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INFLUENCE OF CHROMIUM (Cr^{3+}) SUBSTITUTION ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF NICKEL FERRITE NANOPARTICLES

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ABSTRACT

The nanoparticles of chromium substituted nickel ferrite with the general formula $NiCr_xFe_{2-x}O_4$ (x = 0.0, 0.2 and 0.4) were prepared by sol-gel auto combustion method using ascorbic acid as a fuel. The single phase cubic spinel structures of all the samples were confirmed through X-ray diffraction (XRD) analysis. The lattice constant, X-ray density and bulk density was obtained and their variations with Cr substitution were studied. The lattice constant decreases with Cr substitution. The crystallite size of all the samples was determined using Debye-Scherrer's formula and found to be 28-36 nm which confirms the nanocrystalline nature of the samples. The DC electrical resistivity was studied using two probe technique to understand role of chromium on electrical behaviour. The variation of DC resistivity with temperature exhibits semiconductor behaviour. The resistivity decreases with increase in temperature.

KEYWORDS: Nanoparticles, sol-gel auto combustion, X-ray diffraction.

INTRODUCTION

Ferrites are enclosing of iron oxides and metal oxides and they exhibit certain important electrical and magnetic properties, which makes them broadly useful in technological applications. Ferrite materials are insulating magnetic oxides, unlike most material they possess high permeability, high electrical resistivity, moderate permittivity and saturation magnetization, high Curie temperature, low eddy current and dielectric losses. These characteristics of ferrite materials make them useful in variety of applications. Ferrites represent an important category of materials, which are in great demand due to their numerous applications viz. antenna rod, transformer core, memory storage chips, magnetic resonance imaging (MRI), drug delivery etc [1-4]. Spinel-type oxides of general chemical formula AB_2O_4 have been recognized for a long time. They have given rise to many industrial applications in magnetic recording, batteries, catalysis and biomedicine. Polycrystalline soft ferrites are magnetic semiconductors which cannot be replaced by any other magnetic material for the reason that they are stable, easily manufactured, relatively inexpensive, easily manufactured and have many applications in the field of electronic and telecommunication due to their combined property of magnetic conductor and electrical insulator which is not observed in any other magnetic materials. The important electrical and magnetic properties of the ferrite materials, which decide the application areas, are generally governed by the chemical compositions, preparative conditions and preparative parameters, method of preparation, type and amount of substituent, distribution of cations at available sites [5-7]. Thus, the chemical aspects of the ferrite have become most important in the design and preparation of ferrite materials. Recently, synthesis of nanocrystalline ferro-spinels is one of the interesting fields of material science in material processing and technology. This nano-scale particle exhibits new and interesting properties as compared to the bulk properties. The various synthesis technique, which are used for the synthesis of spinel ferrite powders include microwave refluxing, hydrothermal, sol-gel, co-precipitation, spray-pyrolysis, micro-emulsion [8-13].

The trivalent dopant like Al^{3+} and Cr^{3+}-substituted Ni ferrite finds a wide range of applications at radio and microwave frequency devices. The aim of the present work is to prepare Cr^{3+} doped nickel ferrite $NiCr_xFe_{2-x}O_4$ (x = 0, 0.2 and 0.4) by sol-gel method and to study structural and electrical properties.

