Materials Chemistry and Physics 114 (2009) 505–510

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Review

Structural analysis of Y^{3+}-doped Mg–Cd ferrites prepared by oxalate co-precipitation method

A.B. Gadkari[a,*], T.J. Shinde[b], P.N. Vasambekar[c]

[a] *Department of Physics, GKG College, Kolhapur 416012, Maharashtra, India*
[b] *Department of Physics, KRP Kanya Mahavidylaya, Islampur 415409, India*
[c] *Department of Electronics, Shivaji University, Kolhapur 416004, India*

ARTICLE INFO

Article history:
Received 16 July 2008
Received in revised form 24 October 2008
Accepted 3 November 2008

Keywords:
Nanomaterials
Crystallite size
XRD
Lattice constant
Porosity

ABSTRACT

Polycrystalline ferrites of $Cd_xMg_{1-x}Fe_2O_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) with addition of 5% of yttrium has been synthesized by oxalate co-precipitation method and characterized by XRD, SEM and FTIR techniques. The samples were presintered at 700 °C for duration of 6 h and sintered at 1050 °C for 5 h. The X-ray diffraction measurements confirmed the formation of cubic spinel structure. Lattice constant, X-ray density, physical density, crystallite size, ionic radii on A-site and B-site (r_A, r_B), bond length on A-site and B-site (A–O, B–O) and porosity have been calculated. The lattice constant is found to increase with increase in Cd^{2+} content. The physical densities are about 86.96% of their X-ray density. Average crystallite size lies in the range of 28.86–32.06 nm. SEM study shows that the grain size of the samples increases with increase in Cd^{2+} content. The addition of Y^{3+} reduces the grain growth. The FTIR spectra shows two strong absorption bands in the frequency range 575–435 cm^{-1}, on the tetrahedral and octahedral sites, respectively. Further it shows that Y^{3+} occupies B-sites.

Contents

1. Introduction

Spinel ferrites are important materials due to the wide interest required for various applications in modern technology [1,2]. These materials have been extensively studied due to growing interest in the study of electric, magnetic and structural properties [3]. The basis for the wide range of application is related to the variety of transition metal cations which can be incorporated into the lattice of the parent magnetic structure. Spinel ferrite crystallizes in cubic close packed structure of oxygen ions which occupy two types of interstitial sites. One of them called a tetrahedral (A) site with cation surrounded by the four oxygen ions in tetrahedral coordination. The other interstitial position is known as an octahedral (B) site with cation coordinated by six oxygen ions in the octahedral symmetry. The electric, magnetic and dielectric behavior depends upon structural properties. Therefore X-ray diffraction (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) are especially used for structural investigation. Because of high penetrating power, X-ray can provide important information regarding structural properties of matter. The angle of diffraction and inten-

---

* Corresponding author. Tel.: +91 9423814704.
E-mail address: kashokabg@yahoo.com (A.B. Gadkari).

0254-0584/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2008.11.011

sity of diffracted beam together are the characteristics of particular crystal structure. Since no two atoms have exactly same size and X-ray scattering ability, the intensities of diffracted beam will be unique for every material. This uniqueness helps to identify the structure and determine the structure parameters of the material.

The microstructural study is essential for optimizing the properties of ferrites needed for various applications. These properties are strongly influenced by sintering parameter and composition [4,5]. The presence of other phase than spinel can also affect the properties [5].

Infrared spectroscopy is a technique used for chemical identification, which is based upon the simple fact that the chemical substance shows marked selective absorption in the infrared region. After absorption of infrared radiation, the molecule of chemical substance vibrates in many modes of vibration giving FTIR absorption spectrum, over wide wavelength range. Hence an IR spectrum of chemical substance is the finger print for its identification. A splitting of FTIR band is observed in same spinels containing coordinated John Teller ions. The band may split also due to presence of two different kinds of ions in the sub-lattice. The IR spectroscopy for several ferrites has been reported by Waldron [6], which shows two absorption bands within the ranges 800–200 cm^{-1} in tetrahedral and octahedral site.

Many research groups have studied the effect of trivalent substitution in different ferrites to upgrade their structural, electric and magnetic properties. The effect of the substitution of Gd^{3+} on electric and magnetic properties of Mg–Cd ferrite has been extensively studied by Bhosale et al. [7]. They have found that lattice constant increases with increase in Cd^{2+} content obeying Vegard's law. Karche et al. [8] studied the XRD, SEM and Mossbauer effect of Mg–Cd ferrite by ceramic method. The effect of Cr^{3+} substitution on crystallographic properties of Cd–Co ferrite has been studied by Vasambekar et al. [9] and reported that lattice constant depend on Cd^{2+} content. Electrical transport properties of gadolinium-substituted Mn–Zn ferrites have been studied by Ravinder et al. [10]. Ladagaonkar et al. [11] reported single phase cubic spinel in Nd^{3+}-substituted Zn–Mg ferrite and studied XRD, SEM and IR properties. Verma et al. [12] reported high resistivity Ni–Zn ferrite prepared by citrate precursor method. It is known that addition of rare earth cations into spinel structures of ferrites results in modification of structural, electrical and magnetic properties.

