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Effect of Oxalate Precursor Formation Temperature on Magnetic Properties of NiCuZn Ferrites

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ABSTRACT

Ni-Cu-Zn ferrites with general formula $Ni_{0.5}Zn_{0.5-x/2}Cu_{x/2}Fe_2O_4$ (*with* x = 0.3, 0.4, 0.5 *and* 0.6) *have been synthesized using oxalate precursor method with different precursor reaction temperatures in the range* 10˚*C to* 70˚*C. The Curie temperatures obtained using AC susceptibility measurements are found to be in the range* 150˚*C to* 350˚*C, the measurements also show single domain structure for all the samples except few compositions obtained at* 35˚*C precursor reaction temperature, show a multi-domain behaviour. The saturation magnetization is found to be in the range* 20 *to* 51 *emu/gm, while the magnetic moment is found to be in the range* 0.63 *to* 1.5 *μB. The hysteresis losses were found to be maximum for the samples obtained at precursor reaction temperature of* 35˚*C. The grain size is found to be in the range* 0.4 *to* 2.0 *μm.*

Keywords: *Magnetic Materials*, *Temperature of Chemical Reaction*, *Magnetic Susceptibility*, *Curie Temperature*

1. Introduction

NiZn ferrites have been used in the high frequency applications and also multilayer chip conductor with silver as a suitable material for inner conductor, however co-firing silver with the NiZn ferrites at higher temperature of 1250˚C is unsuitable as the melting point of silver is 961˚C [1,2]. Cu^{2+} can be introduced to reduce the sintering temperature and at the same time enhance sintering process [3, 4]. Ni-Cu-Zn Ferrites having oxygen deficiency have been reported to be useful materials in CO_2 decomposition in reducing green house effect with 100% efficiency [5]. The synthesis of ferrites can be carried out using different methods but the low temperature synthesis and molecular level mixing is reported to be useful in obtaining desired magnetic properties and the reaction kinematics in a chemical process dependent on the temperature at which it is carried out [6]. A combination of lower reaction temperature followed by calcination at suitable elevated temperature for the solid state reaction could be useful for synthesizing the ferrites with required parameters.

Various preparation techniques such as sol gel auto combustion [7], microwave assisted combustion synthesis [8,9], soft chemical method [10-14], combustion synthesis [15] have been used to synthesize ferrites. In the present communication, efforts have been made to synthesize Ni-Cu-Zn ferrites in two steps, involving oxalate co-precipitation at three different reaction temperatures [16], followed by calcination at 600˚C for the completion of the solid state reaction. The choice of calcinations temperature has been based on the fact that ferrous oxalate gets converted into ferrous oxide at 400˚C [17] while the ferrite formation is reported to take place at around 600˚C [18,20]. It has also been reported that there is exothermic peak around 620˚C due to crystallization [21,22].

2. Experimental

Ni-Cu-Zn ferrites with general formula $Ni_{0.5}Zn_{0.5-x/2}Cu_{x/2}$-$Fe_2O_4$ (with x = 0.3, 0.4, 0.5 and 0.6) have been synthesized using AR grade metal sulphates as starting material. The stoichiometric proportions of metal sulphates were

added to 200 ml distilled water. The temperature of chemical reaction was maintained at three different values i.e. 10˚C, 35˚C and 70˚C, using thermally controlled water bath. The chemicals were also maintained at the three temperatures before the chemical reaction was carried out. The reaction temperatures were chosen considering the room temperature of the work place during summer. The summer room temperature is in the range of 35˚C which could be easily maintained. The other two temperatures were chosen which have the variation of more than 25˚C on either side of the room temperature.

Ammonium oxalate was added drop by drop in the flask containing the metal sulphates up to the completion of the chemical reaction. Barium chloride test was used to confirm the completion of chemical reaction. The filtrate was filtered and washed with distilled water and dried using electric lamp. Oxalates in precursor act like a combustion agent which helps in lowering the calcination temperature. Therefore the solid state reaction to obtain the ferrites was carried out in muffle furnace at optimized temperature of 600˚C for 6 Hrs for all samples irrespective of the oxalate reaction temperature. X-ray diffractograms were recorded using Philips PW 1710 powder diffractometer by scanning in the range 20˚C to 80˚C. AC susceptibility measurements were carried out using Helmholtz double coil setup operated at 263 Hz with a constant field of 7 Oe. Hysteresis measurements were done using the hysteresis loop tracer. SEM micrographs were taken on JEOL-JEM-6360 microscopes to obtain the grain size of the samples.

3. Results and Discussions

The XRD patterns indicate the single phase cubic structure for all the samples. The effects of reaction temperatures on the position of most intense (311) peak in the diffraction pattern are shown in **Figures 1 2**, **3** and **4**. The peak is found to shift towards smaller angle for reaction temperature 35˚C for all the compositions, while the peak intensities are found to be maximum for reaction temperature of 70˚C for $x = 0.3$ and 0.4 while for $x = 0.5$ and 0.6 the maximum intensity is observed at reaction temperature of 10˚C. The reaction temperatures show their effects in position as well as the intensity of the (311) peak. The variation in peak intensities and sharpness with reaction temperature has been reported by Qu *et.al* [23]. They have also reported the increase in grain size, lattice constant and Ms with reaction temperature.

