



Identification of a Super Paramagnetic Phase of Titanium Substituted Mn-Zn Ferrites and Its Magnetic and Mossbauer Studies

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Authors' contributions

This work was carried out in collaboration between all authors. Author DJS managed the literature searches, the experimental process, wrote the protocol and wrote the first draft of the manuscript. Author NVN designed the study and helped the analyses of the study performed the spectroscopy analysis and author JI helped in every stages of the experiment and its analyses leading to this paper. All authors read and approved the final manuscript.

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ABSTRACT

The magnetic and Mossbauer studies were carried out in $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with $x=0.10, 0.15, 0.20$. The addition of Ti^{4+} induces considerable improvements of properties such as linear dependence of permeability versus temperature, Curie temperature, isomer shift, hyperfine interactions etc. Samples with $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ for $x=0.10, 0.15, 0.20$ were prepared by usual solid-state reaction method. To achieve equilibrium between the magnetic and core loss properties Titanium is introduced into the base composition of MnZn ferrite. A sublattice assigned to $Ti^{4+}Fe^{2+}$ pairs appeared in the Mossbauer spectra gave information on the local surroundings of iron ions. Increasing of Ti^{4+} shifts secondary maximum of permeability (SMP) to higher

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temperatures is in agreement with the hyperfine magnetic fields observed. The hyperfine magnetic field and electric quadrupole splitting decreases with the addition of Ti. The conduction mechanism is due to hopping of small polarons between Fe^{2+} and Fe^{3+} .

Keywords: Mössbauer; magnetic; isomer shift; permeability; hyperfine magnetic fields; superparamagnetic phase.

1. INTRODUCTION

The properties of ferrites are very sensitive when proper substitutions are done. Instruments working in high frequency are needed in this fourth generation age. These ferrites are widely used in RF range of communication. Substitution of Titanium increases high frequency response of ferrites. This has gained considerable application in recent years because of Giga hertz range applications at present. The addition of titanium produce dilute spin glass behaviour in ferrites. This can enhance the frequency range of Mn-Zn ferrites. Since titanium occurs in various oxidation modes it can be substituted for Fe. The magnetic properties of the ferrites are sensitive to the chemical composition, grain size, sintering temperature, rate of cooling, type and amount of additive etc. Soft ferrites are used in many electronic devices due to their electric and magnetic properties. Manganese zinc ferrites [1] belong to the group of soft ferrite materials with high magnetic permeability and low losses. Non magnetic ions in ferrites are found to change their electric and magnetic properties [2]. Ferrites with the spinel structure or magnetic materials, magnetic ceramics have received special attention as a result of chemical stability as well as high electrical resistivity [3,4]. Ferrites can be represented by the chemical formula AB_2O_4 , where A and B denote metal cations on the tetrahedral (A) and octahedral (B) sites, respectively. The magnetic properties of the spinel ferrite materials originate from the antiferromagnetic coupling between the octahedral and tetrahedral sub-lattices [5]. The magnetic properties of spinel ferrites can be changed scientifically by altering the characteristics of the divalent Me^{2+} cations (Me=Co, Mn, Ni, Zn, Ti, etc.) without changing the spinel crystal structure. Among different ferrite materials, spinel-type ferrites are attractive for the bio-medical application as a result of suitable Curie temperature, magneto-crystalline anisotropy, moderate saturation magnetization and superparamagnetic behavior at room temperature [6]. In the manufacture of MnZn ferrites, titanium dioxide is a well known additive. Nanoparticles of manganese zinc ferrites exhibit

some unusual properties, for example, enhanced coercivity, modified saturation magnetization, super paramagnetism, and metastable cation distributions [7]. These nanoparticles have wide applications in heat transfer devices, drug delivery systems, and medical diagnostics, that is, especially in cancer treatment, and so forth [8,9]. Mn-Zn ferrites possess a spinel structure in which Mn^{2+} , Zn^{2+} , and Fe^{3+} cations are distributed among two interstitial tetrahedral (A-) and octahedral (B-) sites. In general, spinels are classified as normal, inverse, and mixed. In most cases, Mn^{2+} ions tend to Control electrical conductivity of MnZn ferrites in high frequency applications because of eddy current damping losses. Stijntjes et al. [10] and Hanke [11] reported that the substitution of Ti^{4+} contributes by a positive value to the anisotropy constant K_1 . The result of spin-orbit coupling is large and an appreciable contribution to the magnetic anisotropy is found for octahedral Fe^{2+} ions. The present work investigates the effect of Ti^{4+} substitution in $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ system using Mossbauer spectroscopy in correlation with the permeability measurements.

