Structural and Morphological Studies of Spinel Type Nanocrystalline $Co_{0.5}Cr_{0.5}Al_2O_4$

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Abstract

Nanocrystalline $Co_{0.5}Cr_{0.5}Al_2O_4$ spinel was prepared from cobalt and aluminium nitrate solutions by using co precipitation method with ammonia as precipitant. The precipitate was dried at 110^{o}C and then calcinate for 4 h at 900^{o}C. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Scanning electron microscopy (SEM-EDAX) were employed to identify structural phase, vibrational stretching frequencies and surface morphology of sample respectively. This was carried out with the objective of elucidating the effect, if any, of the presence of the dopants on the spinel structure and properties. The spinel structure was clearly exhibited in the prepared samples. We observe that doping concentration increases surface area and the growth of big pores.

Keywords: Cobalt aluminate, Co precipitation, X-ray diffraction, Fourier transforms infrared spectroscopy, Scanning electron microscopy.

Introduction

Recently scientist has great interest in nanocrystalline 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 applications of aluminates are microwave devices, magnetic fluids, heterogeneous catalysis, absorbent materials, pigment catalyst and refractory material [1-3]. Cobalt aluminate ($CoAl_2O_4$) is spinel type oxide which occurs in normal or inverse spinel which having cubic structure. Many methods have been used to prepare the $CoAl_2O_4$ that can provide many advantages over traditional methods, including an ability to control homogeneity and purity of product, to process at lower temperatures, and to control the shape, size. $CoAl_2O_4$ has received attention for different applications due to its scientific properties. It is normally use as a luminescent pigment [4] and as a material for electrical [5, 6] and magnetic [7-9] instruments as well as for thin film technology [10].

From last few years, co precipitation method has been used to prepare a series of mixed-metal oxides, nanoscale, nanomaterials and nonporous oxides, organic-inorganic hybrids. It is very simple and low cost method. In this work, spinel-type $Co_{0.5}Cr_{0.5}Al_2O_4$ was prepared by co precipitation method. The preparation parameters were optimized to study the structural properties.

Experimental Work

Materials

High purity procured was used for the synthesis of the powder. Aluminium nitrate ($Al(NO_3)_39H_2O$), Cobalt nitrate hexahydrate ($Co(NO_3)_36H_2O$), Chromium nitrate ($Cr(NO_3)_39H_2O$) and Ammonia solution 25% (NH_4OH) of Sd fine (GR grade) chemicals were used.

Instruments

Chemical analysis was obtained by X-ray diffraction (XRD) and Fourier transforms infrared spectroscopy (FTIR). X ray measurement of mixed oxide was carried out with Cuk_{α} radiation, λ=1.5405 nm recorded on X-ray diffractometer (PANalytical X'Pert-Pro). Sample was scanned in the range 2θ=10°-90°.The crystallite size of $Co_{0.5}Cr_{0.5}Al_2O_4$ present in the investigated sample was based on X-ray diffraction, line broadening and calculated by using Scherer equation [11]. FTIR Infrared spectra were recorded (3000 Hyperion microscope) 1 wt.% weight sample in KBr. The FTIR spectrum is obtained in the range 400 - 4000 cm^{-1} which shows characteristic bands. The surface morphology was determined by scanning electron microscopy (JEOL JSM 7600F). The samples were mounted on alumina stubs using a liquid carbon paste and then sputter-coated with Au to avoid particle charging. The molar ration was estimated by EDAX.

Synthesis of nanocrystalline $Co_{0.5}Cr_{0.5}Al_2O_4$

Nanocrystalline $Co_{0.5}Cr_{0.5}Al_2O_4$ was prepared using co precipitation synthesis, which involves heating of metal nitrate and aluminium nitrate in stoichiometric proportion $Co_{0.5}Cr_{0.5}Al_2O_4$ sample is prepared from $(Al(NO_3)_3 \cdot 9H_2O)$, $(Co(NO_3)_2 \cdot 6H_2O)$ and $(Cr(NO_3)_3 \cdot 9H_2O)$ which were first dissolved in small amount of distilled water. This mixture was stirred for 2 h at the 80°C temperature. After stirring ammonia was added to this mixture. The collected precipitates comprising of hydroxides of metal ions, and some water contents. This precipitate was filtered-washed with ethanol and distilled water for several times to remove excess of ammonia. The obtained precipitated dark blue in colour was dried at 110°C in oven for 24 h. Then the powder was calcinate at 900°C for 4 h. $Co_{0.5}Cr_{0.5}Al_2O_4$ powder was milled by an agate mortar and pestle and mixed with binder. The paste thus form was screen printed on glass substrate, followed by sintering at 350°C for 2 h.

