Applications of Sn4+ and Zr4+ Substituted Nanoscale Calcium Hexaferrites in Microwave Absorbers and Storage Devices

Asmita D. Deshpande[a], Sharad N. Sable[a], Vivek M. Nanoti[a] , Kishor G. Rewatkar[b]

a Department of Applied Physics, Priyadarshini College of Engineering, Nagpur (India)
b Department of Physics, Dr. Ambedkar College, Deekshabhumi, Nagpur (India)

ABSTRACT

The industrial applications of substituted nanoscale hexaferrites are of immense importance because of their versatile utility in modern technical and scientific world. It has been observed that Sn4+ and Zr4+ Substituted Nanoscale Calcium Hexaferrites have unique feature that their structural and magnetic properties can be tailored and manipulated to the practical extent. This salient feature makes them very useful in the design of microwave absorbers, switching devices and storage devices. Also, by virtue of their nano sized grain structure and improvised magnetic characters over those of earlier reported ferrites, they are not only found to be more economical but also more resolute. Therefore this class of hexagonal ferrites has been reported to be the promising candidate for electronic gadgets like high density recording media, microwave absorption devices, magneto-optic recording media, etc.

In our exhaustive research module, base of calcium hexaferrite is substituted with Sn4+ and Zr4+ with stoichiometric proportions for x ranging for 0 to 5 in the generic formula Ca(Co-Sn)xFe12-2xO19 and Ca(Co-Zr)xFe12-2xO19. But for the present research module, only one combination for x = 2 is taken into explanation as it has shown to be more useful for aforementioned applications. The synthesis of Ca(Co-Sn)2Fe8O19 and Ca(Co-Zr)2Fe8O19 is carried out by recently reported technique i.e. Microwave Induced Sol-Gel Combustion Route. The morphological and structural parameters of the samples are studied by scanning electron microscopy and further by transverse electron microscopy which leads to confirm these samples into category of nanoscale ranging from 11.52 nm to 36.28 nm. The space group for the samples is observed to be p63/mmc as confirmed by Reitveld quantitative analysis. The magnetic characterization of the samples is done by vibrating sample magnetometry. The saturation magnetization (Ms), coercivity (Hc) and retentivity (Mr) of the samples are found in the ranges which are aptly suitable for microwave absorbers, switching as well as storage devices. Further investigation is underway to tailor their properties to fit them for these more demanding applications in the modern technology.

EXPERIMENTAL

The recently reported technique, Microwave Induced Sol-Gel Combustion Route is employed to prepare samples having generic formula Ca(Co-Sn)2Fe8O19 and Ca(Co-Zr)2Fe8O19 respectively. This technique has better advantages over those of others like facile operation, low anneal or calcine temperature, energy efficient and a short reaction rate, etc (1, 2) . The most prominently, the technique provides requisite amount of heat energy to synthesize samples with an average particle size in the range of nm (2). In addition, this route gives ultra fine powder of nano particles with better particle size distribution, excellent chemical homogeneity and more probability of formation of single domain structure (3).

The reactive precursors such as Ca(NO3)2, Fe(NO3)3.9H2O, Co(NO3)2.6H2O and SnCl4 and ZrO(NO3)2 were dissolved into an unionized distilled water at the temperature of 500C for 15-20 minutes. The urea was used as reducing agent to supply requisite energy to initiate exothermic reaction amongst oxidants. The gel produced is then kept for an hour in the room temperature and then it is presintered at 1200C by keeping in the digitally controlled furnace for 30 to 40 minutes. Then the sample is annealed by giving intermittent moderate heat treatments for further few minutes with intermediate grinding and quenching in dry air. The sample so produced is then kept in moist free air tight compartment to avoid possible air born reactions for the further analysis of characterization of the samples (4).

