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IMPROVEMENT THE DIELECTRIC AND IMPEDANCE PROPERTIES OF PB-FREE $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ PIEZOELECTRIC MATERIALS MODIFIED BY Fe_2O_3

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The focus of this study is on the Fe_2O_3-doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ piezoelectric material. This is important to find ecologically acceptable piezoelectric materials. This research aims to obtain a lead-free piezoelectric material because lead is a material that is not environmentally friendly. An alternative solution is a piezoelectric material based on BNT-ST, which in this case is doped with Fe_2O_3 material. The study of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ piezoelectric material prepared by the solid-state reaction method was carried out to determine the optimum composition of the material formed. Doping variations are 0; 2.5; 5; 7.5; and 10 in mol %. The examinations were performed using X-ray diffraction (XRD) spectroscopy, a Scanning Electron Microscope (SEM), and an LCR meter. The Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$produced a new compound in the form of $FeBi_5Ti_3O_{15}$-$Na_2Ti_3O_7$-$SrTiO_3$ with the crystal structure of cubic, orthorhombic, and monoclinic, as well as the increasing crystalline size with the addition of dopants, exclude at 5 mol % and 7.5 mol %. $FeBi_5Ti_3O_{15}$-$Na_2Ti_3O_7$-$SrTiO_3$ also produces varying particle sizes, which are between 0.88–8.23 μm. From the obtained data, the optimum composition of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ was the 2.5 mol % of Fe_2O_3 due to it having the highest dielectric constant (ε_r) and temperature Curie (T_c), and also the lowest material impedance (Z) with the ε_r of 12.037 at T_c of 400 °C and Z of 135 kΩ. The high piezoelectricity, which is indicated by the high value of the dielectric constant and Curie temperature, is possible due to the presence of a greater number of sodium ions in the $Na_2Ti_3O_7$ phase. Sodium ions are ions with good electrical storage capabilities. The increase in dielectric constant in the BNT-ST piezoelectric obtained by the addition of Fe_2O_3 shows that this material can be used as a substitute for lead-based piezoelectric materials so that it is secure for the environment. The piezoelectric material of BNT-ST doped with Fe_2O_3 earned from this research can be applied to obtain electricity with a optimal value when given mechanical pressure

Keywords: piezoelectric, BNT-ST, Fe_2O_3 doping, electric properties, Curie temperature

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1. Introduction

Piezoelectric technology is one of the new Renewable Energy technologies that has been widely used as a source of electrical energy. The working principle of piezoelectricity is a reversible reaction that produces an electric current due to pressure/strain. Today's most widely used piezoelectric material is Lead Zirconate Titanate ($Pb(Zr_xTi_{1-x})O_3$) commonly referred to as PZT [1–5]. One of the critical drawbacks of PZT is that it contains more than 60 % lead (Pb) by weight. This effective lead content creates a hazard during processing (lead evaporates and is released into the atmosphere) and limits applications (e. g. in vitro). It is potentially toxic to the environment during disposal. Over the last few years, the World Health Organization (WHO) has begun to impose strict restrictions on the use of lead, except for the electronics industry, due to the lack of PZT-compliant replacements [6]. Therefore, the researchers began to look for PZT replacement materials with more environmentally friendly materials.

One of the environmentally friendly piezoelectric materials that have recently become a concern for researchers is $Bi_{0.5}Na_{0.5}TiO_3$. Studies on the utilization and modification of $Bi_{0.5}Na_{0.5}TiO_3$ materials to produce increased piezoelectricity have been carried out, including modifying them with $Bi_{0.5}K_{0.5}TiO_3$, $SrTiO_3$ [5, 7–12]; $K_{0.5}Na_{0.5}NbO_3$-Gd_2O_3 [13]; and $BaTiO_3$-$NaNbO_3$ [14]. $Bi_{0.5}Na_{0.5}TiO_3$ has good piezoelectric properties with a Curie temperature of 320 °C, but this value is still lower than the Curie temperature of PZT. The Curie temperature value of a material affects the quality of the material. Next, the piezoelectricity of the material is also influenced by the dielectric properties of the material, whose value is represented by the dielectric constant. Dielectric materials are vital in ferroelectricity because of some of the properties of dielectric materials; namely, they can store electric charge, pass alternating current, and withstand direct current.

