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Electrical, magnetic and microwave absorption properties of multiferroic NiFe$_2$O$_4$-BaTiO$_3$ nanocomposites

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Abstract

Multiferroic nanocomposites of xNiFe$_2$O$_4$/(1-x)BaTiO$_3$ (x = 0, 0.1, 0.2, 0.3, and 0.4) (denoted as NFO-BTO) with the particle size about of 70 nm were prepared by the high energy mechanical milling combined with the thermal annealing methods. The x-ray diffraction patterns show a presence of NiFe$_2$O$_4$ (NFO) and BaTiO$_3$ (BTO) phases. The values of the characteristic parameters of nanocomposites such as the coercive field ($E_c$), the residual polarization ($P_r$), the remanent magnetization ($M_r$), the saturation magnetization ($M_s$), and the coercive force ($H_c$) increase gradually with an increase in NFO concentration. For an applied electric field below 10 kV cm$^{-1}$, the values $P_r$ and $E_c$ are found to be 0.004–0.038 $\mu$C cm$^{-2}$ and 0.7–2.0 kV cm$^{-1}$, corresponding $x = 0.1–0.4$, respectively. Changes in electrical and magnetic properties of composites depend heavily on the NFO content, which will be studied specifically. Additionally, the ability to absorb microwave at room temperature of a representative sample with $x = 0.3$ mixed in acrylic paint (denoted as NFO-BTO-AP) in a frequency range of $f = 12–18$ GHz has also been investigated. It shows a large negative reflection loss ($RL$) with $RL = -39.8$ dB occurring at around 16.8 GHz corresponding to the absorptivity of over 99.9% for an absorbing layer with thickness of 5.5 mm. This suggests that NFO-BTO nanocomposites could be considered as a potential material in the field of absorbing and shielding electromagnetic waves.

1. Introduction

Nowadays, the studies about ferroelectric (FE) and ferromagnetic (FM) materials used as fillers in electromagnetic wave absorbers in the frequency range of 1–20 GHz have received considerable attention and attracted many scientists [1–4]. There are many microwave absorbent materials, which have high absorption efficiencies, such as ferrites [5, 6], magnetics [7], and especially multiferroic composites [8]. They can degrade incoming microwaves by converting them into heat or dissipating them. Due to the influence of structural characteristics, physical properties, ferroelectricity, and ferromagnetism existing in the materials, the microwave absorption and shielding ability of synthetic multiferroic composites are highly effective. Therefore, the researches on multiferroics in the field of microwave absorption and shielding have attracted scientists around the world [8–10]. Multiferroics that may concurrently exhibit several ferroic orders such as ferromagnetism, ferroelectricity, and ferroelasticity, and can be widely applied in advanced electronic components such as DRAM, MRAMs, FeRAMs, magnetoelectric transducers, actuators [11–15], and so on. The magnetic effects in multiferroics are often derived from the coupling between the phases of electrostrictive and magnetostRICTive [16, 17]. The mechanical strain occurs in the FM phase through magnetostriction which is impacted by the FE phase of a multiferroic, stress is generated and induces electric polarization in the FE phase through
microwave absorber. However, its absorption bandwidth is limited. Therefore, studies on BTO-based composites are being viewed as a multifunctional electronic ceramic. Besides, recent studies indicate that BTO is also used as a lead-free ferroelectric material, exhibiting some advanced characteristics, such as high permittivity and good ferroelectric properties [30–33]. Chemical stability, and low toxicity [34–36], which is being viewed as a multifunctional electronic ceramic. Besides, recent studies indicate that BTO is also used as a microwave absorber. However, its absorption bandwidth is limited. Therefore, studies on BTO-based composites have been carried out to improve their microwave absorption [32–34]. It is known that, by adjusting the fabrication conditions, the content, and types of doping, the structure and the physical properties of BTO can be tuned [37–39]. Additionally, BTO is also a lead-free ferroelectric material with wide bandgap and quite high Curie temperature [40–45]. Therefore, BTO was chosen as a typical FE material to create multiferroic composites, such as BaTiO3–NiFe2O4 [26], BaTiO3–CoFe2O4 [41], BaTiO3–Ni0.7Zn0.3Fe2O4 [46], Ba0.9Sr0.1Ti0.9Zr0.1O3–CoFe2O4 [47], Ba0.8Ca0.2Ti0.8Zr0.2O3–CoFe2O4 [48], BaTiO3–CoFe2O4 [49], BaTiO3–BiFeO3 [50], BaTiO3–Ba0.8Sr0.2FeO3 [51], [0.5(Ba0.7Ca0.3Ti3O12)–0.5(Ba0.95Ti5O12)]–Co0.5NiFe2O4 [52]. Among spinel ferrites, nickel ferrite NiFe2O4 does not exhibit a typical ferromagnetic exhibiting the high initial permeability, which is an important character to improve the electromagnetic conversion factor in multiferroic composites [26, 27, 29].