Figures 5, **6** and **7** depict the variation of normalized AC susceptibility with temperature for all the compositions at different reaction temperatures. All the samples at reaction temperature of 10˚C and 70˚C show SD behaviour while two compositions at 35˚C show MD be haviour. The magnetic properties are structure sensitive and the grain size plays a significant role. The Curie temperature, at which the normalized susceptibility drops off sharply, shows a variation with reaction temperature. For synthesis at temperature of 10˚C the Curie temperature is found to be in the range 120 to 220˚C. For the reaction temperature of 35˚C, it is in the range of 220 to 290˚C while for the reaction temperature of 70˚C it is in the range 180 to 260˚C. The value of Curie temperature is found to be minimum for $x = 0.4$ for all the reaction temperatures while its value is maximum for the samples synthesized at 35˚C for all the compositions. The Curie temperature depends mainly on A-B interaction which is determined by the cations present in the sample. The substitution of Cu^{2+} ions in place of Zn^{2+}, changes the magnetic moment on both the sites whereby the A-B interaction changes. The Curie temperature is sensitive to the calcination temperature but in the present case even though the calcination temperature is same for all the samples, there is variation in Curie temperature with composition as well as the chemical reaction temperature indicating the effect of chemical reaction temprature even after calcination.

Figure 8 depicts the hysteresis loops for all the samples studied. The values of saturation magnetization and magnetic moment shown in **Table 1** are found to increase with increase in reaction temperature up to $x = 0.4$ while for $x > 0.4$ the maximum value is observed for reaction temperature of 35˚C. The retentivity for all the samples is found to increase with reaction temperatures. Shrotri *et al*. [10] have reported decrease in Ms with increase in Cu^{2+} content for ferrites with similar composition synthesized at 80˚C. The substitution of Cu^{2+} ions is reported to show canting behaviour for higher concentration [24,11,19] which is also observed in the present case. The variation in magnetization is also found to depend upon the reaction temperature, where it is found to show larger values for reaction temperature of 35˚C which happens to be the room temperature.

The SEM micrographs for the samples with $x = 0.4$ and $x = 0.5$ at the three reaction temperatures studied are shown in **Figures 9** and **10**. Maximum grain size is obtained for $x = 0.4$ which is in the range 0.6 to 1.95 μm for the samples studied. The grain size is found to increase with reaction temperature indicating the effect of reaction history on the grain size. The grain size is found to be maximum for the reaction temperature of 35˚C which happens to be the room temperature.

4. Conclusions

The oxalates co-precipitation reactions were carried out at 10˚C, 35˚C and 70˚C temperatures while the solid state reaction was carried out at 600˚C for all the samples, show variation with composition as well as reaction temperature in the structural as well as magnetic proper-

