CHAPTER 5: Effect of Crystal Field and Magnetic Perturbation on Spin Dynamics of $Dy_2Ti_2O_7$

5.1 Introduction

In chapter 3 and 4, nature and origin of multiple dielectric relaxations of $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ have been analysed and shown the role of crystal field and magnetic 3in-1out/1in-3out spin structure in the generation of dielectric relaxations. This Ising nature of RE spin is responsible for the magnetic frustration in this compound. As explained in the chapter 1, In case of $Dy_2Ti_2O_7$, ac-susceptibility studies show two successive robust magnetic freezing at ~16 K and ~ 4 K temperature, termed as single spin and spin ice freezing, respectively [41], [61], [64]. It has further been reported by Ruminy et al. that Ising spin flipping mechanism is phonon mediated in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ [52]. Signature of this phonon mediated spin flipping mechanism is observed in low temperature dielectric and pyroelectric studies as well [88], [90], [93]. In these cubic pyrochlore lattices, primary electronic order parameters are coupled with secondary structural order parameters of the oxygen sites [123]. It indicates that low-temperature magnetic properties are mainly affected by the magnetic perturbation instead of structural distortion. Studies performed on hybrid RE titanates support this argument and show existence of spin-spin correlations affecting both the magnetic freezing observed at ~16 K and ~ 4 K [67], [68]. However, previous studies based on broad range non-magnetic dilution suggest that observed ~16 K spin freezing is a thermally activated single spin process, which gets affected by the local crystal field environment rather spin-spin correlations [41], [61], [65]. These studies have been performed at higher substitution, due to which real mechanism cannot be concluded decisively. For small substitutions, B site

doped Dy$_2$Ti$_{2-x}$Fe$_x$O$_7$ have been studied by Liu et al, where it has been suggested that the both Dy-Fe interaction and crystal electric field plays important role in the dynamic freezing of the spins at lower temperatures [134]. Pyrochlore A$_2$B$_2$O$_7$ can also be termed as A$_2$B$_2$O$_6$O' because of the site sensitivity of the oxygen sublattice, which is reflected in dielectric measurements of selective substitution in Ho$_2$Ti$_2$O$_7$ and explained in sections 3.2.2.1 and 3.2.2.2. The pyrochlore structure can further be broken in to B$_2$O$_6$ unit formed by a corner-shared BO$_6$ octahedra and an A$_2$O' unit formed by corner-shared A$_4$O' tetrahedral [135], [136]. Crystallographically O' oxygen is termed as O2 as well. When the lattice is distorted using a substituent, its oxygen sublattice surrounding A (16d) or B (16c) site get affected. This in turn decide the dominance of underlying phenomenon, which decides the dynamic freezing of spins at low temperatures [17], [137]. Out of local crystal field distortion and spin-spin interaction, which process plays more significant role has been investigated in this chapter. In order to investigate that which perturbation (structural or magnetic) plays more significant role, we have studied the A-site Fe substituted Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ polycrystalline compound in terms of structural and magnetic distortions. The study performed for a narrow range of dilution $0 \leq x \leq 0.15$ and discussed as follows.

5.2 Results and Discussion

5.2.1 Dielectric properties of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$

Temperature-dependent dielectric permittivity and loss tangent measured at different frequency for x= 0, 0.05, 0.1 and 0.15 compositions are shown in figure 5.1. It has been found that, for substituted compositions, a very broad relaxation occurs in contrast to the well defined distinct relaxations observed at 90K and 36K for x = 0. On increasing Fe concentration, this relaxation becomes pronounced with large frequency dispersion.

