



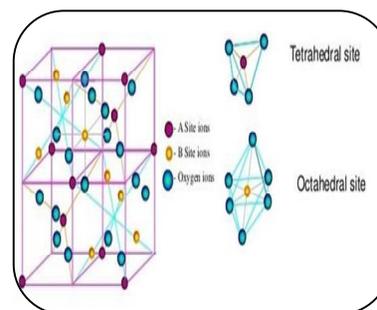
SYNTHESIS, STRUCTURAL ELUCIDATION AND THERMO-KINETIC STUDY OF Ni-Zn-FERRITE-CITRATE PRECURSOR.

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ABSTRACT

Thermal analysis was applied as prime techniques for determination of various kinetic and thermodynamic parameters. TG and DTA curves for the dried precursor sample of $Ni_{0.4}Zn_{0.6}Fe_2O_4$, before sintering was scanned and interpreted. It helps to predict sintering temperature for single phase formation of the compound. Coat-Redfern and Piloyan Novicova method were smeared to study several constraints as function of kinetic mechanisms, activation energies, frequency factor and entropy. With the help of thermal study data, powder X-ray powder diffraction (XRD) pattern was recorded to get single phase compound.



KEYWORDS: Ferrimagnetic; XRD; semiconducting; DC electrical conductivity.

1 INTRODUCTION

Ferrites are the magnetic materials containing iron oxide as the main constituent with various oxides. Oxidic spinel having general formula $Me^{2+}O \cdot Fe_2^{3+}O_3$ where Me^{2+} is divalent metallic ion such as Zn^{2+} , Cu^{2+} , Mg^{2+} , Ni^{2+} etc. Mixed ferrites are the mixture of ions of divalent or trivalent ion, so that a wide range of composition is possible due to variable oxidation state [1-6]. Magnetic mixed-metal oxides containing iron provide the best available combination of semiconductor and magnetic materials with remarkable flexibility in controlling magnetic and electrical properties. It also effects on structural parameters of the system. The above types of oxides have broad technological as well as commercial applications as catalysts [7-15], magnetic devices [16,24], thermistors [16, 25-28], gas sensors and pigments [29-35].

The applicability of these materials mainly depends upon their various physico-chemical properties. Their structural, electrical, magnetic, catalytic and gas sensing activity were depending on their oxidation state, active centers, surface area and smaller uniform sized grains, which crucially depend on the process of synthesis, heat treatment and location of cations over tetrahedral (T_d) and octahedral (O_h) sites. With this view an attempt has made for the thermogravimetric study of as prepared (unsintered) powder Ni-Zn-ferrite-citrate precursor. From the above thermal study sintering temperature of the sample was predicted while single phase crystal structure was confirmed by XRD pattern.

2. EXPERIMENTAL METHODOLOGY:

Desired composition was prepared by sol-gel auto-combustion method using citric acid as precursor [36]. TG and DTA curves for the dried precursor sample of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ (before sintering) were studied by scanning the thermographs in the temperature range of room temperature to 1000°C in static air at the flow

rate of 10°C/min. Its XRD pattern at room temperature was recorded to confirm single phase crystal structure.

For the determination of various kinetic parameters, Coat and Redfern [37] and Piloyan - Novicova [38] methods were employed. From thermal analysis (TG-DTA) various thermokinetic parameters were calculated by mentioned methods and compared.

3. RESULT AND DISCUSSION:

Thermogravimetric curve of the as prepared sample is shown in Fig. 1. A continuous weight loss was observed from TG curve up to 450°C. DTA curve shows one exothermic peak at about 110°C and other around 405°C. At this temperature a decomposition of mixed-metal citrate complex takes place by loss of water and thermal degradation of organic content respectively which results in the formation of stable mixed-metal oxides. Evaluated different kinetic parameters of precursor sample of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ (before sintering) are shown in Table 1. Two step decomposition takes place (Fig. 2 & 3), out of which first stage activation energy (E_a) is in the range of 9.59 to 12.75 kJ mol^{-1} for all the precursors and second stage activation energy was in the range of 59.99 to 193.55 kJ mol^{-1} as listed in Table 2 [39]. There is a good agreement between the values of frequency factor ($\log z$) and Entropy (ΔS) which are calculated by both the Coat-Redfern and Piloyan Novicova methods. The negative values obtained for entropy of activation point out that both the reactions are slower than the normal [40]. Based upon above study, 500°C temperature will be desirable for the formation of single phase spinel phase structure. Hence sample was sintered at 500°C (Fig. 4) and scanned by XRD which reflect that there is no any additional peak rather that single phase cubic spinel structure (JCPDS card No. 82-1142 and 74-2081) or additional phase [41]. Broad peaks at both fronting and tailing can be considered for their nanosized crystalline nature. Form above study it can be considered that there is a thermal study helps lot to decide desirable temperature for sintering to get pure compound.