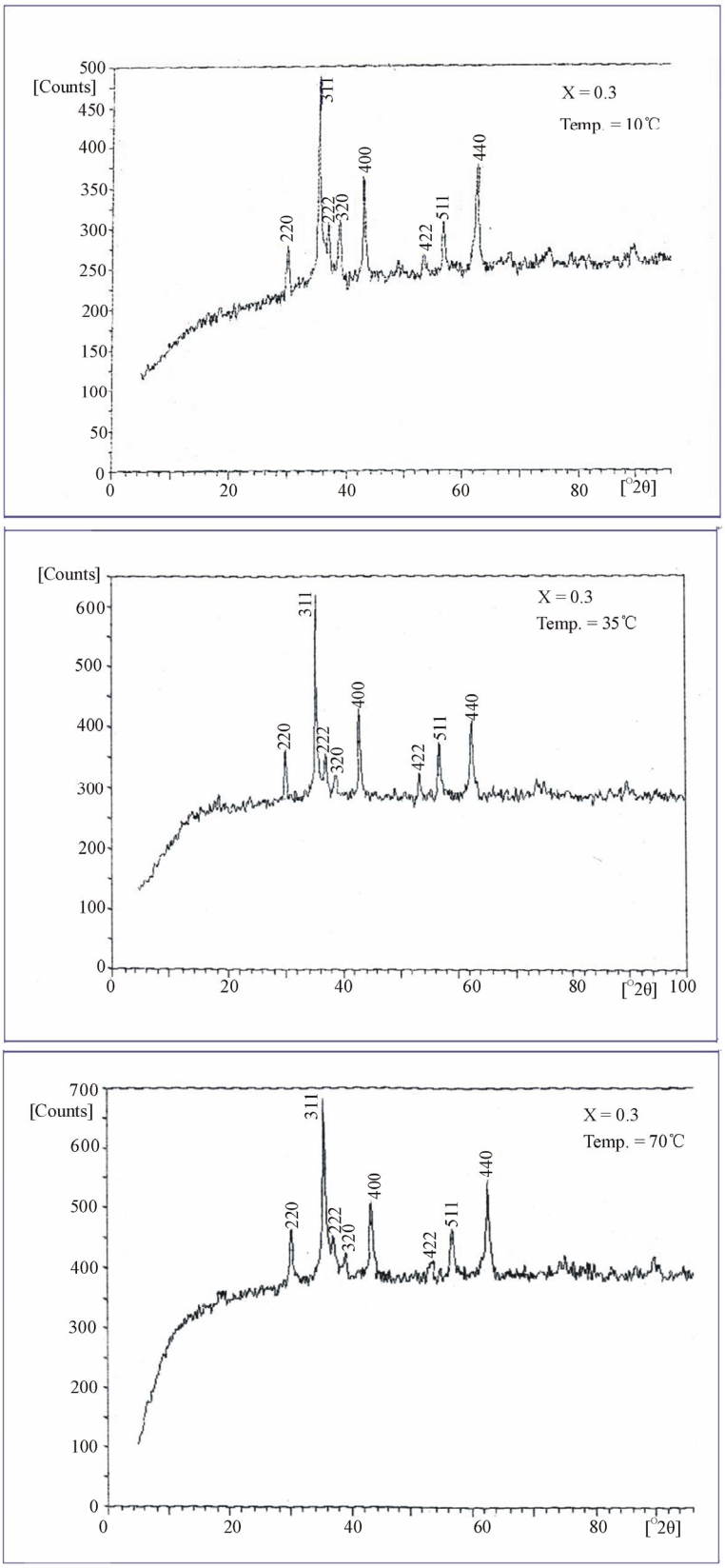


Figure 1. Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.3.

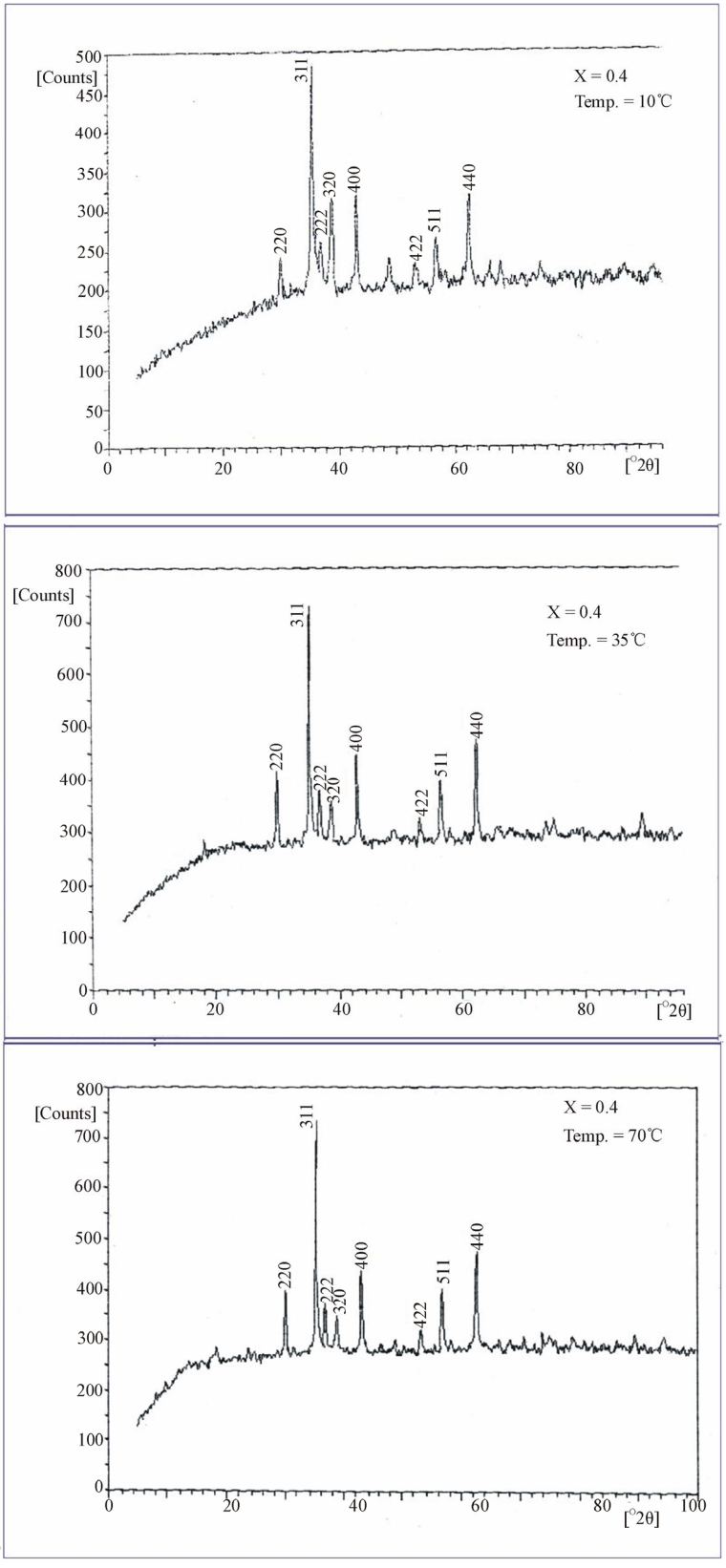


Figure 2. Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.4.

