Journal of Alloys and Compounds 651 (2015) 266–272

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Fabrication, structural, dielectric and magnetic properties of tantalum and potassium doped M-type strontium calcium hexaferrites

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ARTICLE INFO

Article history:
Received 24 January 2015
Received in revised form
30 March 2015
Accepted 28 May 2015
Available online 11 August 2015

Keywords:
Tantalum-potassium doped hexaferrites
Sol-gel method
X-ray diffraction
Dielectric behavior
Magnetic parameters

ABSTRACT

Tantalum–potassium substituted strontium calcium hexagonal ferrites with chemical composition $Sr_{0.5}Ca_{0.5}Fe_{12-2x}Ta_xK_xO_{19}$ (x = 0.0, 0.1, 0.2, 0.3, 0.4) have been synthesized by the sol gel combustion procedure. The structural and morphological characterizations of the synthesized hexaferrites were performed by X-ray diffraction and scanning electron microscopy, respectively. Dielectric and magnetic properties of these samples were also inspected. XRD analysis revealed that all the prepared compounds have pure magnetoplumbite phase and their mean crystallite size was between 34 and 44 nm.The dielectric parameters present resonance type behavior at higher frequency (GHz) region. The dielectric constant increases as the dopant contents increase. The saturation magnetization and remanence show decreasing trend as the concentration of dopants rise in the range of applied magnetic field. The coericivity of all the prepared samples rises with Ta–K concentration and is high enough to be used for longitudinal magnetic recording media.

1. Introduction

Hexaferrites have achieved great attention because of their significant physical and chemical properties during last 50 years. The commencement of extensive research on these ferrites is related to their appealing applications in microwave devices, transformer, computer memory chip, micro strip antennas, radio frequency coils and high density recording media [1,2]. These ferrites can be divided into six categories: 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 Ba, Sr, Pb, Ca and B may be bivalent cations of transition metal like Ni, Co, Zn [3] etc. The M-type hexaferrite structure is based on hexagonal crystal lattice with 64 ions per unit cell on 11 distinct symmetry sites. In this structure, smaller Fe^{3+}cations reside over five different interstitial sites i.e. three octahedral sites (12k, 2a, $4f_2$), one tetrahedral ($4f_1$) and one trigonal bipyramidal site (2b) [4] in which 5 oxygen atoms encircle the Fe^{3+} cation. Good magnetic behavior of these ferrites can be elucidated with the ordering of magnetic moments of the Fe^{3+}cations and the superexchange interaction, in which coupling of three parallel (12k, 2a, 2b) and two antiparallel sites ($4f_1$, $4f_2$) is occurred by O^{2-} anions [5]. These M-type hexaferrites have been broadly studied due to their superb chemical stability, larger microwave magnetic loss, high Curie temperature and moderately large magnetization [6,7]. At higher frequencies, these nanoparticles are considered more valuable than other magnetic materials credited to their remarkable electrical properties such as low eddy current losses and high resistivity [8]. The electrical and magnetic properties of hexagonal ferrites are affected by the route of synthesis, average crystallite size, chemical composition and substituent cations [9–11].

Usually conventional method i.e. solid state reaction is used to prepare the metal oxides which need high temperature i.e. 1200 °C [12]. But it is very hard to prepare pure, strain free, smaller particle size and homogenous nano hexagonal ferrites by solid state method. Therefore, other procedures such as aerosol pyrolysis [13], micro emulsion [14], dehydration and rotary evaporation, chemical co-precipitation [9] and sol–gel combustion [15] have also been applied. In this work, sol gel combustion method was opted to get the nanoparticles with pure phase and smaller mean particle size.

The dielectric, magnetic and electrical properties of the hexagonal ferrites can be altered by the doping of various cations at A (Ca,

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http://dx.doi.org/10.1016/j.jallcom.2015.05.181
0925-8388/

Sr, Ba, Pb) as well as Fe^{3+} sites. Several researchers have substituted many cations and their combinations (bivalent-tetravalent) in M-type hexagonal ferrites [9,16–18]. Literature presents lots of researches on the $SrFe_{12}O_{19}$, $BaFe_{12}O_{19}$, $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ and their substituted derivatives [9,16–19]. However, least attention is given to $Sr_{0.5}Ca_{0.5}Fe_{12}O_{19}$ and its pentavalent-monovalent cations derivatives. Therefore, the major emphasis of this research is to study the influence of tantalum (Ta^{5+}) and potassium (K^{1+}) on the dielectric and magnetic properties of $Ca_{0.5}Sr_{0.5}Fe_{12}O_{19}$. Morphology and crystal structure of the synthesized nano hexaferrites are also discussed in this paper.

2. Experimental

2.1. Chemicals

The chemicals used for the synthesis of the samples were $Fe(NO_3)_3.9H_2O$ (97% Riedel de Haen), $CaCl_2.2H_2O$ (99% Merck), $Sr(NO_3)_2$ (99%Fluka), $TaCl_5$ (99% Aldrich), KCl (99% Merck) and ammonia solution (33% Merck).

2.2. Solution preparation

Solutions of all metal salts were prepared in deionized water except tantalum chloride. Tantalum chloride was not soluble in deionized water. That's why the required amount of this salt was initially dissolved in small amount of aqua regia (3HCl and HNO_3) on a hot plate with magnetic stirrer. Then this dissolved salt solution was transferred into the measuring flask and made the volume of this solution up to the mark by adding the deionized water in it.

