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Rietveld Refinement of Cobalt Doped Magnesium Aluminate Spinel Nanoparticles

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ABSTRACT

Among various transition metals, Co: $MgAl_2O_4$ can be regarded as a good one for applications like high mechanical resistance, high chemical and thermal stability, and low temperature sinterability of spinel type oxide materials. The physical properties like chemical strength, catalytic ability, and high temperature resistivity of cobalt doped magnesium aluminate have been further enhanced. Cobalt-magnesium aluminate crystallizes at relatively higher temperature, i.e. above 850°C as compared to un-doped magnesium aluminate that crystallizes around 800°C. A single phase cobalt doped magnesium aluminate fcc ordered-spinel nanopowder (grain size ~ 20 nm) with a good, chemical homogeneity, is obtained by using co-precipitation method followed by thermal treatment at temperature 1000°C for 4h, in air. Rietveld refinement is performed by FULLPROF program and used to confirm the results of XRD of samples calcined at 850°C and 1000°C (4h).

Keywords : Rietveld Refinement, Magnesium Aluminate, Cobalt, Nanoparticle, XRD.

I. INTRODUCTION

In earlier studies, the structural evolution due to the effect of heat treatment on lattice constant micro-strain and grain size of magnesium aluminate spinel powders prepared by coprecipitation have been reported. Introduction of transition metal in $MgAl_2O_4$ spinel have attracted a lot of interest of researchers and technologists due to its extremely high absorption, emission and luminescence properties [1-2]. Owing to the high mechanical resistance, high chemical and thermal stability, and low temperature sinterability of spinel type oxide materials, $Co_xMg_{1-x}Al_2O_4$ is in great demand for qualified nano inorganic blue pigment [3].

The coprecipitation method and ammonium hydrogen carbonate as precipitating agent, pure and highly dispersed nanoscale powders of Co-doped $MgAl_2O_4$ were synthesized by coprecipitation method at 800°C with particle size in the range of 10-30 nm [4]. Nanocrystalline $Co_xMg_{1-x}Al_2O_4$ spinel pigment has been synthesized via low-temperature combustion route by employing β-alanine as a novel environmentally benign fuel by Torkian et. al. [5]. In nanoscale, the physical properties of Co:$MgAl_2O_4$; like chemical strength, catalytic ability, and high temperature resistivity have been further enhanced. This is due to the fact that nanocrystalline materials have high surface to volume ratio of the grains, 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 [6].

Authors have already reported that the mixed metal oxide spinel $MgAl_2O_4$ belongs to cubic space group Fd3m. A unit cell comprises 8 tetrahedrons and 16 octahedrons. The Mg^{2+} ions are located at the centre of the tetrahedron and coordinated by O^{2-} ions with full T_d symmetry (A site) while the Al^{3+} ions are located at the centre of the octahedron coordinated by O^{2-} ions with T_{3d} symmetry (B site). The doped metal ions can substitute either A site or B site or both depending upon its valency and site type [7-8]. The synthesis route is very important for determining the final properties of inorganic pigment such as color, particle size, and chemical & thermal stability. The liquid combustion method has the advantage of preparing crystalline powders with nano size and high purity at low temperatures [9]. Single crystal of $MgAl_2O_4$ doped with tetrahedral Co^{2+} ions is attractive for laser modulation [10], however, the homogeneous and bulk crystals can hardly be obtained because of the high growth temperature and all kinds of defects embedded in the crystals.

In our previous work, we have reported synthesis of nanocrystalline $Co_xMg_{1-x}Al_2O_4$ spinel pigment via coprecipitation technique followed by heat treatment and characterized by applying different complementary techniques. Doped with some active ions, the spinel behaves as multifunctional material, especially doped with Co^{2+} which can offer a wide choice of solid-state saturable absorbers such as opaque ceramics of Co^{2+}:$MgAl_2O_4$ and Co^{2+}:$ZnAl_2O_4$. Co (2.88 wt%) has been introduced in $MgAl_2O_4$ spinels by chemical coprecipitation technique followed by thermal treatment. In the present work, Rietveld refinement is used to confirm results of XRD of cobalt doped magnesium aluminate.