RESULT & DISCUSSION

The diffraction patterns of samples are taken with Phillips X'pert Diffractometer and Cu-Kα radiation with wavelength, λ=1.542A0. The data is analyzed by using computer softwares. By comparing the patterns with JCPDS standards, the phases in the different samples are determined. It is being observed that most of the hexagonal grains are of same size (2, 5). Using 2θ, observed d-values and intensity calculations, d-value is recalculated and (hkl) planes are finalized. These values confirm the formation of single phase hexagonal ferrites. The lattice parameters a and c are found to be 5.8421 A0 and 21.5378 A0 for Ca(Co-Sn)2Fe8O19 and 5.8758 A0 and 22.6089 A0 for Ca(Co-Zr)2Fe8O19 respectively. The space group for the samples is observed to be p63/mmc as confirmed by Reitveld Analysis as shown in the figure 1. Further it is observed that the internal structure of M-type hexaferrite accommodates three different types of interstitial Fe+3 cation positions: tetrahedral, octahedral and bipyramidal (6).

The transverse electron micrographs given in the figure 2 reveal the remarkable changes in the microstructure, grain size, porosity and homogenous particle size distribution obtained as a perturbation of many dependant parameters like time of synthesis, temperature, process of annealing, intermittent quenching, grinding, etc. It is also come to the notice that the presence of the large crystalline agglomerations is composed of very small discrete crystallites in the samples at the temperature of synthesis (7). The particle size is determined with the help of TEM studies. The size is found to be about 11.52 nm to 36.28 nm respectively confirming the nanoparticle size of these samples as shown in the figure 2. The grains are found to be hexagonal platelets. It is reasonable to confirm that the doping of tetravalent ions does remain responsive to the grain size of these substituted hexa ferrites (7, 8)

.