Increasing the Curie temperature and dielectric constant can be done by substituting the $Bi_{0.5}Na_{0.5}TiO_3$ crystal lattice with ferrite (Fe_2O_3), which raises the formed structure's crystallinity, increasing the ceramic grain size, and increases the magnetoelectric response [15]. Modification of piezoelectric materials has been reported to be successful in increasing the Curie temperature and dielectric constant. Piezoelectric $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) composited using $SrTiO_3$ (ST) and modified using Fe_2O_3 is more environmentally friendly, stable, and has the potential to produce better piezoelectricity values. Therefore, research devoted to the development of a lead-free piezoelectric material based on BNT-ST and modified by Fe_2O_3 is relevant.

2. Literature review and problem statement

Piezoelectric materials are a class of materials that can be polarized using mechanical pressure or an electric field. Examples of piezoelectric materials are Bismuth Natrium Titanate (BNT), Bismuth Natrium Titanate-Strontium Titanate (BNT-ST), Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate ($KNbO_3$), etc. Three parameters can indicate the piezoelectric properties of a material, namely dielectric constant, Curie temperature, and material impedance [16].

Piezoelectric $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ (BNT-ST) is an environmentally friendly electrical energy-producing material compared to the $PbZr_{(0.52)}Ti_{(0.48)}O_3$ (PZT) material which is currently frequently used. PZT has a piezoelectric constant value d_{33}=460 PC/N, coupling factor K_p=0.56, P_r=39.2 μC/cm^2, coercive field E_c=14.9 kV/cm, and a high Curie temperature of 450 °C [17]. However, PZT contains the element Pb (lead) which is toxic. Industrial scale production requires quite a lot of Pb material so it is not profitable because waste gases such as lead oxide (PbO) evaporate and likewise the remaining Pb oxide material in the synthesis process can pollute the environment and be dangerous for health.

To overcome this concern, research and development of lead-free piezoelectric materials has been carried out, one of which is $Bi_{0.5}Na_{0.5}TiO_3$. (BNT). It is necessary to try to modify this material to obtain a material with the desired characteristics. The material modification process can be done by modifying the manufacturing process as has been done by several researchers [18, 19]. In this case, modification is carried out using microwave irradiation [18] and variations in milling time duration [19]. Or by providing additional ingredients known as a doping process, as has been done by other researchers [20–22]. The paper [20] presents the results of research related to the addition of Nd to Strontium hexaferrite. It is demonstrated that the structure, magnetic characteristics, and microwave absorption capability of strontium hexa ferrite change when Nd is added. On the other hand, research on the addition of Ba to BNT is presented in publication [21]. The structure and dielectric characteristics of the material generated are altered by the addition of Ba to BNT. Additionally, research on the topic of adding carbon black to a mixture of polybutylene terephthalate, polyamide 6, and carbon black is reported in the paper [22]. Here, the material's microstructure and mechanical characteristics are altered by the addition of carbon black. The results of the investigation showed that the addition of a material can change its structure, mechanical properties, and dielectric properties. However, questions related to the modification of BNT material, or the effects of adding doping material to BNT have not been revealed in detail. This may be because of the financial constraints and the fact that this topic is beyond the scope of their research focus.

In the development of BNT materials, many doping materials have been added in fairly good quantities in the hope of forming solid solutions that have mechanical and electrical properties comparable to PZT. Research on modifying BNT by adding ST doping ($SrTiO_3$) was carried out by Werner Krauss using the solid-state reaction method, obtaining a Curie temperature value of 335 °C [23]. In making these materials, polyvinyl alcohol can be added to improve the mechanical properties of the material so that it has strong resistance when subjected to high pressure or temperature [24]. The higher the Curie temperature, the better the quality of the piezoelectric material.

Of several ferroelectric doping materials, one of them is Fe_2O_3. Fe_2O_3 material is an ion donor doping material [25]. The use of this doping material is because Fe_2O_3 has a doping ion whose radius is almost the same as the Ti^{4+} ion. Fe_2O_3 has a Fe atom with a 3+ ion whose basic salt color is yellowish brown. The radius of the Fe^{3+} doping ion is 0.67, while the radius of the Ti^{4+} doping ion is 0.68 which occupies position B in the perovskite structure. The addition of the Fe^{3+} doping ion will result in the formation of space at position B in the ABO_3 structure.

