Bimodal to Unimodal Particle Size Distribution Transformation in Nanocrystalline Cobalt – Ferri – Chromites


1*Department of Physics, Saurashtra University, Rajkot, India  
2Government Engineering College, Mavdi - Kankot Road, Rajkot, India  
3Department of Physics, M S University of Baroda, Vadodara, Vadodara, India  
4Government Polytechnic College, Porbandar, India  
5Darshan Institute of Engineering and Technology, Morvi Road, Rajkot, India

*Corresponding Author: kunalbmodi2003@yahoo.com, Tel: +91 9824536994
Available online at: www.isroset.org

Received 29/Dec/2017, Revised 11/Jan/2018, Accepted 05/Feb/2018, Online 28/Feb/2018

Abstract— A meticulous investigation of particle size distribution curves; differential size distribution and cumulative undersize distribution, registered for nano-particulates of spinel structured ferrite system, CoCr2−xFexO4, (x = 0.0, 0.3 and 0.7), prepared through co-precipitation route has been presented. It is established that the distribution transforms from bimodal to unimodal on Fe3+ substitution. This distribution is not monodisperse and having negative skew. The cause for bimodality lies in the growth mechanism and the respective amount of the particles assembled by nucleation and Ostwald ripening. The function of Fe3+ substitution in regulating signature of the distribution patterns has been deliberated and various microstructural parameters have been determined.

Keywords— Nanoparticles, Ferrites, Particle size distribution, Growth mechanism

I.  INTRODUCTION

Particle morphology; i.e. shape, size, and distribution of particles have an effect on scores of physical properties and as a result quality and performance of polycrystalline materials [1]. The growth mechanism may be controlled during granulation or crystallization process. On the other hand, particle size distribution data can be offered graphically or numerically. In graphical form, data are presented in two interrelated forms i.e. differential size distribution (DSD) and cumulative undersize distribution (CUSD) curves [2] (Figure 1). The DSD curve shows relative amount at each particle size and modal and mean (average) particle diameter can be determined. On the other hand, corresponding CUSD curve demonstrates the relative amount at or below a particular size. Measures of central tendency such as the modal diameter and mean diameter can be resolute by means of DSD. The diameter at the peak of the differential distribution is the modal diameter while the mean diameter is the average diameter. The median diameter is an additional measure of central tendency. It is the diameter at the 50th percentile, designated d50. Quartile diameters include d25, d50 and d75.

Various measures of absolute width one can derive given the cumulative distribution. One customary measure is the span, d90 - d10. A dimensionless measure of width is the relative span defined as span/d50. Other relative measures of width comprise percentile ratios such as d90/d10 and d25/d75.

The size distribution determination of manufactured ceramics is highly indispensable for industry and biotechnology. Earlier, a bimodal size distribution was observed for nickel ferrite synthesized by a sol-gel technique for the as-prepared sample and the sample annealed at 300 K with an average particle size of 2 – 8 nm [3]. On the other hand, the bimodal distribution has been reported for nano-particles of nickel ferrite (NiFe2O4), magnesium ferrite (MgFe2O4) and magnetite (Fe3O4) prepared by high energy mechanical milling and other ultrafine mechanically alloyed materials [4]. Very recently, a study on microstructure and properties of bimodal structured ultrafine - grained ferrite steel fabricated by the cold rolling and annealing process of a dual – phase steel has been carried out by Niu et al. [5]. They found that this ferrite steel possesses outstanding mechanical properties and excellent corrosion resistance. Properties of
zirconium oxide and cobalt ferrite layered nano-composite synthesized by the sol-gel method have been studied by Tamm and co-workers [6]. The composite found potential application as a memory material. Eu$^{2+}$ - doped core-shell silica cobalt ferrite functionalized nanoparticles for combined fluorescence and magnetic resonance bioimaging was developed by Kevadiya et al. [7]. These nanoparticles are found to exhibit multimodal microstructure.

The present work aims to examine the particle size distribution curves documented for nano-particles of the spinel structured ferrite system, CoCr$_2$Fe$_x$O$_4$ ($x = 0.0, 0.3$ and $0.7$), in an organized way and to study growth mechanism and microstructural parameters determination.

The article has been written into four distinct sections, introduction, experimental details, results and discussion and conclusion. Introduction section gives fundamental aspects of the work presented, relevant literature survey, high lights of the findings and aim of the present work. The section experimental details contain information regarding the nanoparticles synthesis process and characterization technique employed. In the results and discussion section results are presented in a graphical and tabular manner and discussion and analysis are made. Conclusion part narrates the significant outcome of the present investigation.