Related to the field of electromagnetic shielding, it shown that spinel ferrites can be also used as the microwave absorbers owing to their immense magnetic losses and high resistivity [53]. Studies on the microwave absorption and shielding ability of NFO materials have been specifically shown in previous studies [5, 6]. More specifically, the studies on the absorption and shielding ability of nanocomposites at frequency of not only FM materials [53–56] but also BTO-based composites [8–10, 57]. Recently, Zainal et al researched the microwave wave absorbing properties of xCoFe2O4–(1-x)BaTiO3 composites fabricated by using the ball milling method [8]. The value of the reflection loss of x = 0.5 composite achieved is quite impressive (RL = −40.1 dB) occurred at a frequency of 10.98 GHz [8]. Besides, Sardarian et al successfully fabricated and researched the Fe2O3–BaTiO3–multi-walled carbon nanotubes nanocomposite well mixed with 40% paraffin. They obtained the absorption capacity in a frequency of 12.5–14.3 GHz of this nanocomposite is about 80–90% [9]. However, ability to absorb and shielding the microwave of NFO–BTO nanocomposites have not been specifically and systematically mentioned, especially when mixed them with some kind of paint (for example, acrylic paint: AP). This can be considered as an interesting point when the studies on the ability to absorb electromagnetic waves of multiferroic composites are closer to practical application. It is also shown that the appearance and the change of NFO/BTO ratio can affect the electromagnetic properties, resistivity, and the loss of energy density of multiferroic composites [38]. This directly affects the ability of the material to absorb and shield microwaves. The intrinsic parameters of the individual ferroic orders [59, 60], piezoelectric and magnetostrictive coefficient, and the extent of electromagnetic coupling [26, 27] are greatly influenced by grain size. The smaller the grain size will create more grain boundaries. This is similar to making the scattering centers help to improve resistivity required for electrical poling elastic and developing the mechanical contact for interaction in multiferroics [61–64]. The presence of BTO changes the cation distribution from inverse spinel to mixed spinel structure of NFO. Making a change in the lattice parameters of NFO and BTO, which indicates a strong elastic coupling between them [65]. Several recent studies have also shown that, the cause of the significant enhancement of the remnant polarization (Pr) when NFO content changes are attributed to the change in the structure and resistivity of composites [26, 66]. To improve the ME response and physical properties of BTO-based multiferroic, the methods including sol–gel [26], high energy ball milling [63], solid-state reaction [65], conventional solid state [66] were performed. Accordingly, materials can be successfully fabricated at low temperatures, eliminating the appearance of unwanted secondary phases. Liu et al obtained a coexistence of the FM and FE properties at room temperature in NFO–BTO nanocomposites with particle size of 20 nm, which were fabricated by using the sol-gel method [26]. It is also shown an increase in the saturation magnetization (M_s) while the maximum electrical polarization value (P_m) reduced for NFO increasing. The sol-gel or solid-state reaction methods have been widely used to prepare NFO–BTO composites. However, a combination the high energy mechanical milling with the thermal annealing methods is quite rare. It is known that the residual electrical polarization of materials fabricated by using high energy mechanical milling method is improved significantly due to the influence of lattice distortion and the surface defects [63, 67–69]. In the present work, xNFO–(1–x)BTO (x = 0–0.4) nanocomposites were fabricated by using a combination of the high energy mechanical milling with the thermal annealing methods. The influences of the content of FE and FM phases on their electromagnetic characteristics were systematically analyzed. Additionally, a multiferroic nanocomposite with x = 0.3 exhibiting the typical FE and FM properties were further investigated for the ability...
to systematically absorb and shield microwaves. The obtained results are useful for investigations and application the lead-free multiferroics in the field of microwave shielding and absorption.