II. EXPERIMENTAL

The coprecipitation method was used to synthesize cobalt-magnesium aluminate spinel nanopowders. The high purity reagents $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and ammonia solution were used to prepare cobalt magnesium aluminate cubic spinel nanopowders. A solution of 0.2 M nitrates was prepared in double distilled water, with Co:Mg:Al (molar ratio) = 0.1:0.9:2.0. The solutions of nitrates were mixed together for homogenization. The precursor have been prepared by adding slowly the mixed solution to the ammonia solution under rigours stirring, maintaining the pH 8-9 and temperature 60°C. The precursor was washed with an excess of double distilled water, many time. The washed precipitates of precursor were dried for 24 hrs at 100°C in an oven in the presence of air. The solid so-obtained was grinded in agate mortar pestle to obtain fine powder. The powdered samples were calcined at temperatures 550°C, 700°C, 850°C and 1000°C for 4 hours in presence of air, with heating rate 10°C min^{-1}.

X-ray diffraction experiments were performed at room temperature in a Rigaku Miniflex-II instrument using CuKα radiation (λ = 1.5406 Å), generated at 30 kV and a current of 15 mA. In order to further analyse XRD data of Co:$MgAl_2O_4$, the Rietveld refinement of the XRD data has been carried out. The Rietveld refinement of samples calcined at 850°C and 1000°C (4h) was performed by FULLPROF program taking into consideration Fd3m space group symmetry of the samples.

III. RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD)

Figure 1 depicts the XRD patterns of the samples as-prepared and calcined at temperature 550°C, 700°C, 850°C and 1000°C for 4h in air.

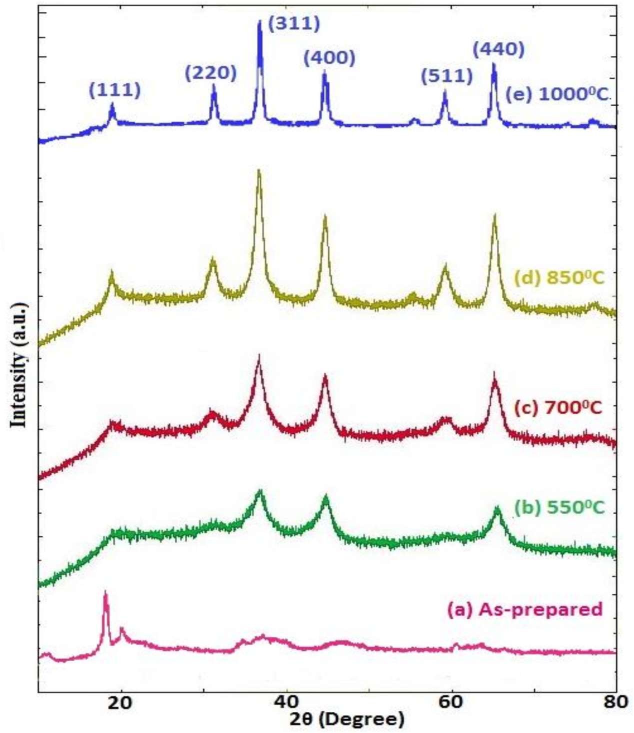

Figure 1 : XRD patterns of as-prepared and heat treated samples of Co:$MgAl_2O_4$.

Diffraction peaks of the sample calcined at 850°C are compared with the standard data of face centred cubic $MgAl_2O_4$ [JCPDS 21-1152] and found in accordance with the diffraction peaks of the standard data. The diffraction peaks are indexed by Miller indices (111), (220), (311), (400), (511), (400), respectively with the help of JCPDS data.

Effects of heat treatment on structure parameter of Co:$MgAl_2O_4$ like lattice constant, spinel phase, crystallites size and microstrain and dislocation density have also been estimated. Figure 2 displays lattice constant vs Nelson-Riley function.