2. EXPERIMENTAL DETAILS

Ferrite samples having the compositional formula $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ with $x=0.10, 0.15, 0.20$ was prepared by solid state reaction method. The initial ingredients MnO, ZnO, TiO_2 , Fe_2O_3 were weighed and mixed in correct Stoichiometric ratio and grinded for ten hours using an agate mortar. Resulting mixture was air dried and pre sintered and grinded for three hours. Granulated powder was then pressed into pellets and toroids. Final sintering was done at 1150°C for 20 hours followed by slow cooling to room temperature. Structural characterization of the samples was carried out by the X-ray diffraction, SEM and EDX analyses [12]. Magnetic measurements were performed at room temperature using vibrating sample magnetometer (Lakeshore 7304) for all samples. The surface morphology and grain structure were studied from the SEM micrograph. The Mossbauer spectra of the samples were recorded at room temperature with Co^{57} source

in rhodium acceleration mode. The computed parameters were obtained by the least squares method.

3. RESULTS AND DISCUSSION

The magnetization measurements at room temperature for $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ for different Titanium concentrations are given in Fig. 1 from the experimental data obtained.

Magnetization increases in applied magnetic field and variation decreases, nearing to saturation value for higher fields. The Fe^{3+} magnetic hyperfine field varied with titanium content. Because of the electron hopping between multiple valence ions, the iron could be present sometimes as Fe^{3+} (magnetic ion) in the nearest neighborhood of the trivalent ion. The saturation magnetization decreases with the increase in Ti

concentration. The low values of coercivity and resonant magnetization indicates the presence of super paramagnetic phase, neither coercivity nor remanence were observed [13-15]. M–H curves indicate the superparamagnetic nature of the particles by the absence of saturation, remanent magnetization, and coercivity. The non-saturation of the magnetization even at the highest applied field also implies the presence of the single domain particles in the superparamagnetic state. The magnetization studies show a decreasing trend with the increase in Titanium concentration. The similarity in the variation of saturation magnetization and initial permeability with the concentration of Ti supports the dependence of initial permeability on saturation magnetization. The decrease in initial permeability can also be due to the effect of anisotropy.

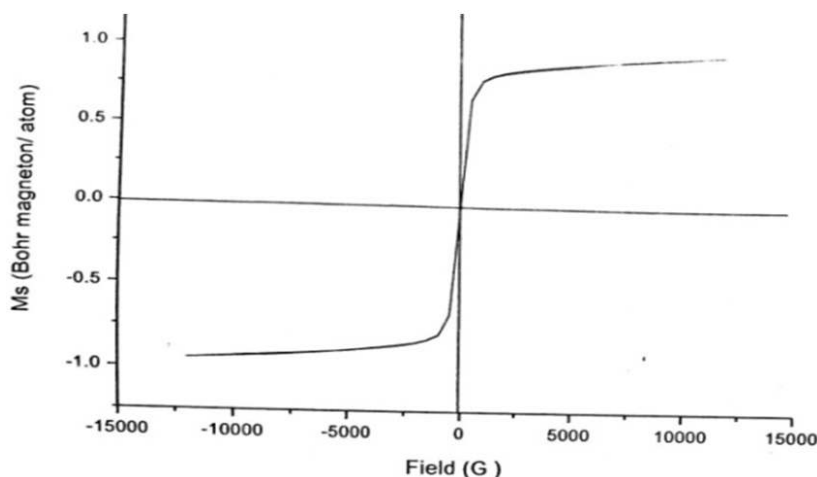


Fig 1.a Variation of Magnetisation with field of $Mn_{0.9}Zn_{0.2}Ti_{0.1}Fe_{1.8}O_4$