MATERIALS AND METHODS

Synthesis

The high purity AR grade ferric nitrate ($Fe(NO_3)_3.9H_2O$), nickel nitrate($Ni(NO_3)_2 \cdot 6H_2O$), chromium nitrate ($Cr(NO_3)_3.9H_2O$), ascorbic acid ($C_6H_8O_6$) and ammonium hydroxide solution (NH_4OH) were used to prepare chromium substituted nickel ferrite nanoparticles ($NiCr_xFe_{2-x}O_4$). These nitrates and ascorbic acid were weighed accurately to have proper stoichiometric proportion required in the final product. The metal nitrate to ascorbic acid ratio was maintained as 1:3 for all the samples. An aqueous solution containing nickel nitrate (0.1 M), chromium nitrate (0.1M) and ferric nitrate (0.2 M) was prepared first and then these solutions were mixed together and stirred for about 1 h. Then ascorbic acid was added in the mixed solution of nickel nitrate and ferric nitrate and stirred it for 1 h until the homogeneous solution is formed. During the stirring process liquid ammonium hydroxide was added drop by drop to obtain pH of 7. The mixed solution was simultaneously heated at 70 ^{0}C for 2 to 3 h to form a sol. The transparent sol was heated at 100 ^{0}C for 1h for removal of water. The sol turns into a viscous brown gel. The temperature of the gel was further increased up to 120 ^{0}C, after some time combustion of the gel takes place and fine powder of chromium substituted nickel ferrite nano particle was obtained. The powder was dried and annealed at 650 ^{0}C for 7 h after confirmation from TG-DTA analysis, and the same powder was used for further characterization.

Characterizations

The ferrite phase formation was investigated by the powder X-ray diffraction technique at room temperature using Philips X-ray diffractometer (PW 3710) working with Cu-Kα radiation. The diffraction patterns were recorded in the 2θ range of 20^0 to 80^0. The electrical properties of the nano-particles were measured using the two probe technique. The measurements were performed in the temperature range 300-800 K.

RESULTS AND DISCUSSION
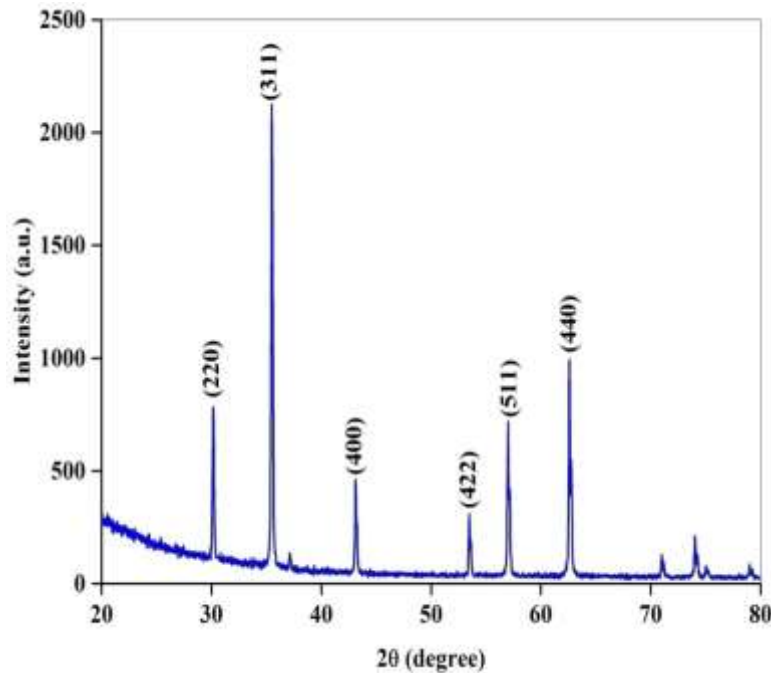
Fig. 1 Typical X-ray diffraction patterns of NiCr$_x$Fe$_{2-x}$O$_4$ (x= 0.2) system

The typical XRD pattern show the reflections (220), (311), (222), (400), (422), (511) and (440) which confirms the formation of cubic spinel structure. No extra peak was detected in the XRD pattern of all the samples studied in the present work. Using XRD data, the lattice parameter has been determined using the method of least squares to an accuracy of ± 0.002 Å and the values are presented in Table 1.

