Dielectric Study at Microwave Frequencies of Phase Transitions in Multiferroic Ceramics

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Multiferroic ceramic solid solutions between the ferroelectric relaxor $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) and "normal" ferroelectric $PbTiO_3$ (PT) - PFW-PT have been synthesized by a modified B-site precursor method and characterized by microwave dielectric measurements. A dielectric dispersion occurring in the frequency range of 100MHz-3GHz and in a broad range of temperatures showed to be a powerful tool to detect electrostrictive and magnetostrictive effects. Anomalies in the temperature dependence of the dielectric parameters (f_R (characteristic frequency) and the dielectric strength $\Delta\varepsilon$ (characteristic of the dispersion)) have been observed at T_N and T_C for all samples, indicating that the coupling between the ferroelectric and antiferromagnetic orders occurs "via strain" and confirming the high sensitivity of microwave dielectric measurements to probe weak transitions in bulk ceramics.

Keywords: *multiferroic, lead iron tungstate, microwave dielectric spectroscopy, phase transitions*

1. Introduction

Ferroelectric materials present a dielectric dispersion in the frequency range of 0.1-1 GHz, which has been attributed to either a relaxation or a resonance process by different authors[1-5]. Nevertheless, the results reported in the literature have not been conclusive enough to distinguish clearly each process.

In spite of still not being clarified, several theoretical attempts have been proposed to explain the origin of this effect. The relation between the high frequency dielectric dispersion and the microstructure of ceramics was expressed by Von Hippel[6] who attributed the piezoelectric resonance of the grain as the principal cause of the observed microwave anomalies. Kittel attributed the decrease of the dielectric constant at the microwave region to the resonance of the domain walls in ceramics[7]. Some others models concerning piezoelectric resonance of individual domains or on correlated hopping of off-centered ferroelectric active ions between several potential walls have been proposed. More recent experimental results confirms the elastic contributions to the high frequency dielectric anomalies, showing that ferroelectric and ferroelastic effects are always coupled each other and either mechanisms, resonance or relaxation-like, are always present without the presence of an intermediate case. For last, magnetoelectric coupling was only observed in the microwave dielectric measurements in many multiferroic materials, which simultaneously display electric dipole moment and magnetic ordering in the same phase[8,9]. At higher frequencies, conductive contributions to the dielectric permittivity can be minimized, suggesting microwave dielectric spectroscopy as an accurate tool to investigate phase transitions in multiferroic materials. On other hand,

the presence of an elastic subsystem in the crystal leads to the emergence of electrostriction which accompanies the FE ordering and changes the crystal size. Thus, in turn, changes the magnetic state due to magnetostriction, and vice versa. A systematic study of the elastic behavior also provides useful information for probing structural phase transitions as well as spin–phonon and electron-phonon coupling. Therefore, microwave dielectric spectroscopy reveals to be a powerful and accurate approach to investigate the ferroelastic contributions in multiferroic – magnetoelectric materials.

Among the single phase multiferroic materials, $Pb(Fe_{2/3}W_{1/3})O_3$-PFW shows both ferroelectric ($T_C\sim180K$) and antiferromagnetic ($T_N\sim340K$) properties[10]. These types of materials, called multiferroics have been used widely as multistate memory elements, electrically controlled ferromagnetic resonant systems, between others. PFW present a complex perovskite-type structure, in which the cations (Fe^{3+}, W^{6+}) are randomly distribute at the octahedral B-site positions. Besides, the Curie temperature is too low for practical applications. PFW can form solid solutions with $PbTiO_3$ (PT) presenting changes of symmetry and a range of temperature, where magnetic and ferroelectric ordering coexists, depending on the PT contents. As the $PbTiO_3$-PT content is increased, the Curie temperature increases, because PT has a transition at a rather high temperature (around 773 K).

In current work, we report the magnetic and microwave dielectric characteristics of $Pb(Fe_{2/3}W_{1/3})O_3 - PbTiO_3$ solid solutions multiferroics ceramics determined in the temperature range spanning both T_N and T_C in the frequency range of 1MHz-3 GHz. The microwave dielectric results characterized the magnetoelectric effect in the PFW-PT

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and demonstrated that the technique is powerful to detect magnetic transitions. Moreover, it was also verified that the magnetoelectric coupling can be arises indirectly via elastic contribution rather than a direct coupling between electrical and magnetic order parameters.