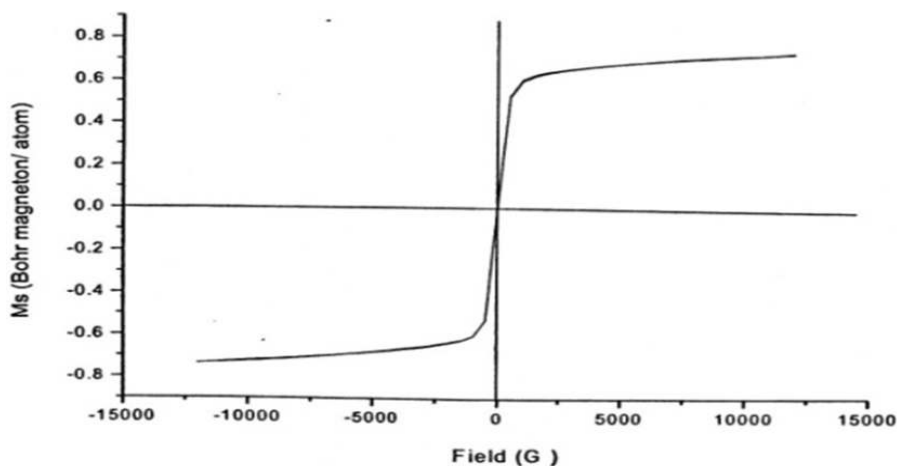


Fig 1.b Variation of Magnetisation with field of $Mn_{0.95}Zn_{0.2}Ti_{0.15}Fe_{1.7}O_4$

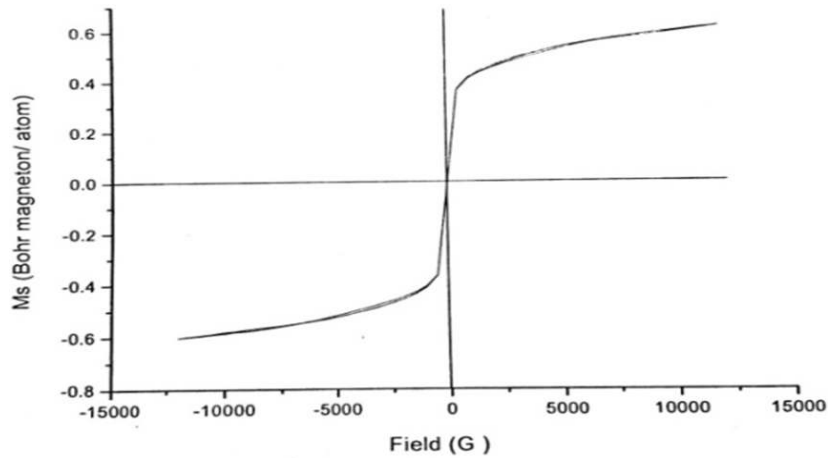


Fig 1.c Variation of Magnetisation with field of $Mn_1Zn_{0.2}Ti_{0.2}Fe_{1.6}O_4$

Fig. 1. Magnetization measurements at room temperature for $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ for different titanium concentrations
 a) $x=0.10$, b) $x=0.15$, c) $x=0.20$

Visser and Johnson [16,17] have developed a non-magnetic grain boundary model to explain the corresponding change in initial permeability. There can be an enrichment of Titanium ions near the grain boundary causing a non-magnetic segregation at the grain boundary. Hence the anisotropy influences the decrease in initial permeability with the increase in titanium concentration (Fig. 2). Permeability calculated from the data measured at various temperatures is plotted in the Fig. 2.

Mossbauer spectrum gives information about the oxidation state of Mossbauer atom, the symmetry of the immediate environment of the Mossbauer

atom and the magnetic interaction between the Mossbauer nuclei. The Mossbauer data of samples were stored in a multichannel analyzer. The Mossbauer spectrum (Fig. 3) clearly shows well defined sextets due to magnetic hyperfine interaction and a doublet due to superparamagnetic component. The Mossbauer data suggest the presence of Ti^{4+} , Fe^{2+} pairs. The iron could be present sometimes as Fe^{3+} and titanium as Ti^{3+} in the nearest neighbourhood of the trivalent iron, varying its magnetic hyperfine field. It is because of electron hopping between multiple valence ions. From the spectrum data we have calculated hyperfine magnetic fields (HMF), Quadrupole splitting (QS), Isomer shift.

