6.1 Introduction

Magnetic nano-particles continue to attract scientific interests due to underlying physics at low dimensions, which generally opens another dominion of applications. The uncompensated surface spins engage at nano scales in a much more crucial way in comparison to the bulk counterpart and contributes to the overall magnetization of the system. With these reduced dimensions, the physical properties are mainly governed by two factors viz., surface and finite-size effect [Alivisatos (1996), Kodama et al.(1997), Sun et al.(2000), Dutta et al.(2003), Allwood et al.(2005)]. In such particles, phase inhomogeneity is now well established at local level, it can be structural or magnetic as the case may be. The structural disorder generally forms inhomogeneous magnetic phases. In magnetic systems, these disorders generally lead to pre-formation of ferromagnetic (FM)/antiferromagnetic (AFM) clusters prior to setting of long-range magnetic order, if the system is getting cooled from paramagnetic regime. This clustered state identified as Griffiths Phase (GP) [Deisenhofer et al.(2005)]. It was initially suggested for randomly diluted Ising ferro-magnets. In case of randomly diluted Ising ferromagnets interchange of the bonds amongst the nearest-adjacent having strength of J and 0 can be considered as distributed randomly with probability p and 1-p. Below a percolation threshold P_C, no long-range magnetic order is established; whereas above that threshold a long-range magnetic phase exists below a temperature recognized as Griffiths temperature (T_G). In the zone in between $T_C < T < T_G$, the system is represented by the coexistence of magnetic clusters within the extensively paramagnetic (PM) phase which is mention as GP.

Griffith phase (GP) singularity is such a form of in-homogeneity of magnetic state, where magnetic spins are gathered as cluster like arrangement above the classical magnetic

ordering i.e. coexistence of short-range FM magnetic clusters within paramagnetic (PM) environment. Under the other condition, the coexistence of short-range ordered AFM clusters inside the PM matrix leads to the non-Griffiths-like phase [Zhou et al. (2010)]. Other than the coexistence of the short range magnetically ordered state in the PM matrix competition between ferromagnetic and antiferromagnetic or ferrimagnetic phases can lead to the presence of Griffiths like phase. For example, Pathak et al has reported a very unusual magnetic characteristic in Rare earth dialuminides $Pr_{0.6}Er_{0.4}Al_2$ coexistence of ferromagnetic and ferrimagnetic, along with metamagnetism in the presence of an applied magnetic field. The Griffiths phase behavior has been observed even at H = 1 kOe in this compound [Pathal et al. (2014)].

The Griffiths phase has also been observed in hole doped double perovskite $La_{2-x}Sr_xCoMnO_6$ having a value of x = 0.0, 0.5, and 1.0. The existence of Griffiths phase is explained on the basis of effects of quenched randomness on the magnetization of a dilute Ising and quenched disordered ferromagnetic system below Griffiths temperature T_G. The quenched disorder is originated from the nucleation of ferromagnetic clusters, which can be enhanced by the competition between the magnetic phases [Mandal et al. (2015)].

As mentioned above, that on reduction of particle size, another disorder gets introduced in the system through the uncompensated coordination at the surface. Many a times this broken crystallographic symmetry of surface percolates with the magnetic disorders in the core of the nanoparticles. Markovich et al. have prepared $Sm_{0.1}Ca_{0.9}MnO_3$ nanoparticles in the range of 25 and 60 nm average size. The Griffiths phase behavior has been observed upto an applied field of at H = 6 kOe in the bulk of this compound, whereas for the nanoparticles having an average size of 25 nm, the Griffiths phase has been observed

even upto an applied magnetic field as high as 15 kOe [Markovich et al. (2013)]. Banik et al. have reported particle size driven transition of the non-Griffiths phase to Griffiths phase in $(La_{0.4}Y_{0.6})_{0.7}$-$Ca_{0.3}MnO_3$ compound. A reduction in lattice distortions together with the quenched disorder having its origin in the ionic size mismatch of the different A site occupant has been attributed for the emergence Griffiths phase in these compound on the size reduction [Banik et al. (2018)].

