STRUCTURAL AND GAS SENSING STUDIES OF CHROMIUM DOPED COBALT ALUMINATE SPINEL COMPOSITE

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ABSTRACT

Chromium doped cobalt aluminate spinel was prepared from cobalt and aluminium nitrate solutions using coprecipitation method by ammonia as precipitant, doped with 0.5 amounts of chromium nitrate. Sample characterizations were carried out by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy. The spinel phase crystallinity, according to the intensity and broadness of diffraction peaks and to the synthesis method. Two characteristic peaks referred to vibrations of the atom in tetrahedral and octahedral holes were found for Al_2-O_3 and Co-Cr, respectively. The morphology and elemental composition of the film was observed through scanning electron microscopy with energy dispersive analysis (SEM-EDAX). The sensor response of prepared film was studied towards different gases like liquefied petroleum gas, carbon dioxide, methane ammonia and ethanol. The film shows the maximum sensing response towards 500 ppm LPG.

Keywords: Coprecipitation, X ray diffraction, Fourier transforms infrared spectroscopy, scanning electron microscopy, gas sensing.

1. Introduction

Semiconductor transition metal oxides are suitable materials for environmental gas sensing applications due to their reproducibility in gas detection. Recently scientist has great interest in nano-crystalline spinel aluminates because of their versatile practical properties and application. The general formula of spinel is AB_2O_4. Aluminates have high thermal stability, mechanical resistance, and low surface acidity. Different application of aluminates is microwave devices, magnetic fluids, heterogeneous catalysis, absorbent materials, pigment catalyst and refractory material [1-3]. Cobalt aluminates ($CoA1_2O_4$) is a thermally and chemically stable pigment of intense blue color (Thenard's blue). Cobalt aluminate is spinel type oxide which occurs in normal or inverse spinel which having cubic structure From last few years, coprecipitation method has been used to prepare a series of mixed-metal oxides, nanoscale, nanomaterials and nonporous oxides, organic-inorganic hybrids. The addition of chromium retards the growth of the bulk cobalt aluminate phase on the surface and forms new phases. The results demonstrate the influence of starting material, complexing agent, annealing temperature, heating time and other parameters on the phase purity and crystallinity of the prepared products [4-6].

2. Materials and methods

Cr^{3+}doped aluminates was prepared using coprecipitation synthesis, which involves heating of metal nitrate and aluminium nitrate in stoichiometric proportions [7].$Co_{0.5}Cr_{0.5}Al_2O_4$ sample, was prepared from $Al(NO_3)_3·9H_2O$,$Co(NO_3)_2·6H_2O$ and $Cr(NO_3)_3·9H_2O$ were weighed and dissolved in distilled water. This mixture was stirred for 2 hr at the 80^0c temperature. After stirring ammonia was added to this mixture. The obtained precipitate was dried in oven for 24 hr at 110^oc.Then the powder was calcinate at 850^oc for 4 hr.

The crystallinity and phase of the powder was observed through X-ray diffraction (XRD) and Fourier transforms infrared spectroscopy (FTIR). X ray measurement of mixed oxide was carried out with cu k_α radiation. Sample was scanned in the range 10^0-90^0.The crystallite size of $Co_{0.5}Cr_{0.5}Al_2O_4$ present in the investigated solids was based on X-ray diffraction line broadening and calculated by using Scherer equation [8]. The FTIR spectrum is obtained in the range 400 - 4000 cm^{-1} which shows characteristic bands. To study the gas sensing behavior, thick film of as prepared powder sample was fabricated by screen printing method and sintering at 200^oc. The surface morphology of the sintered porous film was determined by (JEOL JSM 7600F) scanning electron microscope at the desired magnification with energy dispersive X-ray analysis (SEM-EDAX).The static gas-sensing unit was used to investigate the sensing performance of the fabricated sensor elements. To measure the gas sensing characteristics, desired volume of the test gas was injected into a glass chamber and mixed with air.

3. Results and discussion

3.1. X-Ray diffraction studies

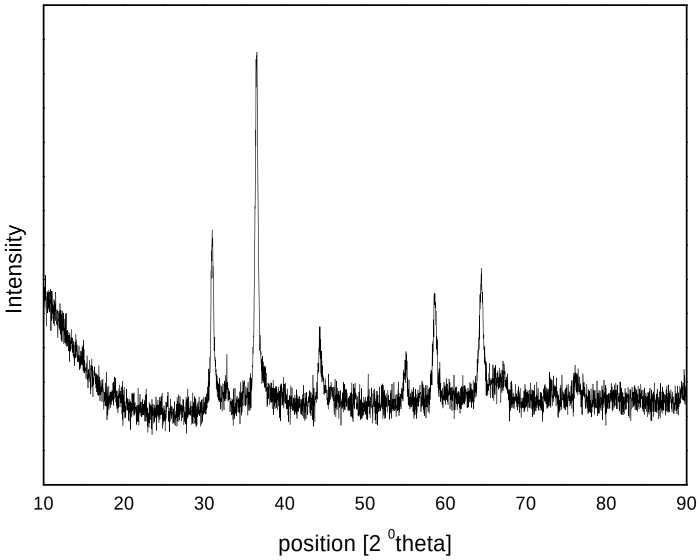

Fig.1.The XRD pattern of $Co_{0.5}Cr_{0.5}Al_2O_4$ powder sample.