2. Experimental Procedure

Fe_2O_3 and WO_3 were milled for 2 h, and then preheated at 950 °C for 3 h to form Fe_2WO_6. Afterward, PbO and TiO_2 were mixed to the Fe_2WO_6, to form $(1-x)Pb(Fe_{2/3}W_{1/3})O_3$-$xPbTiO_3$ (PFW-xPT). The mixture was initially calcined at 800°C for 3 h, reground, pressed in pellets and finally sintered between 830-850 °C for 5 h. The temperature ramps were controlled at 5 °C/min for heating and 2 °C/min for cooling.

This procedure avoids the formation of pyrochlore phase (details can be found elsewhere[11]). The sintered ceramic bodies were cut in disc form and polished to a thickness of 0.5 mm and 2mm in diameter. After that, they were annealed at 873 K for 0.5 h to release mechanical stresses introduced during the polishing. Gold electrodes were sputtered on the samples faces for dielectric measurements. Microwave dielectric measurements were carried out in the temperature range of 80-420 K (network analyzer HP-8719C), while low frequency measurements (HP 4194A) were performed in the range 15-500 K. The temperature dependence of the and magnetic moment m'(T) were measured using a commercial SQUID magnetometer range of temperatures 4K-600K.

3. Results

3.1. *Multiferroics properties*

In a previous work, we reported the structural and electrical proprieties of the system $Pb(Fe_{2/3}W_{1/3})O_3$-$PbTiO_3$. The degree of PbO volatilization during the sintering of PFW was quite low, due to the low sintering temperatures. Relative densities of about 93-99 TD% could be achieved in this route. XRD patterns of the PFW-PT ceramics indicate formation of a major phase with a cubic perovskite-type of structure (space group $pm\overline{3}m$). The average grain size was around 5 μm for all samples and no systematic variation of grain size with change x. All compositions with PT showed relatively high resistivity from 10^7 to 10^8 Ω.m. As can be seen the addition of PT increases the room temperature electrical resistivity of PFW samples. From these results, we concluded that all samples resulted in single phase, dense, with relatively high electrical resistivity, which allowed us to perform the dielectric and magnetic characterizations, which are presented and discussed in this work[11].

Magnetic measurements, Figure 1a, show two characteristic temperatures (T_{N1} = 340 K and T_{N2}~15 K), which have been associated to two types of magnetic ordering for "pure" PFW. At T_{N1} = 340 K the a paramagnetic to antiferromagnetic ordering results from a strong superexchange Fe^{3+}-O-Fe^{3+} interactions. For the other one, a weak superexchange Fe^{3+}-O-W-O-Fe^{3+} interaction, caused by local short range order in the B site, is the responsible mechanism for the magnetic anomaly at lower temperatures (around T_{N2}~15 K). Similar results are shown in Figures 1b-

1d for the PFW-PT samples. As the amount of PT increases it can be observed that characteristic temperature T_{N1} decreases (from 340 K to 134 K for x=0,0 and x=0.30, respectively). Otherwise the lower temperatures magnetic ordering occur at T_{N2}=15 K to 17 K for x=0 and x=0.30, respectively.

In Figure 2 the temperature of the imaginary relative dielectric permittivity (ε´ and imaginary ε" components) for PFW-PT samples are shown as a function of the temperature at frequencies ranging from 1 KHz to 1 MHz.