In some other perovskite oxides like $Sm_{0.5}Sr_{0.5}MnO_3$, $La_{0.7}Sr_{0.3}CoO_3$ and La_2NiMnO_6 (LNMO) on decreasing the particle size from bulk to nano level leads to the phase transformation from the non-Griffiths-like phase to Griffiths-like phase due to the exhaust of AFM interactions [He et al. (2007), Saber et al.(2010)]. It is well defined that quenched random disorder and/or strong competition of FM and AFM exchange interactions are the basic Ingredients to anticipate the Griffiths like phase [Deisenhofer et al. (2005), Jiang et al. (2008)]. The Hallmark of GP is a sharp downturn in the inverse magnetic susceptibility (as a function of temperature) [Griffiths (1969), Salamon et al.(2002), Pramanik et al.(2010)]. The downturn nature in the thermal behavior of χ^{-1} is a significant observation that differentiates GP from marked phase transition and in latter it rises to an upward curvature in χ^{-1} vs T above T_N or T_C, deviating from Curie-Weiss (CW) law. The diminishing of the downturn in χ^{-1} with the continuous increase in field is another typical indication of GP.

The presence of GP in multiferroics can add to a great advantage. Multiferroics (MFs) exhibit either coupling between electronic and magnetic orders offer great opportunities for applications in information storage, spin electronics and magneto-electronics. In the recent scenario the controlling and coupling of various ‘ferro or antiferro’ magnetic orders are of huge interest at room temperature or above [Spaldin et al. (2010), Wang et

al. (2013)]. The improvement in these kinds of couplings at above the room temperature may be executed by various ways like internal chemical pressure i.e. doping and other external disturbance etc. [Hur et al.(2004), Yang et al. (2009)]. The materials which show high magneto-electric coupling as well as coexistence of more than one magnetic interaction, e. g. coincidence of AFM and FM on doping are the most promising candidates for technological applications. [Singh et al. (2008)]. In such a class of materials, the solid solution of $BiFeO_3$-$PbTiO_3$shows several exotic phenomena like weak ferromagnetism, tricritical transition, morphotropic phase transition, isostructural ferroelectric to ferroelectric transition, critical end point, spin reorientation transition and spin glass transition. Here, we are reporting another exotic property i.e. occurrence of Griffiths phase in the $BiFeO_3$-0.25$PbTiO_3$solid solution in the bulk as well as in 300 nm particle size powder.

6.2 Experimental

Powders of BF-0.25PT solid solution with different sizes were synthesized using sol-gel technique the details of which are given in chapter II.

Magnetic measurements at and above room temperature were carried out using a Quantum Design Evercool MPMS3 with a high temperature attachment capable of going up to 1000 K. Temperature dependent magnetization M(T) measurements were carried out on zero field cooled samples while heating under a magnetic field of 100 Oe, 500 Oe, 1000 Oe and 5000 Oe. Magnetization (M) vs applied field (H) hysteresis measurements were also performed at different temperatures up to a field of 5 Tesla.

6.3 Results and discussion

6.3.1 Evidence of Griffith-like phase

Fig.6.1shows the low field (500Oe) magnetization vs temperature curve for bulk and 300 nm sample. The field heating and field cooled magnetization behaviour of these samples are distinctly different. The field heating magnetization shows a typical antiferromagnetic like behaviour having a transition temperature (T_N) at ~ 445K and ~ 473K for bulk and 300 nm sized BF-0.25PT sample respectively. However, when cooled under the field, the magnetization curve shows typical of ferromagnetic materials. In spite of the fact that, this anomaly in the M-T curve appears to mimic a typical paramagnetic (PM) to ferromagnetic (FM) like transition as it is seem from high temperature to room temperature (RT) side.