The Fe_2O_3 addition in the solid-state reaction can increase the density and increase the piezoelectric constant [26]. They also reported that FeO and Fe_2O_3 doping could increase the grain size of KNN-based ceramics. In addition, many researchers have systematically studied the structural, magnetic, electrical, and magnetoelectric behavior of Fe^{3+} ions doped in perovskite ferroelectric ceramics ($BaTiO_3$, $SrTiO_3$, and $KTaO_3$) and these compounds show possible magnetoelectric response at room temperature [27]. So, Fe_2O_3 doping in appropriate proportions is an effective method to improve the densification and electrical properties and produce ferromagnetism in perovskite ferroelectric ceramics. The advantage of adding Fe_2O_3 to the material $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O_3$ (KNLNTS) s demonstrated in the paper [26]. additionally discussed in the article [27] concerning the incorporation of Fe_2O_3 into the $KTaO_3/BaTiO_3$ composite. However, the effect of adding Fe_2O_3 to BNT-ST has not been disclosed in these papers, possibly due to funding constraints and the fact that it is not the focus of their research. Based on the provided description, it seems that Fe_2O_3 would be a good doping material to enhance the electrical properties of BNT-ST.

Fe_2O_3 material can be synthesized from iron sand. Magnetic minerals contained in iron sand deposits are magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and maghemite (γ-Fe_2O_3). Each mineral from iron sand has different properties. Maghemite has a cubic close-packed structure with good chemical equilibrium, while hematite has a rhombohedral structure and is the most stable type but is antiferromagnetic below the Neel temperature (<955 K). One of the iron sand potentials that can be optimized is located on Widarapayung Beach, Binangun sub-district, Cilacap district. This sand contains magnetic minerals in the form of magnetite.

Iron sand is one source of natural magnetite or lodestone, which is a ferrous ferrite ($Fe[Fe_2O_4]$, or Fe_3O_4) that occurs naturally [28]. The sintering process at high temperatures in making ceramic magnets results in a phase change from magnetite (Fe_3O_4) to maghemite (γ-Fe_2O_3). This change is followed by changes in the magnetic properties of the material [29]. Iron sand is needed in piezoelectric applications because it has the potential to increase the dielectric constant and stability of the piezoelectric material [26]. In general, it can be noted that BNT-ST is an alternative material for lead-free piezoelectrics. However, its piezoelectricity performance is still inferior compared to PZT which is currently widely used. On the other hand, Fe_2O_3 is known to increase the piezoelectric properties of a material. Thus, it is worth examining the characteristics of BNT-ST doped with Fe_2O_3, to obtain an environmentally friendly piezoelectric material that has excellent piezoelectricity. Furthermore, it is necessary to look for a BNT-ST-Fe_2O_3 composition that has the desired piezoelectricity.

Fe_2O_3 addition to the BNT-ST piezoelectric material is a fascinating experiment that merits more investigation. This is consistent with the effectiveness of doing so as shown by studies [26] and [27]. Furthermore, it is necessary to identify the ideal composition of the Fe_2O_3 addition to produce the BNT-ST-Fe_2O_3 piezoelectric material, which has excellent electrical properties.

As per the above description, the material modification stage can be completed by altering the manufacturing process [18, 19] or the component material [20–22]. The material in this study was modified to make the necessary corrections. The material that was used in the present investigation to alter the BNT-ST piezoelectric material is called Fe_2O_3. Fe_2O_3, the donor ion doping material, has been shown to increase both the piezoelectric constant value [26] and the magnetoelectric response capability [27]. It was selected as a doping material in the BNT-ST piezoelectric material for these reasons. The next step is to formulate the problems that this study will attempt to solve.

Based on the background that has been described, the problem can be formulated as follows;

– what the characteristics of the Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ piezoelectric material are;

– what is the optimum composition of Fe_2O_3 doping for the $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ piezoelectric material is.

3. The aim and objectives of the study

The aim of the study is to determine the optimum composition of the BNT-ST piezoelectric material doped with Fe_2O_3 to obtain a piezoelectric material that has a high dielectric constant, stable material, and low impedance.

To achieve this aim, the following objectives are accomplished:

– to synthesize Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ using the solid-state reaction method;

– to characterize the Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ sample.

4. Materials and methods

The object of this research is the piezoelectric material of $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ doped with Fe_2O_3.

The object-related hypothesis, which is based on the completed literature review, is that the BNT-ST piezoelectric material's electrical characteristics will be enhanced by the addition of Fe_2O_3. Furthermore, several assumptions are made concerning this study, specifically:

1. The vacuum permittivity value of 8.85×10^{-12} F/m is regarded as constant.

2. Fe_2O_3 synthesized independently from iron sand of the Binangun area, Cilacap is assumed to be equivalent to commercial Fe_2O_3. Fe_2O_3 is synthesized using the solid-state reaction method with a calcination temperature of 850 °C and a calcination time of 3 hours.