For PFW ceramic (Figure 2a) in the temperature range 150K-400K the dielectric permittivity shows at least two peaks in the real and imaginary components, which present a strong dependence on frequency. The peak around 180 K, which can be attributed to a relaxor like ferroelectric ordering (FE), increases the temperature of maximum with the measuring frequency (Figure 2a). The dispersion
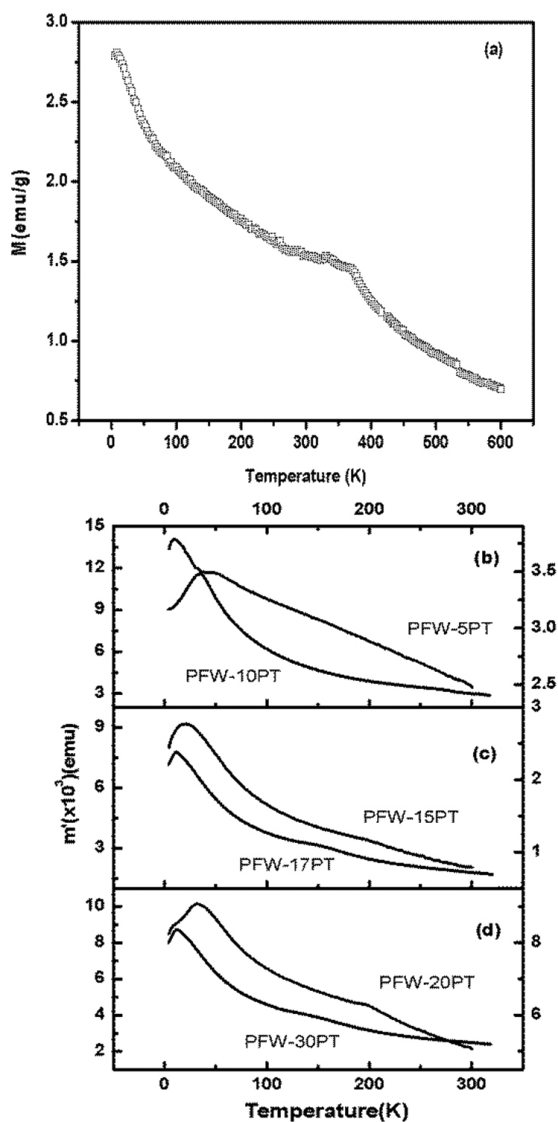

Figure 1. Temperature dependence of the magnetic moments M(T) (dc measurements) for PFW (a) and m'(T) (ac measurements) for PFW-PT system , x= 0.05 and 0.10 (b), 0.15 and 0.17(c) 0.20 and and 0.30 (d).

observed in the real and imaginary part in Figure 2, at temperatures higher than those related to the FE ordering, also shifts towards higher temperatures with increasing frequency, while the permittivity values decreased for higher frequencies characterizing a conductive contribution. As the conductive contributions do not alter the conclusions of this work it will not be no longer discussed. These results are also representative and similar to those measured in the other samples containing PT. Therefore, in Figure 2b only the relative dielectric constant at 100 KHz is shown for the PFW-PT samples. As the PT content in the (1-x)PFW–xPT solid solutions is increased, the maximum dielectric permittivity, corresponding to the FE ordering increases up to x= 0.10, decreasing for higher x values (Figure 2b). Also, the temperature corresponding to the maximum value of the dielectric constant increases from T =180 K for x=0 (PFW) to T=320 K for x=0.3 compound, while the character of the phase transition changes from diffuse, typical for relaxors, to a sharp one, characteristic of "normal" ferroelectrics.

3.2. *Microwave dielectric spectroscopy*

The frequency dependence of the real and the imaginary parts of the electrical permittivity for PFW ceramics is shown in Figure 3. Furthermore a well pronounced relaxation like dielectric dispersion is observed in the microwave region (around 1GHz). As it can be seem the microwave dielectric dispersion does not vanish in the measured temperature
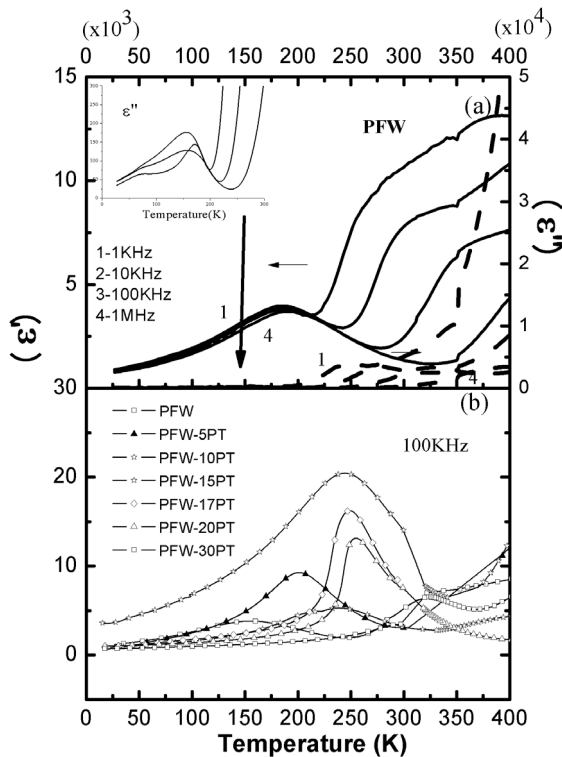
interval, persisting even at temperatures as high as 200 K above T_m.

