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Synthesis, structural, magnetic and dielectric characterizations of molybdenum doped calcium strontium M-type hexaferrites

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Abstract

Molybdenum doped strontium calcium hexagonal ferrites have been synthesized by the sol gel combustion method. The structural and morphological characterizations of the prepared hexaferrites were carried out by X-ray diffraction and scanning electron microscopy, respectively. Magnetic and dielectric properties of these compounds were also studied. X-ray diffraction analysis revealed that all the synthesized samples have single magnetoplumbite phase with average particle size in the range 34–47 nm. The remanent magnetization falls with the concentration of dopant cation in the studied range of magnetic field. The coericivity of all the samples is increased with Mo concentration and is high enough to be used for longitudinal magnetic recording media. The dielectric parameters exhibit the relaxation behavior in higher frequency region and show increasing trend with the molybdenum contents. The high magnitudes of dielectric constant of the synthesized hexaferrites make them suitable materials for miniaturization of microwave devices.

Keywords: A. Powders: chemical preparation; B. X-ray methods; C. Magnetic properties; C. Dielectric properties

1. Introduction

Since their discovery, hexagonal ferrites have continued to be very attention-grabbing group of materials credited to their significant physical and chemical properties. Their captivating applications in microwave devices, micro strip antennas, high frequency transformers, memory core, radar devices [1] and high density recording media [2,3] have enforced several researchers to explore new such materials. The hexaferrite materials are divided into six types: M-type ($AFe_{12}O_{19}$), W-type ($AB_2Fe_{16}O_{27}$), X-type ($A_2B_2Fe_{20}O_{46}$), Y-type ($A_2B_2Fe_{12}O_{22}$), Z-type ($A_3B_2Fe_{24}O_{41}$) and U-type ($A_4B_2Fe_{36}O_{60}$) where A may be Ca, Sr, Pb, Ba and B may be bivalent cations of transition metal like Ni, Co, Zn [4] etc. The basic structural unit in M-type hexaferrtite is the hexagonal crystal lattice in which 64 ions per unit cell on 11 symmetry sites are present. In this crystalline structure, Fe^{3+} cations occupy five different sites namely three octahedral (12k, 2a, $4f_2$), one trigonal bipyramidal (2b) [5] and one tetrahedral ($4f_1$) site in which five oxygen atoms enfold the ferric ions. M-type hexaferrites generally show good magnetic properties which can be explicated by the ordering of magnetic moments of the Fe^{3+} ions and the super exchange interaction. In super exchange interaction, three parallel (12k, 2a, 2b) and two anti parallel sites ($4f_1$, $4f_2$) are paired through oxide anions [6]. These hexaferrites are widely investigated due to their good chemical stability, higher microwave magnetic loss, high Curie temperature and moderately large magnetization [7,8]. These nanomaterials are more useful as compared to other magnetic materials in higher frequencies attributed to their remarkable electrical properties such as high resistivity and low eddy current losses [9]. Several aspects such as fabrication route, average size of crystallite, composition and dopants can affect the electrical and magnetic properties of these M-type hexaferrites [10–12].

Conventional ceramic method is usually utilized to synthesize the nanomaterials in which high temperature i.e. 1573 K [13] is required. However, it is difficult to prepare homogenous, strain free, less mean particle size and single phase hexagonal ferrites by

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this method. Thus other procedures such as aerosol pyrolysis [14], micro emulsion [15], dehydration and rotary evaporation, chemical co-precipitation [10] and sol–gel combustion [16] have also been followed. In this work, we selected the sol gel combustion method for the fabrication of the metal oxides having single phase and small average particle size.

Doping of different cations in nano hexaferrites at A (Ca, Sr, Pb, Ba etc.) as well as at iron site induces variations in their electrical, dielectric and magnetic properties. Many researchers have successfully attempted to substitute a number of cations and their bivalent–tetravalent binary mixtures in M-type hexaferrites [10,17–19]. Literature provides quite a handful reports on the Sr hexaferrite, Ba hexaferrite, Ba–Sr hexaferrites and their substituted derivatives [10,17–20] but rare studies are available on Ca–Sr hexaferrites and its hexavalent cations substituted derivatives. Focus of the present studies was, therefore, to explore the effect of molybdenum (Mo^{6+}) on the magnetic and dielectric properties of $Ca_{0.5}Sr_{0.5}Fe_{12}O_{19}$. The magnetoplumbite structure and grain morphology of the synthesized materials are also discussed in this paper.