3. Because $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ and Fe_2O_3 materials have been heated to 120 °C, it is expected that they are devoid of water.

Ensuing the following is the simplification used in the research project:

1. Piezoelectricity testing of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ material was carried out at a frequency of 1000 Hz.

2. This study did not examine the output voltage.

3. Air pressure's impact was disregarded.

4. Piezoelectricity was tested by applying an electric field and without applying pressure.

The materials used in this study were $Bi(NO_3)_3$ 71 % Merck KGaA 1304-85-4 (source of Bi); Na_2CO_3 99 % Aldrich 497-19-8 (source of Na); TiO_2 97 % Aldrich 13463-67-7 (source TiO_3); $SrCO_3$ 98 % Aldrich 1633-05-2 (source Sr); natural iron sand of Binangun area, Cilacap district, Central Java, Indonesia (source of Fe_2O_3); Aqua Demineralization; Merck absolute ethanol 64-17-5; and Merck KGaA 99 % polyvinyl alcohol. The appliances used are the PPF-UG FiLa shaker mill, PPF-1300 muffle furnace, Krisbow hydraulic pump, and PA 213 OHAUS digital balance. As well, X-Ray Diffraction (XRD) Philips PW 171016, Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) JEOL type JSM-6510 LA Equipment, Inductor-Capacitor-Resistor meter (LCR meter) digital type 4271B. Synthesis of $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$-Fe_2O_3 started by weighing $Bi(NO_3)_3$, Na_2CO_3, TiO_2, $SrCO_3$, and Fe_2O_3 based on the composition of the compound $(0.75-x)Bi_{0.5}Na_{0.5}TiO_3+(0.25-x)SrTiO_3+xFe_2O_3$ where x is 0; 0.025; 0.05; 0.075; and 0.1 in moles and are denoted by FeBS0, FeBS1, FeBS2, FeBS3, and FeBS4. Next, the samples were milled for 3 hours using a PPF-UG shaker mill with the addition of absolute ethanol and dried at a temperature of 120 °C. The dried sample was calcined in a furnace at a temperature of 850 °C to remove impurities in the sample. Then the sample was mashed again for 3 hours using a PPF UG shaker mill to reduce the surface area of the material so that the resulting pressure would be more optimal. The process of producing pellets is as follows. Five drops of 5 % polyvinyl alcohol were added to the sample to form a semi-dry powder (agglomerated powder). Furthermore, the material is ground for 5 minutes so that it is no longer agglomerated and is ready to be formed into pellets by using a Krisbow hydraulic pump. The sample was then pre-sintered for 1 hour at a temperature of 800 °C and sintered at 1100 °C for 2 hours. The material $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$-Fe_2O_3 in pellets was tested for characterization and electrical properties, in the form of dielectric constant and impedance using an LCR meter with an increment of 100 °C. The samples were also tested using XRD (X-ray diffraction) and SEM (Scanning Electron Microscopy) apparatus for composition material and morphology analysis. The dielectric constant was determined using an LCR meter through a furnace. The LCR meter will evaluate the capacitance of the prepared sample as the temperature of the furnace was raised, then the dielectric constant was calculated through the capacitance using the following equation:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}, \quad (1)$$

where ε_r is the relative dielectric constant, C is capacitance (F), d is the distance between the plates (m), ε_0 is the air permittivity (8.85×10^{-12} F/m), and A is the cross-sectional area of the plates.

5. Results of the synthesis and characterization of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$

5. 1. Synthes of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ using the solid-state reaction method

The piezoelectric material $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ doped with Fe_2O_3 has been successfully synthesized using the solid-state reaction method. Fe_2O_3 was synthesized through the milling and calcination of iron sand from the Binangun area of Cilacap (Fe_3O_4), resulting in a material with a dark red color. This color signifies that the Fe_2O_3 formed is of the maghemite type (γ-Fe_2O_3). The synthesized Fe_2O_3 material was then used as a doping agent. The synthesis of $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ doped Fe_2O_3 using the solid-state reaction method was performed by mixing $Bi(NO_3)_3$, Na_2CO_3, TiO_2, $SrCO_3$, and Fe_2O_3. Absolute ethanol was added to this mixture to ensure homogeneity during the milling process. The mixing process is followed by drying to remove water content and calcination to form the desired compound. This process yields a powder with a yellow color, which becomes progressively more brownish as the Fe_2O_3 concentration increases. This suggests the influence of Fe^{3+} ions, as evidenced by the characteristic color of Fe^{3+} salts within the material [25].