The experimental data of Figure 3 can be fitted with a damped harmonic oscillator model as adopted for PLT[12] ceramics, where ε(f,T) takes the form:

$$\varepsilon(f,T) = \varepsilon_{inf} + \frac{\Delta\varepsilon f_R^2}{f_R^2 - f^2 + i\gamma f} \tag{1}$$

where $\Delta\varepsilon(f,T)=\varepsilon(f_0,T)-\varepsilon(f_{inf},T)$ ($f_0 \ll f_R \ll f_{inf}$) is the dielectric strength, $f_R(T)$ the characteristic frequency, $\gamma(T)$ a damping coefficient and $\varepsilon_{inf}(T)$ the high-frequencies contribution by phonons and electronic polarization. $\varepsilon(f_0,T)$ should be interpreted here as the dielectric permittivity at frequencies lower than f_R, without any additional contribution (related to phase transitions or conductive mechanism).

The temperature dependence for $\Delta\varepsilon$ and f_R, reversible in the cooling and heating cycles, is shown in Figure 4. The observed temperature dependence of f_R and $\Delta\varepsilon$ around 200 K, f_R reaches a minimum value, while $\Delta\varepsilon$ goes through a maximum, is associated with that of the dielectric permittivity peak, observed at RF range. Otherwise, remarkable are also the change of f_R curve around 340 K, and the set of "anomalies" around 250 K approximately, which are correlated to the secondary maximums of $\Delta\varepsilon$ at 340K and around 250 K region, respectively. These

Figure 2. (a) Relative dielectric permittivity at various frequencies as a function of the temperature for PFW ceramic and at 100 kHz (b) for $(1-x)$Pb(Fe$_{2/3}$W$_{1/3}$)O3-xPbTiO$_3$ solid solutions (x=0.1-0.30).
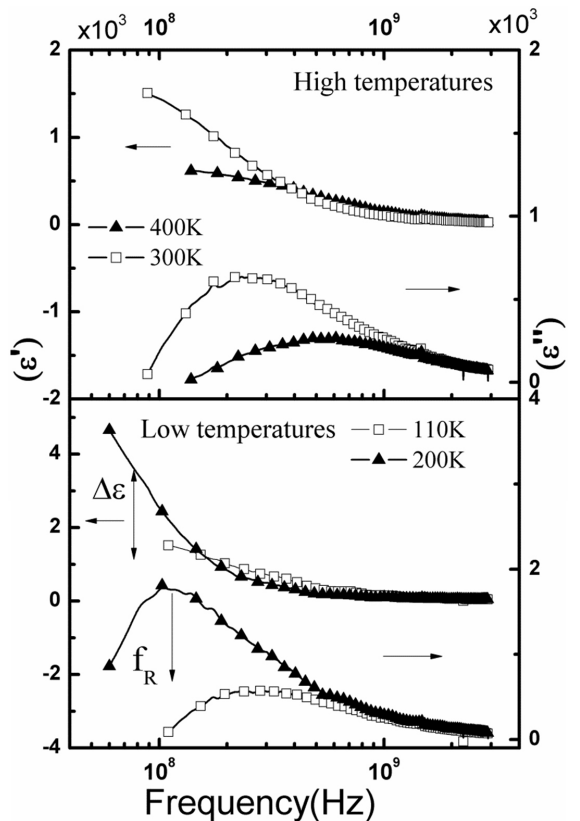
Figure 3. Temperature and frequency dependence of the real (ε') and imaginary (ε'') components of the relative dielectric permittivity of PFW ceramics frequency dependence at various temperatures.

secondary maximums cannot be detected in the radio frequency dielectric measurements. The dielectric anomaly observed around 340 K coincides with the temperature of the paramagnetic-antiferromagnetic ordering ($T_{N1} \approx 340\,K$). Therefore, based on our previous results in multiferroic systems[8,9,13,14], this dielectric anomaly in the PFW system results from a magnetostrictive contribution, due to a spin-lattice coupling, in the paramagnetic-antiferromagnetic ordering.

