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Research Article

Synthesis of Mixed Rb-Zn Ferrites by Novel Solution Combustion Method and Investigation on Their Microstructural Properties

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Microstructural studies have been made on mixed rubidium nanoferrites of varying compositions, that is, $Rb_{0.5-x/2}Zn_xMn_{0.05}Fe_{2.45-x/2}O_4$ prepared by solution combustion method from stoichiometric aqueous solutions of metal nitrates and ethylene glycol. The combustion method is rapid and approach direct conversion from the molecular mixture of precursor solution to the fine nanoparticles of oxide product. The ferrites obtained have been characterized by powder XRD, transmission electron microscopy, and EDXRF studies. Powder X-ray diffraction analysis shows the formation of single-phase structure. The lattice parameter "*a*" has been found to increase with increasing Zn content. Both theoretical and experimental densities show a decreasing trend with decrease in molecular weight. The calculated value of the porosity has been found to be quite low which is a characteristic requirement of good-quality ferrite materials. TEM micrographs indicate the formation of nanosized ferrite particles which is in agreement with the size calculated from XRD data.

1. Introduction

Miniaturization of devices due to advancements in nanotechnology led to an increased interest in physical properties of nanomaterials [1]. Mixed ferrites are the ferrimagnetic oxide materials exhibiting high resistivity, permeability, and low eddy current losses. These novel materials are extensively used in radio, TV, radar, audio-video and digital recording, bubble devices, memory cores of computer, and microwave devices [2–6]. Recently, there has been a surge of interest in the preparation of nanosized mixed alkali metal ferrites as their properties are quite different from bulk of the material of the same composition. Ferrite nanoparticles show unusual magnetic properties which are not observed in bulk material such as single-domain behavior and superparamagnetism [7, 8]. The properties of the ferrite materials, which decide the application areas, are generally governed by the chemical compositions and the procedures followed for preparation. Thus, the chemical aspect has become the most important factor in the design and preparation of ferrite materials. Although several methods have been developed for the synthesis of metal ferrites [9–12], solution combustion route has the advantage of obtaining nanosized and pure ferrites at lower temperature and in shorter time as compared to other conventional methods [13]. Another attractive feature of this method is that no milling of the starting materials is required which avoid the formation of lattice defects in the ferrite obtained [14]. Though several investigations have been reported on the synthesis and characterization of doped lithium, sodium, and potassium ferrites [13, 15], a similar interest on mixed rubidium-zinc ferrites needs to be generated.

2. Experimental Method

Mixed rubidium ferrites of varying composition that is, $Rb_{0.5-x/2}Zn_xMn_{0.05}Fe_{2.45-x/2}O_4$ were prepared by solution combustion method. In these compositions, x varies from 0 to 0.5 in steps of 0.1. Stoichiometric quantities of aqueous solution of respective metal nitrates and ethylene glycol were taken and thoroughly mixed in a beaker. After vigorous stirring at 80°C for 2 hrs, the reaction mixture was combusted

in muffle furnace at 600°C for 30 min. Ethylene glycol used in this method acts as a fuel for the combustion synthesis of ferrites. The final ferrite product is then characterized by X-ray diffractometer (PW3064, X'Pert Pro, Phillips, using a Cu Kα radiation $\lambda = 1.54059$ Å in a wide range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 80^\circ$) with step size of 0.0170 and scan step time of 20.0286 s^{-1}). The size and shape of ferrite particles were analyzed by transmission electron microscope (TEM, Hitachi H-7500). Infrared studies were carried out on Varian 660, FTIR system after preparing pellets with KBr. The elemental analysis of the samples was performed using the EDXRF spectrometer (PanAnalytic, The Netherlands). The Mossbauer spectroscopic studies, magnetic and electrical properties of product ferrite, have already been reported somewhere else [16].

3. Result and Discussions

Figure 1 shows the X-ray diffraction patterns for different compositions from $x = 0$ to 0.5. The diffraction peaks (220), (311), (400), (422), (511), and (440) reveal the existence of only single phase of cubic ferrite (see Supplementary Tables 1–6 in Supplementary Material available online at doi:10.1155/2011/247320) and are comparable to those reported for respective lithium ferrites [5, 17]. IR spectra of all the samples display two main bands in the region ν_1 (630–550 cm^{-1}) and ν_2 (525–390 cm^{-1}) attributed to stretching vibrations of M-O bond in tetrahedral and octahedral sites [18–20], respectively (see Supplementary Figure 1).

