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Characterization of Co-surface modified nanocrystalline $SmFeO_3$ thick film

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Abstract

Samarium orthoferrite $SmFeO_3$ thick films prepared by screen printing technique were surface modified with cobalt chloride. Surface modification was achieved by dipping technique. $SmFeO_3$ thick films were dipped into 0.1 M aqueous solution of cobalt chloride for 5 min. After drying, the modified films were fired in Muffle furnace at 550^0C for 30 min. $SmFeO_3$ powder was analyzed by X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy techniques. The observations depict that powder sample is made up of $SmFeO_3$ nanoparticles. As-fabricated pure and Co-surface modified $SmFeO_3$ thick films were analyzed by Field Emission Scanning Electron Microscope (FE-SEM) to observe its microstructure. The FE-SEM results revealed the formation of nanocrystalline $SmFeO_3$ grains and the porosity of films. For the conformation of Co deposition, the Energy-dispersive X-ray (EDAX) analysis of the Co modified $SmFeO_3$ thick film was carried out. The EDAX analysis showed that Co was successfully deposited on pure $SmFeO_3$ surface with no additional impurities. The effect of Co modification on the surface morphology of pure $SmFeO_3$ thick film was discussed.

Keywords: Surface modification, Orthoferrite, Dipping method, FE-SEM, Nanocrystalline, $SmFeO_3$.

1. Introduction

Scientists have shown great interest in examining the properties of nanostructured semiconductor metal oxides. Various semiconductor metal oxides and their composites have been continuously investigated for different applications. The physical and chemical properties of metal oxides are related to the morphology of material. Methods of synthesis, nature of dopant, concentration of dopant, and annealing temperature have been reported to influence the morphology of material.

Perovskite-type oxides with general formula ABO_3 (A=rare earth and B= transition metals) have shown excellent tunable physical and chemical properties. Among them, rare earth orthoferrites have been employed in various fields including solid state gas sensors [1-3]. Rare earth orthoferrite has orthorhombic distorted structure in which Fe ions prefer central position whereas rare earth ions prefer non-central position [3]. Some of the ABO_3 type rare earth orthoferrites such as $LaFeO_3$ and $SmFeO_3$ have been reported for the detection of oxidizing and reducing gases [4-7]. Particularly, $SmFeO_3$ which belongs to Pbnm space group (#62), exhibited p-type electrical conductivity, oxygen-ion mobility and high catalytic activity towards oxidizing gases [8-10]. Therefore, $SmFeO_3$ can be considered as good sensing material for the detection of oxidizing gases. But $SmFeO_3$ based gas sensors generally operate at high operating temperature because the electrical conductivity of $SmFeO_3$ is extremely small at lower temperature. Further, problem of stability at high temperature in reducing environment arises for $SmFeO_{3.}$ In perovskite structure, nature of A-site and B-site ions controls the electrical conductivity and the stability of material. Therefore, modified $SmFeO_3$ can have enhanced electrical conductivity and stability. Literature survey reveals that $SmFeO_3$ can be modified with Co, Ce, Ni and Mg. S. M. Bukhari et al. examined the effect of Ce doping on $SmFeO_3$ and concluded that Ce-doped $SmFeO_3$ enhanced electrical conductivity as well as stability [11]. H. Zhang et al. prepared $SmFe_{0.9}Mg_{0.1}O_3$ by sol gel method and obtained excellent response towards 0.5 ppm acetone vapour [12]. Mir et al. reported that Ni doping in nanostructured $SmFeO_3$ results in an increase in porosity and decrease in optical band gap energy [13]. Ma Zhao et al. illustrated influence of Co-doping in structural and electrical properties of $SmFeO_3$ nanostructure thereby suggesting that $SmFe_{0.7}Co_{0.3}O_3$ was good material for ethanol sensor [9].But, Co-O bond is weaker than Fe-O bond. Therefore researchers suggested the controlled addition of Co to pure $SmFeO_3$ for increasing electrical conductivity.

