

Structural and Vibrational Response in Al Modified NiCr₂O₄

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Abstract. Pristine and Al doped NiCr₂O₄[NiCr_{2-y}Al_yO₄; $y = 0.0, 0.05$] nanoparticles were prepared using sol-gel auto combustion route. Structural and vibrational studies were examined using X-ray diffraction technique and Raman spectroscopy. From X-ray diffraction pattern it was observed that both samples crystallize in spinel cubic structure with space group $Fd\bar{3}m$. Al doping does not affect the crystal structure. A small amount of Cr₂O₃ is also present in the sample which may due to a higher melting temperature of Cr₂O₃. Average crystallite size decreases when Cr³⁺ ions are occupied by Al³⁺ ions. For vibrational analysis, Raman spectroscopy was performed. All active Raman modes for spinel structure were observed for both samples. Some extra modes between 300 and 400 cm⁻¹ were observed. These modes might be appearing due to Cr₂O₃ phase present in the sample.

INTRODUCTION

Metal oxides with spinel structure have general formula (A_xB_{1-x})[A_{1-x}B_{1+x}]O₄; where x is cation distribution factor, A is divalent (Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Zn²⁺) and B is trivalent (Fe³⁺, Cr³⁺, Al³⁺) cations occupying the tetrahedral and octahedral sites in Face Centered Cubic (FCC) lattice formed by anions (O²⁻). In the above formula divalent is situated at tetrahedral and octahedral sites are filled with trivalent according to the type of spinel structure. These oxides have been a subject of great interest due to their charge ordering, electromagnetic, structural, multiferroic properties. As the oxide possess these rich set of properties, they are useful in many technological applications such as spintronics, electromagnetic sensors, as a catalyst, storage devices *etc.* [1].

Nickel Chromite with formula NiCr₂O₄ crystallizes in spinel cubic structure with space group $Fd\bar{3}m$ above room temperature where nonmagnetic Ni²⁺ ions reside at the tetrahedral site. Due to Jahn- Teller distortion NiCr₂O₄ shows a structural phase transition from cubic ($Fd\bar{3}m$) to tetragonal ($I41/amd$) structure near room temperature. Another structural phase transition from tetragonal to orthorhombic ($Fddd$) was also observed [2]. NiCr₂O₄ shows different magnetic phase transition due to the frustration of spins at a lower temperature. It shows long-range ferrimagnetic transition at $T_C = 75$ K this coinciding with tetragonal to orthorhombic symmetry [3]. Another magnetic phase transition near $T_s = 29$ K was also observed by some researchers and this attributed to antiferromagnetic coupling of the transverse component of magnetic moments [4].

A lot of work has been done on A-site doped NiCr₂O₄ but few work have been reported on Cr site doped NiCr₂O₄. Al³⁺ has higher tendency to occupy octahedral sites as well as ionic radii of Al³⁺ (0.5 Å) is comparable to ionic radii of Cr³⁺ ions thus this does not affect the crystal structure. In the present study, we have synthesized Al doped NiCr₂O₄ nanoparticles by low-temperature sol-gel auto combustion route and the structural vibrational effects have been studied through characterization techniques X-ray diffraction (XRD) and Raman spectroscopy.

EXPERIMENTAL TECHNIQUES

NiCr_2O_4 and $\text{NiCr}_{1.95}\text{Al}_{0.05}\text{O}_4$ samples were prepared by sol-gel auto combustion route by taking nickel nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, chromium nitrate $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ and aluminium nitrate $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ in a stoichiometric ratio. All precursors in their stoichiometric ratio were dissolved in distilled water. The citric acid in a calculated amount was added for making a reaction. To maintain the pH level up to 7. Ammonia was added and 1 ml of ethylene glycol was dropped for defreezing the solution. The neutralized solution was stirred using a magnetic stirrer at 80°C until it becomes viscous and finally formed a very viscous gel. After auto combustion, the NiCr_2O_4 and $\text{NiCr}_{1.95}\text{Al}_{0.05}\text{O}_4$ samples were calcined at 800°C for 4h, further designate as NCO and NCAO respectively.