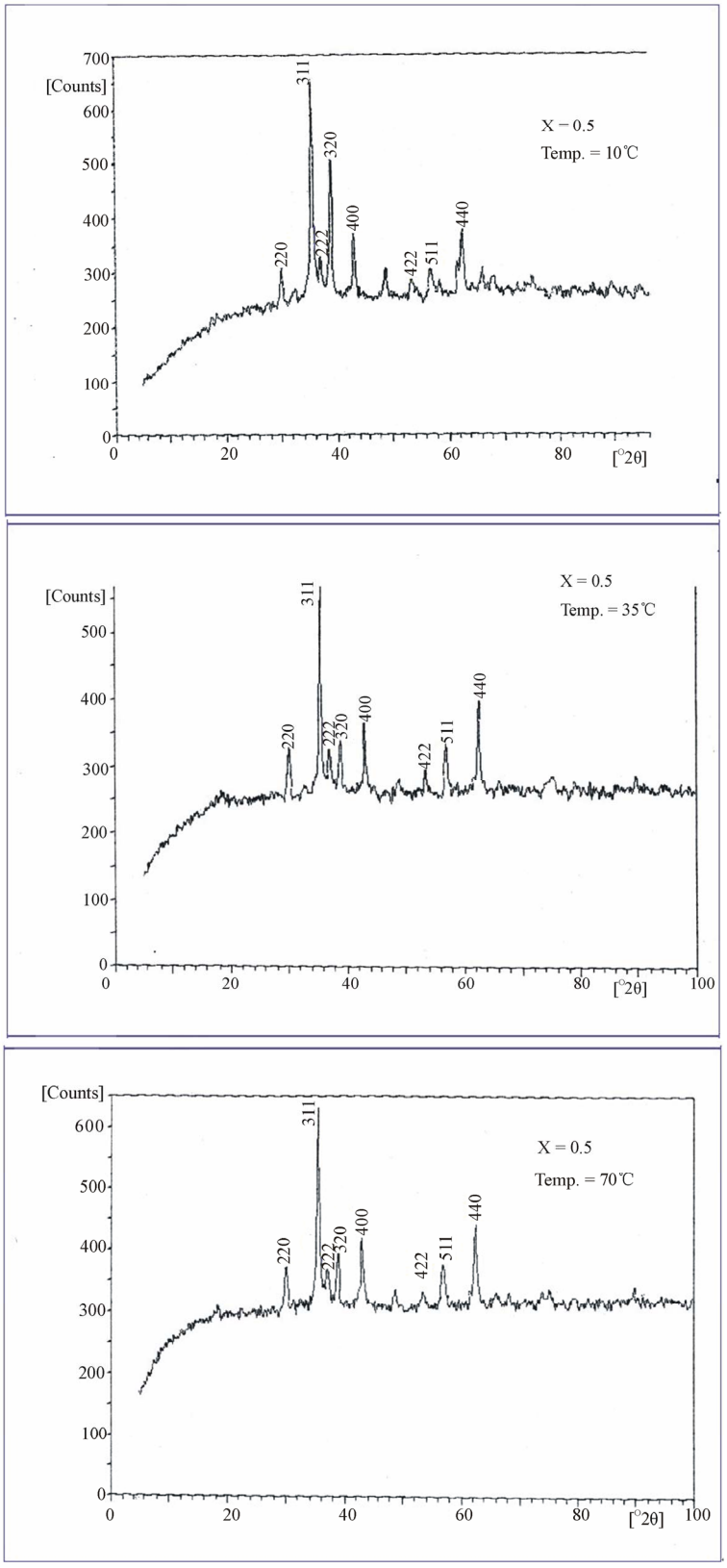


Figure 3. Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.5.