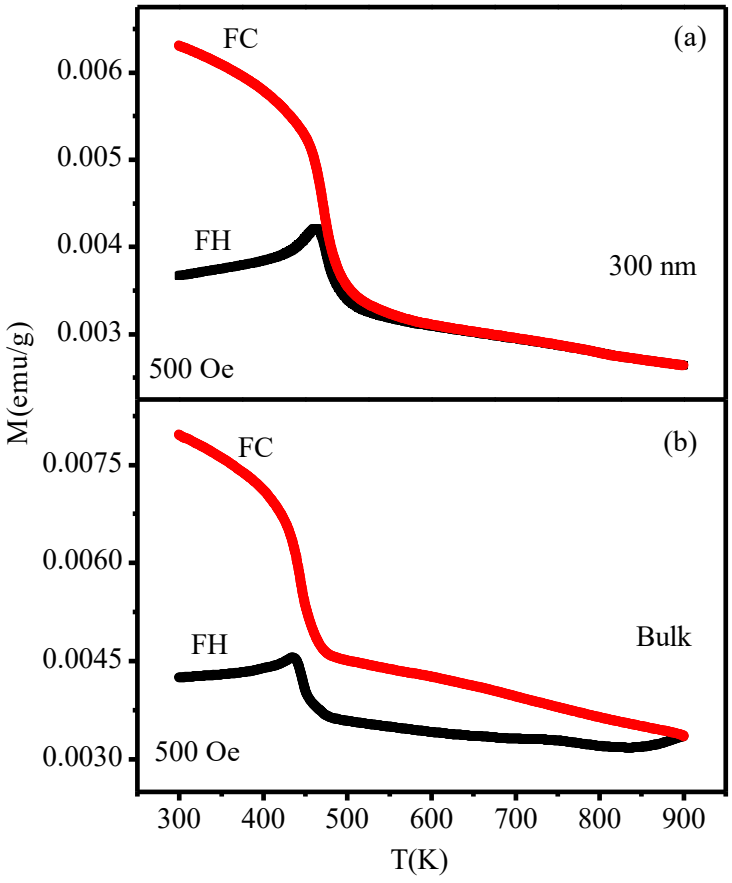

Fig.6.1 The temperature dependence, FH and FC curves of BF-0.25PT (a) 300 nm (b) bulk powder under magnetic field of 500 Oe.

The occurrence of the separation between FC and ZFC curves is usually attribute to the appearance of the spin glass or cluster like state which arises because of magnetic anisotropy [Cullity (1972)]. This observation of magnetization behaviour is one of the typical behaviours of the samples having Griffiths like phase, which shows a clear transition from long range antiferromagnetic to short range antiferromagnetic/ferromagnetic behaviour in the magnetization curve.

This can be understood as, when the disorders in the magnetic lattice is introduces there is a tendency to form large number of cluster and the long-range AFM order is interrupted and uncompensated spins start to narrate for large irreversibility [Kundu et al (2011)]. Increase of the net moment of the grains due to the destabilization of the long-range AFM order in these systems is strongly dominated by inhomogeneous clusters.

Fig. 6.2, represents M-H curves at different temperatures below and above the Neel temperature (T_N). At room temperature, M-H curve show a small ferromagnetic like hysteresis loop, but no saturation was not observed even at an applied filed of 50kOe. This phenomenon supports the canted AFM-like behavior of sample.

The M-H curves at 550K (i.e. above T_N); show a non-linear behavior at low field (H).This kind of nature at low field (< 10kOe) shows the presence of weak magnetization. In order to find out whether these cluster have long range or short range ferro magnetic correlations (FMC), M^2 versus H/M plotted (i.e. an Arrot plot) at above and below the T_N for the 300 nm powder shown in fig. 6.3**.**

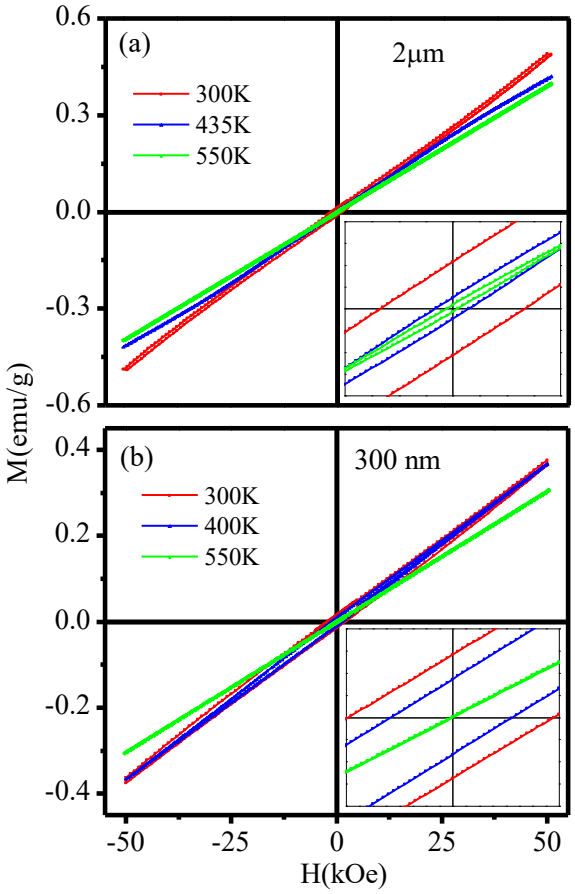

Fig. 6.2 M-H curve for bulk and 300 nm powder at different temperatures.