The crystal structure of both the samples was identified by x-ray diffraction (XRD) technique at room temperature using Bruker D8 Advance X-ray diffractometer with $\text{CuK}\alpha_1$ (1.54 \AA) radiation. The Raman measurements on as-synthesized samples were carried out on LABRAM HR800 spectrometer. The spectrometer comprises of Ar ion laser: Wavelength: 488 nm excitation source.

RESULTS AND DISCUSSIONS

The crystalline structure of NiCr_2O_4 and $\text{NiCr}_{1.95}\text{Al}_{0.05}\text{O}_4$ was observed using X-ray diffraction technique. Figure 1 shows the X-ray diffraction pattern of pristine and Al^{3+} doped NCO. From the figure, it is clear that the diffraction pattern consists of well-resolved peaks, which confirms the polycrystalline and spinel structure formation. The peak position at 30.35° , 35.79° , 37.40° , 43.49° , 53.99° , 57.58° , and 63.20° . The diffraction peaks corresponding to reflection planes (220), (311), (222), (400), (422), (511) and (440) provide a clear evidence for the formation of spinel structure of NiCr_2O_4 . These assigned to spinel cubic structure with space group $Fd\bar{3}m$. Doping of Al ions at Cr site does not influence crystal structure and NCAO also have cubic structure [4].

Both samples have a small amount of Cr_2O_3 present. The ionic radius of Al^{3+} ions (0.51 \AA) is smaller than that of the Cr^{3+} ions (0.63 \AA) and the amount of Cr^{3+} ions substituted by Al^{3+} ions is limited, thus redundant Cr^{3+} ions aggregate on the grain boundaries forming Cr_2O_3 phase, similar was observed by Han *et al.* [5]. When Al^{3+} ions replace Cr^{3+} ions most intense (311) peak also shift to the higher angle side this is attributed to the small ionic radii of Al^{3+} (0.51 \AA) as compared to Cr^{3+} (0.63 \AA).

Crystallite size was calculated theoretically from Scherer's formula $t = 0.9\lambda/\beta\cos\theta$, Where $\lambda = 1.54 \text{ \AA}$ is the wavelength of X-ray used, β is the FWHM and θ is the angle of diffraction. The average crystallite size was calculated as 44 nm for NCO and 37.47 nm for NCAO. The values of lattice parameter, volume and average crystallite size of NiCr_2O_4 samples are depicted in Table 1. From the table, the value of the lattice parameter was found to decrease with the increase in Al^{3+} concentration. This reduction can be explained on the ionic size difference of the component ions. The unit cell is expected to contract to accommodate smaller ions so that the lattice parameter decreases [6].