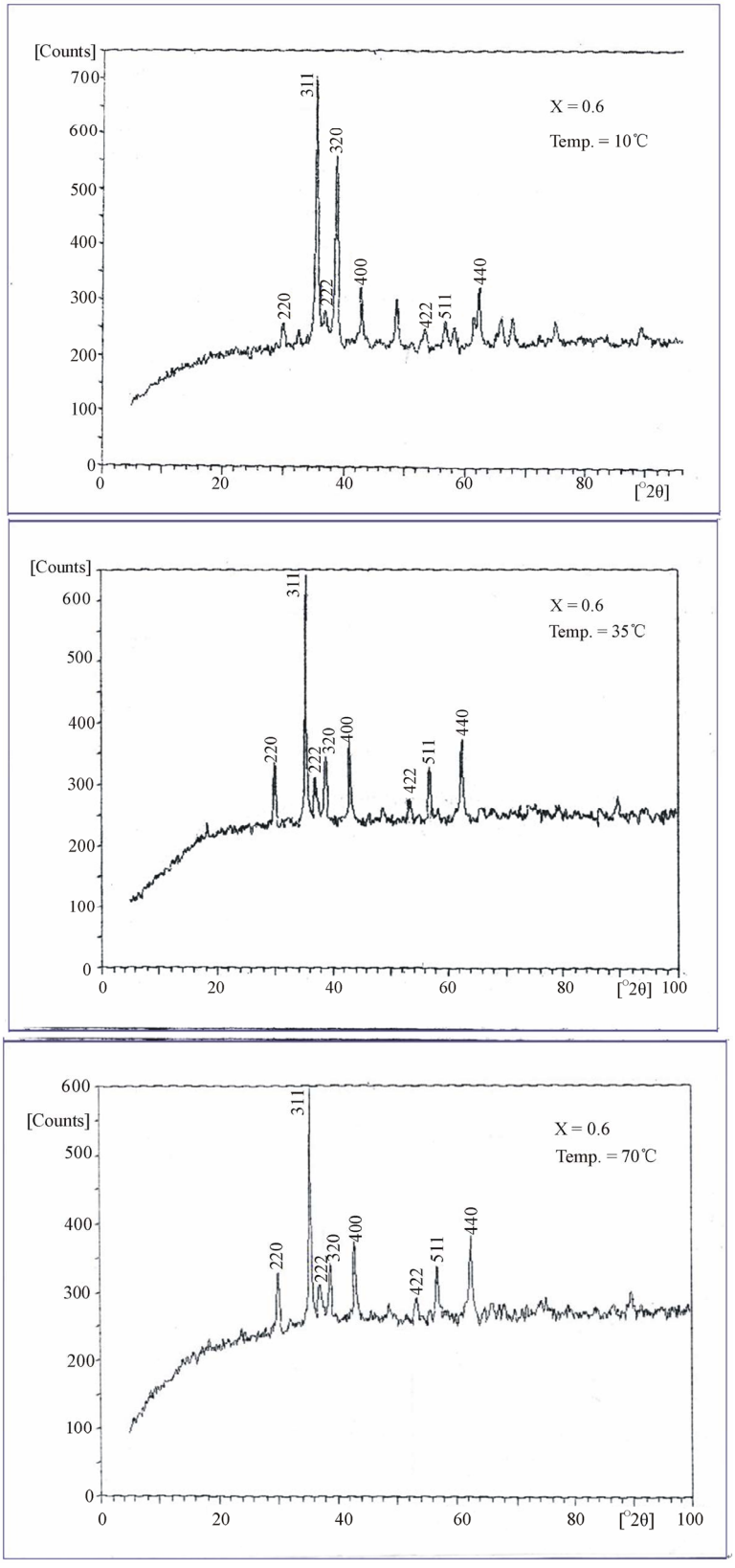


Figure 4. Variation of most intense (311) peak with temperature of chemical reaction for the composition x = 0.6.

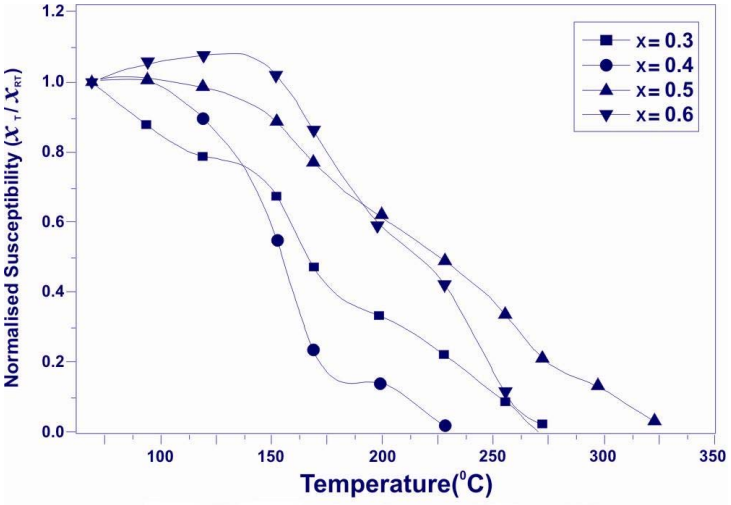


Figure 5. Variation of normalized AC susceptibility for compositions x = 0.3, x = 0.4, x = 0.5 and x = 0.6 at reaction temperature 10˚C.