II. EXPERIMENTAL DETAILS

Nanoparticles of Fe$^{3+}$- substituted spinel structured cobalt chromite, CoCr$_x$O$_4$, with nominal chemical formula, CoCr$_{2-x}$Fe$_x$O$_4$ where $x = 0.0, 0.3$ and $0.7$, have been synthesized by co-precipitation route. The basic solutions were prepared by blending $50$ ml of aqueous solution of CoSO$_4$$\cdot$$7$H$_2$O (cobalt sulfate heptahydrate), Cr$_2$(SO$_4$)$_3$$\cdot$$6$H$_2$O (chromium sulfate hexahydrate) and FeSO$_4$$\cdot$$7$H$_2$O (ferrous sulfate heptahydrate) (procured from Ranbaxy Fine Chemical limited, Mumbai with purity of 99.4%) in stoichiometric proportions. The stoichiometric ratio of chromium/ferric to metal ion was 2:1. A $2M$ solution of sodium hydroxide (NaOH) was used as a precipitant. To prepare experimental solutions double distilled water was used. In order to avoid sequential precipitation of the hydroxides, the starting solution with pH $\sim 3.5$ was added into the precipitant. A suspension with pH $= 10.5$ thus formed comprising dark green intermediate precipitates was then heated and retained at $333$ K for $1$ hour. To promote oxidation reaction during heating hydrogen peroxide (H$_2$O$_2$) was added to the suspension until all the intermediate precipitates turned into dark brownish precipitation of the spinel ferrites. The samples were filtered, washed with acetone repeatedly and dehydrated under vacuum at $473$ K.

The synthesized samples were further characterized by powder X-ray diffractometry (XRD) at $300$ K to confirm the formation of single phase structure. The XRD patterns could be indexed for a face-centered cubic (fcc) spinel structure (space group: $O_h^3$ Fd3m) [8]. The average particle size for the different compositions has been estimated from the X-ray diffraction line broadening using Debye-Scherer formula [8]. It is found that the particle size increases from $17$ nm for cobalt chromites, CoCr$_2$O$_4$ , ($x = 0.0$) to $21$ nm for $x = 0.3$ composition to $33$ nm for CoCr$_{1.5}$Fe$_{0.5}$O$_4$ ($x = 0.7$) composition. The existence of iron appears to facilitate fertilization and particle growth of the ferrite powder at quite a modest temperature. Laser particle size analyzer (model: Helos - BF, make: Sympatec, Germany) has been used to study particle size distribution patterns by dispersing $100$ mg of nanocrystalline ferrite powder in de-ionized water followed by ultrasonication.

III. RESULTS AND DISCUSSION

The differential size distribution and cumulative under size distribution patterns for multiferroic spinel, cobalt chromites, CoCr$_x$O$_4$ ($x = 0.0$) and Fe$^{3+}$ - substituted CoCr$_x$O$_4$ system, CoFe$_{x}$Cr$_{3-x}$O$_4$ with $x = 0.3$ and $0.7$ compositions are depicted in Figure 2. The distribution is bimodal (double-peaked) for $x = 0.0$ composition while for $x = 0.3$ and $0.7$ compositions it is unimodal (single peaked). Furthermore, particle size distribution is not mono disperse (all one size) for all the three compositions.

The origination of the bimodality lies in the growth mechanism by which the particles are formed. In chemical growth techniques such as co-precipitation, which is employed here, growth arises from preliminary nucleation and growth via a ‘seed and grow’ mechanism pursued by Ostwald ripening. For tinier particle systems, where the growth has been cramped, some indigenous seeds persist in the colloid. For the larger particle systems, a considerable percentage of the seeds have been noticed in the ripening mechanism accelerate a more homogeneous distribution of particle size [9].

The phenomenon in which tiny particulates in solution dissolve and deposit on sizable particles in order to reach a more thermodynamically steady state wherein the surface to area ratio is minimized is known as Ostwald ripening. This happens to owe to fact that molecules on the surface of particles are energetically unsteady than those within. Therefore, the unstable surface molecules often go into solution shrinking the particle over time and increasing the number of free molecules in solution. When the solution is supersaturated with the molecules of the shrinking particles, the free molecules will redeposit on the larger particles. Thus, tiny particulates diminish in size before they vanish and the sizable particles grow even bigger. The shrinking and growing of particles will bring about a larger mean diameter of a particle size distribution.
Figure 1. Illustrative differential size distribution and cumulative undersize distribution curves [2].

A vigilant examination of Figure 2 shows that for \( x = 0.0 \) composition two well-separated peaks are observed. The peak on the left-hand side is with more intensity and asymmetric in nature i.e. the curve tails to the left more than to the right, that means the skew is negative; while the peak on the right-hand side is with less intensity but symmetric one i.e. has zero skew. The skew is positive if curve tails to the right more than to the left. The reference point for tailing is concerning to the modal diameter.

