The impact of the particle size of the $BaFe_{12}O_{19}$ magnetostrictive phase on the electrical properties of $(K_xNa_{1-x})NbO_3$ magneto-electric composites

Matheus Cavallaro Conti [a], Jose Antonio Eiras [b], Fabio Luis Zabotto [c]

[a] Materials Engineering Department, Center of Exact Sciences and Technologies (CCET), Federal University of São Carlos (UFSCar), São Carlos, Brazil, matheus.c.conti@gmail.com

[b] Department of Physics, Center of Exact Sciences and Technologies (CCET), Federal University of São Carlos (UFSCar), São Carlos, Brazil.

[c] Department of Physics, Center of Exact Sciences and Technologies (CCET), Federal University of São Carlos (UFSCar), São Carlos, Brazil.

Abstract. This study is aimed at investigating the impact of the particle size of the $BaFe_{12}O_{19}$ magnetostrictive phase on the electrical properties of $(K_xNa_{1-x})NbO_3$ magneto-electric composites. This perovskite-structured material presents significant technological potential due to its intriguing ferroelectric properties and its role as a substitute for commonly utilized ferroelectric matrices such as PZT and PMN-PT. The viability of incorporating KNN into multiferroic magneto-electric composite systems aligns with sustainability objectives, given that its nanostructures eschew lead (Pb), a heavy metal with pronounced toxicity, both in its composition and processing pathway. Consequently, in the pursuit of optimizing the physical characteristics of the KNN/BaM system, samples featuring distinct particle sizes were synthesized via Spark Plasma Sintering (SPS), a non-conventional sintering technique. Electrical properties were assessed through impedance spectroscopy. Overall, regarding electronic, nuanced variations were observed with alterations in particle size, including heightened dielectric dispersion correlating with augmented average grain size of the composite post-powder mixing and SPS sintering.

Keywords. Magneto-electric composites, Ferroelectricity, Spark Plasma Sintering.

1. Introduction

Ferroelectric materials exhibit a unique property wherein atoms with positive charges displace from the center of the unit cell in relation to negative charges, resulting in the generation of an electric dipole. This characteristic renders them highly attractive for various technological applications, including their utilization as magnetic detectors at ambient temperatures and in the development of ferroelectric random-access memories (FeRAM). Moreover, recent investigations have unveiled their potential for solar energy harvesting [1].

In industrial settings, the predominant ferroelectric systems comprise PZT and PMN-PT. However, the inclusion of lead in both the material composition and the manufacturing process leads to the generation of undesirable toxic byproducts. Consequently, there exists a compelling incentive to explore alternative systems such as KNN/BaM composite.

In light of this, the present study endeavors to investigate the influence of varying particle sizes of the magnetostrictive component on the electrical properties of the system. Through a systematic exploration of these parameters, insights into the optimization of novel ferroelectric composite materials can be garnered, thereby advancing their potential for diverse technological applications.

2. Reviewing

2.1 Dielectric Materials Polarization

Dielectric materials can be defined as those which, in the presence of an external electric field, undergo a rearrangement of charges such that the field inside them is neutralized [2,3]. Therefore, the application of an external electric field causes charge displacement, resulting in the induction of electric polarization. An external electric field interferes with the symmetry of the material's charge distribution, resulting from the displacement of the electron cloud (electronic polarization), the displacement of ions in the crystal lattice (ionic polarization), the orientation of pre-existing dipoles (dipolar polarization), and the ordering and redistribution of spatial charges possibly present in material defects (space charge polarization). These contributions differ concerning their response to the frequency spectrum of the electric field oscillation. Thus, dielectric properties are modified when subjected to different frequencies of the electric field. This is a parameter of utmost importance in the study of dielectric materials [3,4]..

2.2 Dielectric Dispersion

The total dielectric polarization is the result of all contributions in the dielectric. Thus, the contribution to polarization in the electronic and ionic mechanisms is largely due to the relative displacement of the participating particles, unlike the dipolar, which predominates the rotation of dipoles present in the material [5]. Thus, polarization can be divided into elastic displacement, from the first two mechanisms, and orientational polarization in the last two. Each of these contributions can be separately analyzed through spectroscopic analysis in the case of the application of an alternating electric field. Through the system's electrical response as a function of frequency, it is possible to determine the contribution of each mechanism, each occurring in a specific characteristic frequency range. The regions in which ε varies more sharply are called dispersion regions, each corresponding to a polarization mechanism.