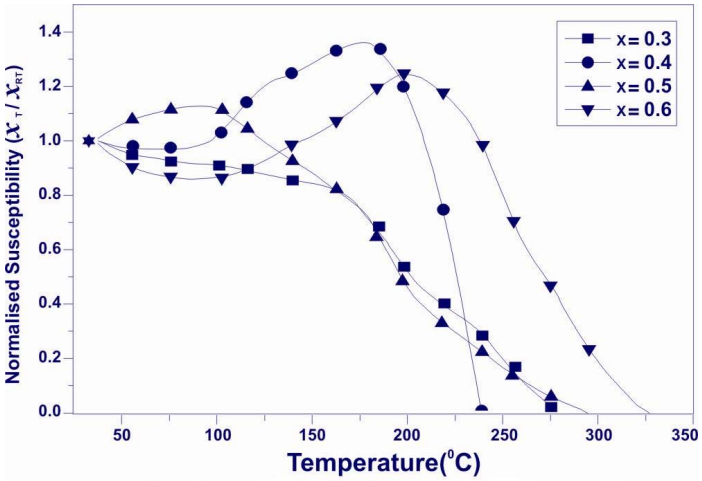


Figure 6. Variation of normalized AC susceptibility for compositions x = 0.3, x = 0.4, x = 0.5 and x = 0.6 at reaction temperature 35˚C.

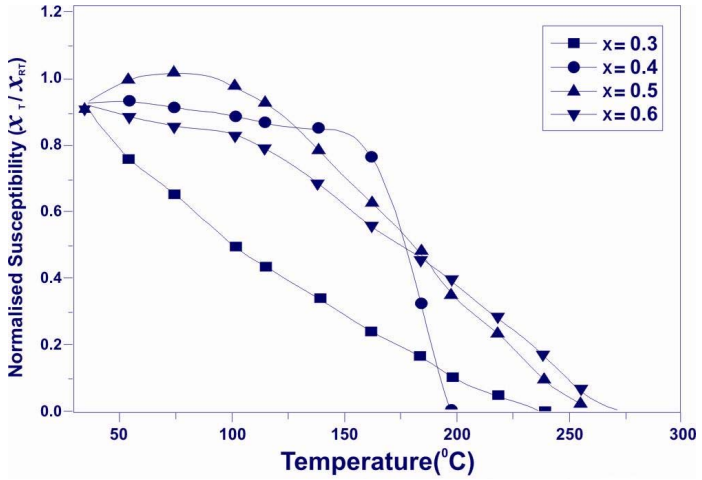
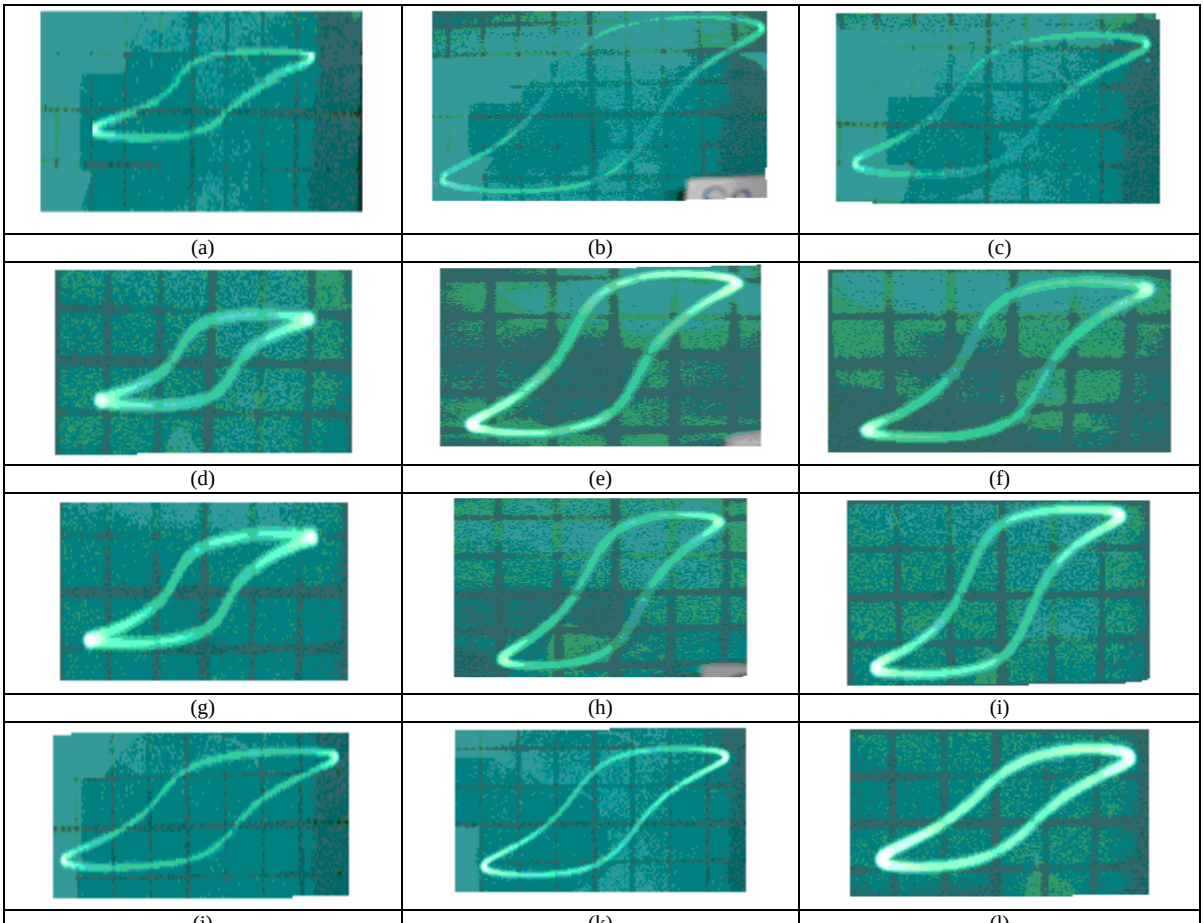
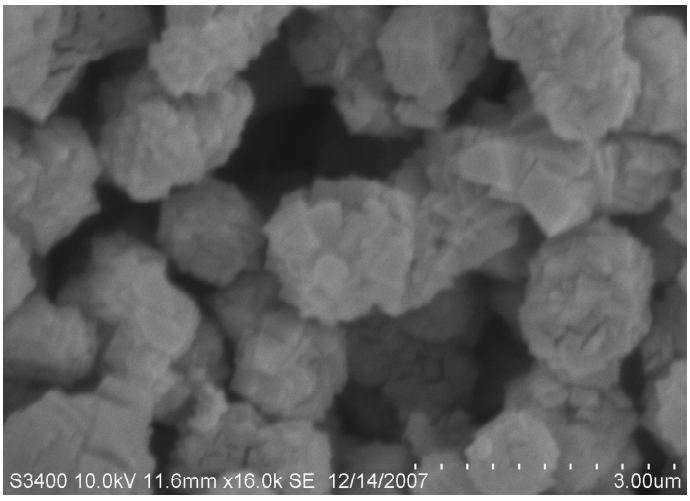