The ferrite materials can be prepared by different methods [13] such as solid-state reaction [14], hydro-thermal [15], decomposition [16], sol–gel [17], and co-precipitation [18]. The ceramic method requires high sintering temperature leading to evaporation of certain elements like Zn, Cd, Li, etc. resulting in formation of chemical inhomogenity [19]. During milling and grinding there may be a loss of some material which leads to non-stoichiometry in the final product. Chemical method overcomes the limitations of ceramic method. The high density ferrites with fine particle size can be obtained by co-precipitation method. High density homogenous and fine grained ferrites prepared by co-precipitation method are reported by us [20]. There are several reports on divalent and trivalent metal ions added ferrites prepared by ceramic method [7–10]. But the reports on trivalent rare earth added Mg–Cd ferrites prepared by co-precipitation method are rarely available in literature. The present work reports the compositional dependence of structural behavior of yttrium-added Mg–Cd ferrites prepared by co-precipitation method and characterized by XRD, SEM and FTIR technique. The phase formation of samples, compositional variation of lattice constant '*a*', and crystallite size '*D*' and X-ray density 'ρ_x', have been determined using powder X-ray diffraction method. The effect of yttrium addition on granular structure is studied by SEM. The absorption band is studied by FTIR spectroscopic method. From absorption bands details regarding functional group and their linkage can be correlated which depends upon atomic mass, ionic radius, cation, anion bond length, etc.

2. Experimental details

2.1. Preparation of $Mg_{1-x}Cd_xFe_2O_4 + 5\%\ Y^{3+}$

Polycrystalline ferrite with general formula $Mg_{1-x}Cd_xFe_2O_4$ (0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) with 5% addition of Y^{3+} were prepared by the oxalate co-precipitation method using sulphates of analytical reagent (AR) of grade. The high purity starting materials $MgSO_47H_2O$ (purity 99.99%, Sd fine), $3CdSO_48H_2O$ (purity 99.99%, Sd fine), $FeSO_47H_2O$ (purity 99.5%, Thomas Baker) and $Y(SO_4)_38H_2O$ (purity 99.9%, Alafa Aesar) were used in desired stoichiometric proportion and dissolved in distilled water. The pH of the solution was maintained at 4.8 by adding drop wise concentrated H_2SO_4 [21]. The resulting solution was heated at 80 °C for 1 h in order to complete the ionization of metal sulphate. The solution of ammonium oxalate (AR) was added in the solution by stirring until the process of precipitation is completed [13]. The process of precipitation can be explained by chemical reaction as below:

$$CdSO_4 + 2H_2O + C_2O_4{}^- \rightarrow CdC_2O_42H_2O + SO_4{}^{2-}$$

$$MgSO_4 + 2H_2O + C_2O_4{}^- \rightarrow MgC_2O_42H_2O + SO_4{}^{2-}$$

$$FeSO_4 + 2H_2O + C_2O_4{}^- \rightarrow FeC_2O_42H_2O + SO_4{}^{2-}$$

$$YSO_4 + 2H_2O + C_2O_4{}^- \rightarrow YC_2O_42H_2O + SO_4{}^{2-}$$

The resultant precipitation containing the solid solution of cadmium oxalate, magnesium oxalate, ferrous oxalates and yttrium oxalates, was digested on sand bath for 1 h in order to settle down the precipitate at bottom of the beaker. Further it was filtered by using Whatman filter paper no. 41 with the help of suction flask operating on the vacuum pump and finally washed with distilled water in order to remove sulphate ions. The absence of sulphate ion in the filtrate was confirmed with barium chloride test. The co-precipitate product was dried and presintered at 700 °C for 6 h in air [21]. The rate of heating and cooling was 80 °C h^{-1}. The presintered powder was milled in an agate motar with AR grade acetone as a base and pressed in the form of pellets at pressure of 7 tones cm^{-2} by using hydraulic pressure machine. Polyvinyl alcohol 2 wt% was used as a binder. The size of pellets was 1.3 cm diameter. The pellets were finally sintered at 1050 °C for 5 h in air followed by slow cooling in the furnace at room temperature.

2.2. Experimental techniques (XRD, SEM, FTIR)

The ferrite phase formation of sintered powder was confirmed by powder XRD technique using a Philips PW-3710 X-ray diffractometer with Cu Kα radiation (λ = 1.5424 Å). For each sample a scan has been performed from 20° to 80° with a step size of 0.02°. The X-ray tube was excited at 40 kV and 30 mA. The crystallite size is calculated by Scherrer formula. The morphological feature of fractured surface of the sintered pellet at 1050 °C was examined with a scanning electron microscope (model JEOL-JSM 6360). SEM images give the information regarding the intergranular and intragranular pores as well as sub-structural defects within the grains. FTIR absorption spectra of powdered sample were recorded on a PerkinElmer spectrum one spectrometer by KBr pellet technique between 350 and 800 cm^{-1}. The physical density of palletized samples was measured by using Archimedes principle.

3. Result and discussion

3.1. Characterization

3.1.1. XRD analysis

The XRD patterns of $Mg_{1-x}Cd_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) with addition of 5% yttrium are presented in Fig. 1. The allowed planes in the diffraction patterns confirm the formation of cubic spinel structure. The planes corresponding to peaks (2 1 0), (2 2 0), (3 1 0), (3 1 1), (4 0 0), (4 2 2), (3 2 1), (3 3 3)/(5 1 1), (4 4 0) and (5 3 3) have been observed. It further shows that there is no impurity present except the YFeO$_3$. The yttrium ion induces second phase indexed by planes (2 1 0) (3 1 0) and (3 2 1) which corresponds to orthoferrite (YFeO$_3$). The ASTM card shows that this type of phase can appear such as in YFeO$_3$ [22]. The appearance of second phase is mainly explained due to high reactivity of Fe^{3+} ions with Y^{3+} ions near or on the grain boundaries. Although the radius of Y^{3+} ions is (0.95 Å) the phase contains a small quantity of yttrium in the