume and hence the lattice parameters. The enhancement of the bond length is schematically shown in Fig. 1(g).

The variation of lattice parameters after the ion irradiations with the different ion fluences is illustrated in Fig. 2(a–c) respectively. The lattice parameter enhanced after C, Li and Ag ion irradiation in the studied fluence range as indicated in the shifting in the XRD peaks towards the lower angle side [31]. The variation of the FWHM of the main XRD peak ~28.51° with the change in ion fluence for C, Li and Ag ion irradiation is shown in Fig. 2(d). A sharp increase in the FWHM was observed with increasing ion fluence. Moreover, the intensity of the XRD peak decreased with ion irradiation. The so obtained results confirm the loss of crystallinity after SHI irradiation. However, the variation in lattice parameter is also directly correlated with the strain present in the material. The Williamson-hall analysis method [32] was taken into account to get an idea of the microstrain present in the materials and the variation of