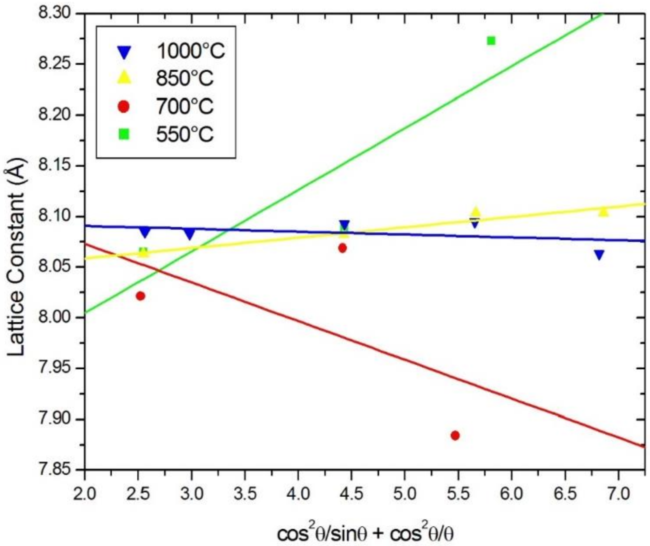

Figure 2 : Lattice constant vs Nelson-Riley function

Figure 3 illustrates that the lattice constant increases with increasing calcination temperature. The increase in lattice constant is due to the fact that the ionic radius of Co^{2+} (0.74 Å) is larger than that of Al^{3+} (0.45 Å) and demonstrates that the Co^{2+} ions actually enter the crystal lattice and retain the cubic spinel structure.

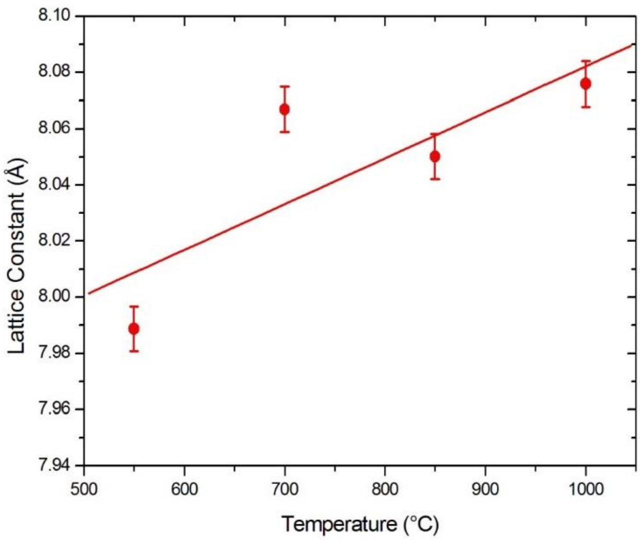

Figure 3 : Lattice constant versus calcination temperatures for 4 h.

The effect of temperature on degree of order in Co:$MgAl_2O_4$ spinel nanopowder is studied and estimated value of degree of order is given in Table 1. The data clearly reveal that the degree of order in Co:$MgAl_2O_4$ spinel nanopowder increases with increasing calcination temperature (Figure 3).

Table-1 Estimated value of grain size and degree of order

Calcined Sample	Crystallite size $D_{D\text{-}S}$ (nm)	Crystallite size $D_{W\text{-}H}$ (nm)	Strain (ε)	Lattice constant (Å)	X-ray density (g/cm³)	Dislocation density $\rho \cong \frac{1}{D_{XRD}^{2}}$	Degree of ordered phase
550°C(4h)	3.40	2.35	0.0367	7.8831	3.673	0.1815	0.7348
700°C(4h)	5.75	4.36	0.0129	8.1494	3.324	0.0527	0.6957
850°C(4h)	7.78	5.37	0.0121	8.0382	3.464	0.0347	0.8850
1000°C(4h)	15.09	19.33	0.0034	8.0965	3.390	0.0027	0.9901