On increasing \( \text{Fe}^{3+} \)-substitution \((x)\) in the system, \(\text{CoCr}_2\_\text{Fe}_x\text{O}_4\), for \( x = 0.3 \) and 0.7 compositions, right hand side peak gets disappeared and only left hand side peak is observed. Furthermore, it is also observed that with \( \text{Fe}^{3+} \)-substitution, left hand side peak get broader and more symmetric. Concerning the role of \( \text{Fe}^{3+} \)-substitution \((x)\) for \( \text{Cr}^{3+} (2-x) \) in the system, \( \text{CoCr}_2\_\text{Fe}_x\text{O}_4 \), it is found that when the concentration of \( \text{Fe}^{3+} \) is less than the concentration of \( \text{Cr}^{3+} \) i.e. for \( x = 0.3 \) and 0.7 compositions, uni-modality is observed. In order to support our argument particle size distribution curves for \( x = 0.9 \) and \( x = 2.0 \) \((\text{CoFe}_2\text{O}_4)\) compositions [10] are also included in Figure 3. As \( \text{Fe}^{3+} \) concentration is approximately equal to \( (x = 0.9) \) or greater than \( \text{Cr}^{3+} \) ion concentration \((x = 2.0)\) in the system, bimodality starts to appear \((x = 0.9)\) and clearly seen for \( x = 2.0 \) composition.

It leads to conclude that Cr: Fe ratio plays a very important role in governing particle size distribution in the system. Furthermore, on increasing \( \text{Fe}^{3+} \)-concentration, broadening of peak corresponds to small size particles (LHS peak) increases but the intensity of the peak remains unaffected. Above observations suggest that on increasing \( \text{Fe}^{3+} \)-content, size distribution in small size particles becomes broader and the population remains almost constant. The overall effect is an increase in particle size on \( \text{Fe}^{3+} \)-substitution as supported by XRD patterns and transmission electron micrographs analysis [2,8].

There are various measures of width. One of them is the full width at half maximum (FWHM). It is acquired by drawing a horizontal line at 50% of the maximum and taking the difference between the two places it intersects the distribution. The half width at half maximum (HWHM), is another measure of width and is described as FWHM/2. A relative fractional measure of width is derived by dividing HWHM by the measure of central tendency from which it was extracted, the modal diameter (HWHM/modal diameter).

The size of the particles shown in Figure 2 is in micrometer (μm) order. These particles were agglomerates which were found to break further and further to submicron level with
more and more powerful ultrasonic de-agglomeration techniques.

Figure 3. Particle size distribution curves for \( x = 0.9 \) and 2.0 compositions of CoCr\(_2\)Fe\(_4\)O\(_{12}\) spinel ferrite system [10].

Table 1. Measurement of central tendency and width for CoCr\(_2\)O\(_4\) (\( x = 0.0 \)), CoCr\(_1\)Fe\(_3\)O\(_4\) (\( x = 0.3 \)) and CoCr\(_1\)Fe\(_3\)O\(_4\) (\( x = 0.7 \)) compositions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LHS Peak</th>
<th>RHS Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modal diameter</td>
<td>85 ( \mu )m</td>
<td>70 ( \mu )m</td>
</tr>
<tr>
<td>Average diameter</td>
<td>95 ( \mu )m</td>
<td>103.29 ( \mu )m</td>
</tr>
<tr>
<td>FWHM</td>
<td>177.5 ( \mu )m</td>
<td>105 ( \mu )m</td>
</tr>
<tr>
<td>Span</td>
<td>246.5 ( \mu )m</td>
<td>103.29 ( \mu )m</td>
</tr>
<tr>
<td>Relative span</td>
<td>4.93 ( \mu )m</td>
<td>3.12 ( \mu )m</td>
</tr>
<tr>
<td>Quartile ratio</td>
<td>8.12 ( \mu )m</td>
<td>7.0 ( \mu )m</td>
</tr>
<tr>
<td>Median diameter</td>
<td>55 ( \mu )m</td>
<td>33.15 ( \mu )m</td>
</tr>
<tr>
<td>Relative percent measure of width</td>
<td>104.4 %</td>
<td>75 %</td>
</tr>
</tbody>
</table>

The important parameters such as: modal diameter, mean/average diameter, full width half maximum (FWHM), span (\( d_{50} - d_{10} \)), relative span (\( d_{50}/d_{25} \)), quartile ratio (\( d_{75}/d_{25} \)) and median diameter (\( d_{50} \)), for CoCr\(_2\)O\(_4\) (\( x = 0.0, 0.3 \) and 0.7 compositions) are determined and summarized in Table 1.