Thus, from the literature survey on $SmFeO_3$ it is clear that the physico-chemical properties of are associated with grain size and surface morphology. For this reason, synthesis of doped $SmFeO_3$ nanomaterials of well defined morphology has become an area of interest. Sol-gel method, co-precipitation method, hydrothermal method etc have been frequently used for the synthesis of $SmFeO_3$ nanoparticles. For the addition of dopants to pure material, doping technique and dipping technique are regularly employed. Doping technique involves the addition of dopants in desired proportion at the time of synthesis of material. On the other hand, with dipping technique, additives can be deposited on the surface of pristine material. Modification of $SmFeO_3$ by doping technique was adopted by most of the researchers.

In present work, an attempt has been made to modify screen printed nanocrystalline $SmFeO_3$ thick film with Co by dipping technique. As-prepared Co-surface modified $SmFeO_3$ thick films are characterized by different characterization techniques.

2. Experimental

Preparation of nanocrystalline $SmFeO_3$ powder by sol-gel method was described in earlier publications [14]. The procedure includes mixing of stoichiometric amounts of samarium nitrate, iron nitrate and citric acid monohydrate (in the proportion 1:1:1). The mixture was grounded into Agate mortar for 30 min. Ethylene glycol was added to the mixture provided with constant stirring at 75^0C for 2 h. The sole was then dried into gel which was finally calcinated in Muffle furnace at 800^0C for 4 h to obtain powder sample.

The formulation of thixotropic paste of $SmFeO_3$ powder follow the procedure described elsewhere [15-17]. The paste was screen printed on the glass substrate to obtained pure $SmFeO_3$ thick films. These films are allowed to dry and then fired in Muffle furnace for 30 min at 550^0C.

For surface modification, 0.1 M aqueous cobalt chloride solution was taken in Petri dish to which $SmFeO_3$ films are dipped for 5 min. After natural drying, Co-modified $SmFeO_3$ thick films were again fired for 30 min at 550^0C. The films so prepared are named as "Co-surface modified $SmFeO_3$ thick film".

EXPERT-PRO PW 3071 powder diffractometer was used to obtain X-Ray Diffraction (XRD) pattern of pure $SmFeO_3$ powder. To obtain the information about the functional groups and the vibrational modes present in the system, Fourier Transform Infrared (FTIR) spectrum of $SmFeO_3$ powder was recorded on Shimadzu NIR spectrophotometer in the range of 400-4000 cm^{-1}.

The morphological and the elemental analysis of the films were carried out by Field Emission Scanning Electron Microscope (FE-SEM) coupled with Energy Dispersive X-ray Spectrometer (EDAX) (JSM- 7610F, JEOL Japan operated at 15 kV).

3. Results and Discussion

3.1 XRD analysis

XRD pattern of pure $SmFeO_3$ powder prepared by sol-gel method is already presented in earlier publication [10]. The results confirmed that $SmFeO_3$ powder has orthorhombic structure and Pnma space group. Applying Debye Scherrer's formula, the average crystallite size was calculated as 50.08 nm.

3.2 FTIR analysis

Fig. 1 depicts FTIR spectrum of pure $SmFeO_3$ powder sample. Two prominent absorption peaks are seen at 554 cm^{-1} and 411 cm^{-1} which confirms the formation of $SmFeO_3$ crystal structure (orthorhombic perovskite). Peak obtained at 554 cm^{-1} is ascribed to Fe-O stretching mode of vibration. Another peak obtained at 411 cm^{-1} corresponds to O-Fe-O bending mode of vibration. The absorption peaks around 2931 cm^{-1} corresponds to C-H vibration mode. Band around 1112 cm^{-1} is ascribed to C-O bond. On exposure to ambient atmosphere, carbonate species are adsorbed on the surface and results in above bands.