Furthermore, at lower temperature (<50 K), for x= 0.05 and 0.1 compositions a sharp decrease in the dielectric permittivity takes place whereas for x= 0.15 composition, it gradually increases. In these cubic materials having Fd$\bar{3}$m space group dielectric permittivity is originated by the orientational polarization of lattice. At higher temperatures, polar lattice vibrations are larger, which get slowed down with decreasing temperature due to which an increase in the dielectric permittivity takes place [114], [138].
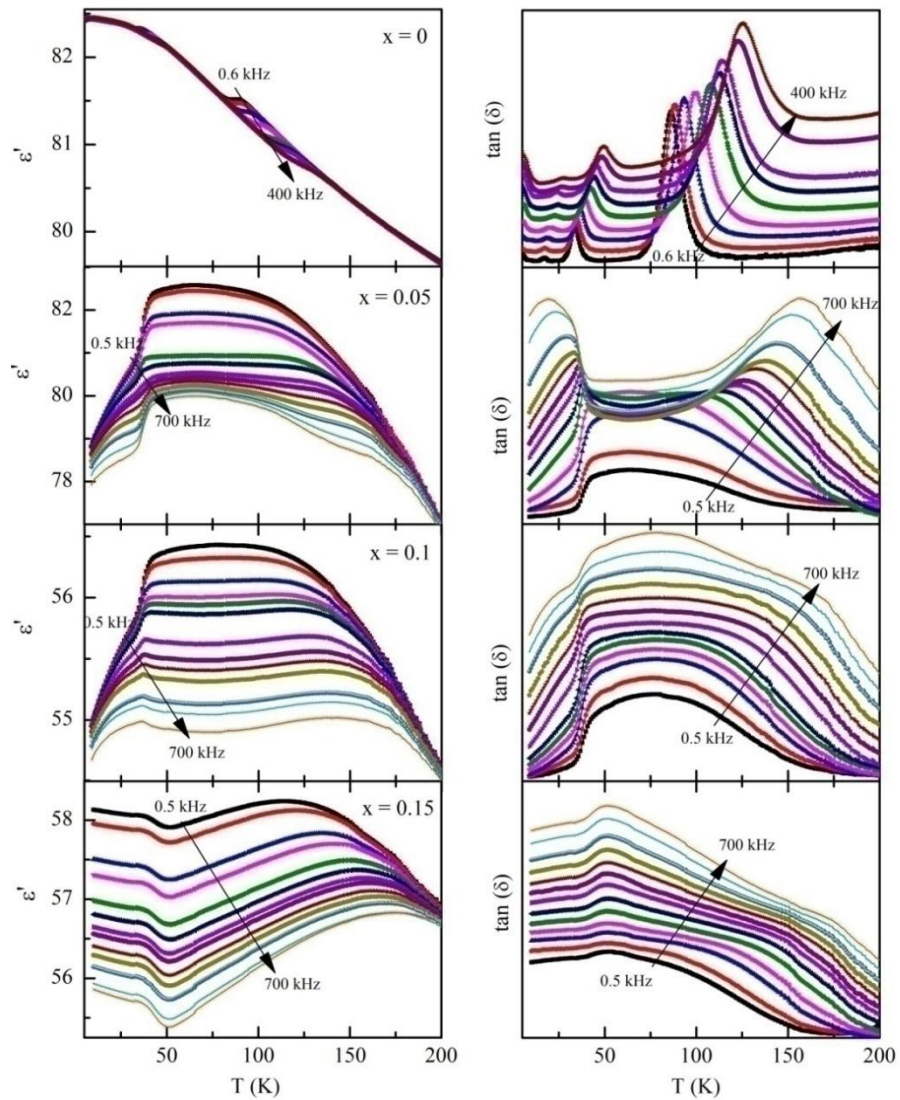

Figure 5.1: Temperature dependence of the dielectric permittivity and loss spectrum of polycrystalline Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ compound for (a) x= 0 (b) x= 0.5 (c) x= 0.1and (d) x= 0.15 compositions at various frequencies.

As discussed in chapter 3, both 90 K and 36 K dielectric relaxations in DTO are distinctly related to the distortion at the O1 and O2 site oxygen positions. The local motions of these distorted oxygen ions have larger amplitude than the polar lattice vibrations. On decreasing temperature, because of the larger amplitude, oxygen ions no longer follow the applied time varying field, resulting a relaxation phenomena to takes place in the dielectric permittivity measurement [114], [138]. On Fe substitutions, due to its smaller ionic size than Dy, it generate a random static displacive disorder of multiple amplitude of polar lattice vibrations [114]. In order to study the role of Fe substitution, structural analysis has been performed in $Dy_{2-x}Fe_xTi_2O_7$ as explained here.

