Structural and Phonon Modes Study of Nano Ceramics $CoAl_2O_4$ Synthesized by Sol-Gel Route

Bhargav Pathak[1,a)], A. Yadav[2], Pankaj Choudhary[1, b)], M. Varshney[1], A. Mishra[1]

[1]*Material Science Laboratory, School of Physics, Vigyan Bhawan, Devi Ahilya University, Khandwa Road Campus, Indore 452001, India.*
[2]*Department of Physics, Medi-Caps University, Pigdamber, Indore 453331, India.*
[a)]bhargavpathak.phy@gmail.com
[b)]pankaj.7007@rediffmail.com

Abstract. $CoAl_2O_4$ nano ceramic was successfully synthesized via sol-gel auto combustion technique and the obtained nano-sized powder is annealed at 800° C for 8h. The annealed powder is examined by x-ray diffraction (XRD) and Raman spectroscopy at room temperature. The diffraction peaks of the annealed $CoAl_2O_4$ are well crystalline and correspond to cubic inverse-spinel structure with space group *Fd*-3*m*. Raman spectroscopy also confirms the formation of single phase structure. Crystallite size and the strain are obtained using Williamson-hall method and found to have values ~17 nm and -2.41×10^{-3}, respectively. The negative strain in crystal structure is attributed to the shrinking of structure in order to get stability in nano ceramics. In vibrational study we are confirming inverse spinel structure via Raman spectroscopy. The quadruplicate splitting of peak related to A_{1g} mode at 694 cm^{-1}, 715 cm^{-1}, 735 cm^{-1} and 758 cm^{-1} attributed to structural symmetry.

INTRODUCTION

Royal blue colored ceramic cobalt aluminate has attracted extensive interest in photo electrochemical catalysis (PEC). Its spinel structure allows the wide range of cationic substitution at tetrahedral and octahedral sites giving rise to applications in different domains such as catalyst, pigments, super durable coating, magnetic materials and also in semiconductor devices. Moreover cobalt aluminate possesses inverse spinel structure $[B^T(AB)^OO_4]$. This type of spin cation distribution of spinel structure has been given a lot of attention because it allows understanding of the correlations between the structure and its properties such as color, diffusivity, magnetic behavior and optical properties, which are heavily based on better occupation with these two metal sites. [1 - 3].

The crystallite dimension of $CoAl_2O_4$ has fundamental importance in particular properties to the material. More precisely, when cobalt aluminate is in the form of micron-sized pigment Reportedly, $CoAl_2O_4$ ceramic pigments possess excellent covering and coloring ability. This compatibility with most thermoplastic opens the window for its applications in various domains such as rapid developing 3D printing, inkjet printing, as a catalyst, pigment layer on luminescent materials. Its nature to resists solar exposure and atmospheric agents, it has been widely used for color filter for automotive lamps, coloration of plastics, fibers, rubber, glass, ceramic bodies, paint and porcelain etc. Among the other uses of this material it is likely to show promising optical applications because of its thermally and chemically stable behavior at nano size pigments [4, 5].

The aim of this work was to achieve the nano particles of $CoAl_2O_4$ using a sol- gel method. This technique for processing various materials helps to save time and energy. Sol-gel method gives advantage over controlling size and homogeneity of crystallite size; it will be interesting to see the impact of particle size on the structure of $CoAl_2O_4$ and also the coloring ability of the aluminates. For the structural confirmation of the synthesized sample we have performed the x-ray diffraction. We have also studied the vibrational phonon modes with the help of the Raman spectroscopy.

EXPERIMENTAL DETAILS

Cobalt blue was synthesized using precursor nitrates $Co(NO_3)_2$ and $Al(NO_3)_3 \cdot 9H_2O$ with using citric acid $C_6H_8O_7$ as a fuel. For the desired amount of oxide yield, the precursors were calculated and mixed using magnetic stirrer, dissolved in distilled water placed in a beaker. After successive mixing, ammonium hydroxide (NH_4OH) is added in order to balance pH. 1 ml of Ethylene glycol is added for gel formation and after 4 hr of stirring and heating at 180 °C, gel gets evaporated and we get cobalt aluminate in nitrate form as a yield.