Table 1 shows the lattice constant variation as a function of "x." The value of lattice constant increases with increasing Zn content (x) in the composition. The lattice constant "a" can be calculated theoretically by the following relation [21]:

$$a = \left(\frac{8}{3}\sqrt{3}\right)\left[(r_A + r_O) + \sqrt{3}(r_B + r_A)\right], \quad (1)$$

where r_O is the radius of oxygen ion, r_A and r_B are the ionic radii of tetrahedral (A) and octahedral (B) site, respectively. This clearly indicates that there exists a correlation between the ionic radii and the lattice constant. In order to estimate r_A and r_B in the case of more than one ion present at a site, it is necessary to know the cationic distribution of the composition. According to the thumb rule if the radius of the substituted ion is smaller than that of the displaced ion, the lattice shrinks and the lattice constant reduces. Similarly, when the substituted ion of larger ionic radius replaces the metallic ion of smaller ionic radius from the regular lattice, the lattice constant is expected to increase. Figure 2 shows the variation of lattice constant with Zn content, that is, a regular increase with increase in the "x" value. This is attributed to the substitution of larger Zn^{2+} cation (0.083 nm) for smaller Fe^{3+} cation (0.067 nm). Rubidium ferrites, like other alkali metal ferrites [22], have inverse cubic structure in which all the Rb^+ ions occupy octahedral position along with half of the Fe^{3+} ions and remaining Fe^{3+} ions occupy tetrahedral site. The addition of Zn^{2+} ions which have strong affinity for tetrahedral site, only Fe^{3+} ions present at tetrahedral site get replaced, results in an increase in lattice parameter. The inverse structure of the ferrite is also supported by the cationic distribution obtained from Mössbauer spectrum for Rb-Zn ferrites [16].

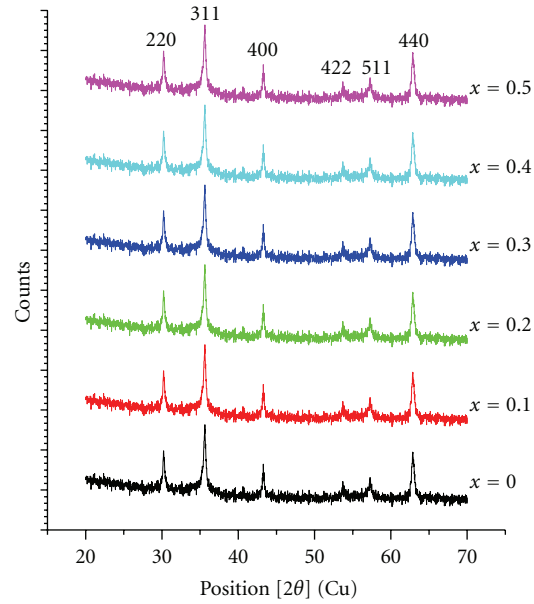

Figure 1: X-ray powder diffraction pattern for different compositions.

The theoretical or X-ray density (d_{XRD}) of the prepared rubidium series has been calculated by using the relationship [23]:

$$d_{XRD} = \frac{8M}{Na^3}, \quad (2)$$

where M is Molecular weight of the ferrite, N is Avogadro's number, and a is lattice constant obtained from the different XRD patterns. Figure 3 exhibits the variation of theoretical/X-ray density (d_{XRD}) and experimental density as a function of Zn content and shows a regular decrease with increasing "x" value. This may be attributed to a decrease in molecular weight of the ferrite.

The experimental/bulk density ($d_{Exp.}$) has been calculated for the prepared compositions by Archimedes principle. The magnitude of observed and calculated densities have been found to be comparable. Both parameters show a downward trend with increasing magnitude of "x." However, the X-ray density for any given composition is higher than that of the experimental density and this difference is primarily due to the porosity of the material.

The percentage porosity for all the compositions was calculated by using the equation:

$$\left[1 - \frac{d_{Exp.}}{d_{XRD}}\right] \times 100. \quad (3)$$

The calculated value of the porosity (Table 1) has been found to be quite low which is a characteristic requirement of good quality ferrite materials. The low porosity values may be attributed to high temperature sintering of the pellets.