5.2.2   Structural analysis

The diffraction pattern shown in the figure 2.3 in chapter 2 has been analyzed using Rietveld refinement. The refinement was done using space group $Fd\bar{3}m$ by considering Dy^{3+}, Ti^{4+} and O^{2-} ions are at the 16d, 16c and 48f site (O1) & 8b site (O2) crystallographic sites respectively. Figure 5.2 shows the Rietveld fit of the HRXRD pattern of $Dy_{2-x}Fe_xTi_2O_7$ samples in the measured 1.5 to 7.1 Å^{-1} Q range. The obtained fit is remarkably good, indicating that the samples are defect free and having intended stoichiometry. Refinement by switching the Fe site from A to B has been also tried but due to insignificant difference of Fe and Ti atomic scattering factor no decisive conclusion has been made. However, the best fit was obtained when Fe has been confined to A-site only. Inset of the figure 5.2 shows a gradual shifting in the (844) peak position towards the higher Q side with composition. The shifting in the x-ray diffraction peaks towards the higher Q side indicating the gradual decrease in the lattice constant with increasing Fe substitution. This observation is further confirmed from the obtained values of lattice constant from the Rietveld refinement. The

obtained values of structural and fitting parameters are listed in table 5.1. Whereas, obtained values of bond lengths and bond angles with varying compositions are summarized in table 5.2.

Table 5.1: Composition, the length of unit cell volume, variable coordinate x in the 48f-site, reliable parameters (Rp, Rwp and Rexp) and goodness of fit χ^2.

Composition	a (Å)	x (48f)	Rp	Rwp	Rexp	χ^2
x= 0	10.1267(4)	0.326(1)	18.4	12.8	9.57	1.80
x= 0.05	10.1208(1)	0.328(1)	18.5	12.2	10.03	1.47
x= 0.1	10.1143(1)	0.328(1)	19.7	12.6	10.53	1.43
x= 0.15	10.1077(1)	0.328(1)	19.4	12.0	10.56	1.30

Table 5.2: Values of bond length and bond angle as obtained by the Rietveld refinement for $Dy_{2-x}Fe_xTi_2O_7$.

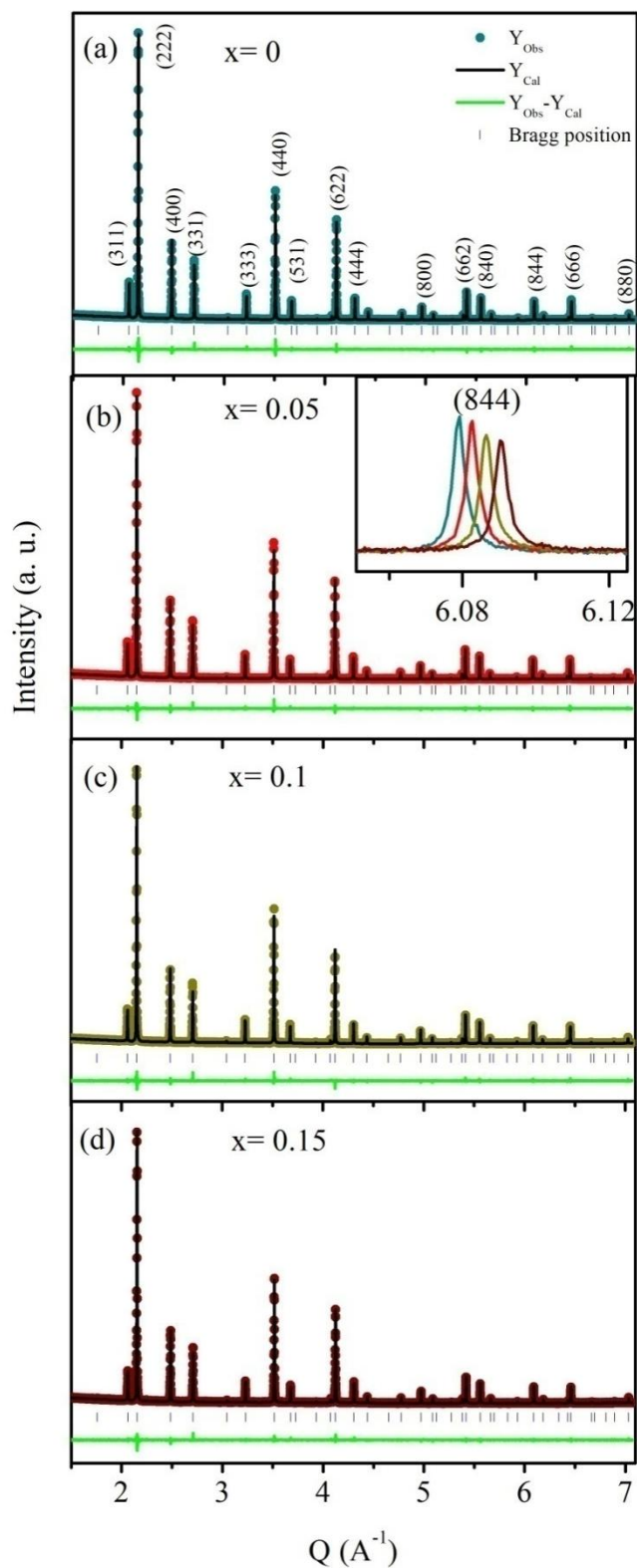| Composition	Bond length (Å)			Bond angle (^{0})	
	Dy/Fe-O2	Dy/Fe-O1	Ti-O1	O1-A-O1	O1-Ti-O1
x= 0	2.1925(0)	2.511(3)	1.949(1)	63.07(4)	84.74(1)
x= 0.05	2.1912(1)	2.496(3)	1.956(1)	63.27(5)	84.02(1)
x= 0.1	2.1898(1)	2.495(3)	1.954(1)	63.25(5)	84.09(1)
x= 0.15	2.1884(1)	2.494(3)	1.952(2)	63.24(5)	84.12(1)