It is well established fact that if at higher field side, the linear extrapolation of Arrot plot provides a positive intercept on the Y-axis i.e.(M^2-axis), it shows existence of spontaneous magnetization with long-range FMC, while on the other side a negative intercept shows short-range FMC [Tong et al. (2008) and Pramanik et al. (2010)].

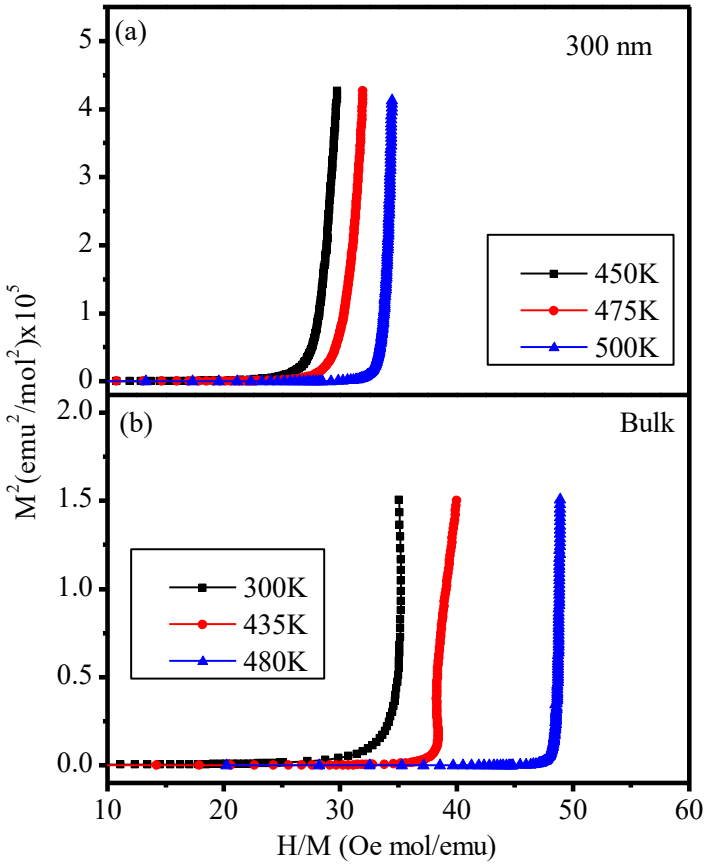

Fig.6.3 Arrott plots of isotherms at different temperatures around T_N for (a) 300 nm and (b) bulk powder.

In our case, the above-mentioned linear extrapolation shows a negative intercept on the M^2-axis for both the sample, thus establishing that there is a presence of short-range FMC in nano BF-0.25PT sample.

The measurements of susceptibility using DC magnetic field as a function of temperature at different applied fields reveals a strong sign of GP in the nano-BF-0.25PT powder. The inverse magnetic susceptibility (χ^{-1}) shows a noticeable strong field dependent downturn on moving towards the magnetic phase transition (T_N) from the high temperature region i.e. paramagnetic side. Fig. 6.4 shows the plot of χ^{-1} with temperature. It can be divided

into three regions (i) Long range AFM ordered, (ii) short range AFM/FM cluster (GP phase) and (iii) paramagnetic region.