Table 1: Variation of various XRD parameters with composition "x" for $Rb_{0.5-x/2}Zn_xMn_{0.05}Fe_{2.45-x/2}O_4$.

Composition (x)	Molecular weight	Density (d_{XRD}) g/cm^3	Density (d_{Exp}) g/cm^3	Porosity (%)	Lattice parameter "a"
0	246.70	5.613	5.331	5.03	8.359
0.1	246.16	5.581	5.329	4.50	8.369
0.2	245.63	5.545	5.285	4.62	8.381
0.3	245.09	5.499	5.249	4.54	8.398
0.4	244.56	5.462	5.172	5.30	8.411
0.5	244.02	5.415	5.132	5.37	8.429

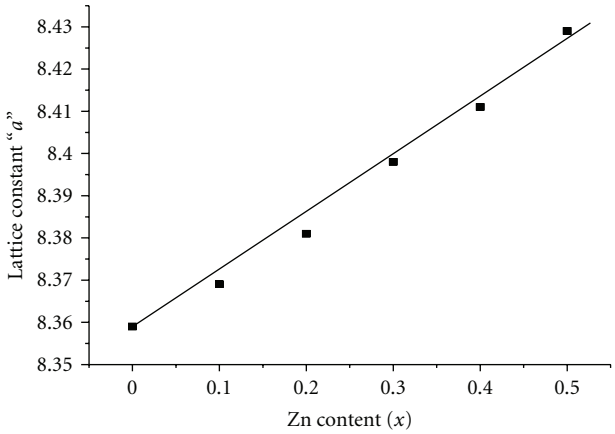

Figure 2: Variation of lattice constant "a" with Zn content.

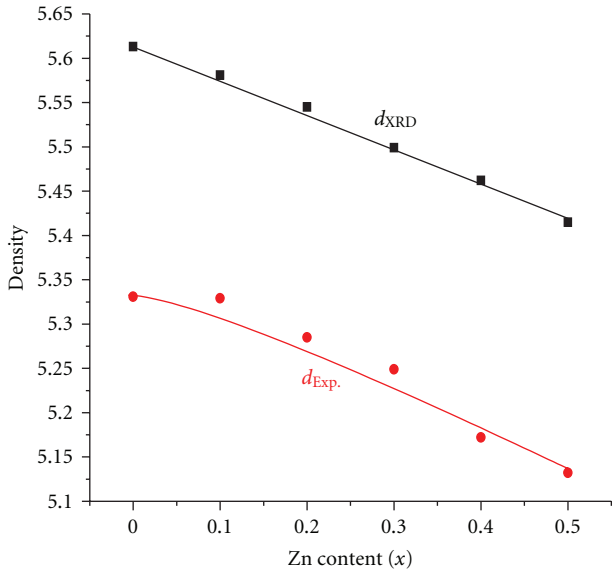

Figure 3: Variation of theoretical (d_{XRD}) and experimental density ($d_{Exp.}$) with Zn content (x).

The particle size has been calculated from the XRD data by using Scherrer formula [24]:

$$D = \frac{\lambda}{\beta \cos\theta}, \quad (4)$$

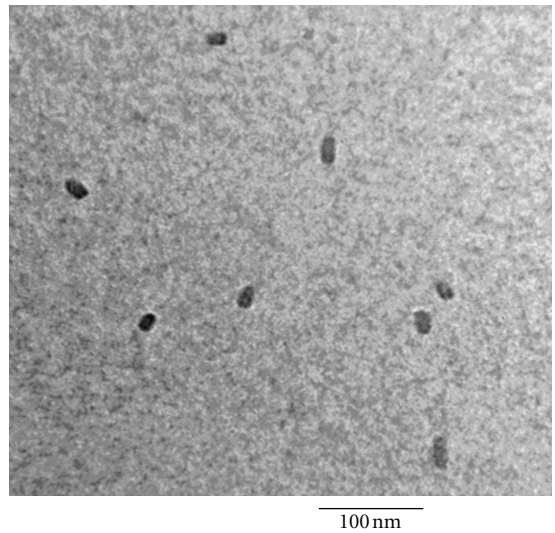

Figure 4: TEM structure of $Rb_{0.5-x/2}Zn_xMn_{0.05}Fe_{2.45-x/2}O_4$ with x = 0.3.