Otherwise, the comparatively smaller anomaly detected around 250K, also observed in the magnetic measurements (Figure 2), must also be caused by magnetostrictive contribution (spin-lattice coupling) denominated as T_{inst} region. These instabilities were investigated through magnetic, anelastic and XANES measurements and the experimental data revealed that the observed magnetoelectroelastic instabilities, around 250K, and are associated with valence fluctuations of the iron ions in this region of temperature, configuring a charge-frustrated electronic structure[15].

It can be seem (Figure 4b), at the magnetic ordering temperature, a decrease in f_R is observed, followed by a decrease with the same previous trend. In fact, the dashed line that fits the points at temperatures below the antiferromagnetic ordering and above the ferroelectric, has the same slope of paramagnetic phase. Namely, the AFM ordering only caused a decrease in f_R, without modifying behaviorist temperature dependence. This would agree with the by Smolenskii´s propose (despite not having
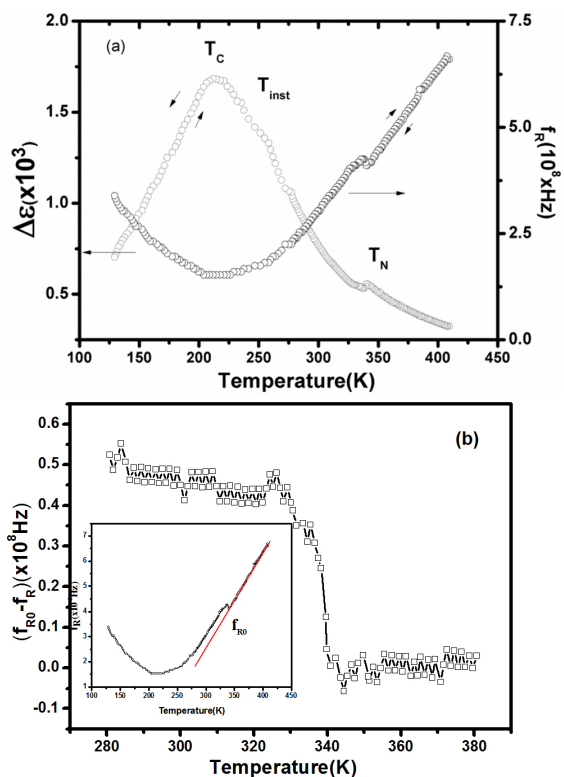
experimental evidence): for materials where $T_N > T_C$, all the laws for ferroelectricity remain in effect, since the existence of AFM order will not influence the establishment of electric order[16].

Generalizing these results for all PFW-PT samples, Figure 5 shows the temperature dependence for $\Delta\varepsilon$ and f_R: all curves have a minimum in f_R dependence and a maximum in $\Delta\varepsilon$ at the same temperature, correspond with FE phase transitions. In the same form, at T_N, all samples show a local maximum in the dielectric strength and a change in characteristic frequency.

Transition temperatures for ferroelectric (FE) and antiferromagnetic (AFM) phases are condensed in phase diagram of Figure 6. Néel and Curie temperatures of AFM and FE phases are indicated with different symbols for points measured with different techniques: magnetic (□) and dielectric (●) usual spectroscopy and by microwave dielectric technique (▲).

First, the diagram shows how while the establishment of the temperature of magnetic ordering decreases, the ferroelectric transition temperature increases with the addition of $PbTiO_3$ (PT) in the system. The temperatures where both orders coexist vary with the percentage of PT, and for some percentage between 10 and 15% to about 13% of PT, the two orders are simultaneously at temperature of approximately 235 K. Although lower than room temperature, this is relatively high compared to most multiferroic materials in literature. Second, it can be seen
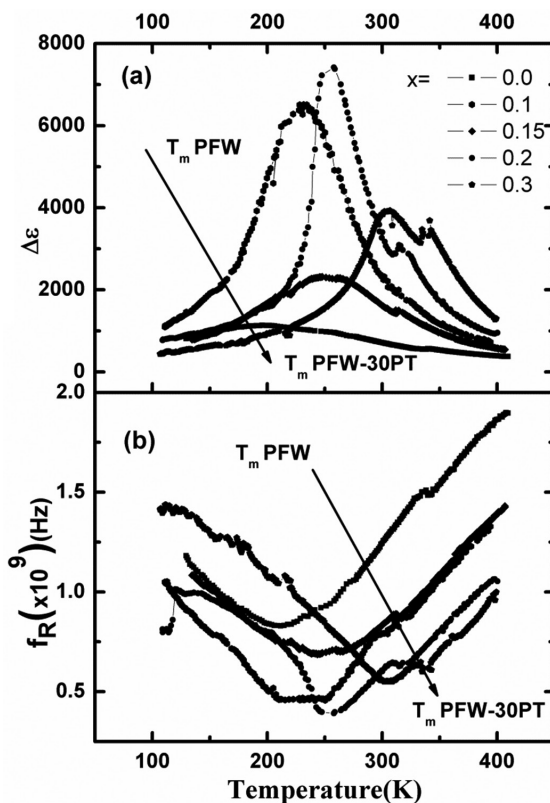