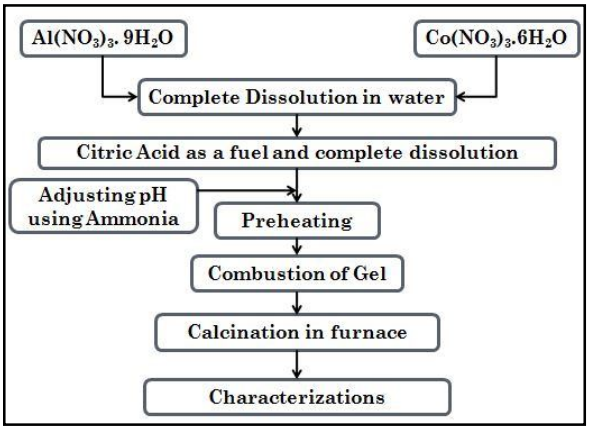

FIGURE 1 Procedure steps of sol-gel auto combustion method

It is then calcined at 800 °C in order to get it in oxide formed $CoAl_2O_4$. The oxide in bulk form of $CoAl_2O_4$ is used for structural characterization such as X-ray diffraction and Raman spectroscopy. The procedure schematic is shown in form of flow chart Figure 1

X-ray diffraction was performed on Bruker D8 setup at room temperature with Cu-k_α as a source (1.5406 Å) in the 2θ range from 10° - 70° with working voltage of 40 *kV* and current 40 *mA*. Raman measurement was done in the range 400 -900 cm^{-1} using LABRAM - 800 with argon laser at 488 *nm*.

RESULTS AND DISCUSSION

The x-ray diffraction (XRD) profile of $CoAl_2O_4$ nano ceramics is shown in Figure 2. From the XRD pattern, it is observed that planes present at (220), (311), (400), (422), (511), (440) confirms that $CoAl_2O_4$ ceramics crystallizes have cubic spinel structure with space group *Fd3m*. The sharpness of the each peak shows the crystallinity of the compound. Lower particle size can be expected from the broadening of FWHM peak. The lattice parameters for $CoAl_2O_4$ cubic unit cell is estimated to be $a = b = c = 8.1$ Å. The crystallite size of the prepared ceramics was estimated from averaging the full width at half-maxima (FWHM) of the obtained XRD profile the peaks are fitted to pseudo voigt function.

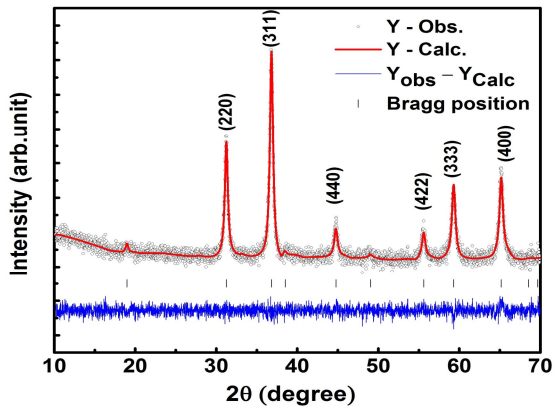

FIGURE 2 XRD pattern of $CoAl_2O_4$ nano ceramics

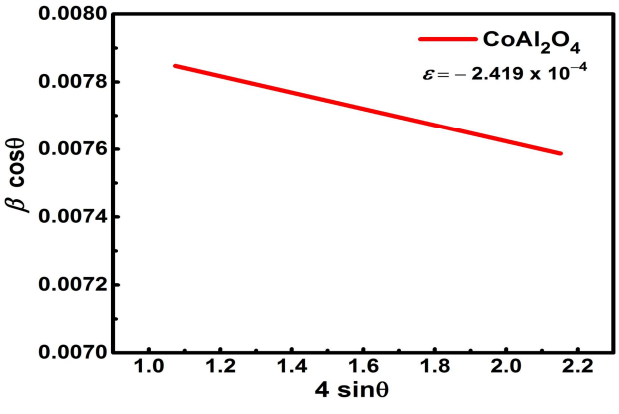

FIGURE 3 Williamson-Hall strain plot

X-ray peak broadening is not only affected by crystallite size but also strain. The strain is calculated by using Williamson–Hall plot method and derived from formula β_{hkl} = (Kλ/ D cosθ + 4ε tanθ); strain is denoted as ε. By rearranging the formula we get β_{hkl} cosθ = [4ε sinθ + (Kλ/ D)]. Thus comparing it with straight line equation y = m x + c; the slope of β_{hkl} cosθ as a function of 4sinθ, the slope gives value of the strain (ε) = -2.41×10^{-4} and the crystallite size is obtained from the intersecting β_{hkl} Cosθ is ~17 *nm*. Thus particle sizes are validated by W-H method giving averaged similar crystallite sizes. The dislocation density is calculated 3.046×10^{15} m^{-3} using $1/D^2$, where D is particle diameter [3].