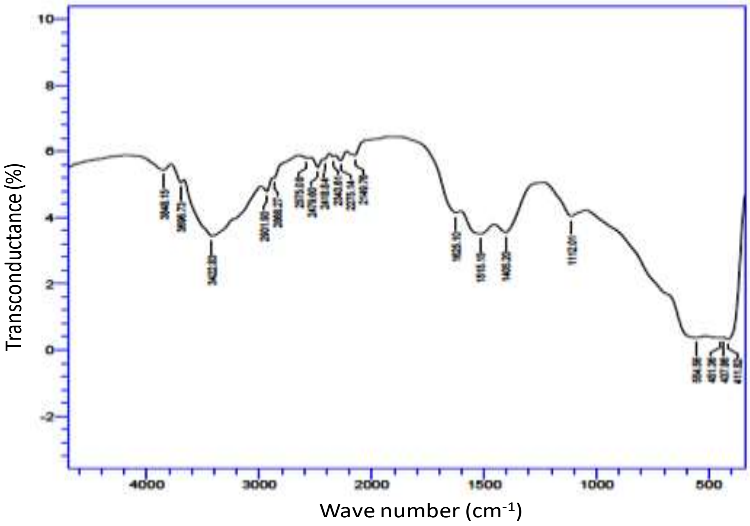

Fig. 1: FTIR spectrum of pure $SmFeO_3$ powder.

3.3 FE-SEM analysis

To analyze the microstructure of Co-modified $SmFeO_3$ thick film, field emission scanning electron microscope was used. The FE-SEM image of Co-surface modified $SmFeO_3$ thick film is shown in Fig. 2.

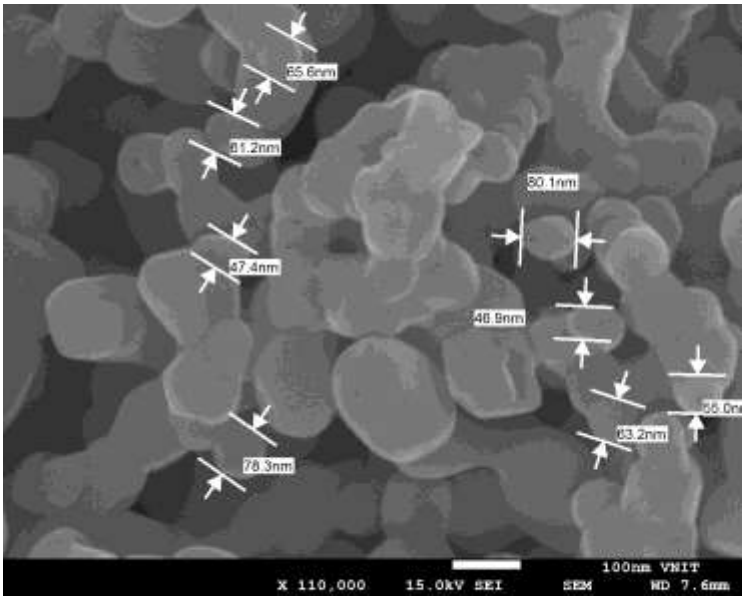

Fig. 2: FE-SEM image of Co-surface modified $SmFeO_3$ thick film (dipping time 5 min).

Crystalline, nanostructured $SmFeO_3$ particles are observed on the surface of film. The particle size ranges from 47 nm to 80 nm. Particles are irregular in shape and distributed non-uniformly. The spherical morphology is observed for some particles and the agglomerations of some fine particles are also observed. A careful observation of micrograph depicts that some smaller particles are distributed around larger grains. These smaller particles may be Co species and can be confirmed from elemental analysis. The micrograph depicts that the average particle size for $SmFeO_3$ is 62 nm which is less than the average particle size (84 nm) observed for undoped $SmFeO_3$. Thus, Co doping has reduced the particle size which is consistent with the observations reported in other works [9]. Particle size is considered to be an important parameter affecting the sensitivity of sensor. Smaller size of nanoparticles tends to increase the sensitivity of sensor. The surface of film seems to be smooth and porous due to the presence of large numbers of $SmFeO_3$ grains. Therefore Co-surface modified $SmFeO_3$ thick film may favor the adsorption and desorption processes in gas sensing mechanism.