Figure 5.2: High resolution x-ray diffraction pattern and Rietveld refinement of polycrystalline Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ compound for various compositions. Inset of figure 1(b) shows the systematic variation of lattice constant.

It can be clearly seen from the table 5.2 that Fe substitution produced significant static displacive structural distortion in the lattice. It has been found that nature of distortions at the O1 and O2 site of the oxygen positions are quite different. The magnitude of displacive disorder occurring at the O1 site (~0.68%) is significantly larger than that of the O2-site (~0.18%) for x= 0.15 composition. These results confirm that substituted Fe ion locally distorted the lattice mainly occurring at the Dy, O1 and O2 sites.

The magnitude of these random displacive disorders is getting increases with increasing Fe concentration. Structural analysis shows that the magnitude of disorder at O1 site oxygen position is larger than the O2 site. These analyses suggest that on increasing Fe substitution, 90 K dielectric relaxation become more pronounce in comparison to the 36 K dielectric relaxation. This could be the possible reason for the observed dielectric behavior of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$. These structural and dielectric observations suggest that Fe substitution will be significantly affecting the lattice geometry locally, which becomes pronounced with increasing Fe concentration.

5.2.3   Temperature dependent ac susceptibility of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$

To study the effect of Fe-substitution on the low temperature magnetic properties, temperature-dependence of the magnetic ac-susceptibility of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ has been measured. Figure 5.3 shows the temperature-dependent χ' and χ'' of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ measured at 1 kHz. It has been found that both ~16 K and ~4 K spin freezing in χ' and χ'' observed in the case of DTO disappeared for all the Fe substituted compositions. This is quite surprising because previous studies, based on broad range of non-magnetic and lower magnetic moment containing rare earth dilution, suggest that both freezing are robust in nature [41], [65], [67], [68]. The observed behavior in this case clearly indicates that Fe substitution is strongly