2.3. Fabrication of $Sr_{0.5}Ca_{0.5}Fe_{12-2x}Ta_xK_xO_{19}$ ($x = 0.0–0.4$)

Tantalum and potassium substituted M-type Sr–Ca hexaferrites with nominal composition $Sr_{0.5}Ca_{0.5}Fe_{12-2x}Ta_xK_xO_{19}$ (x = 0.0, 0.1, 0.2, 0.3, 0.4) have been prepared by the sol gel combustion procedure. In this method, solutions of all metal salts in equal volumes were mixed in a 2000 ml beaker. To this mixture 250 ml of 0.195 M citric acid solution 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 metal salts and chelating agent were homogenized on a hot plate with magnetic stirrer. The mixed solution was then neutralized to pH 7 by dropwise addition of 4.0 M ammonia solution. The evaporation of neutralized solution was done by heating it at 300–353 K on a hot plate with continuous stirring, until it became a viscous gel. Increasing the temperature upto 673 K led to ignition of the gel. Finally, ash burnt powders were annealed in air at the temperature of 1223 K for 6 h in a furnace (VULCAN™ A-550) to attain the magnetoplumbite phase in the synthesized hexaferrite.

2.4. Characterization

The magnetoplumbite phase of the synthesized hexaferrites was identified by PAnalytical X-ray diffractometer using CuKα as radiation source. The synthesized materials were characterized by Scanning electron microscope (JEOL-JSM-6700F) to envisage their shape, grain size and morphology. The dielectric properties of these samples were measured as a function of frequency in the range 1.0 MHz–3.0 GHz at room temperature by RF Impedence/Material Analyzer, Agilent E4991A. The magnetic parameters of the synthesized materials at ambient temperature were investigated by using Lake Shore-74071 vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. XRD analysis

X-ray diffraction analysis was applied to observe the magnetoplumbite phase of the $Sr_{0.5}$ $Ca_{0.5}Fe_{12-2x}Ta_xK_xO_{19}$ (x = 0.0, 0.1, 0.2, 0.3, 0.4) samples. The indexed powder XRD patterns of the synthesized ferrites are illustrated in Fig. 1. All the peaks were compared with ICSD pattern having reference code 01-080-1197. The XRD patterns corroborate the formation of pure magnetoplumbite phase in all the synthesized materials. The minor shift in peak position may be ascribed to the doping of tantalum and potassium. The average crystallite sizes of all the synthesized hexaferrites were calculated by Scherrer's formula (Eq. (1)) [20].

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

Here λ is wavelength of X-rays used i.e. 1.541 Å, β is full width at half maximum, θ is Bragg's angle and K is Scherer's constant i.e. 0.9. The average crystallite size was in the range of 34–44 nm that is much smaller than many of those already reported [21,22]. To achieve the suitable signal to noise ratio, the crystallite size less than 50 nm is desired in the high density recording media [23]. In the current work, the prepared samples have crystallite size enough small (<50 nm) to obtain the suitable signal to noise ratio in high density recording media.

3.2. SEM analysis

The morphology and grain size distribution of the undoped Sr–Ca hexaferrite and its Ta–K doped derivative were explored by scanning electron microscopy (SEM) as presented in Fig. 2a and b, respectively. It can be seen that in the undoped compound (Fig. 2a) the particles have a plate like hexagonal morphology. The surface seems to be the mixture of several nanoparticles and their clusters are produced by agglomeration. The particles show regular orientation and narrow range of grain size. Similar grain size distribution and their orientation have also been reported by Wang et al. [24]. By the substitution of tantalum (Ta^{5+}) and potassium (K^{1+}) in calcium strontium hexaferrite (Fig. 2b), the surface looks less agglomerated and the grain size distribution is relatively broad. The

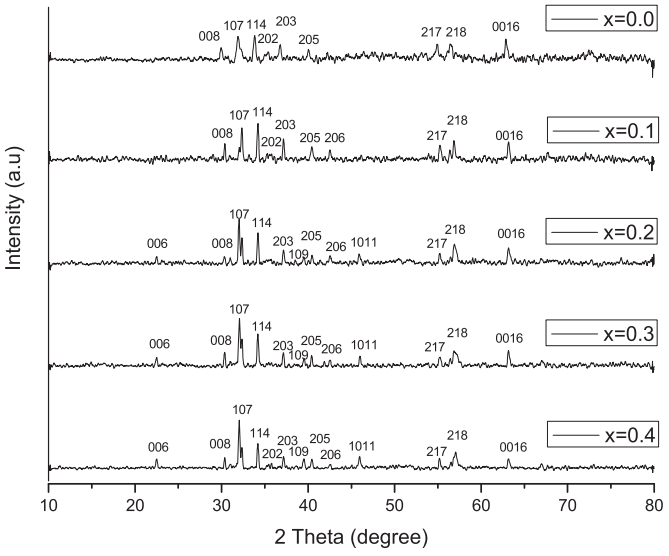

Fig. 1. Indexed powder XRD patterns of $Sr_{0.5}Ca_{0.5}Fe_{12-2x}Ta_xK_xO_{19}$ (x = 0.0, 0.1, 0.2, 0.3, 0.4) samples.