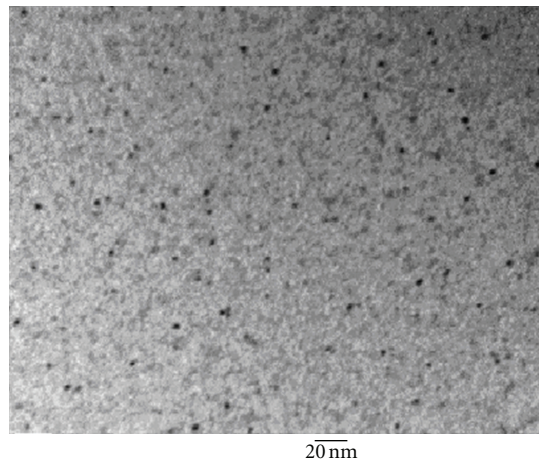

Figure 5: TEM structure of $Rb_{0.5-x/2}Zn_xMn_{0.05}Fe_{2.45-x/2}O_4$ with x = 0.5.

where λ is the wavelength of X-ray used and "β" is the full width of diffraction line at half maximum and θ is the Bragg's angle. The particle size calculated from XRD powder data and TEM studies reveal the formation of nanosized ferrite particles with average particle size of 10–15 nm (Figures 4 and 5). The elemental analysis for the

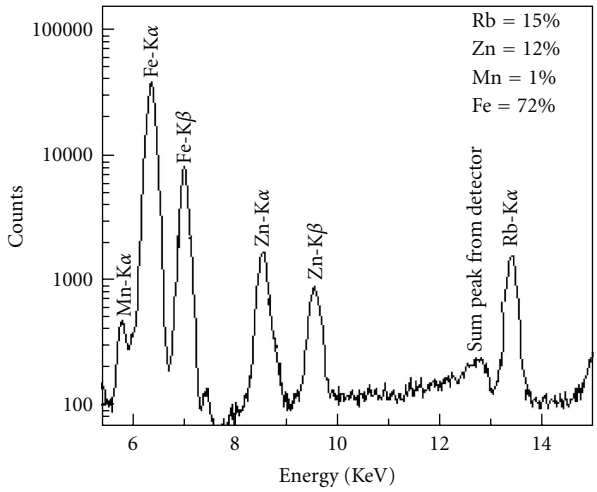

Figure 6: EDXRF graph for the composition $x = 0.3$.

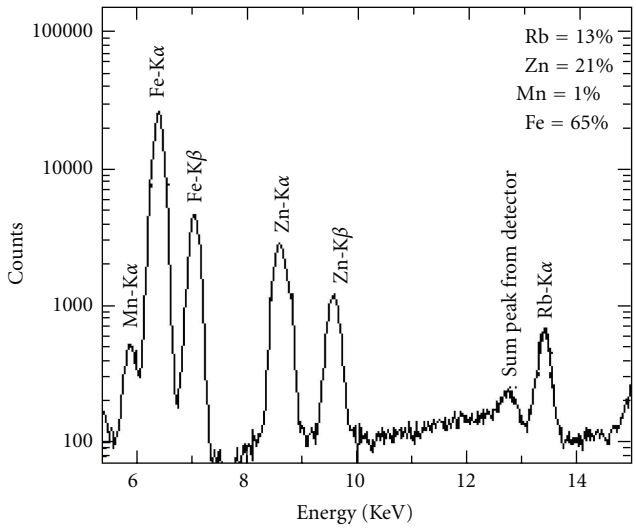

Figure 7: EDXRF graph for the composition $x = 0.5$.

different composition was characterized by EDXRF studies (Figures 6 and 7), the values obtained agreed with the calculated ones (with ±10% error).

4. Conclusion

A series of doped rubidium ferrites were successfully prepared by novel solution phase combustion method by using metal nitrates and ethylene glycol solutions. By making use of this method, stoichiometrically pure and nanosized ferrites particles have been obtained at lower temperature and in shorter time as compared to the conventional ceramic method. X-ray powder diffraction studies reveal the formation of single-phase nanoferrite particles which ensures the high purity of materials, also confirmed by the EDXRF studies. The lattice parameter "a" has been found to increase with increasing Zn content (x) which is due to the larger cationic radii of substituent Zn^{2+} ions. TEM micrographs show the formation of nanosized ferrite particles with average grain size of 10–15 nm.

Acknowledgment

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