CONCLUSION:

Single phase cubic spinel $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ were formed by polymerized complex process. TG-DTA study helps to decide single phase formation of compound. Various kinetic and thermodynamic parameters studied from TG-DTA are well agree with each other in both the methods and indicate desirable sintering temperature. XRD pattern reflects nanosized crystalline phase of desired compound.

REFERENCES

- [1] B. Viswanathan and V. R. K. Murthy, Ferrite Materials: Science and Technology, (Narosa Publishing House, New Delhi, 1990).
- [2] Alex Goldmann, Handbook of Modern Ferromagnetic Materials, (Kluwer Academic Publishers, Boston 1999).
- [3] G. Blasse, Philips Res. Rep. Suppl. 3 (1964) 96.
- [4] J. B. Goodenough, Prog. Solid State Chem. 5 (1971) 145.
- [5] B. D. Cullity, Fabrication to Magnetic Oxides (Addison Wiley New York, Chap. 6, 1972).
- [6] A. Brosevan, J. M. Grochou, P. F. Bongors, A. L. Stuists, Mater. Sci. Eng. 3 (1988) 317
- [7] P. P. Hankare, P. D. Kamble, S. P. Maradur, M. R. Kadam, U. B. Sankpal, R. P. Patil, R. K. Nimat, P. D. Lokhande, J. Alloys Compd. 487 (2009) 730.
- [8] R. J. H. Voorhoeve, J. P. Remeika, L. E. Trimbe, Annals of the New York Academy of Sciences, Catalitic Chem. 272, 1 (1976) 3.
- [9] S. S. Deshpanade, S. U. Sonavane, R. V. Jayaram, Catal. Commun. 9 (5) (2008) 639.
- [10] D. H. Zhang, H. B. Li, G. D. Li, J. S. Chem. Dalton Transactions (47), (2009) 10527.