IV. CONCLUSION

The detailed analysis of particle size distribution curves recorded for nanoparticles of Fe\(^{3+}\)-substituted cobalt chromite, CoCr\(_2\)O\(_4\), leads to conclude that: the distribution transforms from bimodal to unimodal on Fe\(^{3+}\) substitution. This distribution is not monodisperse and having negative skew. The size of particles is of micrometer order and ultrasonic de-agglomeration is required before further analysis. The cause for bimodality lies in the growth mechanism and the respective amount of particles formed by nucleation and Ostwald ripening. The substitution of Fe\(^{3+}\) ions and Cr : Fe ratio in the system effectively control size distribution and a population of particles. Various microstructural parameters can be determined from the differential size distribution and cumulative undersize distribution curves.

ACKNOWLEDGMENT

The authors, K.B.M., P.Y.R., and N.H.V., are grateful to University Grants Commission, New Delhi, for supporting financial assistance under the Major Research Project scheme, junior research fellowship and Dr. D.S. Kothari post-doctoral fellowship respectively.

REFERENCES

AUTHORS PROFILE

Dr. Kunal B. Modi obtained Master of Science from Department of Physics, Bhavnagar University, Bhavnagar in the year 1991. He completed Ph.D. in the year 1996 and currently working as a Professor in Department of Physics, Saurashtra University, Rajkot, since 1998. He has published more than 100 research papers in internationally reputed journals including Inorganic Chemistry and Physical Chemistry physical journals. His main research work focuses on catalytic activity in ferrites and characterization nano-oxide materials and their applications. He has 20 years of teaching experience and 27 years of research experience. He has guided 25 M.Phil. and 7 Ph.D. students and at present 8 students are working under his guidance. He has got 4 national awards and many state-level prizes in his credit.

Dr. Jayant A. Bhalodia completed Ph. D. in the year 1994. He is currently working as an Associate Professor at Department of Physics, Saurashtra University, Rajkot since 2003. He did his Ph. D. in the field of High-T_c Superconductivity and published 50 research papers in standard reputed journals. He has received several research prizes.

Dr. Tushar K. Pathak completed his Master of Science from Department of Physics, Saurashtra University, Rajkot in the year 2005. He is completed his Ph.D. in the year 2014 and currently working as an Assistant Professor in Applied Science & Humanities Department, Government Engineering College, Rajkot. He has published more than 10 research papers in reputed international journals and conferences. He has 4 years of teaching and 7 years of research experience.

Ms. Pooja Y. Raval completed her Master of Science and M.Phil. from Department of Physics, Saurashtra University, Rajkot in the year 2014. She is pursuing Ph.D. at Department of Physics, Saurashtra University, Rajkot since 2016. Currently, she is working as a UGC MRP-JRF. She has visited ICTP, Italy and Dubai for attending workshops. She has published more than six research papers in experimental and theoretical physics in high impact factor journals.

Ms. Pooja R. Pansara completed her Master of Science from Department of Physics, Gujarat University, Ahmedabad in the year 2014. Presently she is pursuing Ph.D. at Department of Physics, Saurashtra University, Rajkot since 2016. She has published a couple of research papers in reputed journals.

Dr. Nimish H. Vasoya received Master of Science and M. Phil.degrees from Department of Physics, Saurashtra University, Rajkot in the year 2006. He is completed Ph.D. in the year 2013 and currently working as Associate Professor in Department of Physics, Sanjaybhai Rajguru Science College, Rajkot, Gujarat since 2008. He has published more than 23 research papers in reputed international journals. He has received Dr. D. S. Kothari Post Doctoral Fellowship from UGC. His main research work focuses on Scaling and modeling of the various experimental dielectric. He has 10 years of teaching experience and 13 years of Research Experience.

Mr. Chetan R. Kathad obtained pursued Master of Science degree from Department of Physics, Saurashtra University, Rajkot in the year 2005. He is completing Ph.D. in from 2014 and currently working as Assistant Professor in Department of Physics, government Poly technique, Porbandar, Gujarat since 2015. He has published more than 5 research papers in reputed international journals. His main research work focuses on Photo-catalytic activity in ferrites. He has 3 years of teaching and research experience. He has cleared NET and SLET examinations.

Dr. Suraj J. Shah obtained Master of Science from Department of Physics, Saurashtra University, Rajkot in the year 2009. He has completed Ph.D. in the year 2016 and currently working as an assistant professor in Department of Physics, Darshan Institute of Engineering, Rajkot, Gujarat since 2010. He has published more than 5 research papers in international journals. His main research work focuses on photo-catalytic activity in ferrites. He has 7 years of teaching and research experience.