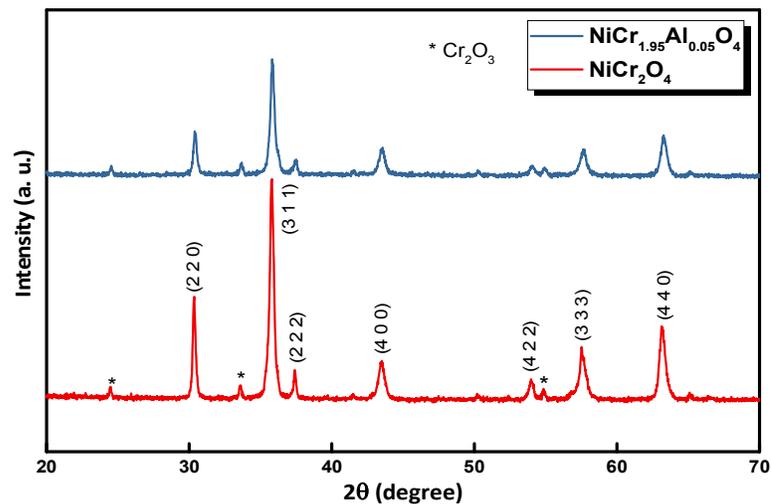


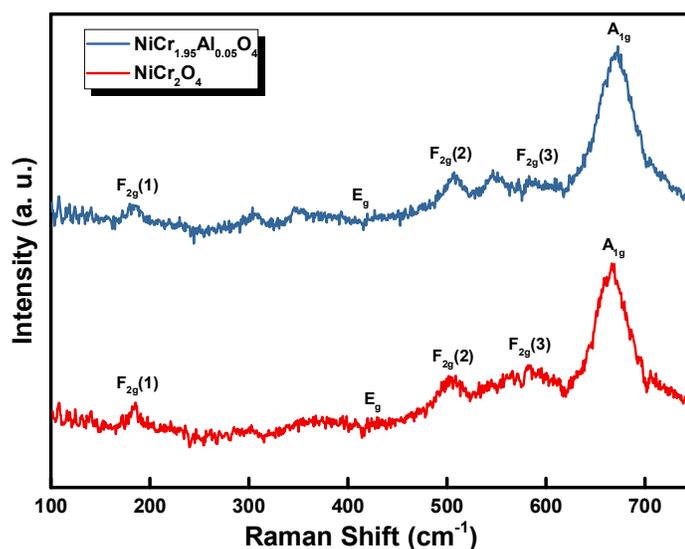
FIGURE 1. X-Ray Diffraction Patterns of $\text{NiCr}_{2-y}\text{Al}_y\text{O}_4$ ($y = 0.0, 0.05$) samples.

TABLE 1. Lattice Parameters, Volume and Average Crystallite Size for NiCr₂O₄ and NiCr_{1.95}Al_{0.05}O₄ samples

Sample	Space group	Lattice Parameter (a) (in Å)	Volume (in Å ³)	Average Crystallite Size (in nm)
NiCr ₂ O ₄	<i>Fd3m</i>	8.32	575.96	44.00
NiCr _{1.95} Al _{0.05} O ₄	<i>Fd3m</i>	8.30	573.81	37.47

Vibrational spectra of NCO and NCAO were recorded using Raman spectrograph in frequency ranges from 100 cm⁻¹ to 750 cm⁻¹ at room temperature. There are five active Raman modes predicted from group theory for spinel structure as A_{1g}, E_g and 3F_{2g}. Figure 2 shows the Raman spectra of NCO and NCAO. For prepared NCO and NCAO samples, we have observed eight active Raman modes. Lowest wave number F_{2g}(1) mode was observed at 183.22 cm⁻¹ for both samples E_g mode was observed at 427.42 cm⁻¹. F_{2g}(2) and F_{2g}(3) modes were observed at 508.27 cm⁻¹ and 583.59 cm⁻¹ respectively [7].

Some extra active modes between 300 cm⁻¹ and 400 cm⁻¹ arise due to Cr₂O₃ present in the sample all these Raman bands could be attributed to Cr(III) species (crystalline Cr₂O₃), which is consistent with the XRD results [8]. The most intense A_{1g} was observed at 667.67 cm⁻¹ for NCO and 673.19 cm⁻¹ for NCAO sample. This shift is due to the higher stretching vibration of Al-O bond as ionic radii of Al³⁺ is less as compared to Cr³⁺. This shift confirms that Al ions successfully occupied the Cr ions.

**FIGURE 2.** Raman spectra of NiCr_{2-x}Al_xO₄ (x = 0.0, 0.05) recorded at room temperature.

CONCLUSIONS

NiCr₂O₄ and NiCr_{1.95}Al_{0.05}O₄ chromite were synthesized by sol-gel auto combustion technique. X-ray diffraction pattern confirms that both samples have spinel cubic structure with space group *Fd3m*. The most intense (311) peak shows a little shift at higher angle and crystallite size decreases with Al doping both are attributed to small ionic radii of Al ion as compared to Cr³⁺ ion. Raman spectra show all five active Raman modes for spinel structure. Some extra modes were also observed which might be arises due to a small amount of Cr₂O₃ present. The most intense mode shows a clear shift which confirms that Al³⁺ ions occupied Cr³⁺ ions successfully.

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