Table 1. Lattice constant (a), unit cell volume (V), molecular weight (M), X-ray density (d_x) and bulk density (d_B) of

$NiCr_xFe_{2-x}O_4$ system

x	a (Å)	V (Å)³	M (gm)	d_x (gm/cm³)	d_B (gm/cm³)
0.0	8.388	590.34	234.61	4.650	5.2812
0.2	8.352	582.80	228.83	4.547	5.2140
0.4	8.323	576.95	223.07	4.449	5.1362

The observed behaviour of lattice constant can be explained on the basis of the relative sizes of ionic radii. The ionic radius of Cr^{3+} (0.64Å) ions is smaller than the ionic radius of Fe^{3+} (0.67 Å) ion. Replacement of larger Fe^{3+} cations by smaller Cr^{3+} cations in the nickel ferrite causes decrease in lattice parameter. Similar variation of lattice parameter was observed for other Cr^{3+} substituted spinel ferrites [14, 15]. Table 1 indicates that lattice constant decreases almost uniformly as observed from the change in the chromium concentration x. The decrease in volume means the shrinkage of unit cell may be attributed to the substitution of smaller size Cr^{3+} ions (0.64 Å) in place of larger size Fe^{3+} ions (0.67 Å).

The particle size of the Cr substituted nickel ferrite powders was calculated by using the most intense peak (311) and using the Debye-Scherrer formula and was found to be 28 nm, 32 nm and 36 nm for x = 0.0, 0.2 and 0.4 samples respectively.

The bulk density (d_B) of the samples was evaluated by using the Archimedes principle. It is observed that density decreases with increasing chromium concentration x. The values of bulk density are given in Table 1. The X-ray density (d_x) was calculated according to the relation;

$$d_x = \frac{8M}{N_a a^3} \qquad (1)$$

where, numerate factor denotes the number of formula units in a unit cell, M is the molar mass, N_a is the Avogadro's, number and a^3 is the unit cell volume computed from the values of lattice constant. The values of unit cell volume and X-ray density are given in Table 1. The unit cell volume and X-ray density both decreases with increase in chromium concentration x. The decrease in X-ray density is attributed to the fact that unit cell volume decreases more than the negligible rise in the molar masses of the doped metal cations.

The transport properties of the systems were investigated by using room temperature resistivity measurement. The values of room temperature resistivity as a function of chromium concentration x and it is observed that the increase resistivity with rise of Cr^{3+} concentration x the relatively low resistivity at lower concentration is due to high mobility of the electrons between the ions with different valance at B-site. The variation of room temperature resistivity with Cr^{3+} concentration x is shown in Fig.2.

The room temperature drift mobility (μ_d) of $NiCr_xFe_{2-x}O_4$ ferrites was also calculated by using resistivity data and employing the relation and obtained to be in the range of 9.30×10^{-12} to 7.32×10^{-12} (cm- (V-cm)$^{-1}$) [16];

$$\mu_d = \frac{M}{N_a B_{Fe} d_m e \, \rho} \qquad (2)$$

where, M is molecular weight of the sample, N_a is the Avogadro's number, B_{Fe} number of Fe ions; e is charge of electron and ρ is the room temperature resistivity. The drift mobility values decreases with chromium concentration x.

The DC electrical resistivity measurements were carried out with varying temperature using two probe technique. The measurements were recorded in the temperature range 300-800 K. The resistance (R) of each sample was measured at regular interval of 10 K. Using the values of 'R' and dimensions of pellet, the resistivity ρ of each sample was evaluated and variation of resistivity with temperature is shown in Fig. 2.
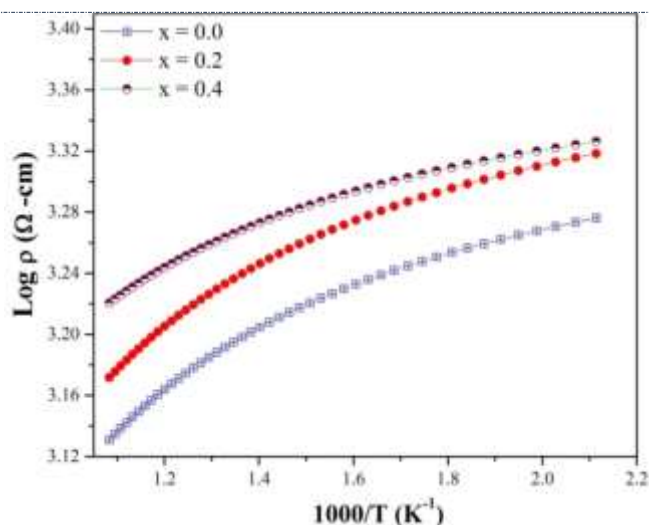
Fig. 2. Variation of Log ρ with 1000/T of NiFe$_{2-x}$Cr$_x$O$_4$