affecting both magnetic freezing. Such a sensitivity of spin dynamics can be associated either with alteration in crystal field acting on Dy^{3+} site or magnetic perturbations.
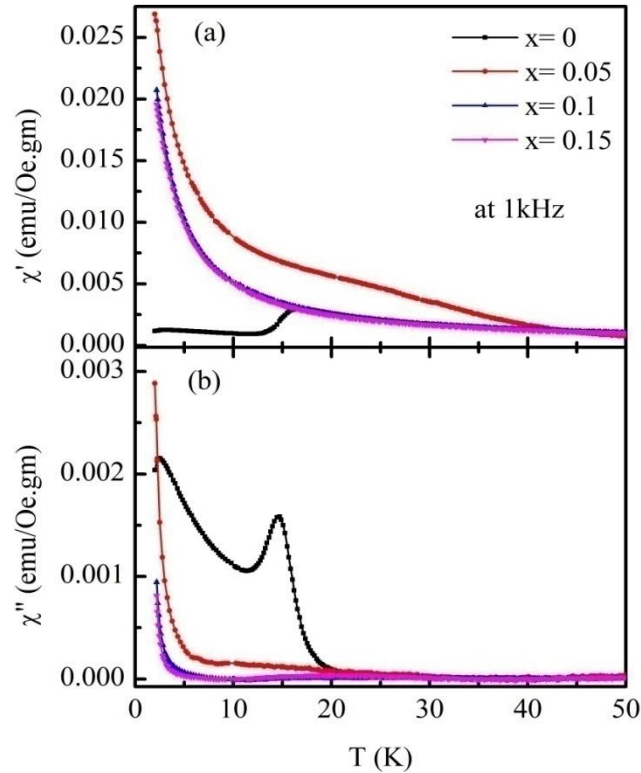

Figure 5.3: Real (a) and imaginary (b) part of magnetic ac-susceptibility verses temperature at 1 kHz frequency of polycrystalline Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$.

As discussed, substituted Fe ion can affect the magnetic behavior either through substitution induced structural distortions or via magnetic perturbation. In case of structural distortions, displacement in ionic position alters the crystalline electric field. This means that if any significant alteration in crystalline electric filed takes place, mainly crystal field acting on the Dy^{3+} site, it must modify the splitted electronic level of the Dy^{3+} ion in Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$. To investigate the effect of altered crystal field on the electronic level of the Dy^{3+} ion, optical UV-vis and Photo-Luminescence measurement has been performed. Since, these

measurements gives spectra associated electronic transition occurring from different electronic levels. It means that if any alteration in crystal field acting on Dy^{3+} site takes place it must be reflect in optical responses.

5.2.4   Optical analysis of $Dy_{2-x}Fe_xTi_2O_7$

5.2.4.1 **UV-vis absorption spectra**

To study the effect of Fe-substitution induced lattice distortions on crystal electric field acting on Dy^{3+} ion, UV-vis absorption spectra of $Dy_{2-x}Fe_xTi_2O_7$ has been recorded and shown in figure 5.4. Although this data is at room temperature, it is sufficient enough to give clue about the energy states of Dy^{3+} in $Dy_{2-x}Fe_xTi_2O_7$. It has been observed for Fe substituted compositions that peak intensity of some of the transitions gets increased without any significant change in the peak positions.
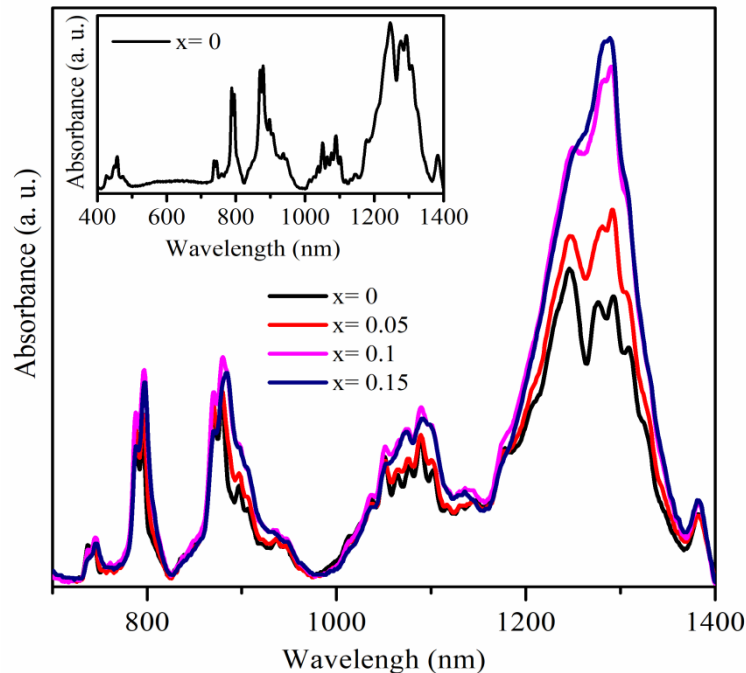