2. Experimental details

Five multiferroic samples of $x$NFO-(1-$x$)BTO with $x = 0, 0.1, 0.2, 0.3,$ and 0.4 (denoted as C0, C1, C2, C3, C4) were fabricated from high purity NiO, Fe$_2$O$_3$, BaO and TiO$_2$ powders ($\geq 99.9\%$) by using high energy mechanical milling combined with the thermal annealing methods. Initially, the mass of chemicals was calculated and weighed according to the nominal formula to create two separate NFO and BTO compounds via the high-energy mechanical milling method on a Spex-8000D machine with a speed of 875 rpm for 3 h in air. The powdered mixture of each compound after being grinded was pressed into pellets under the pressure of $7000 \text{ kg cm}^{-2}$, and then annealed for 5 h at $700 \text{ °C}$ in air. After that, these samples were grinded by the hand on the brain code mortar to create smooth powders. Next step, to create C0-C4 samples, the masses of NFO and BTO were estimated according to the x-ray diffraction (XRD) patterns using an Equinox 5000 device (Thermo Scientific, with $\lambda = 1,5406 \text{ Å}$ of Cu-K$_\alpha$ radiation) and a field emission scanning electron microscopy (FE-SEM) images using S4800 equipment (Hitachi). The composition maps analyses for samples were surveyed on an Aztec EDX equipment made by Oxford Instruments (UK). The electrical and magnetic properties were investigated through hysteresis curves measured by the Precision LC II Model 609 and vibrating sample magnetometer systems. All measurements were performed at room temperature. Additionally, a powder sample with $x = 0.3$ (C3 sample) was selected to mix well with acrylic paint (AP) in a weight ratio of 1:2, respectively, to make a NFO-BTO-AP mixture. After that, this mixture was coated on the flat aluminum (Al) plates of $100 \times 100 \text{ mm}^2$ area. The thicknesses ($t$) of the NFO-BTO-AP layers were changed from 2.0 to 5.5 mm ($t = 2.0, 4.0, 5.0,$ and $5.5 \text{ mm}$). Microwave absorption characteristics of these absorbing layers were carried out at room temperature in the free space using a ZNB20 Vector Network Analyzer in a frequency range of 4–18 GHz.

3. Results and discussion

The XRD patterns of C0-C4 samples are showed in figure 1. We find that the C0 sample to be a single phase of BTO, corresponding to a tetragonal structure, denoted by a set of Miller indices (hkl), such as (100), (110), (111), (002), (210), (211), and (220). With an increase in the NFO content, XRD patterns of the C1-C4 samples appear some characteristic peaks NFO phase corresponding to a cubic structure (denoted by asterisks). It is clear that except for the characteristic peaks of BTO and NFO, there is no appearance of any new XRD peaks or displacement of XRD peaks. This indicates that the phases of BTO and NFO coexist, do not react to form any new phase. The morphology and particle size of samples were analyzed via SEM images. SEM images of two representative samples of C0 and C4 are presented in figures 2(a) and (b), respectively. We see that the particles are pseudo-spherical with the size of about 70 nm. The grain boundaries are blurred. Many small particles are clumped to form clusters with larger size. Changing the NFO content is almost un-change the particle size in samples.

Based on the EDX spectroscopy obtained from an attached function of FE-SEM device, the presence of the elements in composites has been detected. The EDX spectrum of two representative samples of C0 and C4 are presented in figures 2(c) and (d), respectively. They show the full presence of the elements including Ba, Ti, Fe, Ni and O, which are derived from the original chemicals without any foreign elements in all samples. The percentage of atomic analyzed from the EDX spectrum is quite consistent with those expected of composites.