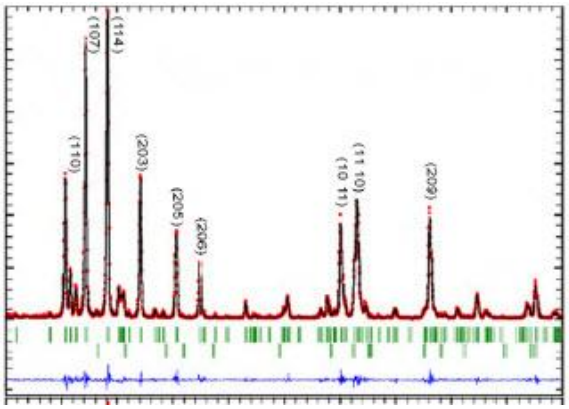

Figure 1 (a) : Reitveld Qualitative Analysis for $Ca(Co\text{-}Sn)_2Fe_8O_{19}$

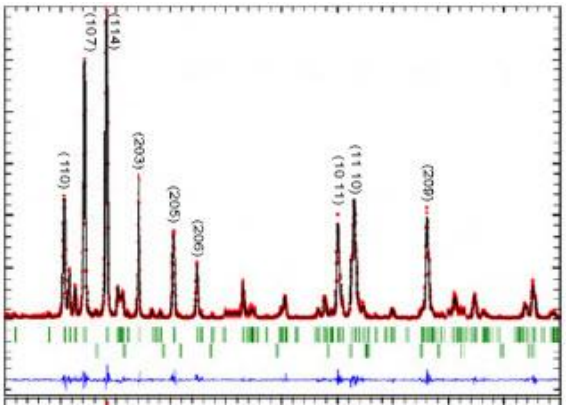

Figure 1 (b) : Reitveld Qualitative Analysis for $Ca(Co\text{-}Zr)_2Fe_8O_{19}$

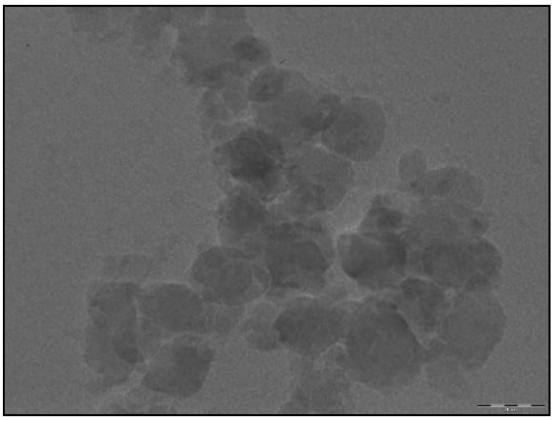

Figure 2 (a) TEM for Ca(Co-Sn)2Fe8O19

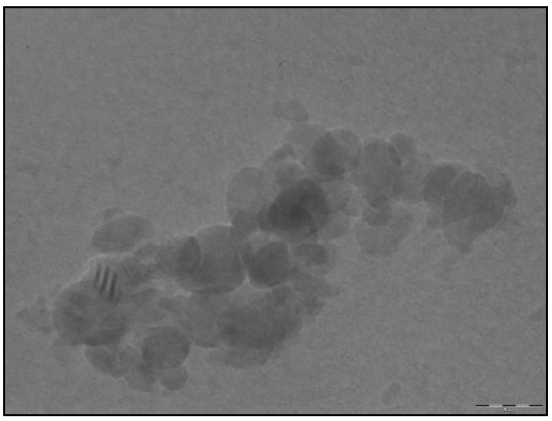

Figure 2 (b) TEM for Ca(Co-Zr)2Fe8O19

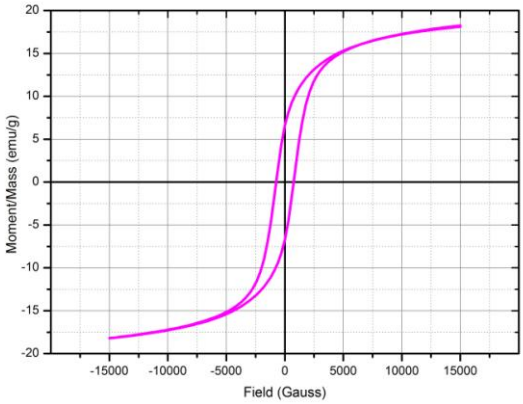

Figure 3 (a) Hysteresis Curve for Ca(Co-Sn)2Fe8O19

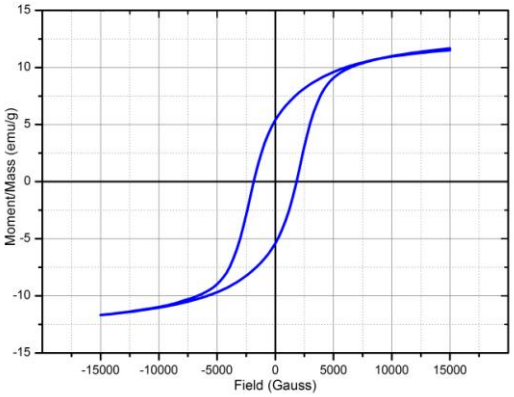

Figure 3 (b) Hysteresis Curve for Ca(Co-Zr)2Fe8O19

The magnetic properties of the two samples synthesized are tabulated in table (1).

Sample	Saturation Magnetization (M_s)	Remanant Magnetization (M_r)	Coercivity (H_c)
$Ca(Co\text{-}Sn)_2Fe_8O_{19}$	17.087 emu/g	8.758 emu/g	9209 G
$Ca(Co\text{-}Zr)_2Fe_8O_{19}$	11.613 emu/g	5.997 emu/g	2143 G

Table (1) : Magnetic Properties of Ca(Co-Sn)2Fe8O19 and Ca(Co-Zr)2Fe8O19

From the hysteresis curves and magnetic parameters of the samples, it can be attributed that with the substitution of Sn4+; Ms, Mr and Hc are found to be more than those for the substitution of Zr4+ into the pure base of CaFe12O19. The application of a magnetic sample for a specific device depends on the relevant properties of such sample (9). One of these properties is the coercivity of the magnetoplumbites. The coercivity of the material Hc should be reduced as low as possible. High coercivity is the demand of a hard magnet while low coercivity is the need of a soft magnet (3, 9). The former is needed for data storage applications. The later is needed for information storage recording media. The origin of coercivity lies in the magnetic anisotropy, which is particularly uniaxial for the hexagonal close packing of the hexaferrites. In view of improvisation of the hexaferrites testing various magnetic properties is of great importance. The stoichiometry of the sample is so chosen that the desired improvement in the coercivity, remanance as well as saturation magnetization is expected (10).