Figure 7. Variation of normalized AC susceptibility for compositions x = 0.3, x = 0.4, x = 0.5 and x = 0.6 at reaction temperature 70˚C.

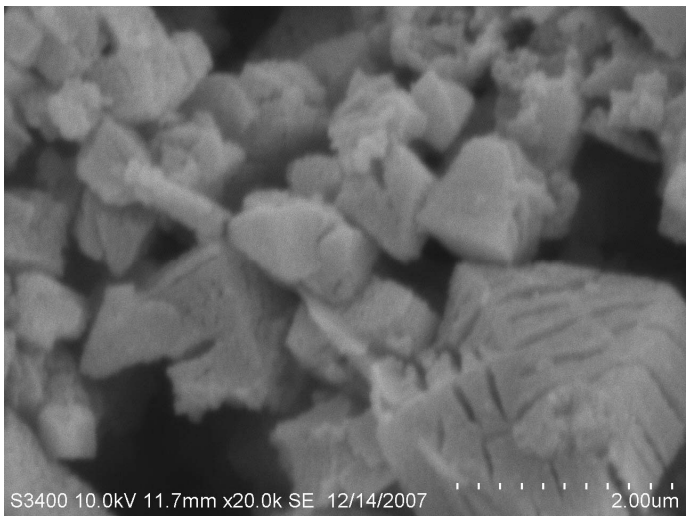


Temperature	X = 0.3	X = 0.4	X = 0.5	X = 0.6
10˚C	a	d	g	j
35˚C	b	e	h	k
70˚C	c	f	I	l

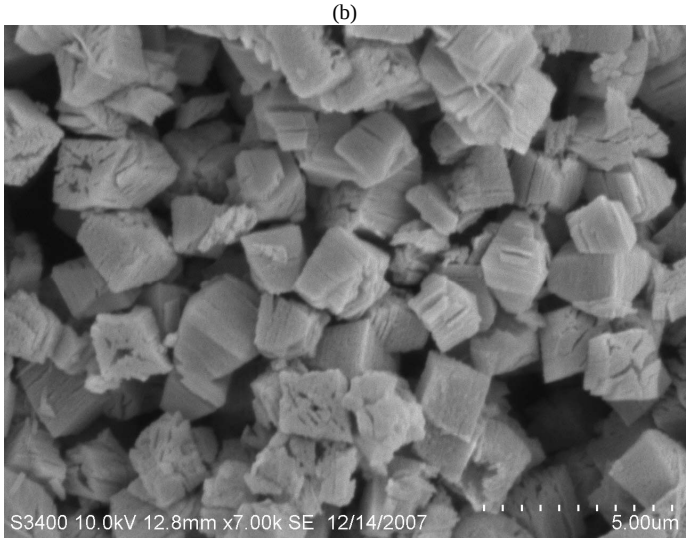
Figure 8. The hysteresis loops for compositions x = 0.3, x = 0.4, x = 0.5 and x = 0.6 at reaction temperatures 10˚C, 35˚C and 70˚C.