2.3 Magneto-Electric effect

The term magneto-electric, first predicted by Pierre Curie in 1894, was coined by Debye in 1926 to describe the linear magneto-electric effect and later established by Dzyaloshinskii in 1959 [6,7,8]. This term represents the coupling between the electrical and magnetic effects, respectively, of the electric charges of electrons and ions and the electron spins present in materials called multiferroics. The search for materials with such property led Van Suchtelen in 1972 to propose obtaining the magneto-electric effect through composite materials, in which the mechanical coupling between piezoelectric and ferromagnetic phases results in the desired effect [9,10,11]. Satisfactorily, the effect in $BaTiO_3/CoFe_2O_4$ composites resulted in a magneto-electric effect ≅ 130 mV [cm * Oe], showing a significant improvement compared to single-phase multiferroics [9]. Currently, based on these findings, magneto-electric composites with $BaTiO_3$, $PbTiO_3$, $Bi_4Ti_3O_{12}$ combined with ferrites as the magnetic phase are common. These particulate composites, at room temperature, exhibit values between 3 mV and 115 mV. Therefore, this work addressed an environmentally friendly alternative to heavy metal. Ferro Electromagnetic materials, single-phase multiferroics in which ferroelectric and ferromagnetic ordering coexist, are rare and potential candidates for industrial applications due to their intrinsic magneto-electric coupling. However, as seen earlier, the magneto-electric effect can be sufficiently satisfactory for technological applications in composite materials, i.e., those that exhibit ferroelectric and/or ferromagnetic properties. Assuming a composite system subjected to a magnetic field, strain (deformation) will be induced due to the ferromagnetic component of the sample through the magnetostrictive effect, which transmits stress to the piezoelectric component (polarized ferroelectric phase), which, via mechanical coupling, induces electrical polarization as a function of the deformation of the ferromagnetic phase [10]. In general, composite systems exhibit indirect or extrinsic magneto-electric coupling, in which this effect is achieved through a strain/stress process between two distinct coupled phases.

2.4 Grain Size Influence

The influence on the dielectric, ferroelectric, and piezoelectric properties of the ferroelectric phase as a function of the average grain size is a widely studied topic, with numerous works in the literature [12,13,14]. The sharp decay of dielectric and pyroelectric properties when the average grain size is less than approximately 100 nm, referred to as a critical particle size value, has also been observed and studied [15,16]. These observed impacts on properties stem from a stress that compresses the grain interior, resulting from the reduction in the average particle size. This leads to a decrease in the Curie temperature and spontaneous polarization [17]. Furthermore, the reduction in domain wall mobility is inhibited, directly inferring from the decrease in the material's relative permittivity value. Regarding magneto-electric properties, the reduction in grain size has caused a decrease in the value of the magneto-electric coefficient. According to Yue et al., studies have shown that the decrease in grain size of the ferroelectric phase, along with an increase in the grain size of the magnetic phase, led to a decrease in the value of the magneto-electric coefficient. This research utilized $PbZr_{52}Ti_{48}O_3$ (PZT) $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF) systems [18].

2.5 Composite materials processing

The magneto-electric coupling depends on the mechanical coupling between the constituent phases of the composite, the ferroelectric phase (KNN), and the ferromagnetic phase (BaM) in the case of this research, which directly implies the importance of material processing to determine its specific properties of the constituent phases. Research conducted by [19,20] in BaTiO3-Ni(Co,Mn)Fe2O3 composite systems was pivotal in establishing control parameters that maximize the material's magneto-electric coefficient. The result of this study established that during processing, it is essential that: the constituent phases exhibit chemical equilibrium; material porosity be minimized to optimize the mechanical coupling of the phases; sintering be controlled to prevent diffusion between the constituent phases; piezoelectric and magnetostrictive coefficients be optimized; both phases should have high resistivity values, thereby avoiding dielectric breakdown during electrical polarization; and, the maximization of the composite's electrical polarization state. Thus, the processing of composite materials for magneto-electric studies must be rigorously controlled to exhibit high magneto-electric coupling coefficients. Therefore, the fabrication of dense samples with intact phases, as well as the use of matrices with appropriate chemical, ferroelectric, and ferromagnetic properties, is of paramount importance. Given that these conditions are difficult to achieve in practice, as polycrystalline materials during sintering undergo diffusion between constituent phases and therefore a decrease in the electrical resistivity of the composite phases [9,19,20,21], Spark Plasma Sintering (SPS) was used in this research as a non-conventional sintering method. This technique allows for better control of microstructural characteristics and magneto-electric coupling in composite systems, through greater control over excessive grain growth and reduced diffusion between phases during sintering.