Figures 3 and 4 show the EDX mappings for two representative samples of C0 and C4, respectively. Homogeneous spatial distributions of Ba, Ti, O, Ni, and Fe elements were observed. These results indicate that BTO and NFO phases are uniformly distributed as expected. $M(H)$ curves measured at room temperature for samples are displayed in figure 5. Clearly, all $M(H)$ curves exhibit the FM characteristics. For the C0 sample, its $M(H)$ curve has almost no hysteresis, the value of the magnetization is very low ($M_{sat} = 6.2 \text{ emu g}^{-1}$ at the magnetic field of 10 kOe, see upper inset in figure 5), suggesting a weak FM order exists in BTO nanoparticles. The origin of this weak FM could be associated to the oxygen vacancies on the surfaces of BTO nanoparticles [39, 65, 70]. However, the value of magnetization of samples increases when the contribution from the magnetic moments of NFO increased [26, 71]. This is related to the stronger strength of FM interactions in NFO grains than that in BTO grains [39]. The change of some magnetic parameters (including $M_s$, $M_r$, and the coercive force ($H_c$)) with NFO concentration is performed in the below inset in figure 5. Herein, the $H_c$ value increases gradually from 372.1 to 519.3 Oe, the $M_s$ values increases from 1.7 to 6.2 emu g$^{-1}$, and the $M_r$ values increases.
Figure 1. Powder XRD patterns of the C0-C4 samples.

Figure 2. (a) and (b) SEM images, (c) and (d) EDX spectra for C0 and C4 samples, respectively.
from 4.4 to 15.2 emu g\(^{-1}\) when NFO concentration increases from \(x = 0.1\) to 0.4, respectively. With the soft FM nature and high value of \(M_s\), NFO-BTO could be used as an absorbing material [54].

In a previous study, Sarkar et al also pointed out NFO doping has the role of improving the magnetic parameters in NFO-BTO composites [27]. For pure NFO, its \(H_C\) value is about 65 Oe, which is lower than that of NFO-BTO composites [27, 43]. The FM and FE interfaces and the magnetic domain boundaries have been expanded, and some structural defects have been also strengthened when NFO increasing. These may contribute to the pinning of magnetic moments, [39, 45, 66]. The FE BTO particles have the role as the pores, which break the magnetic circuits in composite [39]. Besides, the increase in \(M_s\) value confirms that most of the spins in samples are oriented following the applied magnetic field [25, 27, 39]. To predict the nature of magnetic orderings and the order of the magnetic transition in samples, the Arrott plots (\(M^2\) versus \(H/M\) curves constructed from the initial magnetization curves \(M(H)\) at room temperature) have been performed and displayed in figure 6. Clearly, there is an existence of FM ordering and a characteristic of second-order magnetic transition in all the samples, corresponding to the presence of curvature and positive slope of these Arrott plots [61].

Figure 7 shows the hysteresis \(P(E)\) curves measured at different voltages from 100 to 900 V for NFO-BTO composites. The nature of BTO is a FE material. We see that the hysteresis \(P(E)\) curve has a narrow nature and curvature when examined in the electric field generated by the applied external voltages of 100–900 V. Nevertheless, the observed \(P(E)\) loops do not show the saturation status yet, which could be related to the leakage...
currents in the sample. This behavior is also agreed with previous studies on BTO family \cite{26, 47, 50–52, 58}.

With an increase in NFO content, the hysteresis curves tend to expand gradually in the shape of a fingerprint. The cause of this fingerprint curve shape can be explained by two main reasons. The first is the heterogeneity of phases in the samples (where the material has two FE (BTO) and FM (NFO) phases). Second, due to the

Figure 5. $M(H)$ curves of composites measured at room temperature. The upper inset shows $M(H)$ curve for C0 sample. The below inset shows the changes of $M_s$, $M_r$, and $H_c$ with NFO concentration.