- [11] P. Srivastava, I. P. S. Kapoor, G. Singh, J. Alloys Compd. 485 (2009) 88.
- [12] M. Florea, M. Alifanti, V. I. Parvulescu, D. Mihaila-Tarabasanu, L. Diamandescu, M. Feder, C. Negrila, L. Frunza, Catal. Today 141 (3-4) (2009) 361.
- [13] K. George and S. Sugunan, Catal. Comm. 9 (13) (2008) 2419.
- [14] T. Nitadori, S. kurihani, M. Misono, J. Catal. 96 (1986) 221.
- [15] V. Polshettiwar and R. S. Varma, Tetrahedron 660 (5) (2010) 1091.
- [16] S. Zahi, Materials and Design 31 (4) (2010) 1848.
- [17] V. L. Reena, C. Pavithran, V. Verma, J. D. Sudha, J. Physical Chem. B 114 (8) (2010) 2578.
- [18] D. Guo, X. Fan, G. Chai, C. Jiang, X. Li, D. Xue, Appl. Surface Sci. 256 (8) (2010) 2319.
- [19] C. N. Chanaswamy, A. Natayanswamy, N. Ponpandian, K. Chattopadhyaya, H. Guerault, J. M. Grenche, J. Phys.: Cond. Matter 12 (2000) 7795.
- [20] M. K. Roy and H. C. Verma, J. Magn. Magn. Mater. 306 (2006) 98.
- [21] W. J. Yeh, C. Blengeri, A. Abburi, D. N. McIlroy, J. Superconduct. and Novel Magn. 23 (2010) 1151.
- [22] S. D. Shenoy, P. A. Joy, M. R. Anatharaman, J. Magn. Magn. Mater. 269 (2004) 217.
- [23] S. Chigirinsky, M. Kustov, N. Dempsey, C. Ndao, R. Grechishkin, Reviews on Advanced Materials Science 20 (1) (2009) 85.
- [24] R. Huang, D. Zhang, K. J. Tseng, IEEE Transactions on Electromagnetic Compatibility 50 (Part 2), (2008) 597.
- [25] S. Jagtap, S. Rane, S. Gosavi, D. Amalnerkar, J. Europ. Ceram. Soc. 28 (13), (2008) 2501.
- [26] R. C. Kambale, P. A. Shaikh, Y. D. Kolekar, C. H. Bhosale, K. Y. Rajpure, Mater. Lett. 64 (4) (2010) 520.
- [27] B. K. Kuanr, V. Veerakumar, K. Lingam, S. R. Mishra, A. V. Kuanr, R. E. Celinski, J. Appl. Phys. 105 (7) (2009) 07A520.
- [28] J. Mürbe, J. Töpfer, International J. Appl. Ceram. Tech. 4 (5) (2007) 415.
- [29] S. L. Darshane, R. G. Deshmukh, S. S. Suryavanshi, I. S. Mulla, J. Am. Ceram. Soc. 91 (8) (2008) 2724.
- [30] P. P. Hankare, S. D. Jadhav, U. B. Sankpal, R. P. Patil, R. Sasikala, I. S. Mulla, J. Alloys Compd. 488 (2009) 270.
- [31] C. V. Gopal Reddy, S. V. Manorama, V. J. Rao, J. Mater. Sci. Lett. 19 (2000) 775.
- [32] Abd El-Ghaffar, M.A. Ahmed, N.M. Youssef, J. Coatings Tech. Res. 7 (2010) 703–713
- [33] S. Zhuiykov, T. Nakano, A. Kunimoto, N. Yamazoe, N. Miura, Electrochemistry Commun. 3 (2001) 97.
- [34] M. Stranzenbach, E. Gramckow, B. Saruhan, Sens. Actuators B 127 (2007) 224.
- [35] M.G. Baron, R. Narayanaswamy, S.C. Thorpe, Sens. Actuators B 29 (1995) 358
- [36] P.P. Hankare, U.B. Sankpal, R.P. Patil, R. Sasikala, I.S. Mulla, A. K. Tripathi, K.M. Garadkar, J. Alloys Compd. 496 (2010) 256.
- [37] A. W. Coat and J. P. Redfern, Nature 201 (1964) 68.
- [38] G. O. Piloyan and O. S. Novikova, Russ. J. Inorg. Chem. 12 (3) (1967) 313.
- [39] N. S. Gajbhiye, G. Balaji, Thermochemica Acta, 153 (1988) 337.
- [40] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Introduction to Ceramics, Wiley, New York, 1975, p. 904.
- [41] JCPDS card No. 82-1142 and 74-2081.

Table No. 1 Evaluation of kinetic parameters of precursor sample of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ (before sintering) $W_0 = 5.7716$ mg

Sr. No	Temp. ($^{\circ}\text{C}$)	Residual Weight (wt) mg	$\alpha = \frac{W_t - W_f}{W_0 - W_f}$	$\ln [\alpha / T^2]$	$g(\alpha)$	$\ln [g(\alpha) / T^2]$	$1000 / T$ (K^{-1})
1	50	5.7170	0.9222	-11.6363	1.4422	-11.1893	3.0959
2	75	5.6702	0.8556	-11.8604	1.2399	-11.4893	2.8735
3	100	5.6312	0.8000	-12.0663	1.1056	-11.7427	2.6809
4	125	5.6078	0.7667	-12.2386	1.0339	-11.9395	2.5125
5	150	5.5844	0.7334	-12.4049	0.9672	-12.1280	2.3640
6	175	5.5688	0.7111	-12.5505	0.9250	-12.2874	2.2321
7	200	5.5532	0.6889	-12.6908	0.8844	-12.4409	2.1141
8	225	5.5376	0.6667	-12.8266	0.8453	-12.5892	2.0080
9	250	5.5142	0.6334	-12.9759	0.7889	-12.7561	1.9120
10	275	5.4986	0.6111	-13.1050	0.7528	-12.8964	1.8248
11	300	5.4674	0.5667	-13.2697	0.6834	-13.0823	1.7452
12	325	5.4440	0.5334	-13.4157	0.6337	-13.2432	1.6722
13	350	5.4128	0.4889	-13.5846	0.5702	-13.4308	1.6051
14	375	5.3660	0.4223	-13.8099	0.4798	-13.6821	1.5432
15	400	5.2646	0.2778	-14.3042	0.3003	-14.2261	1.4858
16	425	5.1242	0.0778	-15.6495	0.0794	-15.6294	1.4326
17	450	5.0852	0.0223	-16.9704	0.0224	-16.96481	1.3831
18	475	5.0774	0.0112	-17.7285	0.0112	-17.72566	1.3368