Result and discussion

X-Ray analysis

X-Ray diffraction patterns of the samples annealed at 900°C for 4 h obtained by the cobalt, chromium and aluminium nitrate by co precipitation route [12]. The XRD pattern of Fig.1 show peaks corresponding to cobalt aluminate spinel-like phase. As the concentration of the chromium was increased single-phase of cobalt aluminates were 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 patterns were rather complicated, which implied that the material was composed of mixed phases. There were no extra peaks in XRD pattern. We observe powder crystallinity with higher doping concentration of Cr, which had well developed crystalline structure. The addition of chromium retards the growth of the bulk cobalt aluminate phase on the surface and forms new phases. The major peaks of $CoAl_2O_4$ were generated at 30.98, 32.79, 36.48, 44.33, 55.09, 58.65, 64.48, 67.23, and 76.30 corresponding to hkl reflection at 220, 311, 400, 422, 511, 440 and 620 respectively. The peaks at 36.48° was the most intensive and the average crystallite sizes (D) were measured from Scherrer's equation [13]:

$$D=0.9\lambda/\beta \cos\theta$$

Where D is the crystallite size, λ is the wavelength of incident X-rays (0.15405 nm), β is the peak width at half height and θ corresponds to the peak position.The crystallite size of $Co_{0.5}Cr_{0.5}Al_2O_4$ powder is about 20.1 nm. It can be seen that the higher the annealing temperature, the larger the grain size.

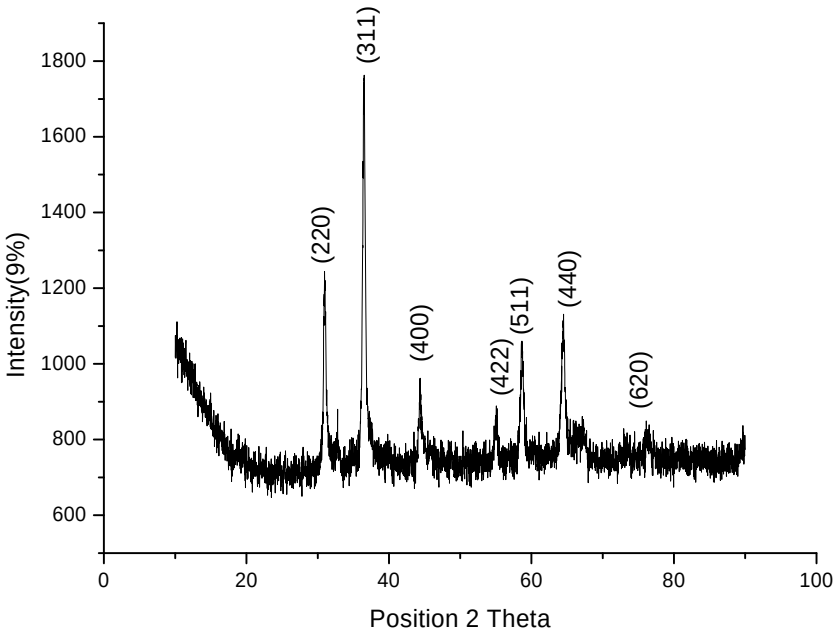

Fig. 1: The XRD pattern of $Co_{0.5}Cr_{0.5}Al_2O_4$ sample.

FTIR analysis

Fig. 2 shows the FTIR spectrum of the $Co_{0.5}Cr_{0.5}Al_2O_4$ sample obtained after calcinating at 900°C for 4 h. Several absorptions are observed in FTIR spectrum. All 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}.The $CoAl_2O_4$ powders were confirmed by FTIR. 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.

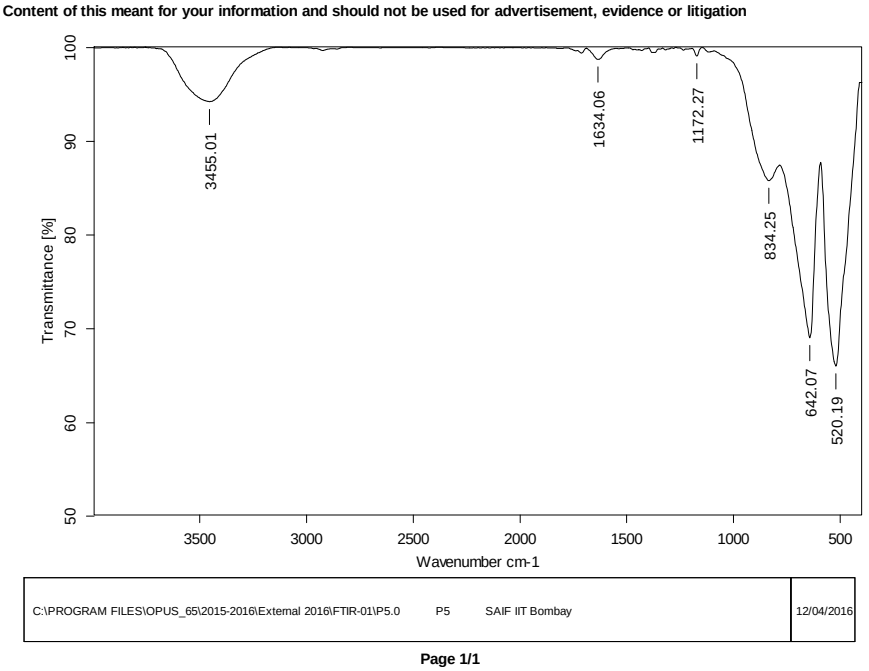

Fig. 2: FTIR spectrum of $Co_{0.5}Cr_{0.5}Al_2O_4$ calcinated at 900°C for 2 h.