Figure 5.4: Room temperature UV-vis spectrum of polycrystalline $Dy_{2-x}Fe_xTi_2O_7$ in 700-1400 nm wavelength range. Inset shows the UV-vis spectrum in 400-1400 nm wavelength range for x=0 composition.

In Dy$_2$Ti$_2$O$_7$ compound, due to local crystal field, $^6H_{15/2}$ free ion state of the Dy^{3+} splits in multiple excited states. The absorption spectrum is associated with the electronic transitions from $^6H_{15/2}$ ground state to multiple excited levels of the Dy^{3+} ion. Based on previous studies, these observed transitions can be assigned as $^6H_{9/2}$ +$^6F_{11/2}$ (1300 nm), $^6H_{7/2}$ +$^6F_{9/2}$ (1100 nm), $^6H_{5/2}$ (940 nm), $^6F_{7/2}$, (890 nm), $^6F_{5/2}$ (870 nm), $^6F_{3/2}$ (790 nm) and $^4F_{9/2}$ (455 nm)[131], [139]. An increase in the peak intensity, mainly $^6H_{9/2}$ +$^6F_{11/2}$ (1300 nm) transitions indicate an increase in the population of electrons in these levels. Whereas, insignificant change in the peak positions indicate the negligible effect of Fe substitution on the existing local crystal electric field acting around the Dy ion.

5.2.4.2 Photo- Luminescence spectra

Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ has been further analyzed using Photo-luminescence recorded at an excitation wavelength of 455 nm. In Dy$_2$Ti$_2$O$_7$, due to pronounced crystal field acting on Dy^{3+} ion, separation between the ground state and excited state of the f-orbital are larger in comparison to other rare earth compound. Figure 5.5 shows the emission spectra of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ recorded in 450-850 nm wavelength range. Luminescence spectrum shows broad emission transitions observed at 517 nm, 685 nm, 735 nm and 828 nm. Broadening in the emission spectra in these compounds is associated from the formation of intra-electronic band of the f-orbitals which are ascribed to the $^4F_{9/2} \rightarrow ^6H_{15/2}$ (517 nm), $^6H_{13/2}$ (685 nm), $^6H_{11/2}$ (735 nm), $^6H_{9/2}$ (782 nm) and $^6H_{7/2}$ (828 nm) transitions. It has been noted that in DTO that the separation between the ground state $^6H_{15/2}$ and $^6H_{13/2}$ excited state is ~170 nm whereas in Dy^{3+} doped Dy^{3+}-doped Lu$_3$Ga$_5$O$_{12}$ nano-garnets it is ~100 nm [139]. This observation also confirms the larger splitting between the ground state and excited state is responsible for the Ising nature of spin in these compounds when compared to other rare earth oxides.