Figure 6. Arrott plots of the samples C1 (a), C2 (b), C3 (c) and C4 (d) obtained at room temperature.
contribution of the NFO phase, the resistivity of the material decreases gradually and the electrical conductivity forms a number of conduction channels causing large leakage currents in the material sample. The results of this study are completely consistent with studies on BTO-based multiferroics [47, 50–52, 70, 71]. Additionally, the hysteresis curves tend to expand, the $E_C$ value gradually increases from 0.4 to 2.0 kV cm$^{-1}$, the $P_r$ value increases gradually from 0.004 to 0.038 $\mu$Cc m$^{-2}$ for C0–C4. These increases are attributed to the pinning effect arising that relate to the presence of FM phase in composites [50–52]. The high internal polarization led to the enhancement of $P_r$ and $P_m$ [70]. According to Ciomaga et al [72], the FE properties of composites could be weakened by the presence of NFO phase. The positive and negative counterpart values of $E_C$ and $P_r$ are not asymmetry, corresponding to the presence of an internal electric field, which is caused by the short distance, off-center and as well as the inherent movement of bound electrons [72]. Regarding the studies of multiferroic BTO-based composites with other FM phases fabricated by using mechano-chemical activation technique [71], high energy ball milling [50] and solid-state reaction methods [39, 51, 52, 73] have shown similar results. To improve the electrical and magnetic properties of multiferroics, besides changing the fraction of the FM and FE phases, the fabricated methods also greatly affect their characters, as shown in table 1. It shows the multiferroic parameters obtained for NFO-BTO composites in this work and some similar multiferroics prepared by using solid-state reaction method [66]. BTO exhibited $P_r = 1.5 \mu$C cm$^{-2}$ and dropped sharply to about 0.9 $\mu$C cm$^{-2}$ for $x = 0.05–0.25$, and then gradually decreased to 0.66 $\mu$C cm$^{-2}$ for $x = 0.45$ under an applied electric field of 50 kV cm$^{-1}$. For sol-gel method [26], under electric field range of 40–50 kV cm$^{-1}$, NFO-BTO multiferroics exhibited a gradually decrease from $P_m = 3.75$ to 0.69 $\mu$C cm$^{-2}$ when the NFO content gradually increased from $x = 0$ to 0.6 [26]. For solid-state reaction method, BTO reached $P_r = 7.7 \mu$C cm$^{-2}$ and dropped sharply, reaching 2.0 $\mu$C cm$^{-2}$ for $x = 0.1$, and then gradually increased to 6.6 $\mu$C cm$^{-2}$ for $x = 0.2$ under electric field of 35 kV cm$^{-1}$ [39]. Meanwhile, studies on the electrical polarization characteristics of materials in low electric fields (below 10 kV cm$^{-1}$) have not been studied in detail. For materials prepared by using the high-energy mechanical milling method, due to the influence of defects in the lattice, the leakage current tends to increase gradually, which strongly affects the FE properties of the material. This is significantly different from the sol-gel

\[ \text{Figure 7. Ferroelectric hysteresis P(E) curves of the samples C0 (a), C1 (b), C3 (c), C4 (d) under the applied voltages of 100–900 V measured at room temperature.} \]
Table 1. Multiferroic characters $P_m, P_r, E_c, M_s$, and $H_c$ at room temperature for NFO-BTO and some similar composites fabricated by using different methods.