The X-ray diffraction patterns of $Co_{0.5}Cr_{0.5}Al_2O_4$ powders are shown in Fig. 1. X-ray diffraction patterns of the samples annealed at 850^oC for 4 h obtained by the cobalt, chromium and aluminium nitrate by co precipitation route [9].The XRD pattern of fig.1 shows peaks corresponding to cobalt aluminate spinel-like phase. As the concentration of the chromium was increased single-phase of cobalt aluminates was not obtained for the composites with higher amounts of chromium added is present regardless of the used synthesis method. The spinel phase crystallinity, according to the intensity and broadness of diffraction peaks and to the synthesis method. The addition of chromium retards the growth of the bulk cobalt aluminate phase on the surface and forms new phases. The average crystallite sizes (D) were measured from XRD peaks based on the Scherrer's equation [10]: D= 0.89k/(b cosθ), where k is the wavelength of X-ray, θ the diffraction angle and b the true half-peak width. The crystallite size of $Co_{0.5}Cr_{0.5}Al_2O_4$ powder sample is 20.3 nm.

3.2. Fourier transforms infrared spectroscopy

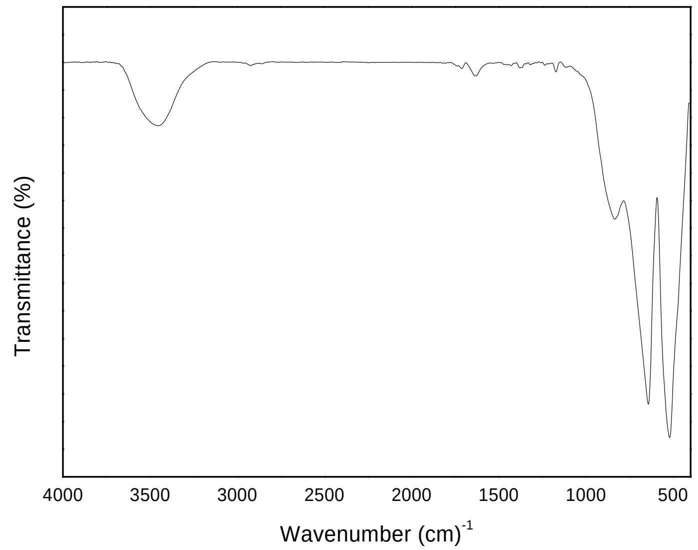

Fig.2: FTIR spectra of $Co_{0.5}Cr_{0.5}Al_2O_4$ powder sample.

Figure shows the FTIR spectrum of $Co_{0.5}Cr_{0.5}Al_2O_4$ at 850°C for 4 h. Several absorptions are observed in FTIR spectrum. The spectra exhibit a common broad band near 3455.01cm^{-1} due to the OH-stretching vibrations of free and hydrogen-bonded 1634.06cm^{-1}. Two characteristic peaks referred to vibrations of the atom in tetrahedral and octahedral holes were found at 642.07 and 520.19cm^{-1} for Al_2-O_3 and Co-Cr, respectively. The $Co_{0.5}Cr_{0.5}Al_2O_4$ powder sample was confirmed spinel phase by FTIR.

3.3. Scanning electron microscopy with energy dispersive analysis:

SEM was used to study morphological features. Fig. 3 shows the SEM micrograph of the $Co_{0.5}Cr_{0.5}Al_2O_4$ thick film. The porous structure of the particle can be observed, with different pore sizes, which is consistent with the higher values for surface area and pore volume. SEM image of thick film sensor surfaces are highly porous and this makes it highly suitable for sensing application. Energy dispersive X-ray analysis was carried out during SEM analysis to determine elemental composition of the film. The EDAX spectrum of $Co_{0.5}Cr_{0.5}Al_2O_4$ thick films is shown in Figure 4. EDAX Spectrum confirms the presence of chromium in the doped samples.