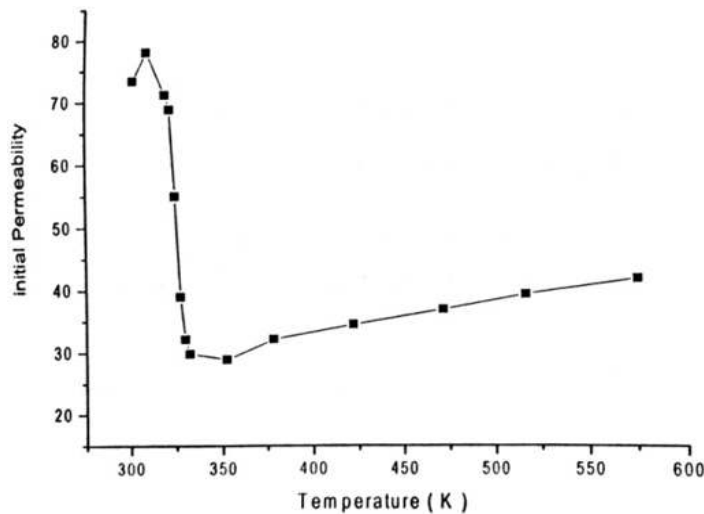


Fig 2.a Variation of initial permeability with temperature of $Mn_{0.9}Zn_{0.2}Ti_{0.1}Fe_{1.8}O_4$

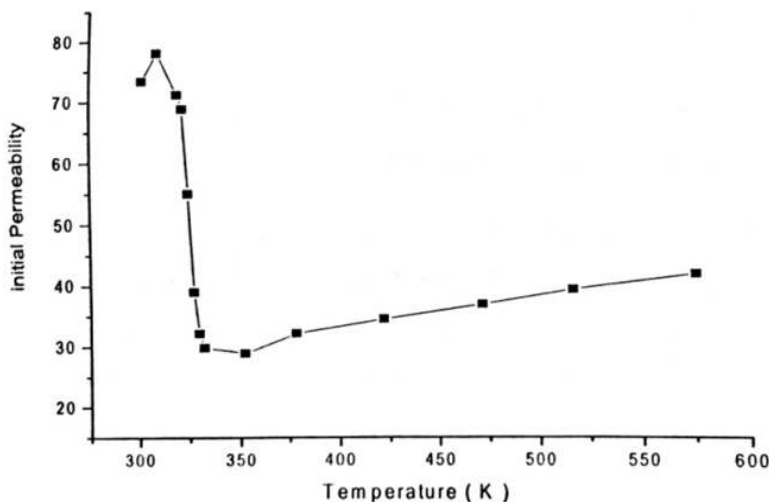


Fig 2.b Variation of initial permeability with temperature of $Mn_{0.95}Zn_{0.2}Ti_{0.15}Fe_{1.7}O_4$

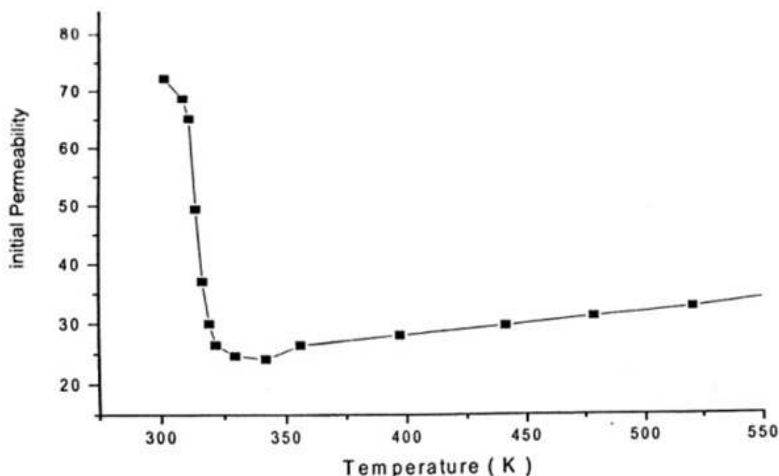


Fig 2.c Variation of initial permeability with temperature of $Mn_1Zn_{0.2}Ti_{0.2}Fe_{1.6}O_4$

Fig. 2. Variation of initial permeability with titanium concentration
 a) $x=0.10$, b) $x=0.15$, c) $x=0.20$

The increase in titanium concentration decreases the HMF of A and B sites as shown. As x increases the iron ratio decreases indicating that the octahedral sites are occupied in a larger proportion by $Ti^{4+}Fe^{2+}$ pairs.