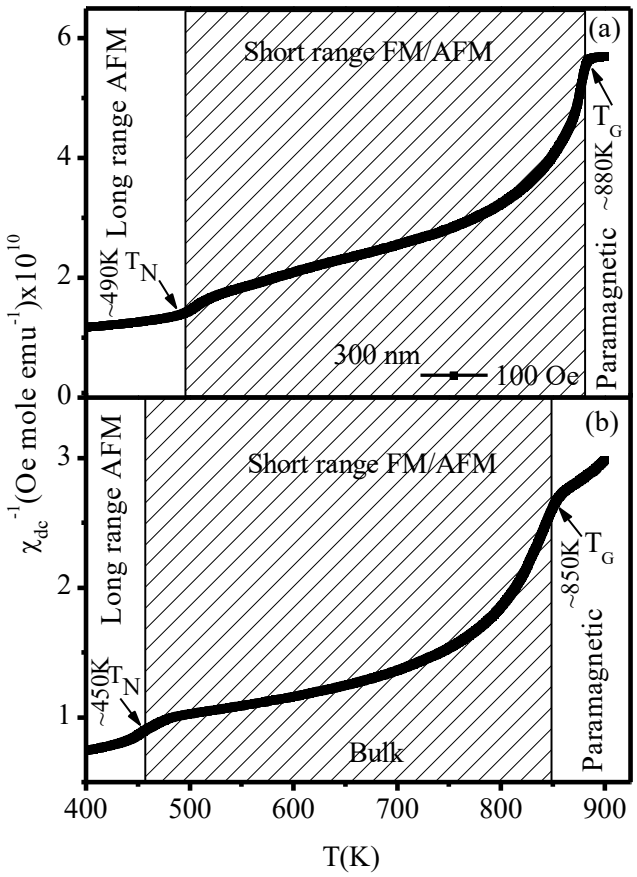

Fig.6.4 Temperature variation in inverse dc susceptibility (χ_{dc}^{-1}) measured in 100 Oe field are plotted for (a) 300 nm (b) bulk powder of BF-0.25PT.

A GP-like behavior clearly exists below a critical temperature where DC magnetization shows downturn. The onset of this downturn is denoted as T_G below which the FMC emerges in the PM matrix. This deviation i.e. downturn in the inverse magnetic susceptibility gets gradually suppressed with increasing field (H) as shown in the fig. 6.5. As evident from the downturn in the χ^{-1} with temperature plot, an applied field of 5 kOe was sufficient enough to quench the Griffiths singularity, whereas for bulk samples we

still observe the downturn in the χ^{-1} with temperature plot even at applied field of 5 kOe. Another distinct feature is the high value of T_G in this system. The values of T_G for the 300 nm sample of BF-0.25PT are found to be ~880 K, whereas for bulk BF-0.25PT this value is 850 K. It will not be out of place to mention that the Griffiths phase has been observed in most of the systems at temperatures well below the room temperature. The BF-0.25PT is probably the only system to the best of our knowledge to have such a high value of T_G where the Griffiths phase has been observed up to a temperature of 880K in the nanoparticle of BF-0.25PT.

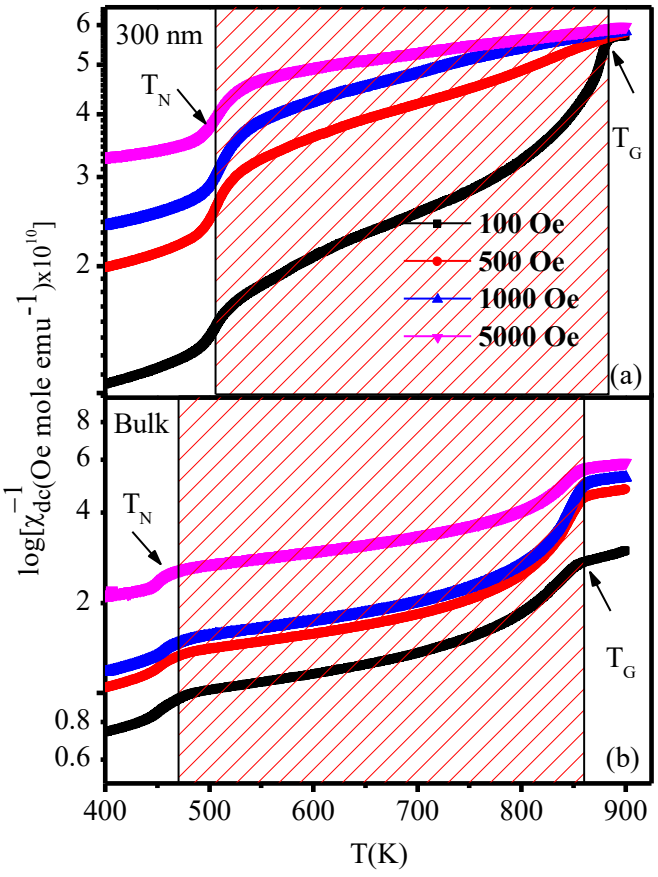

Fig.6.5 Temperature variation in inverse dc susceptibility (χ_{dc}^{-1}) measured in 0.1, 0.5, 1 and 5kOe field are plotted for (a) 300 nm (b) bulk powder of BF-0.25PT.

