Internal friction in particulate composites of \((x)\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4 - (1-x)\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3\) in the vicinity of the structural phase transition temperatures

A V Kalgin and S A Gridnev
Voronezh State Technical University, 14 Moskovsky prospect, Voronezh 394026, Russia
E-mail: kalgin_alexandr@mail.ru

Abstract. The internal friction in particulate ceramic composites of \((x)\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4 - (1-x)\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3\) \((x = 0, 0.1, 0.2, 0.3, 0.4, \text{and} 0.6)\) in the vicinity of the phase transition temperatures was studied. We observed the influence of the composite composition on the exponent that characterizes a temperature dependence of the internal friction near the ferroelectric Curie point. The reason for this influence is shown to be the doping of the \text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3\) ferroelectric phase with atoms of the \text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4\) ferrite phase that occurs during high-temperature sintering of composite samples.

1. Introduction
In modern solid-state physics, special attention is paid to systems with structural phase transitions (PT) of different natures because in these systems the anomalies of some physical parameters (heat capacity, dielectric constant, magnetic susceptibility, etc.) are observed in the vicinity of the Curie temperatures \(T_C\). These anomalies are usually discussed in terms of the Landau thermodynamic theory and different microscopic models as well.

In most cases, at a temperature \(T \rightarrow T_C\), some theories predict a simple power dependence of physical parameters on temperature in the form \(A(T - T_C)^p\), where \(A\) is a temperature-independent factor and \(p\) is the exponent obtained from thermal, dielectric, magnetic and other measurements.

The main task of theoretical and experimental research is to determine the values of exponents and to reveal regularities and reasons for their variations in systems of different natures. The solution of this task makes it possible to reveal the limits for various theoretical approaches and to predict general features of the physical parameter variation for systems at a temperature \(T \rightarrow T_C\).

Until now, the effect of the composite structure and composition on the exponent value has been studied in simple and complex systems using mainly measurements of the dielectric permittivity and magnetic susceptibility \([1, 2]\). At the same time, this influence has rarely been studied by the internal friction method characterized by the high structural sensitivity that is often unattainable by other methods.

Therefore, this study seeks to investigate the effect of the composition of particulate composites of \((x)\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4 - (1-x)\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3\) [hereafter, \((x)\text{MZF} - (1-x)\text{PZT}\)] on the exponents characterizing the temperature dependences of the internal friction \(Q^{-1}\) near the magnetic and ferroelectric Curie points.
The magnetoelectric composites were chosen due to their multifunctional properties and potential applications based on the magnetoelectric effect in these materials (the possibility of mutual conversion of magnetic and electric fields). Besides, there exists a unique correlation between the ME response and internal friction $Q^{-1}$ in composites [3].

2. Experiment

Samples of particulate magnetoelectric ($x$)MZF–(1-$x$)PZT composites, where $x = 0, 0.1, 0.2, 0.3, 0.4,$ and $0.6$, were prepared using the conventional ceramic technology. Mixtures of powders of the $\text{Mn}_0.4\text{Zn}_0.6\text{Fe}_2\text{O}_4$ (MZF) ferrite with the Curie point $T_K = 473$ K and $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ (PZT) ferroelectric with $T_K = 593$ K taken in stoichiometric ratio were sintered in air for 5 h at a temperature that was varied from 1373 to 1463 K as the MZF content in the mixture was increased from 0.1 to 0.6 mass fraction.

The prepared samples contained only initial phases (the ferrite phase with the spinel structure and the ferroelectric phase with the perovskite structure). This was confirmed by micrographs obtained using a Quanta 2003D scanning electron microscope and by X-ray diffraction patterns obtained using a DRON-3 diffractometer with FeK$\alpha$-radiation and a Ni-filter [4]. Samples were 12 x 2 x 2 mm$^3$ in size.

We measured the internal friction $Q^{-1}$ in composites depending on temperature using an inverted torsion pendulum. The temperature in the measuring chamber was controlled and measured by a chromel-alumel thermocouple; the measurement error was less than ± 0.5 K.