Table No 2 Thermokinetic parameters of the precursor samples of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ (before sintering)

Method	steps	TGA Activation energy (E) kJ mol^{-1}	Frequency factor (log z)	Entropy (ΔS) kJ mol^{-1}
Coat- Redfern	I	11.38	5.86	-135.88
	II	193.55	7.52	-88.19
Piloyan Novicova	I	10.91	5.95	-137.99
	II	192.55	7.64	-89.02

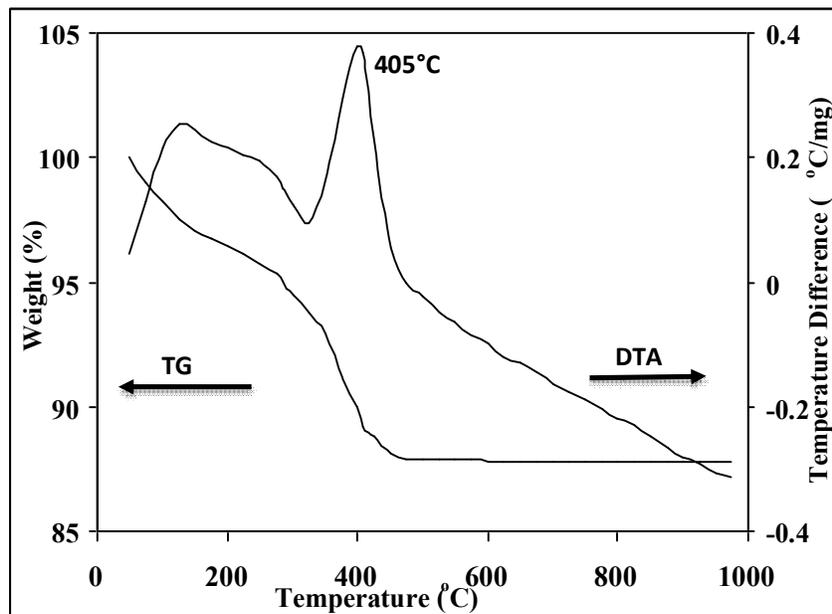


Fig. 1 TGA and DTA curve for precursor sample of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ (before sintering)

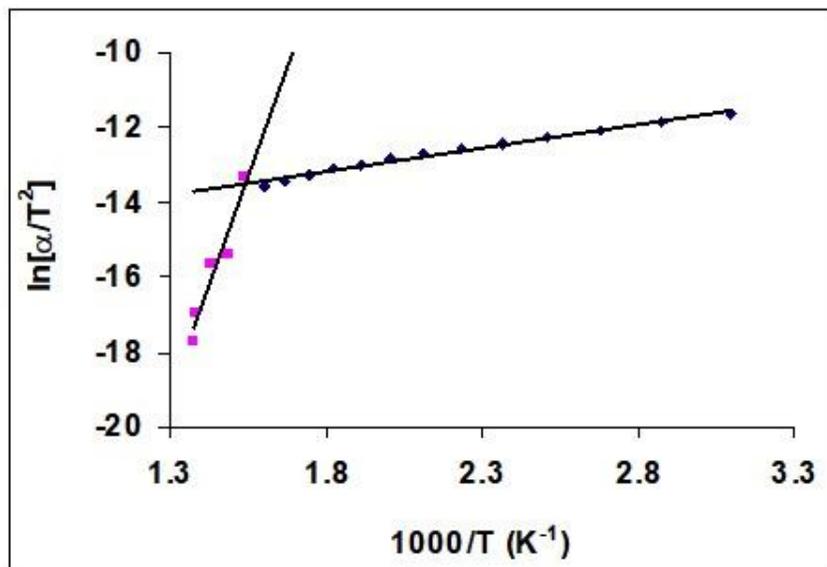


Fig. 2 Graph of $\ln[\alpha/T^2]$ Vs. $1000/T$ for precursor sample of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ (before sintering)