Figure 4. (a) Dielectric susceptibility at 80MHz and (b) dependence of the characteristic frequency (fR0 - fR) change versus temperature for PFW ceramics.

Figure 5. Temperature dependence of the characteristic coefficients of the microwave dispersion (a) characteristic frequency (f_R) and dielectric strength ($\Delta\varepsilon$) for PFW-PT ceramics.
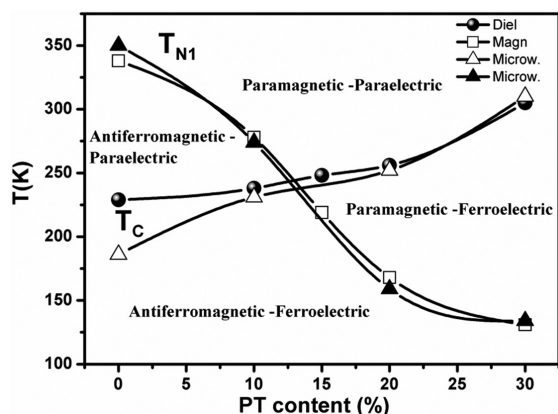
Figure 6. Transition temperatures for ferroelectric and antiferromagnetic ordering in (1-x) Pb (Fe$_{2/3}$W$_{1/3}$) O$_3$-xPbTiO$_3$ samples, with x = 0.0, 0.05, 0.10, 0.15, 0.17, 0.20 and 0.30 depending on the concentration of PT (x), measured by different techniques: dielectric impedance spectroscopy, magnetic susceptibility and dielectric microwave impedance spectroscopy.

that the temperatures measured by microwave dielectric techniques is very close for the observed by conventional measurements, confirm the effectiveness of this technique for detect both magnetic and ferroelectric phase transition.

Therefore, unless another unknown ordering superimposed over the magnetic ordering, this dielectric anomaly is caused by the magnetoelectric coupling in the PFW-PT system. This result demonstrates the high sensitivity of microwave dielectric measurements to probe weak transitions in bulk ceramics, as proposed before.

For last, we can observe a maximum in Δε at the same temperature of T$_N$ for the PFW samples, for all samples of the solid solution. What is surprising is that the maximum was observed near 350 K not only in pure PFW but also in PFW-xPT ceramics although T$_N$ should decrease with rising PT concentration. A decreased in f$_R$ was obtained for all samples at the same temperature. A similar behavior was obtained for acoustic emission for Dul'kin et al.[15] and explained by different chemical compositions in the cores and shells of PFW-PT ceramic grains: Ti cations go practically only in the cores and the shells remain unchanged with Ti doping, i.e., two different magnetic phase transitions in the cores and the shells of PFW-xPT ceramics were expected, whereas the AFM temperature in the shells will be independent of PT concentration. In effect, the morphotropic phase boundary composition 0.68PFW-0.32PT were analyzed in situ by TEM as a function of temperature from 16 to 300K for Li et al.[16] and core–shell structure was detected at room temperature. Additional studies are necessaries to establish the origin of this phenomenon, but by this technique, we demonstrate the influence of the lattice dynamic at this temperature.

4. Conclusions

In conclusion, we investigated MW dielectric properties at microwave frequencies of Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$ – PbTiO$_3$ solid solutions, which confirmed the existence of elastic contribution at the temperatures of antiferromagnetic (T$_N$) and ferroelectric (T$_C$) ordering. The experimental results observed at MW frequencies measurements revealed clearly that the magnetic transition and instabilities can be correlated to spin-lattice coupling.

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