Crystallite size of Co:$MgAl_2O_4$ spinel nanopowder is estimated by Debye-Scherrer equation and Williamson-Hall plot (W-H plot) and presented in Table 1. The graph is plotted between Sin(θ_{hkl}) and β_{hkl}Cos(θ_{hkl}) as shown in Figure 4. The grain size and micro-strain of Co:$MgAl_2O_4$ do not change significantly in the calcination temperature range 550°C to 850°C (4h). In contrast, an increase in crystallite size and a decrease in micro-strain are noticed in a sample heated at 1000°C (4h). The increase in grain size may be attributed to the fact that the ionic radius (0.74 Å) and atomic mass of Co^{2+} (59 a.m.u.) is larger than that of ionic radius (0.45 Å) and atomic mass (27 a.m.u.) of Al^{3+}, respectively.

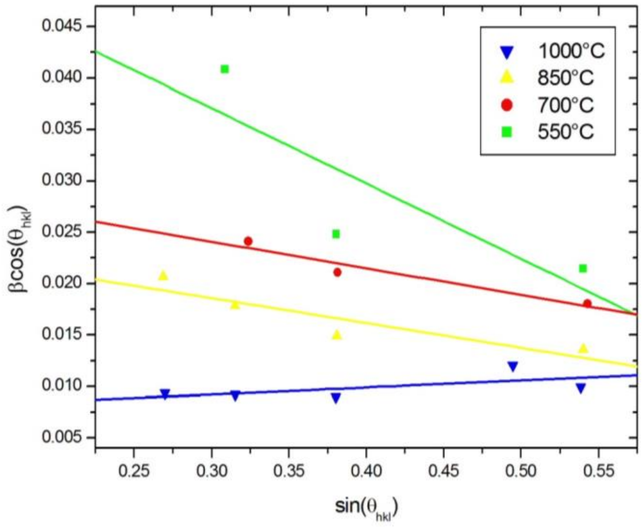

Figure 4 : *Williamson-Hall plot of calcined of Co:$MgAl_2O_4$ spinel nanopowders*

Further, by knowledge of average crystallite size and an empirical relation $\rho \cong \frac{1}{D_{W-H}^{2}}$, dislocation density of Co:$MgAl_2O_4$ cubic spinel nanocrystallites is obtained and given in Table 1. As calcination temperature is increased, the density of dislocation decreased as a result of less nucleation sites being available during crystallization upon heating, which in turn lead to the comparatively larger crystallite size.

3.2 Rietveld Refinement

In order to further analyse XRD data of Co:$MgAl_2O_4$, the Rietveld refinement of the XRD data has been carried out. The Rietveld refinement of samples calcined at 850°C and 1000°C (4h) was performed by FULLPROF program taking into consideration Fd3m space group symmetry of the samples. Figure 5 & 6 displays Rietveld refinement of the samples annealed at 850°C and 1000°C (4h), respectively.

Background parameters, scale factor, isotropic thermal parameters, lattice parameters, half-width parameters (*u*, *v*, *w*), occupancy and atomic positions were refined and the refined values of the lattice constants with the reliability parameters R_p (profile fitting R-value), R_{Bragg} (Bragg R-value), R_F (Crystallographic R_F factor values) and χ^2 (chi-square) are represented in Table 2.