| Sample | $x$ | $E_{max}$ (kV cm$^{-1}$) | $P_m$ (μC cm$^{-2}$) | $P_r$ (μC cm$^{-2}$) | $E_c$ (kV cm$^{-1}$) | $M_r$ (emu g$^{-1}$) | $M_s$ (emu g$^{-1}$) | $H_c$ (Oe) | Method | References |
|--------|-----|---------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|------------|--------|------------|
| xNiFe$_2$O$_4$ - (1-x) BaTiO$_3$ | 0.0 | 8.8 | 0.038 | 0.004 | 0.4 | — | 1.0 | 105.8 | High energy ball milling | This work |
| | 0.1 | 4.5 | 0.045 | 0.011 | 0.7 | 1.8 | 4.4 | 372.0 |
| | 0.2 | 3.5 | 0.048 | 0.015 | 0.8 | 3.1 | 8.2 | 485.0 |
| | 0.3 | 5.0 | 0.056 | 0.024 | 1.3 | 4.9 | 11.7 | 507.6 |
| | 0.4 | 4.5 | 0.069 | 0.038 | 2.0 | 6 | 15.2 | 519.3 |
| xNiFe$_2$O$_4$ - (1-x) BaTiO$_3$ | 0 | 50 | 5.01 | 1.5 | 9.36 | — | — | Solid state reaction | [66] |
| | 0.05 | 3.18 | 0.902 | 7.15 | 0.092 | 1.84 | 57.10 |
| | 0.15 | 1.25 | 8.70 | 0.28 | 6.84 | 47.91 |
| | 0.25 | 0.98 | 0.902 | 10.11 | 0.46 | 11.08 | 47.37 |
| | 0.35 | 0.87 | 0.870 | 10.73 | 0.76 | 15.90 | 38.32 |
| | 0.45 | 0.74 | 0.660 | 10.12 | 1.22 | 22.66 | 38.07 |
| xNiFe$_2$O$_4$ - (1-x) BaTiO$_3$ | 0.1 | 40–50 | 3.75 | — | 0.5 | 3.5 | — | Sol-gel | [26] |
| | 0.2 | 2.08 | — | — | 1.2 | 7 | — | |
| | 0.3 | 1.07 | — | — | 2.0 | 10 | — | |
| | 0.4 | 1.05 | — | — | 2.2 | 15 | — | |
| | 0.5 | 0.71 | — | — | 2.4 | 20 | — | |
| | 0.6 | 0.69 | — | — | 2.7 | 24.1 | — | |
| xNiFe$_2$O$_4$ - (1-x) BaTiO$_3$ | 0 | 35 | 18 | 7.7 | 4.5 | — | — | — | Solid state reaction | [27] |
| | 0.1 | 7 | 2.0 | 7.2 | 0.18 | 5 | 22 | |
| | 0.2 | 9 | 6.6 | 18.1 | 0.26 | 9.5 | 22 | |
| | 0.3 | 52 | 50 | 34.4 | 0.75 | 15 | 27 | |
| (1-x)BaTiO$_3$-xCoFe$_{1.8}$Zn$_{0.2}$O$_4$ | 0.1 | 15–20 | 3.18 | 0.66 | 4.48 | 0.44 | 8.9 | — | Solid-state reaction | [73] |
| | 0.2 | 4.72 | 0.87 | 3.14 | 0.49 | 14.9 | — | |
| | 0.3 | 5.25 | 0.91 | 2.86 | 1.76 | 21.5 | — | |
| | 0.4 | 7.15 | 2.07 | 5.92 | 1.95 | 28.6 | — | |
| (1-x)Ba$_{0.9}$Sr$_{0.1}$Zr$_{0.1}$Ti$_{0.93}$O$_4$ - xNiFe$_2$O$_4$ | 0.0 | 40–50 | 18.45 | 8.8 | 18.8 | — | 2.0 | — | Mechanochemical activation | [74] |
| | 0.1 | 26.95 | 12.3 | 15.6 | — | 3.2 | — | |
| | 0.2 | 41.1 | 15.5 | 23.3 | — | 4.5 | — | |
| | 0.3 | 15.55 | 7.2 | 22.0 | — | 8.0 | — | |
| | 0.4 | 8.0 | 12.0 | 32.0 | — | 11.6 | — | |
| (1-x)Ba$_{0.95}$Yb$_{0.05}$TiO$_3$-xCoYb$_{0.1}$Fe$_{1.9}$O$_4$ | 0.03 | 35 | 3.29 | 1.52 | 13.3 | 0.819 | 1.9 | 746.0 | Solid state reaction | [49] |
| | 0.06 | 7.52 | 4.24 | 17.2 | 1.42 | 3.71 | 831.8 | |
| | 0.09 | 7.21 | 4.95 | 23.2 | 1.97 | 527 | 854.5 | |
or the solid-state reaction methods, suggesting that the manufacturing methods and conditions have a great influence on the physical properties of NFO-BTO multiferroics. In this work, although materials are polarized in an external electric field of approximately a few kV cm$^{-1}$, the polarization value is small. However, the simultaneous improvement of both electrical and magnetic properties of materials becomes efficient and systematic. Besides, the tendency obtained in these results is completely consistent with previous study on BTO-based multiferroics, which were fabricated by using the high-energy ball milling method [50].

To choose a material with high loss that has effective absorption and shielding of electromagnetic waves, in this study we perform some analyses and evaluation of the loss and energy storage capacity of the materials [75–80]. Therefore, in the following contents, we will consider and have specific and relevant discussions. The useful recoverable energy storage density and the energy storage efficiency can be obtained from the expressions [80]:

$$W_{UE} = \int_0^{P_{max}} E_{applied} dP_{induced}$$  \hspace{1cm} (1)

$$\eta_{P-E} = \frac{W_{UE}}{W_{UE} + W_{LE}} \times 100$$ \hspace{1cm} (2)