CONCLUSION:

The substitution of Sn+4 and Zr4+ in Calcium hexaferrites by replacing Fe3+ is found to be successful by recently reported technique i.e. Sol Gel Combustion Route (11). The Reitveld qualitative analysis of the samples confirms the formation of hexaferrites and ‘a’ & ‘c’ values of the sample ensure them into the category of hexaferrites (12). Further, the morphological and structural studies have confirmed the space group of samples to be p63/mmc (7, 12). The transverse electron microscopy of the samples has cataloged them as nanoscale hexaferrites. The significant aspect of the samples is their structural and magnetic properties can be tailored and modulated within the practical limits from the point of view of applications (13). On the firm background of structural and magnetic parameters of Ca(Co-Sn)2Fe8O19 and Ca(Co-Zr)2Fe8O19, it can be attributed that former is more useful for switching devices as its hysteresis curve is more thin like saw tooth wave between logic 0 and logic 1 state (14, 16). Similarly, later can be used in storage devices as its coercivity (Hc) can be manipulated as per the maximum volume of the data to be stored (5, 15). But it is evident that both can be used for microwave absorbers with some tailoring in their structural as well as magnetic properties (16).

REFERENCE

[1] Sang Won Lee, Sung Yong AN, In-Bo Shim, Chul Sung Kim; Journal of Magnetic and Magnetic Materials 290-291 (2005) 231-233

[2] G.B.Teh, N. Saravanan, D.A. Jefferson; Material Chemistry and Physics 105 (2007) 253-259

[3] Gruskova; IEE Trans. Magn. 30(2) (1994) 6062

[4] M. Edrissi, R. Norouzbeigi; Material Science, Volume 23, No. 4, 2007

[5] D. Lisjak, M. Drofenik; Eur. Ceram. Soc. 24 (2004) 1845.

[6] V.M. Nanoti, D.K. Kulkarni, C.S. Prakash; Materials Letters 24 (1995) 171-173

[7] V.M. Nanoti, C.S. Prakash, D.K. Kulkarni, G.M. Rao; Journal of Magnetism and Magnetic Materials 140-144 (1995) 2089-2090

[8] K.G. Rewatkar, N. M. Patil, S. R. Gawali; Bulletin of Material Science, Vol. 28, No.6 (2005) 585-587.

[9] K.G. Rewatkar, N.M. Patil, S. Jaykumar, D.S. Bhowmick, M.N. Giriya, C.L. Khobragade; Journal of Magnetism and Magnetic Materials 316 (2007) 19–22

[10] T. Gonzalez-Carren, M.P. Morales, C.J. Serna; Mater.Lett. 43 (2000) 97.

[11] Mali, A. Ataie; Journal of Alloys and Compounds 399 (2005) 245-250

[12] S. Ounnunkad, P. Winotai; Journal of Magnetism and Magnetic Materials 301 (2006) 292-300

[13] N. Rezlescu, C. Doroftei, E. Rezlescu, P. D. Popa; Journal of Alloys and Compounds 451(2008) 492-496.

[14] M.M. Hessien, M.M. Rashad, K. El-Barawy; Journal of Magnetism and Magnetic Materials 320 (2008) 336-343

[15] G. Litsardakis, I. Manolakis, C. Serletis, K.G. Efthimiadis; Journal of Magnetism and Materials 316 (2007) 170-173

[16] Sharad N. Sable, Kishor G. Rewatkar, Vivek M. Nanoti; Journal of Materials Science and Engineering-B 168 (2010) Volume 168, Issues 1–3, 157-160