3. Methods

Preparation of systems according to particle sizes:

- KNN/BaM@1 – BaM with agglomerate size greater than 200 µm (i.e., did not pass through the 60 mesh sieve);
- KNN/BaM@2 – BaM with agglomerate size smaller than 200 and greater than 75 µm (i.e., passed through the 60 mesh sieve but not through the 120 mesh sieve);
- KNN/BaM@3 – BaM with agglomerate size smaller than 200 and greater than 75 µm (i.e., passed through the 120 mesh sieve but not through the 200 mesh sieve);
- KNN/BaM@4 – BaM with agglomerate size smaller than 75 and greater than 35 µm (i.e., passed through the 200 mesh sieve but not through the 400 mesh sieve).

Tab. 1 - Mass of KNN and BaM used in the preparation of the systems according to particle sizes.

	KNN (g)	BaM (g)
KNN/BaM@1	(4,0046±0,0001)	(1,0027±0,0001)
KNN/BaM@2	(4,0034±0,0001)	(1,0073±0,0001)
KNN/BaM@3	(4,0006±0,0001)	(1,0053±0,0001)
KNN/BaM@4	(4,0750±0,0001)	(1,0011±0,0001)

The selection of powders with different BaM granulometries was performed through sieving using 60 mesh, 120 mesh, 200 mesh, and 400 mesh sieves. To achieve the desired average particle size, high-energy milling was applied for 24 hours at 200 rpm to reach smaller grain sizes and a heat treatment at 1200°C at a rate of 5°C/minute for 3 hours to reach larger grain sizes. After separating the different grain sizes of the ferromagnetic phase, KNN was mixed in a ratio of 4:1 (KNN/BaM) by mass **Tab. 1**.

3.1 Electrical Permittivity

The real and imaginary electrical permittivity of ceramics as a function of temperature and frequency were determined from the values of conductance (G) and susceptance (B) using impedance spectroscopy technique. For this purpose, an impedance analyzer, a laboratory-produced furnace, and a cryostat were employed. Through the complex admittance defined by Y = G + iB, the real (ε') and imaginary (ε'') parts of the dielectric constant (permittivity) were obtained. Considering the sample as a parallel-plate capacitor [22]:

$$\varepsilon' = \frac{Bd}{\omega A \varepsilon_0} \tag{1}$$

$$\varepsilon'' = \frac{Gd}{\omega A \varepsilon_0} \qquad (2)$$

where G is the conductance, B is the susceptance, ε is the dielectric permittivity of vacuum, ω is the frequency of measurement, d is the thickness, and A is the surface area of the sample. Additionally, the energy dissipation (or dielectric losses of the material) can be obtained by the following equation:

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (3)$$

This value obtained by dividing the imaginary part by the real part of the permittivity (3) is a parameter of utmost importance in the analysis of the technological application of a material. The samples were made with silver electrodes, cured at 590°C at a rate of 5°C/minute for 1 hour, and analyzed in the frequency range of excitation field from 100 Hz to 10 MHz between 25°C and 450°C, at a rate of 5°C/minute, during cooling.

4. Results and discussion

From the perspective of dielectric properties, despite all being formed by the same KNN system in the same proportions and microstructural characteristics, the change in the average particle size of the BaM phase drastically influenced the dielectric properties, as seen in **Fig. 1**, which represents the real part of the electric permittivity of the systems for frequencies of 1 kHz and 1 MHz.

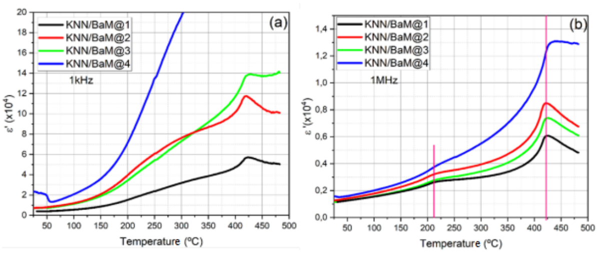

Fig. 1 - Dielectric properties as a function of temperature for the different samples in frequencies from 1kHz (a) to 1MHz (b). Pink bars indicate phase transition temperatures expected for the KNN system.

It is noted that properties characterizing the phase transition of KNN remained unchanged, regardless of the size of the BaM phase cluster, as indicated by the pink lines in **Fig. 1**. However, there is an increase in the conductive contribution for samples with a smaller average cluster size. This fact may be associated with the increased contribution of conductivity at the grain boundary of the ferroelectric phase, associated with the accumulation of the BaM phase in this region, creating percolation regions. Considering that the SPS process itself results in samples with reduced aspects, the continuation for nonlinear and magneto-electric characterizations were hindered since they require the application of high electric fields. Thus, studies are ongoing to discuss the efficiency of the reoxidation process of the prepared samples to restore their ferroelectric properties by increasing the electrical resistivity of the composite particulate systems.