3. Results and discussion

The measurement data for $Q^{-1}$ in composites near the structural phase transition temperatures are shown in figure 1.

![Figure 1](image1.png)

**Figure 1.** Temperature dependences of internal friction at a frequency of 30 Hz and a heating rate of 2 K/min for ($x$)MZF–(1-$x$)PZT composite samples with various $x$, mass fraction: $1 - 0$, $2 - 0.1$, $3 - 0.2$, $4 - 0.3$, $5 - 0.4$, and $6 - 0.6$. The inset shows the temperature dependence of the composite shear modulus for the sample with $x = 0$.

![Figure 2](image2.png)

**Figure 2.** Dependences of $\lg(Q^{-1})$ on $\lg[(T_c - T)/(T_c - T_0)]$ for ($x$)MZF–(1-$x$)PZT composite samples with various $x$, mass fraction: $1 - 0.6$ and $2 - 0.2$. $Q^{-1}_0$ is the value of $Q^{-1}$ at the temperature $T_0$. 


The $Q^{-1}(T)$ dependences have a maximum at temperatures of 565, 538, 528, 519, 493, and 514 K for the samples with $x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.6, respectively. The observed maximum can be attributed to the first-order structural ferroelectric phase transition (FPT). It is accompanied by a characteristic step-like increase in the composite shear modulus $G$ with temperature. As an example, the $G(T)$ dependence for the composite sample with $x = 0$ is presented in the insert in figure 1. Both $Q^{-1}(T)$ and $G(T)$ anomalies are close to the temperature of the tetragonal-cubic FPT in PZT and far from the temperature of the magnetic PT in MZF.

It should be noted that no $Q^{-1}$ anomalies were observed near the magnetic PT temperature (see figure 1). This can be explained by the substantial smallness (by approximately an order of magnitude) of a $Q^{-1}$ maximum for pure MZF as compared to $Q^{-1}$ maxima for all composite samples.

The nature of the $Q^{-1}$ maximum in PZT can be related to the fluctuation mechanism of losses at the first-order phase transition [5]. According to this mechanism, PT occurs by the fluctuation nucleation of a new phase and subsequent growth of the nuclei of a supercritical size, i.e., because of the phase boundary motion through a system of point defects leading to the internal friction. In the case of small amplitudes of sample oscillations, the expression for the $Q^{-1}(T)$ maximum is written as:

$$Q_{m}^{-1} = \frac{G a^2 V}{k T_m} \cdot \frac{\dot{m}}{\omega},$$

where $G$ is the shear modulus; $a$ is the spontaneous strain at $T_C$; $V$ is the volume of a new-phase nucleus; $\dot{m}$ is the phase transformation rate; $k$ is the Boltzmann constant; $T_m$ is the temperature of the $Q^{-1}$ maximum; and $\omega$ is the frequency.

As it follows from equation (1), the internal friction $Q_{m}^{-1}$ should be directly proportional to the heating rate ($\dot{m}$) and inversely proportional to the frequency of a sample oscillation ($\omega$) under other equal conditions. It was this dependence that was found in the investigation of the internal friction dependence on the heating rate in composites of $(x)$MZF–$(1-x)$PZT near $T_c$ [6].

Figure 1 shows that the maximum of $Q^{-1}$ decreases in height, broadens, and shifts to lower temperatures with $x$ at the same frequency. It appears natural to relate the decrease in the maximum height to the increase in the number of point defects that pinning domain walls moving under the mechanical stress in PZT. The increase in the number of point defects leads to larger fluctuations of the composition of PZT in the composite and to a broader distribution of the local Curie temperature over the bulk of PZT. Consequently, the $Q^{-1}$ maximum becomes more diffuse. The shift of the $Q^{-1}$ maximum to lower temperatures, which was revealed in our experiment, is associated with the substitution of Ti atoms (with the ionic radius $R_{\text{Ti}} = 0.064 \text{ nm}$) by Fe atoms (with the ionic radius $R_{\text{Fe}} = 0.067 \text{ nm} > R_{\text{Ti}}$) [7]. Because of the decrease in the chemical pressure at such substitution, the internal field acting on ferroelectric active ions in unit PZT cells decreases. Consequently, the disordering of the polar state of PZT will occur at a lower temperature.