3.4 EDAX analysis

Using energy dispersive X-ray spectrometer, elemental compositions of Co-surface modified $SmFeO_3$ thick film are determined. Fig. 3 shows the EDAX spectrum for Co-surface modified $SmFeO_3$ thick film. The sharp peaks observed in EDAX spectrum confirm the presence of Sm, Fe, O and Co on the film. No other peak is observed in the spectrum indicating the purity of sample. From EDAX spectrum, wt% of Sm, Fe, O and Co are observed and presented in table 1.

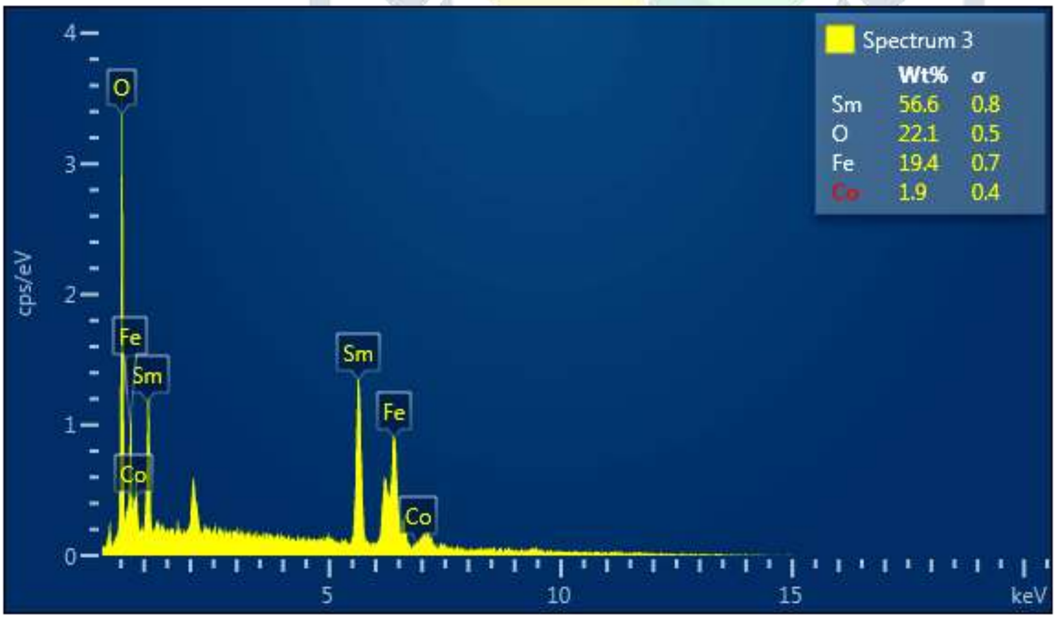

Fig. 3: EDAX spectrum of Co-surface modified $SmFeO_3$ thick film (dipping time 5 min).

Table 1: Elemental composition of Co-surface modified $SmFeO_3$ thick film (dipping time 5 min)

Sample	Elemental composition (wt%)			
	Sm	Fe	O	Co
Co-modified $SmFeO_3$	56.6	19.4	22.1	1.9

Co may have replaced Sm or Fe or both in perovskite structure of $SmFeO_3$ during surface modification. For 5 min dipping time, concentration of Co deposited on the surface of pure is 1.9 wt%

4. Conclusions

Co-surface modified $SmFeO_3$ thick films are successfully prepared by simple dipping technique. As prepared Co- surface modified $SmFeO_3$ thick film has crystalline microstructure and porous surface. Average grain size is reduced from 84 nm to 64 nm due to Co surface modification. Deposition of Co species on $SmFeO_3$ surface is confirmed from EDAX spectrum.

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