

Synthesis and structural characterization of Co doped MgAl_2O_4

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Abstract: Among metal oxide spinel structure, transition metal M doped spinels $\text{M}:\text{MgAl}_2\text{O}_4$ have attracted interest of researchers as well as technologists due to potential laser material because of its strong emission. $\text{Co}:\text{MgAl}_2\text{O}_4$ is considered as a good candidate for such application, as it has excellent absorption, emission and luminescence properties. In present study cobalt doped magnesium aluminate spinel have been synthesized from aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using chemical coprecipitation. Ammonia solution was used as precipitation agent with pH maintained between 8 to 9. The filtrate so obtained was dried at 110°C for 24 hrs. The fine powder was heat treated at different temperature from 550°C to 1000°C for 4h in temperature controlled furnace. Structural characterization of heat treated samples was carried out using X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). Size of the particles was estimated using Debye-Scherrer formula.

Introduction

Metal oxides of spinel structure comprise an important class of compounds with a variety of interesting electrical, magnetic and optical properties. Among these, transition metal M doped spinels $\text{M}:\text{MgAl}_2\text{O}_4$ have attracted a lot of interest of researchers as well as technologists due to its potential use as a new laser material because of its strong emission. $\text{Co}:\text{MgAl}_2\text{O}_4$ can be regarded as a good candidate for such application due to its excellent absorption, emission and luminescence properties. Contrary to bulk compounds, the physical properties like chemical strength, catalytic ability, high temperature resistivity can be enhanced in nanoscale crystallites of MgAl_2O_4 . This is due to the fact that nanocrystalline materials have high surface to volume ratio of the grains, have quantum confinement of charge carriers, enhanced contribution towards the electrical properties from grains and grain boundary regions, creation of holes and defects in grains, and possibility of band structure modification.

The mixed oxide spinel MgAl_2O_4 belongs to cubic space group $\text{Fd}\bar{3}\text{m}$. A unit cell comprises 8 tetrahedrons and 16 octahedrons. The Mg^{2+} ions are located at the center of the tetrahedron and coordinated by O^{2-} ions with full Td symmetry (A site) while the Al^{3+} ions are located at the center of the octahedron coordinated by O^{2-} ions with T3d symmetry (B site). The doped metal ions can substitute either A site or B site or both depending upon its valency and site type. The location of the substituted ions is crucial in determining the overall properties of the doped MgAl_2O_4 . In present study we synthesised $\text{Co:MgAl}_2\text{O}_4$ using coprecipitation technique and structural characterization was carried out.

Experimental

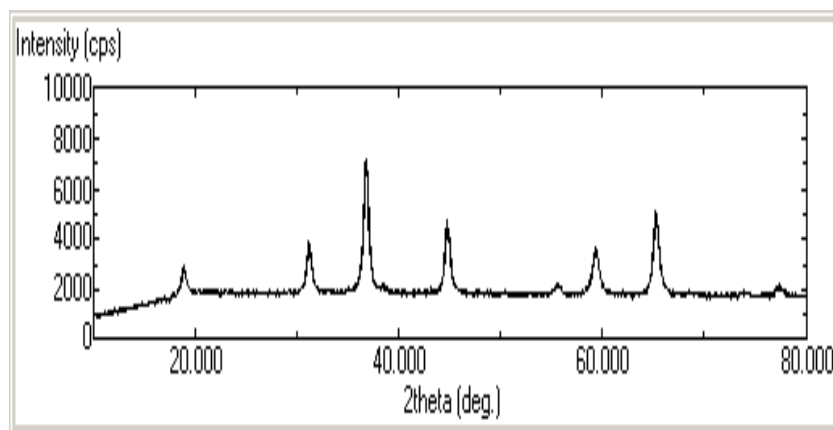
Cobalt substituted magnesium aluminate $\text{MgAl}_{0.9}\text{Co}_{0.1}\text{O}_4$ sample was prepared by the chemical coprecipitation method. The chemicals used in the synthesis of samples were $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ and NH_3 (Sigma-Aldrich). Aqueous solutions of aluminium nitrate and magnesium nitrate in the molar ratio ($\text{Al/Mg} = 2$) with the required stoichiometric amount of cobalt nitrate solution were mixed in a beaker and heated slowly up to 60°C with constant stirring. Then, NH_4OH solution was added until the pH of the solution reached a value of 11–12. The solution of all the samples was prepared in double deionized water. The precipitates were washed several times with double deionised water until the solution pH reached 7. These samples were then dried at 100°C in an oven and annealed at different temperatures.

In order to investigate the structural characterization X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analysis were performed on samples in powdered form.

Results and Discussion

XRD:

Diffraction pattern of the annealed sample is shown in Fig. 1. XRD pattern of the sample annealed up to 550°C (4h) shows that peaks of double hydroxide disappeared. Interestingly, four new broad peaks at $2\theta \sim 19.02^\circ$, 36.86° , 44.84° , 65.44° appeared which could be assigned peaks of spinel phase.