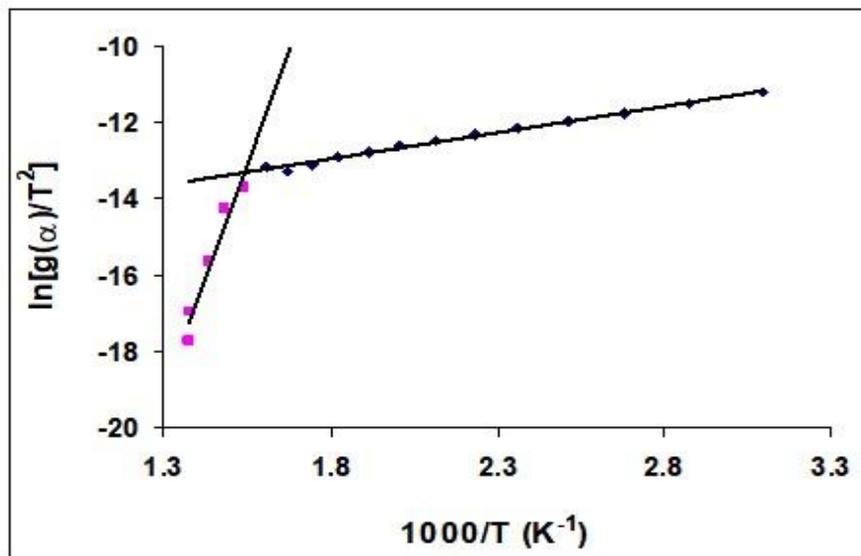


Fig. 3 Graph of $\ln [g (\alpha) / T^2]$ Vs. $1000/T$ for precursor sample of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ (before sintering)

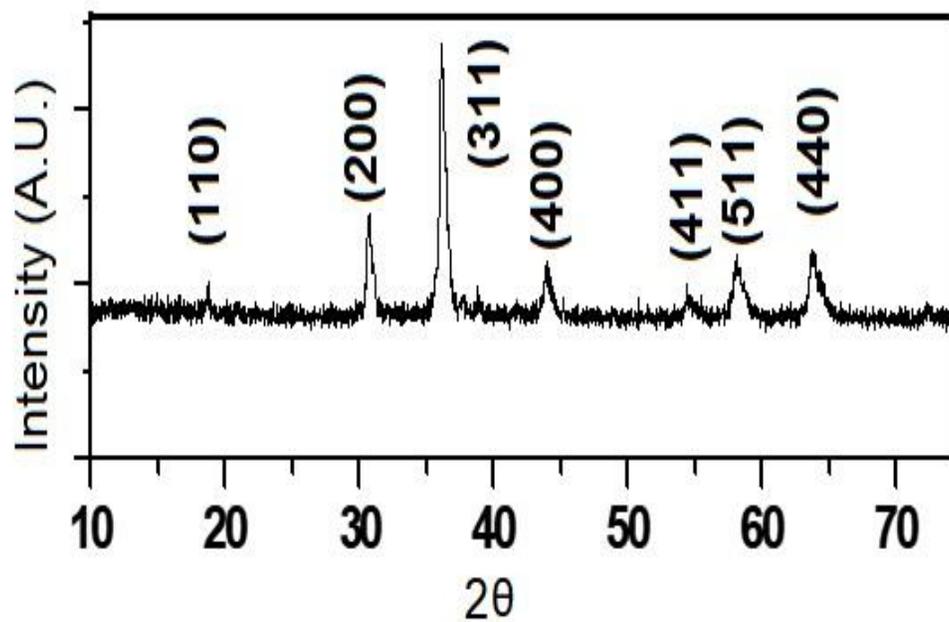


Fig. 4 XRD pattern of sintered $Ni_{0.4}Zn_{0.6}Fe_2O_4$ at $500^\circ C$