Figure 3 shows the plot of $\beta \cos\theta$ as a function of 4sinθ for $CoAl_2O_4$ nano ceramics. It represented by the sum of the contributions of crystallite size and strain present in the material. Assuming that the strain present in nano ceramics is uniform and considering the isotropic nature of the crystal structure [6].

Figure 4 shows the vibrational study of cobalt aluminate at room temperature over range from 400 cm^{-1} to 900 cm^{-1}. This study is performed in order to have idea of phonon vibrational modes obtained for Co based aluminate in inverse spinel structure. We have obtained four vibrational raman modes assigned the known active for the spinel structure: The intense peak observed at 498 cm^{-1} is assigned as the aggregate of the Al–O and Co–O symmetrical stretching due to local lattice effect at octahedral site (O_h) having the symmetry E_g. among the Mean intensity peaks, at 526 and 617 cm^{-1} are generated by asymmetric and symmetric Al–O stretching vibrations, which confirms second and third mode of F_{2g} symmetry, respectively. Here we report an aberration of quadruplicate splitting of peak related to A_{1g} mode. Instead of a single peak related to A_{1g} mode intense peak splits into four peaks at 694 cm^{-1}, 715 cm^{-1}, 735 cm^{-1}, 758 cm^{-1}, respectively. This might be attributed to the contraction and stretching of the Al–O bonds and confirms that A_{1g} vibration have tendency of possessing the symmetric nature [7].

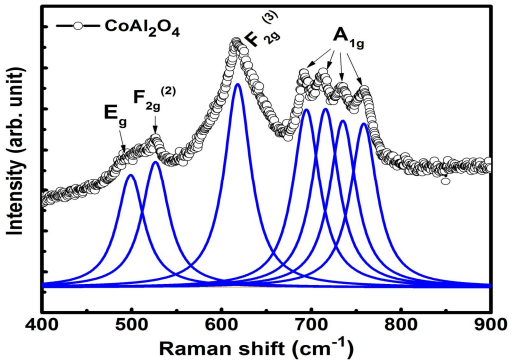

Figure 4 Raman spectra of $CoAl_2O_4$ nano ceramics at room temperature.

Hence, the Raman spectroscopy study confirms the formation of the $CoAl_2O_4$ inverse spinel phase.

CONCLUSION

In conclusion, we have successfully synthesized the cobalt aluminate via sol-gel method. It has inverse spinel structure with space group *Fd*3*m*. The particle size we have obtain is calculated as ~17 *nm* crystallite size and strain is ~17 *nm* and -2.41×10^{-4} using Williamson-hall plot method. The negative strain in the structure provides the structure stability and allows the different chromophores for the cationic substitution and opens window for possible application areas. The trivalent Al^{3+} provides the structural stability while divalent transition metal ions Co^{2+} provides the color property. In addition of confirming the four Raman modes for spinel structure, here we have explained the quadruple splitting of A_{1g} mode and material has shown the luminescence nature which opens the window for the wide range of application due to its structure stability and reported optical properties.

ACKNOWLEDGMENTS

UGC-DAE CSR, Indore as an institute is acknowledged for extending its experimental facilities and financial assistance.

REFERENCES

1. A. Walsh, S. H. Wei, Y. Yan, M. M. Al-Jassim and J. A. Turner, Physical review B **76**, 165119 (2007).
2. Y. Tang, C. Wu, Y. Song, Y. Zheng, K. Zhao, Ceramics International (2017).
3. H. Irfan, M. Racik K. and S. Anand, Journal of Asian Ceramic Societies (2018).
4. X He, F Wang, H. Liu, L. Niu, X. Wang, J. Am. Ceram. Soc. 1–11 (2018).
5. A. Khazaei, L. J. Ghalebabakhani, E. Ghaderi, M. Tavasoli, A. R. Moosavi-Zare, Applied Organometallic Chemistry (2017).
6. A. Yadav, Dinesh Varshney, Modern Physics Letters B 1750153 (2017).
7. T. YU., Z X Shen, Y. Shi and J Ding, J. Phys.: Condense Matter **14** (2002).