The electric quadrupole splitting decreases with increase in titanium concentration. It is a measure of deviation of structure from cubic symmetry. The area of the doublet increases with increase in titanium concentration. It indicates the superparamagnetic phase in the sample. So this decrease is due to the variation in super

exchange interaction with the migration of Zn^{2+} ions from B-site to A-site [18].

Mossbauer studies also show that isomer shift (mm/s) (Fig. 4) at B-site increases with increase in titanium concentration. The isomer shift values of A-site is due to Fe^{3+} and in B-site can be a mixed valency of Fe^{3+} and Fe^{2+} [19,20]. This shift represents overlap of the electronic wave function with the probe site nucleus. The redistribution of electronic charges in the orbitals may also contribute to the observed increase in isomer shift [21].

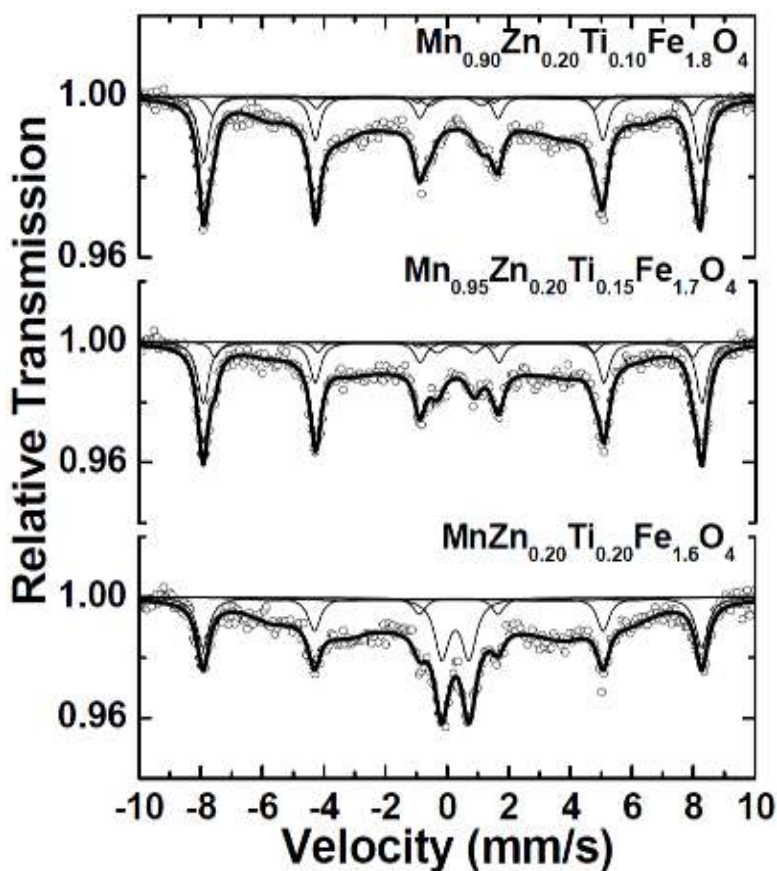


Fig. 3. Mossbauer spectrum of $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ for different titanium concentrations, with $x=0.10, 0.15, 0.20$