SEM analysis.

The surface morphology of prepared $Co_{0.5}Cr_{0.5}Al_2O_4$ thick film is shown in Fig. 3. Numbers of grains are observed in SEM image. The figure shows that the grown sample consist of spherical grains having porosity. The SEM micrograph of the film shows the presence of small particles of variable shape and size along with micro pores. Energy dispersive X-ray diffraction analysis confirms the presence of metal ions, shown in Fig.4. The molar ratio was determined by EDAX was found to be Al :Co: Cr = 21.55:15.07:13.06.

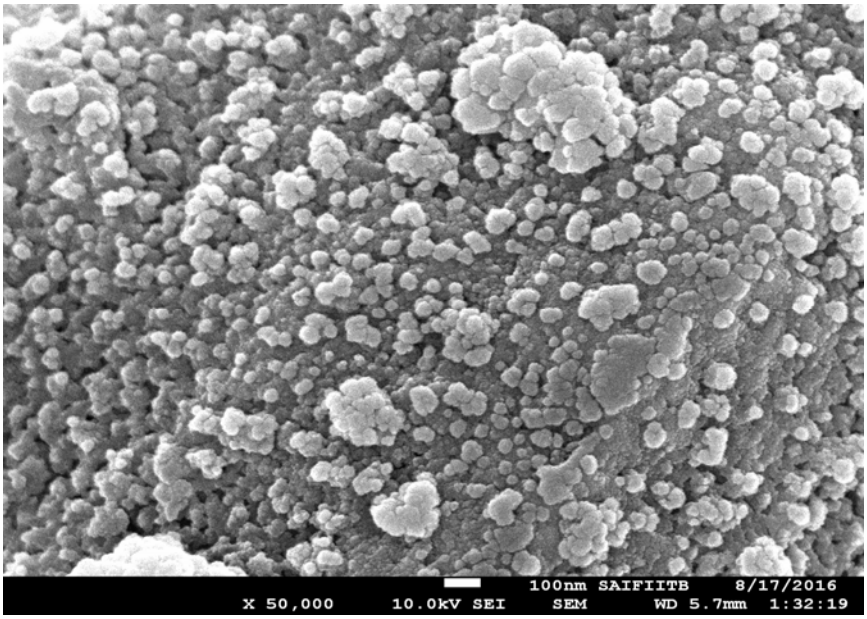

Fig. 3: SEM image of $Co_{0.5}Cr_{0.5}Al_2O_4$ thick film.

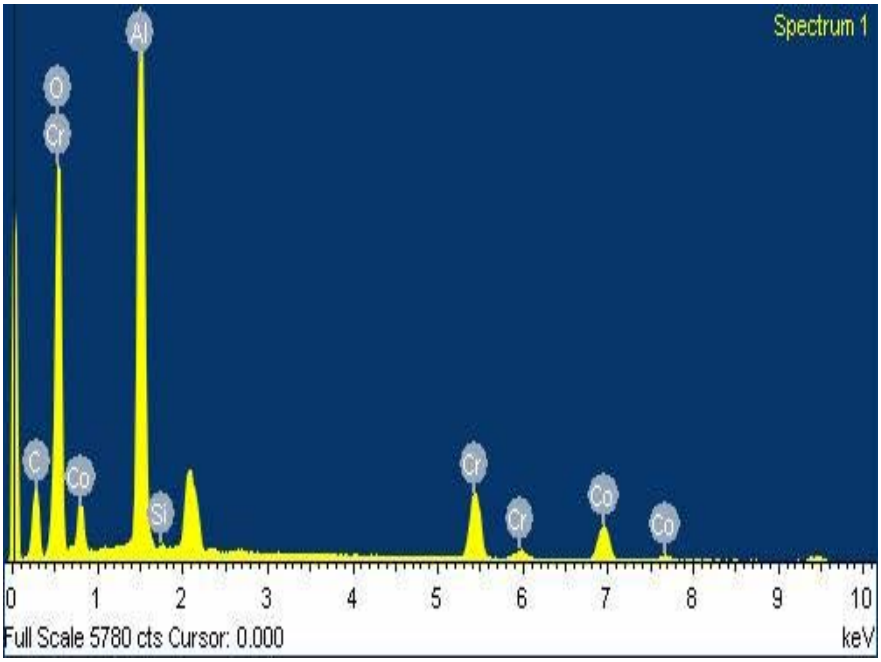

Fig. 4: EDAX spectra of $Co_{0.5}Cr_{0.5}Al_2O_4$ thick film.

Conclusions

In this work nanocrystalline $Co_{0.5}Cr_{0.5}Al_2O_4$ was prepared by coprecipitation method. The XRD result proved that at 900^oC spinel phase is present and the sample is crystalline in nature. Doping also leads to a general increase in surface areas and the development of larger pores. The XRD result proved that at 900^oC spinel phase is present and the sample is crystalline in nature. A SEM picture shows the presence of grains. EDAX analysis confirms the presence of Co, Cr and Al.

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