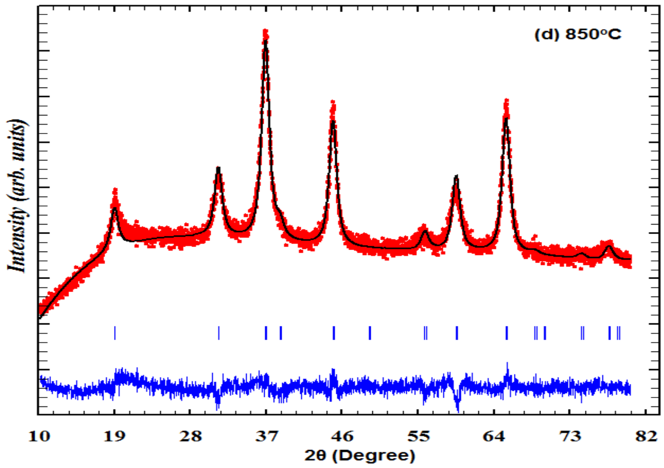

Figure 5 : *Rietveld refinement of Co:MgAl₂O₄ powder calcined at 850°C (4h).*

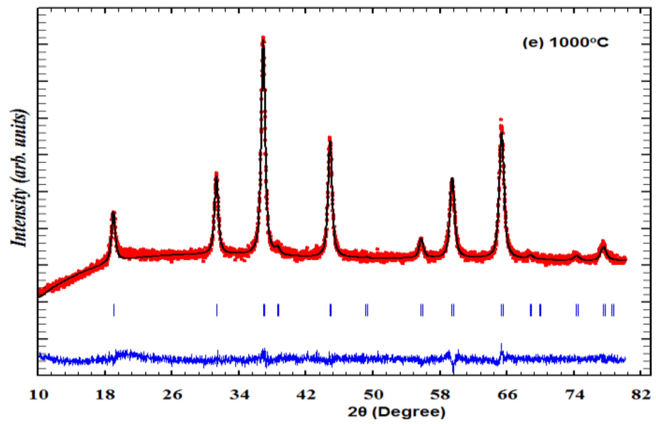

Figure 6: *Rietveld refinement of $Co:MgAl_2O_4$ powder calcined at 1000°C (4h).*

The improved values of R_p, R_{Bragg} and χ^2 are found for the sample calcined at temperature 1000°C. This result suggest that single phase ordered $Co:MgAl_2O_4$ nanopowder can be successfully obtained by coprecipitation technique followed by heat treatment at 1000°C (4h) in air.

Table 2 : Rietveld refinement parameters of $Co:MgAl_2O_4$

Calcined Sample	Lattice Constant (Å)	Volume (Å³)	Density (g/cm³)	χ^2	R_{Bragg}	R_p	R_F
850°C (4h)	8.0641	524.4	4.037	2.61	4.06	2.86	2.34
1000°C (4h)	8.0744	526.4	3.839	2.24	4.57	2.64	4.03

Lattice parameter of $Co:MgAl_2O_4$ of the samples calcined at 850°C (4h) and 1000°C (4h) were estimated by Nelson-Riley function and Rietveld refinement. It is found that the lattice parameter estimated by Nelson-Riley function and Rietveld refinement is comparable for the sample calcined at 1000°C (4h). This result suggests that Nelson-Riley function can also be a good tool for estimation of lattice parameter for a single phase structure.

IV. CONCLUSION

Using the precursors: $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and ammonia solution, as a catalyst, $Co:MgAl_2O_4$ cubic spinel nanopowder were prepared by coprecipitation method and subsequent thermal heating at temperatures 550°C, 700°C, 850°C and 1000°C for 4h, in air. The structural properties of $Co:MgAl_2O_4$ nanopowder were investigated by XRD. Cobalt-magnesium aluminate crystallizes at relatively higher temperature, i.e. above 850°C as compared to undoped magnesium aluminate that crystallizes around 800°C. An increase in lattice constant is observed, which is due to the fact that the ionic radius of Co^{2+} (i.e., 0.745 Å) is larger than that of Al^{3+} (0.45 Å). Result of Rietveld refinement confirms ordered and single phase $Co:MgAl_2O_4$ nanopowder can be successfully obtained by coprecipitation technique followed heat treatment 1000°C. Nelson-Riely function is a good tool for estimation of lattice parameter for a single phase structure. Results of XRD studies were confirmed by Rietveld refinement.

Finally, it is concluded that the lattice parameter estimated by Nelson-Riley function and Rietveld refinement is comparable for the sample calcined at 1000°C (4h). This result suggests that Nelson-Riley function can also be a good tool for estimation of lattice parameter for a single phase structure.

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