Furthermore, in the luminescence emission spectra, no change in the peak position has been observed for all measured compositions. This suggests that Fe substitution induced lattice distortions do not affect the local crystal field acting on the Dy^{3+} ions in the Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ compound.
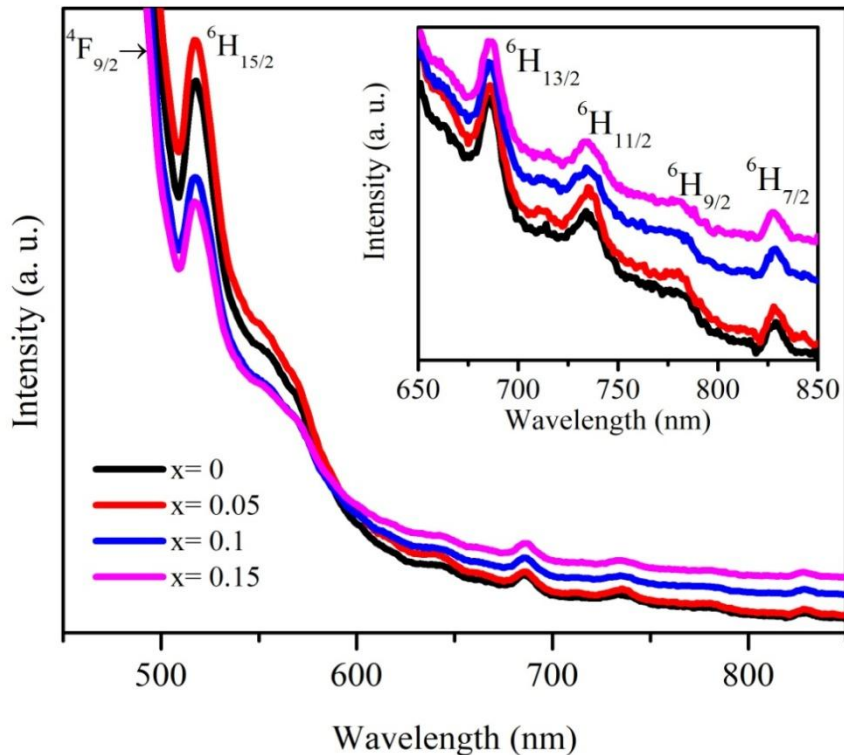

Figure 5.5: Room temperature luminescence spectrum of polycrystalline Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ compound recorded at 455 nm excitation wavelength. Inset shows the enlarge spectra in the wavelength region 650-850 nm.

UV-vis and Photo-luminescent optical analysis of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ compound concludes that effect of Fe substitution induced structural distortion on the crystalline electric field acting on Dy^{3+} ions is insignificant. It also suggests that alteration in crystalline electric field acting on Dy^{3+} ions may not be the primary reason for the observed magnetic behavior in Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$. As discussed above, out of the two possibilities, the observed magnetic behavior of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ can be explained in terms of magnetic perturbation.