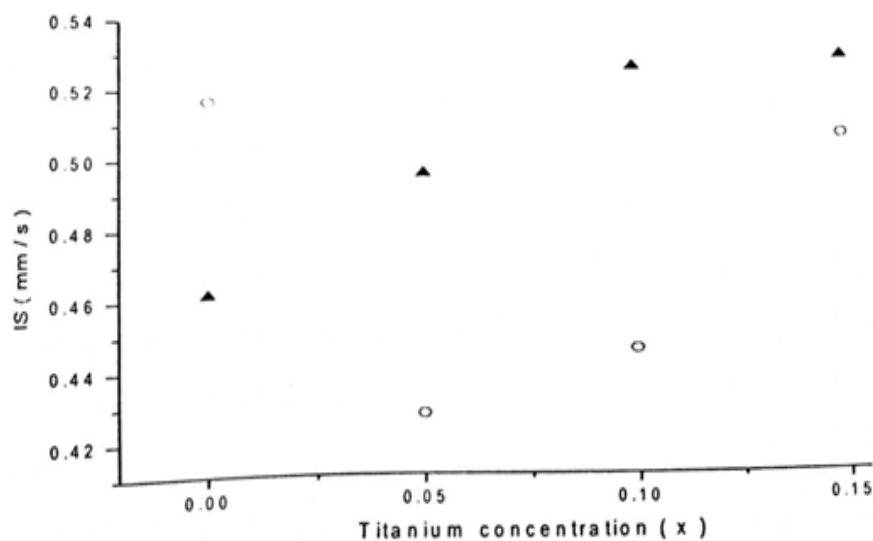


Fig. 4. Plot of isomer shift with titanium concentration of $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ with $x=0.10, 0.15, 0.20$

Table 1. Mossbauer data

Sample	Γ (mm/s)	Δ (mm/s)	Δ (mm/s)	BHF (T)	AREA (%)
$Mn_{0.9}Zn_{0.2}Ti_{0.1}Fe_{1.8}O_4$	0.54±0.1	0.40±0.03	1.68±0.06	-	04.204
	2.37±0.3	0.58±0.08	-.11±0.10	25.39±0.65	38.101
	1.52±0.3	0.35±0.07	0.18±0.15	38.00±0.58	15.265
	0.40±0.0	0.35±0.01	-0.09(f)	48.34±0.20	08.971
	0.41±0.0	0.39±0.00	-.23± 0.01	49.99±0.05	33.458
$Mn_{0.95}Zn_{0.2}Ti_{0.15}Fe_{1.7}O_4$	0.53±0.09	0.39±0.05	1.20±0.05	-	05.459
	2.87±0.68	0.58(f)	-0.13(f)	22.55±0.86	39.629
	1.75±0.8	0.38(f)	-0.19(f)	37.38±1.25	10.030
	0.35±0.08	0.37±0.02	-0.07(f)	48.10±0.16	06.694
	0.42±0.02	0.40±0.02	-.22± 0.01	50.20±0.04	38.186
$Mn_1Zn_{0.2}Ti_{0.2}Fe_{1.6}O_4$	0.55±0.03	0.39±0.01	0.88±0.01	-	18.719
	2.28±0.55	0.47(f)	-0.21± 0.12	23.62±0.92	31.558
	1.99±0.42	0.33(f)	-0.11±0.12	36.09±0.79	25.090
	0.48±0.02	0.39±0.01	-0.20±0.02	50.19±0.05	24.631

4. CONCLUSION

The Mossbauer spectra of titanium doped Mn-Zn ferrites are fitted with two sextets corresponding to two non-equivalent sites and one doublet due to the superparamagnetic phase. The sextet with larger BHF is due to the octahedral Fe^{3+} ions and the pattern with the smaller field arises from Fe^{3+} ions at the tetrahedral site. The BHF of A and B sites decrease with the increase in titanium concentration. The doublet can be due to the quadrupole splitting of the nuclear level of B-site caused by the superparamagnetic components in the sample. The hyperfine magnetic field and electric quadrupole splitting decreases with the addition of Ti. The conduction mechanism is due to hopping of small polarons between Fe^{2+} and Fe^{3+} . From investigations showed that the addition of Ti^{4+} enhanced the properties of the samples prepared. In addition, the increase in Ti^{4+} causes a shift in the secondary maximum permeability (SMP) to higher temperatures. Higher frequencies (up to 100GHz) and higher bandwidths (mm wave range) are used in microwave technology. Ferrite elements are widely used in microwave devices, isolators, circulators, phase shifters etc. Due to very high specific resistance, remarkable flexibility in tailoring the magnetic properties, price and performance considerations make Ferrites the first choice materials for microwave applications. However the frequency range of operation, the power handling capacity and the temperature sensitivity of ferrite devices should be improved. Magnetic properties of high permeability ferrites with titanium ions confirm that Ti^{4+} ions make pairs with Fe^{2+} ions and occupy the octahedral sites in the crystalline lattice.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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