where $E_{applied}$ is the applied electric field, $P_{induced}$ is the induced polarization, $\eta_{P-E}$ is the energy storage efficiency, $W_{UE}$ and $W_{LE}$ are the recoverable useful energy storage density and the lost energy density, respectively. The results show that with the applied voltages below 500 V, the $P(E)$ curves of samples do not degenerate. For higher applied voltages, the $P(E)$ curves degenerate with a stronger trend. Figure 8 shows the $P(E)$ curves and the dependences of $W_{UE}$, $W_{LE}$, and $\eta_{P-E}$ on NFO content of samples measured at 500 and 900 V. From figures 8(a) and (b), we see that the $P(E)$ curve tends to expand gradually with increasing NFO content. It means that the energy loss could increase (figures 8(c) and (d)). Namely, at 500 V, the loss of energy density tends to increase approximately 30 times, from 0.012 to 0.04 mJ cm$^{-3}$, for $x = 0$–0.4, respectively. The energy storage efficiency decreases from approximately 80% to 31.6% as shown in figure 8(c).

With an increase in the external electric field, the strength of leakage current in the samples also increases, so the loss of energy density will increase. At 900 V, the loss of energy density increases from 0.045 to 0.14 mJ cm$^{-3}$ and the stored energy density decreases from 72.3 to 22.4%, with NFO content increasing from 0 to 0.4.
Therefore, in this work, we coated NFO-BTO-AP layers on Z (change in resistivity and deformation of the lattice in the samples. This result has great significance for the practice of carrying out material-oriented studies in the field of microwave absorption and shielding. In the next content we selected C3 sample BTO-AP layers with several thickness on samples. Accordingly, based on the re

matching (100 mm)

mean that the acrylic paint is transparent to microwave. Whereas, the value of

absorbing layer with (RL)

leading to a large negative value of absorbing layer with

at Al plates.

value of absorber, for example: [81–83].

\[ RL = 20 \log \left| \frac{Z - Z_0}{Z + Z_0} \right| \quad (3) \]

\[ Z = Z_0(\mu_r/\varepsilon_r)^{1/2}\tanh[i(2\pi f/\varepsilon)(\mu_r/\varepsilon_r)^{1/2}] \quad (4) \]

where Z and Z_0 are impedances of the absorbing layer and the free space (337 \Omega), respectively; \mu_r is the complex magnetic permeability and \varepsilon_r is the complex electric permittivity of sample. As we known, the impedance matching (Z = Z_0 = 337 \Omega) is a mechanism, which is often applied in explaining the microwave absorption capacity of materials. Therefore, in this work, we coated NFO-BTO-AP layers on flat Al plates (with area of 100 \times 100 mm^2), where Al plates used as the reference material with 100% of reflection into the back of the samples. Accordingly, based on the reflection coefficient (|S_{11}|), the value of Z and RL of absorbing layers can be assessed following the equations [83, 84].

\[ Z = Z_0(1 + S_{11})/(1 - S_{11}) \quad (5) \]

\[ RL = 20 \log \left| S_{11} \right| \quad (6) \]

Figure 9 shows frequency dependences of the reflection coefficient |S_{11}| (figure 9(a)) and the reflection loss RL (figure 9(b)) at f = 12–18 GHz obtained for NFO-BTO-AP layers with different thicknesses (t = 2.0–5.5 mm) compared with those of an acrylic paint layer (AP). One can see that the acrylic paint layer has no effect in this frequency region

The value of |S_{11}| and RL parameters are approximately unit and zero, respectively. It means that the acrylic paint is transparent to microwave. Whereas, the value of |S_{11}| parameter tends to decrease in NFO-BTO-AP composite as the thickness of this composite layer increases. It is noteworthy that the |S_{11}| value of absorbing layer with t = 5.5 mm decreases to almost zero at a resonant frequency of about 16.8 GHz, leading to a large negative RL value (RL = −39.8 dB).

Table 2 shows some parameters (resonant frequency f, minimum RL, and the absorbing bandwidth at RL = −10 dB) related to the microwave absorption of NFO-BTO-AP composites with different thickness and comparison with some similar composites [8, 11, 82]. It is clear that these parameters depend not only on the nature of the composites, but also on the thickness of the absorbing layers. An appropriate ratio of the FE and FM phases can significantly improving the RL value of absorber; for example: RL below −40 dB has been obtained for composites of 0.5CoFe_2O_4−0.5BaTiO_3 [8] and (1-x)BaTiO_3-(x)Fe_3O_4-paraffin at x = 0.5–0.8 [11]. Besides, the impedance of the absorption layer changes due to the thickness of composite changed, leading to a strong effect on the value of RL. For NFO-BTO-AP composite, RL value is found to be −9.3, −16.5 and −39.8 dB for t = 4.0, 5.0, and 5.5 mm, respectively. The value of RL achieved at t = 5.5 mm is significant