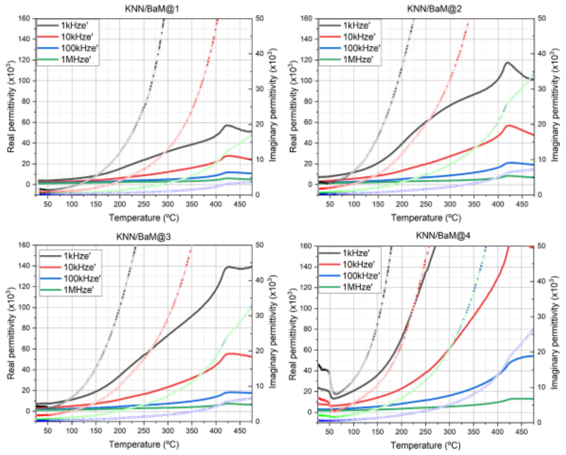

Fig. 2 - Real and imaginary permittivity of the samples KNN/BaM with different particle sizes at different frequencies according to the temperature.

The expected phase transition temperatures can be better observed in **Fig. 2**, in which for the samples KNN/BaM@1, KNN/BaM@2, and KNN/BaM@3, near 200°C, the ferro-ferroelectric transition is noted, and after 400°C, the ferro-paraelectric transition. The sample KNN/BaM@4 almost does not present a ferroelectric behavior.

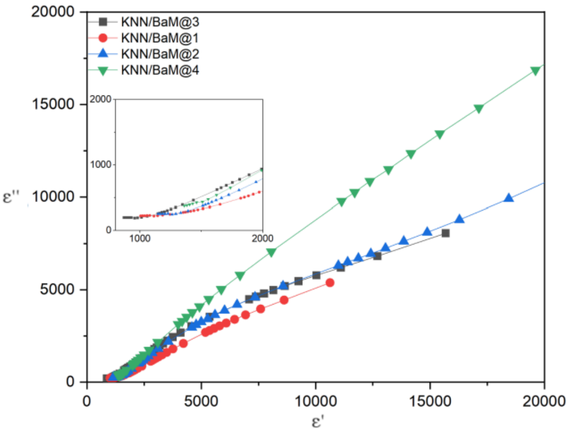

Fig. 3 - Real permittivity vs. imaginary permittivity, at room temperature, of KNN/BaM samples with different grain sizes.

In **Fig. 3**, it is noted that for the coarser powder, the permittivity is lower and has a single contribution, while for the powders KNN/BaM@2 and KNN/BaM@3, they present two dielectric contributions. Additionally, in regions of higher frequencies, powders with intermediate grain sizes undergo more evident saturation. In the coarser powder, this saturation is less evident. In consonance, at lower frequency values, samples with smaller particle sizes present much higher permittivity values, which may result from interface effects or even a relaxation due to the Maxwell-Wagner effect.

For better visualization of the permittivity behavior as a function of frequency, **Fig. 4** was plotted. Upon analysis, it is possible to note that, for larger coarse grains (above 200 nm), the tangent presents a maximum value near frequencies of 1000 Hz.

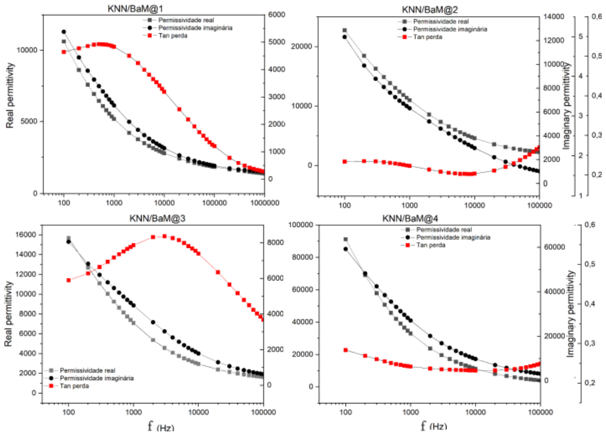

Fig. 4 - Real permittivity, imaginary permittivity and tan loss vs. frequency for the different samples.

On the other hand, the other samples present a peak maximum at lower frequencies, where the permittivities present an increase of up to an order of magnitude. It is also possible to note that the samples follow a very similar curve pattern, meaning an increase in electrical permittivity with smaller grain size. This growth is associated with dielectric loss, which is also higher with decreasing grain size. The most distinct curves occur at the extremes, which is expected. Despite the defined increasing order, there is a reversal between the intermediate powders (KNN/BaM@2 and KNN/BaM@3), where the coarser grain size overlaps.