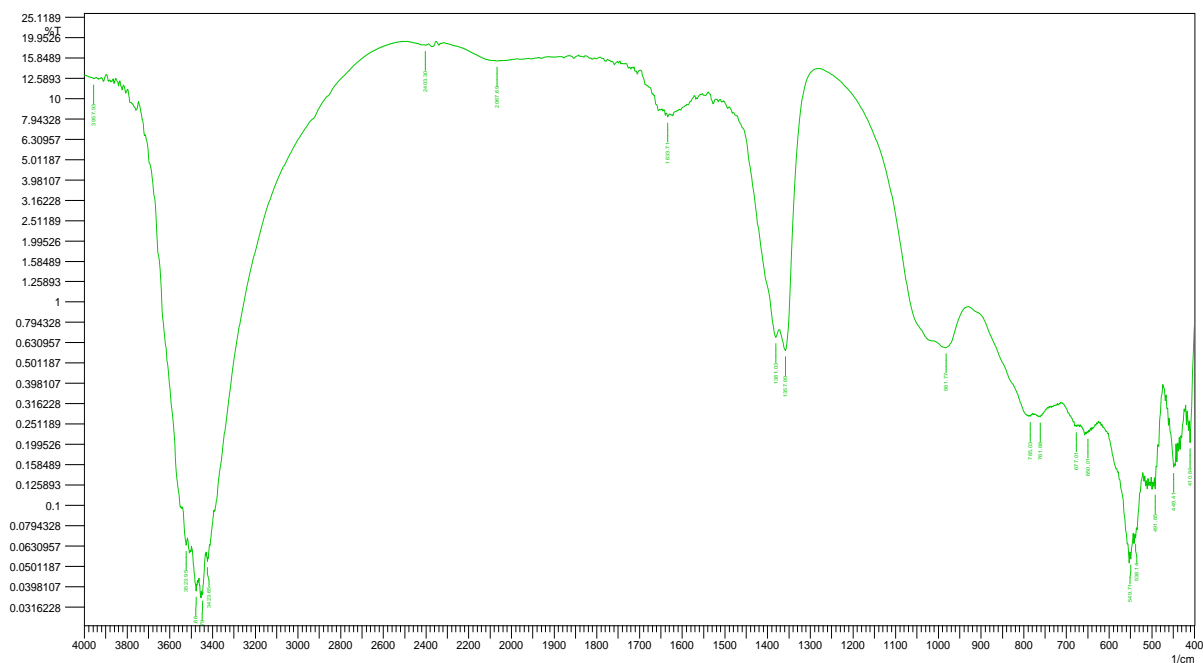


[Fig:-1]

The disappearance of the double hydroxide implies its decomposition whereas appearance of new broad peaks indicate initial phase of $\text{Co:MgAl}_2\text{O}_4$ spinel due to interfacial interaction between magnesium and aluminium at molecular level. The rise in calcination temperature up to 700°C (4h) increased the intensity of the different peaks which suggests improvement in crystallinity. In addition, weak broad peaks at $2\theta \sim 31.34^\circ$ and 59.52° were noticed in this pattern. When annealing temperature was increased up to 850°C and hold for 4h (d), strengthening and sharpness in the diffraction peaks at $2\theta \sim 19.02^\circ, 31.34^\circ, 36.86^\circ, 44.84^\circ, 59.52^\circ, 65.42^\circ$ can be seen. The XRD pattern is consistent with standard data of face centred cubic $\text{Co:MgAl}_2\text{O}_4$; and hence these peaks could be indexed by Miller indices (111), (220), (311), (400), (511), (400), respectively. The size of well developed crystalline $\text{Co:MgAl}_2\text{O}_4$ powders is estimated by Debye– Scherrer formula using XRD pattern, $d = (0.9\lambda) / (\beta \cos\theta)$, where d is the grain size, λ is the wavelength of the X-ray used, θ is the diffraction angle, β is the full width at half maxima of the peak. The average size so calculated corresponding to prominent peak (311) was 7 nm.

FTIR:

FTIR Spectroscopy provides valuable information about the phase composition and bonding in the samples. The FTIR of annealed sample is shown in Fig. 2 within the spectral range of $4000\text{-}400\text{ cm}^{-1}$.



[Fig:-2]

FTIR spectrum of as-prepared sample shows three distinct strong absorption bands centered around 1333, 1636, 3461 cm^{-1} . The absorption band centred around 3450 cm^{-1} could be assigned as the stretching vibration of H-O-H molecule, while band around 1380 cm^{-1} could be ascribed presence of nitrate groups. The H-O-H band overlaps with surface hydroxyl group vibration and result in the broadening of the band. The band centred around 1641 cm^{-1} is due to the banding modes of H-O-H absorbed at surface of the product. In general, the band over range of 1000-400 cm^{-1} corresponds to metal oxygen bonds (M-O-M). In our case, the bands noted around 669 and 554 cm^{-1} may be assigned as hydroxide of magnesium and aluminium. When the sample was annealed up to 550⁰C (4h), evaporation of nitrate group is a noticeable event. Besides, bands of double hydroxide of magnesium and aluminium are weakened, when the sample was annealed up to 700⁰C for 4h, weak bands around 690 and 505 cm^{-1} appeared, which could be assigned AlO_6 group and Mg-O stretching vibrations, respectively. The presence of absorption band around 3450 cm^{-1} and 1640 cm^{-1} even at high temperatures indicate that water molecules exist in the structure. The appearance of small amount of water molecule is most probably due to the inter absorption during the compaction of powder specimen with KBr. The FTIR results support XRD data of respective samples.

References:

- [1] J ahmad et al. Physica B 406 (2011) 254-258.
- [2] M J Iqbal et al. Mat. Sci. Eng. B 136 (2007) 140-147.