![Figure 9](image.png)
compared with other BTO-based composites [8, 11, 82]. Especially the absorbing bandwidth value at $RL = -10$ dB is found to be in a frequency range of over 3.5 GHz. This is higher than five times in comparison with that of BaTiO$_3$ pure reported by Yue Huang et al [11]. Although the absolute value of $RL$ obtained for NFO-BTO-AP layer with $t = 5.5$ mm is slightly smaller than that of $(1-x)$BaTiO$_3$-$x$Fe$_3$O$_4$ paraffin composites with $t = 1.7–2.2$ mm at $x = 0.5–0.8$ [11], combining NFO-BTO composite with acrylic paint brings it closer to the applications in the field of electromagnetic wave shielding.

According to Phong et al [85], based on the reflection coefficient $|S_{11}|$, the percentage of absorbed incoming energy (absorptivity) can be calculated as following.

$$\text{Absorptivity(%) = } (1 - |S_{11}|^2) \times 100\% \quad (7)$$

Figure 10(a) shows the percentage of absorbed incoming energy depend on the frequency calculated for NFO-BTO-AP composites with different thicknesses of 2.0–5.5 mm on flat Al plates. It shows that the absorptivity of composite layer with $t = 2.0$ mm is unstable and quite low. However, the absorptivity increases significantly and smoothly on thicker NFO-BTO-AP layers. The energy in electromagnetic wave in high frequencies can be absorbed of over 90% by NFO-BTO-AP layers with thicknesses of 5.0 and 5.5 mm. Interestingly, the absorption of electromagnetic wave of NFO-BTO-AP layer with thicknesses of 5.5 mm can
reach over 99.9% at 16.8 GHz. This suggests that NFO/BTO-AP can be used as an electromagnetic wave shielding material.

According to Xuan et al [83], the impedance matching mechanism in the absorber can be effectively used to explain the nature of the microwave absorption effect. Accordingly, when the values of the impedance of absorbing layer and the free space are matched, the energy of the microwave in the absorbing layer will be completely dissipated. Then the minimum $RL$ peak will be appeared at the resonant frequency corresponding to $Z/Z_0 = 1$. Figure 10(b) shows the real and imaginary parts of $Z/Z_0$ depend on the frequency calculated for NFO-BTO-AP layer with thickness of 5.5 mm. We can see that the real part of $Z/Z_0$ is approached to the unit at 16.8 GHz corresponding to the minimum $RL$ position on the reflection loss spectrum. This result suggests that the resonance occurring in the NFO-BTO-AP layer is consistent with the impedance matching mechanism. According to equation (3), the value of $RL$ will be approached to $-\infty$ when $Z = Z_0$, and absorbing layer becomes an absolute absorption. However, the absolute absorption only occurs when the imaginary part of impedance must be zero [83]. In this work, our results show a deviation of the imaginary part from zero at 16.8 GHz, implying that the impedance matching condition does not respond completely. Therefore, the negative value of $RL$ parameter degrades only to a finite extent ($-39.8$ dB).

4. Conclusion

In summary, a systematic study was performed on NFO-BTO multiferroics that fabricated by using a combination of high energy mechanical milling with thermal annealing methods. XRD data confirms the successful preparation composites of two separate phases NFO and BTO. Herein, NFO randomly dispersed in BTO matrix with particle size about of 50 nm. The FE and FM parameters of composites significantly improved with NFO-doping. The values of $H_c$, $M_r$, $M_s$, $P_m$, $P_r$, $E_c$, and $W_{LE}$ gradually increase as NFO concentration increases, relating to an increase in the lattice deformations and/or defects. Especially, with the $x = 0.3$ sample, when stuffed in acrylic paint to make NFO-BTO-AP composite, it has shown to be a potential candidate for microwave absorbing and shielding application. Remarkably, microwave absorption percentage is over 99.9% corresponding to $RL = -39.8$ dB at $f = 16.8$ GHz observed for NFO-BTO-AP composite with thickness of 5.5 mm on a flat Al plate. This suggests a good potential application of multiferroics in a high performance microwave absorbing field.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of competing interest

The authors declare that we have no competitive financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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