(a)

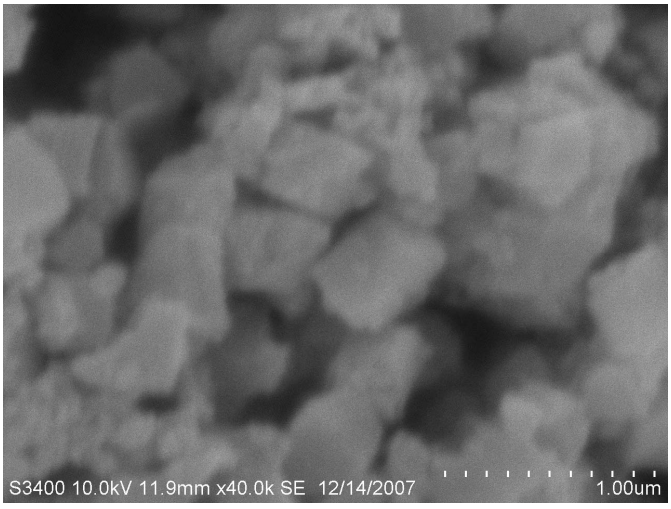


(b)

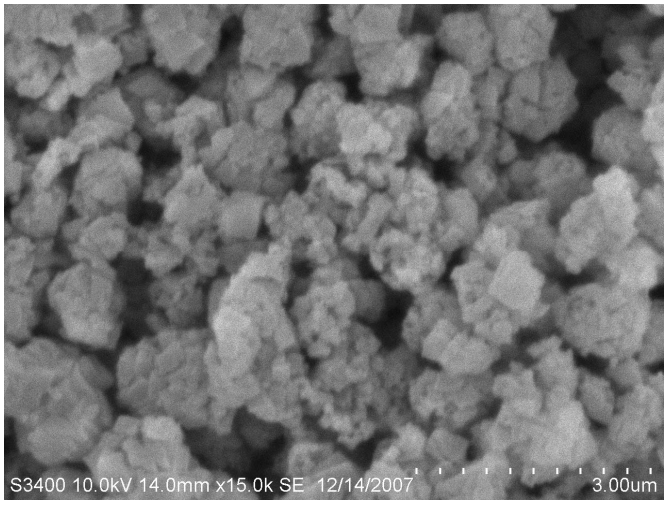


(c)

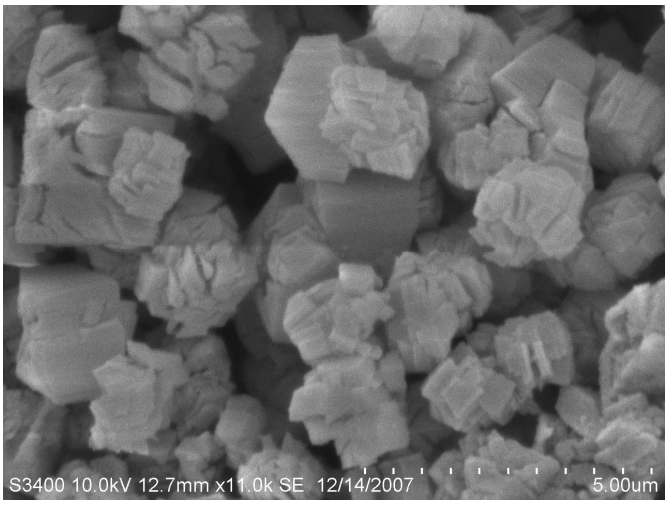
Figure 9. SEM micrographs for x = 0.4 at reaction temperatures (a) 10˚C, (b) 35˚C and (c) 70˚C.



(a)



(b)



(c)

Figure 10. SEM micrographs for x = 0.5 at reaction temperatures (a) 10˚C, (b) 35˚C and (c) 70˚C.

Table 1. Variation of magnetic properties with composition and chemical reaction temperature.

Temperature of reaction (˚C)	Composition parameter x	Ms (emu/gm)	Magnetic moment (μ_B)	Retentivity (emu/gm)	Curie Temperature (˚C)	Grain size (μm)
10	0.3	32.06	1.00	20.04	180	-
	0.4	20.25	0.63	14.17	120	0.6
	0.5	28.57	0.89	22.85	220	0.4
	0.6	28.51	0.67	17.59	175	-
35	0.3	42.97	1.33	35.29	260	-
	0.4	50.44	1.57	38.95	220	1.0
	0.5	46.18	1.43	32.98	260	0.6
	0.6	38.17	1.21	27.43	290	-
70	0.3	47.02	1.46	37.12	220	-
	0.4	51.05	1.58	39.03	180	1.95
	0.5	46.07	1.43	35.83	250	1.5
	0.6	37.09	1.15	28.53	260	-

ties, indicating the effect of chemical reaction history on the properties of ferrites. The temperature of chemical reaction may conveniently be used to synthesize ferrites with suitable properties.

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