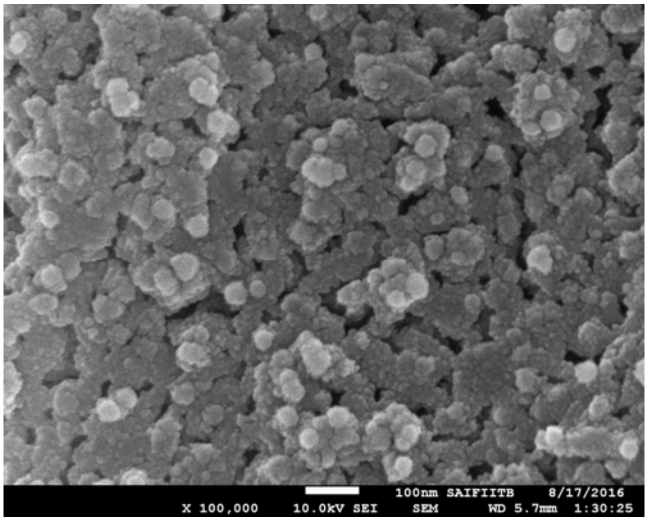

Fig.3: SEM image of $Co_{0.5}Cr_{0.5}Al_2O_4$ based thick film.

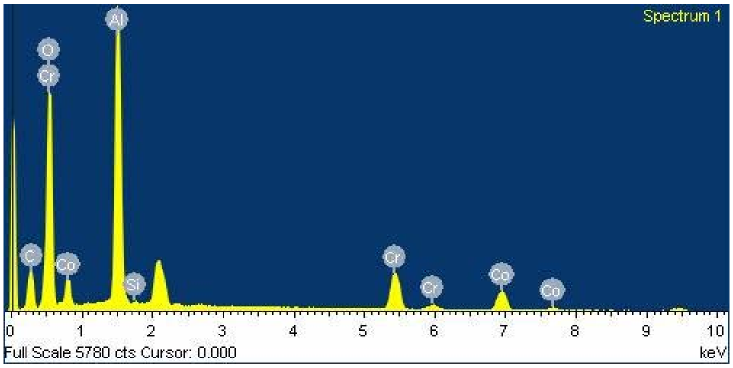

Fig. 4: EDAX spectra of $Co_{0.5}Cr_{0.5}Al_2O_4$ based thick film.

3.4. Gas sensing test

The gas sensing properties of $Co_{0.5}Cr_{0.5}Al_2O_4$ have been studied towards LPG, CO_2,CH_4, C_2H_5OH, NH_3. The temperature is varied between 298 to 408 K. Both adsorption and combustion of the reducing gases occur on the surface of the sensors. The depletion of the lattice oxygen might be responsible for the sensitivity of the sensor to the gases. The response of the $Co_{0.5}Cr_{0.5}Al_2O_4$ film to LPG, CO_2, CH_4, C_2H_5OH, NH_3 was measured at different operating temperature and results are shown in Figure 5. From figure it is clearly seen that, sample $Co_{0.5}Cr_{0.5}Al_2O_4$ shows the maximum sensor response 13.31 towards 500 ppm LPG. A sensor could selectively detect LPG at lower operating temperature without serious interference from other tested gases.

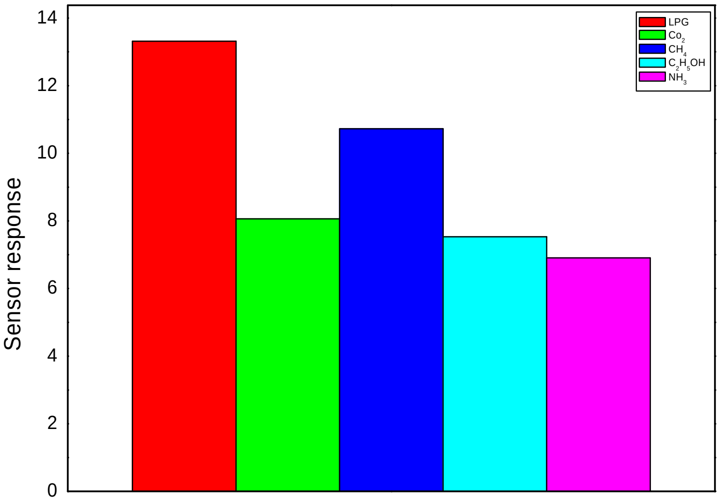

Fig.5: Sensor response of $Co_{0.5}Cr_{0.5}Al_2O_4$ towards different gases at 348 K.

3.5. Conclusion

Spinel type $Co_{0.5}Cr_{0.5}Al_2O_4$ oxide material was successfully prepared by coprecipitation route. The XRD spectra suggested the formation of a spinel phase for $Co_{0.5}Cr_{0.5}Al_2O_4$ composite. The vibrational stretching frequency corresponding to the composites was confirmed by FT-IR spectroscopy. Microstructure of the film was studied with Scanning electron microscope (SEM) with EDAX. It was found that $Co_{0.5}Cr_{0.5}Al_2O_4$ thick film sensor shows maximum response to 500 ppm LPG at 348 K. This new approach enriches the preparation method of $Co_{0.5}Cr_{0.5}Al_2O_4$ and brings new opportunity for the application of $Co_{0.5}Cr_{0.5}Al_2O_4$ nanomaterials as gas sensors. It can be used as selective gas-sensing materials to LPG.

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