2. Experimental

2.1. Chemicals

The chemical precursors used for the synthesis of the compounds were $CaCl_2 \cdot 2H_2O$ (99% Merck), $Sr(NO_3)_2$ (99% Fluka), $Fe(NO_3)_3 \cdot 9H_2O$ (97% Riedel Dehaen), MoO_2Cl_2 (99% Aldrich) and ammonia solution (33% Merck).

2.2. Solution preparation

Solutions of the desired metal salts were prepared in deionized water except that of molybdenum salt. To prepare the solution of molybdenum salt, the compound was dissolved in small volume of aqua regia (3HCl and HNO_3) on a hot plate with magnetic stirrer and transferred into a 250 ml measuring flask. The volume of the solution was then made upto the mark with deionized water to get the desired concentration.

2.3. Synthesis of $Sr_{0.5}Ca_{0.5}Fe_{12-x}Mo_xO_{19}$ ($x=0.0$–0.4)

The title compounds have been prepared by the sol gel combustion route. In a typical preparation, aqueous solutions of all precursors in equal volumes were mixed in a 2000 ml beaker. To this mixture, 0.195 M citric acid solution (250 ml) was added as chelating agent. The molar ratio of citric acid to total moles of metal ions was adjusted as 1:1.5. The solutions of all the precursor salts and chelating agent were homogenized for half an hour on a hot plate equipped with magnetic stirrer. Then 4.0 M ammonia solution was added drop wise to this solution for its neutralization (pH 7.0). The neutralized solution was heated at 300–353 K on a hot plate with uninterrupted stirring for evaporation of the solvent until it transformed into a viscous gel like material. To convert the gel into ash powder, it was ignited by raising the temperature upto 673 K. In the last step, the product was annealed in air at the temperature of 1223 K for 6 h in a furnace (VULCAN™ A-550) to get the single magnetoplumbite phase of the sample.

2.4. Characterization

Identification of magnetoplumbite phase of the prepared hexaferrites was carried out by PAnalytical X-ray diffractometer using CuKα as radiation source. The morphological characterization of the synthesized ferrites was examined by scanning electron microscope (JEOL-JSM-6700F). A vibrating sample magnetometer (Lake Shore-74071) was utilized to study the magnetic properties of the prepared compounds. The dielectric properties of these synthesized samples were studied at ambient temperature in the frequency range of 1.0 MHz to 3.0 GHz by using a RF Impedence/Material Analyzer, Agilent E4991A. The samples used for dielectric analysis were used in the form of pellets having dimensions 0.10 cm in diameter and 0.14–0.26 cm in thickness.

3. Results and Discussion

3.1. XRD analysis

The indexing of powder XRD patterns of the synthesized samples was carried out by reference ICSD pattern having code 01-080-1197 and is displayed in Fig. 1. All the peaks in the XRD pattern of the samples matched well with the reference pattern approving the formation of single magnetoplumbite phase in the synthesized hexagonal ferrites. Slight shifts observed in the peaks position may be due to the doped cation. The mean particle sizes of all the prepared compounds were calculated by Scherrer's formula (Eq. (1)) [1].

$$D = k\lambda/\beta \cos\theta \quad (1)$$

Here λ is wavelength of X-rays used i.e. 1.541 Å, β is full width at half maximum (FWHM), θ is Bragg's angle and K is Scherrer's constant i.e. 0.9. The mean crystallite size was obtained in the range 34–47 nm which is much smaller than

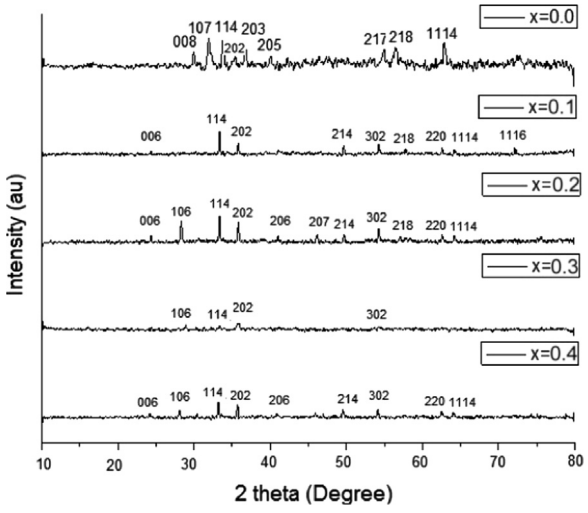

Fig. 1. Powder XRD patterns of $Sr_{0.5}Ca_{0.5}Fe_{12-x}Mo_xO_{19}$ ($x=0.0$, 0.1, 0.2, 0.3, and 0.4) compounds.