It follows the Arrhenius plot. This graph shows that by increasing temperature, the resistivity of NiCr$_x$Fe$_{2-x}$O$_4$ ferrites decreases. This is the property of semiconductor in the nanocrystalline ferrites. It can be seen from Fig. 2 that resistivity increases with increase in chromium concentration x. The increase resistivity is attributed to the decrease in Fe^{2+} due to the substitution of Cr^{3+} ions. The conduction mechanism in the present samples can be explained on the basis of Verwey's hopping mechanism. According to Verwey, exchange of electron between ions of the same element present in different valence state and distributed randomly over equivalent crystallographic lattice state i.e. Fe^{3+}↔Fe^{2+} [17].

CONCLUSION

Nanocrystalline chromium substituted nickel ferrite (NiCr$_x$Fe$_{2-x}$O$_4$) was produced by using sol-gel auto combustion method. The X-ray powder diffraction shows that a cubic spinel phase was formed for all the samples. The crystallite size of the powders calculated by the Scherrer's method found to be in the range of 28 - 36 nm. The lattice parameter of the system decreases with increase in chromium concentration x. The resistivity increases as chromium concentration x increases.

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REFERENCES

[1] J. Ferre, S. Lemerle, V. Mathet, C. Choppert, J. Magn. Magn. Mater.260 (2003) 234–243.
[2] M. Mozaffari, J. Amighin, J. Magn. Magn. Mater. 260 (2003) 244–246.
[3] Suman Rashonlel, N.D. Sharma, S.P. Taneja, Ajay Gupta, Ind. J. Pure Appl. Phys. 43 (2005) 44–50.X. Chu, B. Cheng, J. Hu, H. Qin, M. Jiang, Sensors & Actuat, B 129 (2008) 53.
[4] G. Blasses, Philips Res. 14 (1964) 68.
[5] W.C. Kim, S.J. Kim, S.W. Lee, C.S. Kim, J. Magn. Magn. Mater. 226 (2001) 1418.
[6] Lijun Zhao, et al., Mater. Lett. 60 (2006)1.
[7] Jyotsendu Giri, T.Sriharsha, D.Bhadur, J. Mater. Chem. 14 (2004) 875.
[8] A. Dias, Mater. Resea. Bull. 35(2000)1439.
[9] A. Chargles, N. O'Connor, E. Kolesnichenko, C. Carpenter, S. W. Zheu, A. Kumbhar, S.Jessica and A. Fabrice, Synthetic Metal. 122(2001)547.
[10] A.S. Albuquerque, M. Drofenik, A. Znidarsic, Am. Ceram. Soc. 82 (1999)133.
[11] Dae Soo Jung, Hee Chan Jang, Man-Jong Lee, Kyeong Youl Jung, and Yun Chan Kang, J. Ceramic. Sco. of Japan 117 (2009)1069.
[12] P. Holec, J. Plocek, D.Niznansky, J.Poltierova Vejpravova, J Sol-Gel Sci Technol 51 (2009) 301.
[13] Chandrasekaran, G., S. Selvandan and K. Manivannane, J. Mate.Sci.: Materials in Electronics, 15 (2004) 15.

[14] Rezlescu, N., E. Rezlescu, C. Pasnicu and M.L. Craus, J. Phys. Condens. Matter, 6(1994) 5707.

[15] M.W. Zemansky, Heat Thermodynamics, McGraw- Hill- York, (1968) 460.

[16] Ghazanfar, U., Siddiqi, S. A., & Abbas, G. (2005). Materials Science and Engineering: B, 118(1), 132-134.

[17] Kumar, G. R., Venudhar, Y. C., Raghavender, A. T., & Kumar, K. V. (2012). Journal of the Korean Physical Society, 60(7), 1082-1086.