5.2.5 Effect of magnetic field on the spin dynamics of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$

As observed, both ~16 K and ~4 K, spin freezing get suppressed even by a very small dilution (x= 0.05) (as shown in figure 5.3), confirms that both magnetic freezing are highly sensitive to the nature of neighboring magnetic site. Such sensitivity cannot be possible without existence of strong spin-spin correlations. It can be suggested that, similar to 4 K spin ice freezing where spins are highly correlated because of dipolar interaction, 16 K freezing also have strong spin-spin correlation. This argument is further supported by the order of Mydosh parameters (p) ~0.18 observed for this freezing [41]. Moreover, for further investigation, magnetic ac-susceptibility of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$ has been measured for x= 0.05 and 0.15 compositions at 0 T, 0.5 T and 1 T dc bias magnetic field at 1 kHz frequency as shown in figure 5.6. It has been found that for x=0.05 composition, spin ice freezing of 4 K reappears at 0.5 T applied dc field, followed by reappearance of 16 K freezing at higher applied field of 1 T. On the other hand in case of x= 0.15 composition, both spin freezing reappeared at higher magnetic field in comparison to that of the x-0.05. Further, their nature is also slightly different at lower magnetic fields. The larger magnetic field needed to observed these freezing for x= 0.15 composition further suggests the non-monotonic dependency of spin dynamics on the concentration of the substituted Fe ion. The reappearance of both of the magnetic freezing clearly indicates that applied magnetic field suppresses the spin fluctuations as induced by the Fe spin, which depends on the composition of Dy$_{2-x}$Fe$_x$Ti$_2$O$_7$.
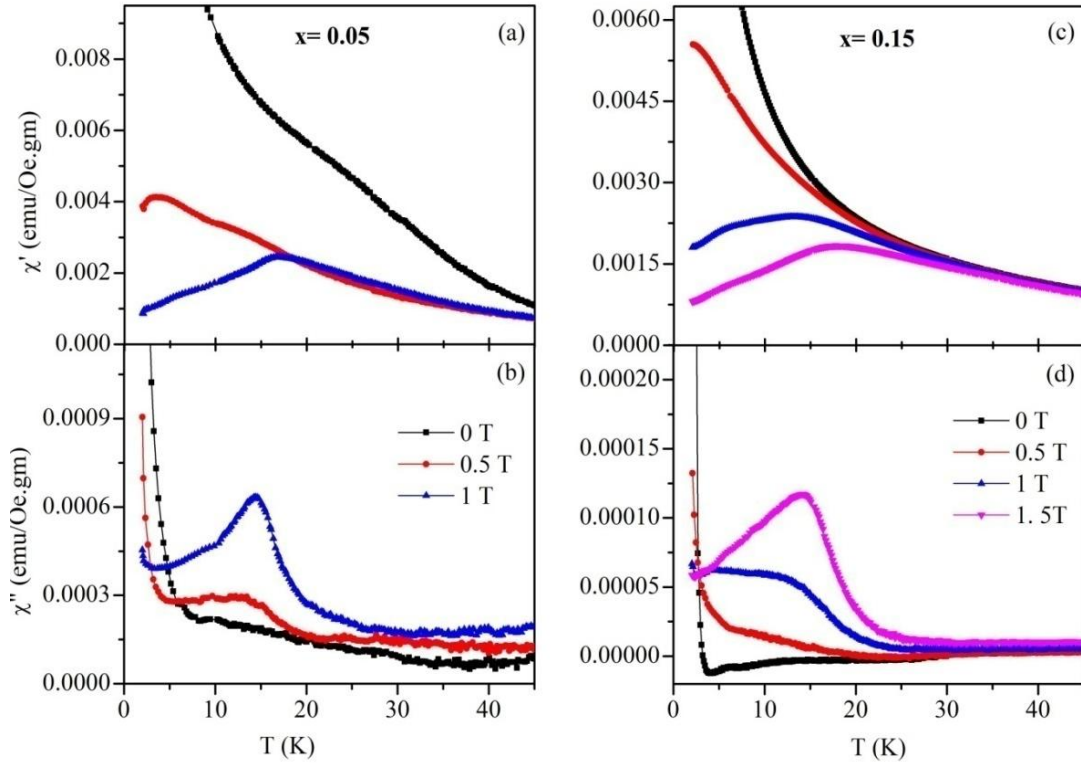
Figure 5.6: Temperature dependent (a) real and (b) imaginary part of magnetic ac-susceptibility measured at 0 T, 0.5 T and 1 T for $Dy_{2-x}Fe_xTi_2O_7$ (x= 0.05 and 0.15) at 1 kHz frequency.

This observation shows the Fe spin behaves differently in comparison to Dy^{3+} ion's being an Ising spin. In case of Dy^{3+} ion, its f-orbital is strongly shielded by the outer s, p and d orbitals and do not participate in the chemical bonding. The ground state is splitted by the acting crystal electric field which in turn becomes responsible for the Ising nature of spin. This crystal field induced spin confinement along local <111> axis of the crystallographic structure. This does not apply for Fe spin because in this case outermost d-orbitals take part in the Fe3d-O2p covalent bonding. This means that substituted Fe spin behaves as Heisenberg-like and highly fluctuating in nature than the neighboring Dy Ising spin. On application of the magnetic field, Fe spins gets aligned along the field direction in contrast to

its local <111> axis (for Dy ion). This spin alignment of Fe suppresses the spin fluctuation and modifies the nature of freezing as well, which could be the possible explanation for the disappearance of the observed 16 K and 4 K frozen spin state on Fe substitution.

5.3 Conclusion

The structural, dielectric, optical and magnetic study of polycrystalline $Dy_{2-x}Fe_xTi_2O_7$ compound reveals that both magnetic freezing observed at ~16 K and ~4 K in ac-susceptibility is highly susceptible to magnetic substitution rather lattice distortions. In field dependent magnetic ac susceptibility both the magnetic freezing reappears with modified nature. These results further suggest that because of strong spin-spin correlation, spin dynamics non-monotonically depend on the nature and dynamics of neighboring magnetic ion's spin.