5. Conclusion

In summary, this research investigated the electrical and magnetic behaviors of a particulate composite system of barium hexaferrite in a KNN matrix. Regarding the electrical part, it was observed that permittivities increase at lower frequencies, and concurrently with this, the tangent of dielectric loss also increases.

6. Acknowledgement

This work has been supported by the following Brazilian research agencies: FAPESP (Grant #2021/01399-0).

7. References

[1] S. S. D. Santos, M. L. Marcondes, I. P. Miranda, P. Rocha-Rodrigues, L. Vitória Credidio Assali, A. Lopes, H. M. Petrilli and J. P. Araujo, *J. Mater. Chem. C*, 2021, DOI: 10.1039/D1TC00989C.

[2] Reitz, J. R.; Molford, F. J.; Christy, R. W. *Fundation of Eletromagnetic Theory*. 4. ed.: Addison-Wesley, 1993.

[3] Rippel, A. R. V. *Dieletrics and Waves. Massachusetts: MIT Press*, 1954.

[4] Uchino, K. Ferroeletric Devices. 1. ed. *New York: Marcel Dekker*, 2000.

[5] Kittel, C. Introduction to Solid State Physics. *John Wiley and Sons. 4 ed.*, 1971.

[6] Currie, P. *Journal de Physique Théorique et Appliquée*. v.3, 1894. 32

[7] Debye, P. *Zeitschrift fur Physik. v.36*, p.300, 1926.

[8] Dzyaloshinskii, I. E. On the Magneto-Eletrical Effect in Antiferromagnets. *Soviet Physics Jetp-Ussr,* v.10, n.3, p.628-629, 1960.

[9] Suchtelen, J. V. Product Properties: A new application of composite materials. *J. Philips. Res. Rep.*, v.27, p.28-37, 1972.

[10] Ce-Wen Nan, et al. Multiferroic magnetoeletric composites: Historical perspective, status, and future directions, *APL* 103, 031104, 2008.

[11] Priya, S.; Islam, R.; Dong, S.; Viehland, D. Recent advancements in magnetoelectric particulate and laminate composites. *Journal of Electroceramics*, v.19, p.147-164, 2007.

[12] Choudhury, S., et al. Effect of grain orientation and grain size on ferroelectric domain switching and evolution: Phase field simulations. *Acta materialia*, v. 55, n. 4: p. 1415-1426, 2007.

[13] Kang, B.-S.;Gu-Choi, D.Choi, S.-K. Effects of grain size on pyroelectric and dielectric properties of Pb0. 9La0. 1TiO3 ceramics. *Journal of Materials Science: Materials in Electronics*, v. 9, n. 2: p. 139-144, 1998.

[14] Martirena, H.Burfoot, J. Grain-size effects on properties of some ferroelectric ceramics.

Journal of Physics C: Solid State Physics, v. 7, n. 17: p. 3182, 1974.

[15] Lu, C., et al. The effect of grain size on domain structure in unsupported thin films. *Journal of Physics: Condensed Matter,* v. 8, n. 42: p. 8011, 1996.

[16] Sakaki, C., et al. Grain size dependence of high power piezoelectric characteristics in Nb doped lead zirconate titanate oxide ceramics. *Japanese journal of applied physics*, v. 40, n. 12R: p. 6907, 2001.

[17] Islam R. A.; Priya, S. Progress in Dual (Piezoelectric-Magnetostrictive) Phase Magnetoelectric Sintered Composites. *Advances in Condensed Matter Physics*, v. 2012, n. p. 2012.

[18] Yue, Y.; et al. Size effects on magnetoelectric response of multiferroic composite with inhomogeneities. *Physica B: Condensed Matter,* v. 478, n. p. 36-42, 2015.

[19] Boomgaard, J. V. D.; Run, A. M. J. G. V.; Suchtelen, J. V. Magnetoelectricity in piezomagnetic-magnetostrictive composites. *Ferroeletrics*, v.10, n.1, p.295, 1976.

[20] Boomgaard, J. V. D.; Run, A. M. J. G. V.; Suchtelen, J. V. Piezoelectric-piezomagnetic composites with magnetoelectric effect. *Ferroeletrics*, v.14, n.1, p.405. 1976.

[21] Ryu, J.; Priya, S.; Uchino, K.; Kim, H. E. Magnetoelectric effect in composites of magnetostrictive and piezoelectric materials. *Journal of Electroceramics*, v.8, n.2, p.107-119, 2002.

[22] Barsoukov, E.; Macdonald, J. R. Impedance spectroscopy: theory, experiment and applications, *John Wiley and Sons*, 2005.