To establish the presence of Griffiths phase, the inverse of magnetic susceptibility of the temperature dependence must follow the power law relation:

$$\chi^{-1}(T)\alpha(T-T_C^R)^{1-\gamma} \text{.....(6.1)}$$

Where, γ is the exponent of susceptibility, which values lies in between 0 and 1 for the GP [Jiang et al. (2007) and (2008)].The value of $T_C^R = T_N$ has been used for value of λ in both the PM as well as GP region for both the bulk as well as 300 nm powder size sample. The value of γ as obtained from fitting of χ^{-1} data using equation 1 has been obtained to be 0.051 and 0.126 for bulk and 300nm respectively for BF-0.25PT powder and shown in figure 6.6.

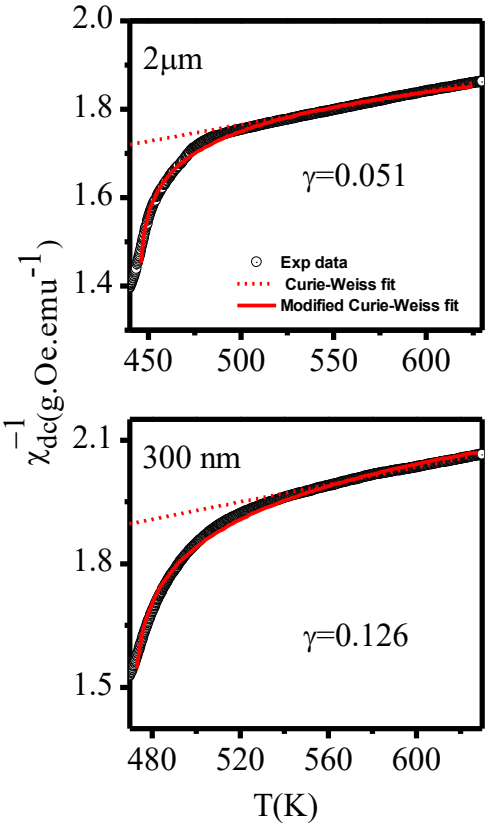

Fig.**6.6** Temperature variation with inverse dc susceptibility (χ_{dc}^{-1}) measured in 500 Oe field are plotted for (a) 300 nm (b) bulk powder of BF-0.25PT.

When compared with the other systems e.g. nanoparticles of $Sm_{0.1}Ca_{0.9}MnO_3$ as reported by Markovich et al a fit of Eq. (1) to χ^{-1} data gives T_C = 95K with γ= 0.66 and T_C=115K with γ = 0.52 for 25 nm and 60 nm sized samples, respectively [Markovich et al (2013)] . Similarly, Banik et al has reported a value of γ = 0.977 for $(La_{0.4}Y_{0.6})_{0.7}$-$Ca_{0.3}MnO_3$ nanoparticles [Banik et al. (2018)]. The value of γ for other bulk systems having the Griffiths phase has invariably been reported between 0.3 to 0.9.

The obtained values thus confirm the conclusive presence of Griffiths like phase in bulk and nano bismuth ferrite-lead titanate systems. Such a presence of Griffiths like phase even up to 880K has not been reported yet. This unique observation provides another tool to control the magnetic ordering in the BF-xPT multiferroic systems towards the $BiFeO_3$.

6.4 Conclusions

Samples of BF-0.25PT having a size of 300 nm and bulk has been investigated for their magnetic behavior in the temperature range of 300-900K. The deviation in the inverse susceptibility behavior from Curie-Weiss law and increase in susceptibility exponent with reduction of size indicates the evolution of the Griffith's phase in BF-0.25PT around T_N. The Griffith's phase to paramagnetic transition has been found to be at extremely high temperature up to 880 K for 300 nm sized BF-0.25PT particles and upto 850K for bulk. The presence of Griffith's Phase is inferred due to magnetic frustration with decreasing size, where the disordered surface plays a very important role. The deviation between field heating and field cooled magnetization curves is observed in these samples and attributed to the appearance of the short range magnetically ordered cluster state that arises due to the underlying magnetic disorder. Such a presence Griffiths phase at high temperatures opens another avenue to control the magnetic ordering in multiferroic Bismuth ferrite-lead titanate systems