Temperature dependences of $Q^{-1}$ near $T_C$ were supposed to be approximated by the following power function:

$$\lim_{T \to T_k} Q^{-1} = f(\omega, T) \cdot \left| \frac{T - T_k}{T_k} \right|^p,$$

where $p$ is the exponent that is equal to unity for the mechanism studied in detail in [6].

It was interesting to relate the value of $p$ to the structure and composition of composites. For this purpose, we determined the exponent $p$ from temperature dependences of $Q^{-1}$ in $(x)$MZF–$(1-x)$PZT composites and revealed a dependence of $p$ on the composite composition. To find the parameter $p$, the $Q^{-1}(T)$ dependences (figure 1) were plotted in coordinates of $\lg (Q^{-1}_0/Q^{-1})$ on $\lg ((T_k - T)/(T_k - T_0))$ (figure 2). The experimental points were revealed to fall well on a straight line and the slope gives
\( p = 0.99 \) over a temperature interval of \( 51 < T_K - T < 106 \) K for the composites with \( x = 0.6 \) and \( p = 0.91 \) over a temperature interval of \( 70 < T_K - T < 113 \) K for the composites with \( x = 0.2 \).

One can see that the temperature dependences of \( Q^{-1} \) for the composites studied are quite well approximated by equation (2), where \( p \) takes values from 0.91 to 1.06 depending on the composite composition (figure 3).

Consequently, the parameter \( p(x) \) reflects the composition variations occurring in the ferroelectric phase of the composite quite well. According to the theory [5], \( Q^{-1} \) is equal to zero in the paraelectric phase. In fact, the \( Q^{-1}(T) \) dependence is observed in a certain temperature range above \( T_c \) in the paraelectric phase that can be related to the smearing of FPT owing to composition fluctuations and thermal fluctuations of the order parameter.

Since \( p \) decreases with \( x \) (figure 3) and FPT becomes more smeared with \( x \) (figure 1), it is natural to expect that there should be a clear correlation between \( p \) and the smearing parameter of the ferroelectric phase transition \( \Delta T \). The estimation of the width of the \( Q^{-1}(T) \) maxima, \( \Delta T \), at their half-height for various composite samples confirms this conclusion. The relationship between \( p \) and \( \Delta T \) is appeared to be inversely proportional (figure 3).

Since the cause of the increase in the degree of the FPT smearing with \( x \) in the composite was revealed, and a relation between \( p \) and \( \Delta T \) was found, we came to conclude that the reason for the decrease in \( p \) with \( x \) is the increase in the content of doping atoms in the ferroelectric phase, which are diffusively removed from the magnetic phase during high-temperature sintering of composite samples. Thus, the exponent \( p \) can be used as an indicator of the defectiveness degree for the ferroelectric phase in composites. We have not seen this approach mentioned before in the literature and believe that it offers certain advantages in material science.

4. Conclusions

Samples of particulate magnetoelectric composites of \((x)MZF-(1-x)PZT\) \((x = 0, 0.1, 0.2, 0.3, 0.4, \) and \( 0.6 \)) were prepared using ceramic technology. The prepared samples were used to measure \( Q^{-1} \) over a temperature range of ferroelectric and magnetic structural phase transitions. A pronounced \( Q^{-1} \) maximum was found in temperature dependences of \( Q^{-1} \) that is due to the ferroelectric phase transition. The maximum behavior agrees rather well with conclusions of the thermodynamic theory that predicts the increase in the \( Q^{-1} \) maximum height with the heating rate. The temperature dependence of \( Q^{-1} \) near \( T_c \)
was approximated by a power function. The exponent $p$ reflecting the smearing degree decreases with $x$ in samples of $(x)\text{MZF}-(1-x)\text{PZT}$. The decrease in the parameter $p$ with $x$ is attributed to the substitution of PZT lattice atoms by MZF lattice atoms arising during high-temperature sintering of composite samples.

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