The powder is then ground using a mortar, a process that maximizes the contact surface area between particles. At this stage, 5 % PVA is added to the material, which serves to enhance its mechanical properties, providing strong resistance under high pressure and temperature conditions. The material is subsequently compacted under an external magnetic field, which aligns the spin direction within the crystals. The powder is compressed to form flat cylindrical pellets, which are then solidified and subjected to sintering for further heating, resulting in a coin pellet with a diameter of 1 cm and a thickness of 0.4 cm. The pure BNT-ST sample without doping is white, furthermore, the addition of Fe_2O_3 causes the color of the sample to change to yellow, and the more Fe_2O_3 added causes the color of the sample to change to brownish.

5. 2. Characterization of the Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ samples

The results of the LCR meter test are as follows. The dielectric constant is a factor that makes a specific substance reduce the electrostatic force between two separate charged objects under vacuum conditions. The magnitude of the value of the dielectric constant illustrates that the material can store electric charge along with one of the functions of the capacitor as a charge store. Testing the dielectric constant is carried out at various temperatures starting with room temperature up to a temperature of 500 °C in a frequency of 1000 Hz using an LCR meter. The graph of the constant dielectric test against temperature can be seen in Fig. 1.

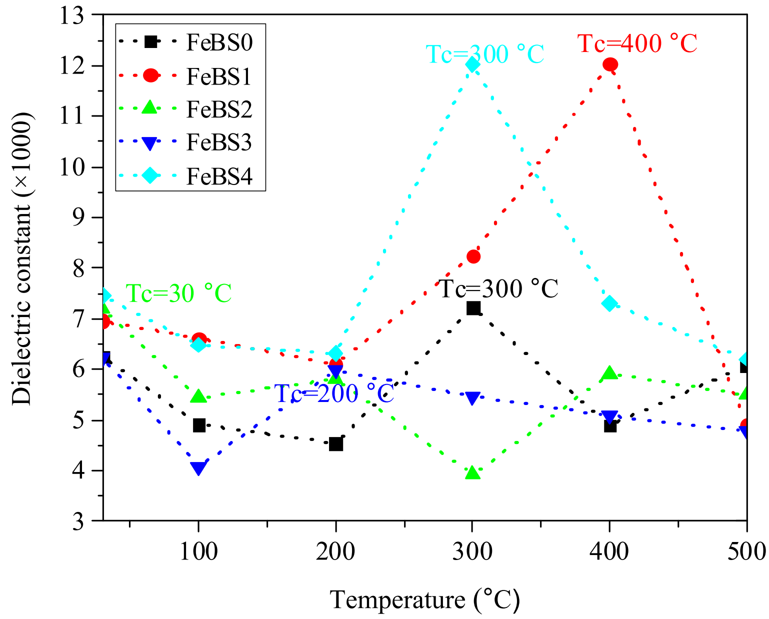

Fig. 1. Dielectric constant and Curie temperature of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$

The sample that produces the optimum polarization ability is the sample of FeBS1 when compared to other concentration variations. Therefore, FeBS1 can have high electrical stability with an optimal temperature of 400 °C. The FeBS1 sample shows the high piezoelectricity which is characterized by the high dielectric constant. The sample that has the lowest piezoelectricity is the FeBS2 sample with a dielectric constant of 5,975 at a temperature of 30 °C. However, the FeBS2 sample still has an increase in the dielectric constant at temperatures of 100 °C and 200 °C, although the constant dielectric increase is not higher than the optimum condition of the FeBS2 sample. The effect of material impedance on temperature with a frequency of 1000 Hz is shown in each sample variation in Fig. 2.

All samples showed the highest impedance values in the range of 30 °C to 200 °C. Furthermore; the material impedance decreases at a temperature of 300 °C. It again increases at a temperature of 400 °C. In contrast to the dielectric constant, the relative dielectric constant has a low value at a temperature of 30 °C to 200 °C. However, at a temperature of 300 °C, the dielectric constant value will increase again, except for the FeBS2 sample. The summary of the results for the dielectric constant, Curie temperature, and impedance is presented in Table 1.

Next, the results of the XRD test are as follows (Fig. 3, 4).

Table 1

Summary of dielectric constant, temperature Curie, and impedance result of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$

Sample	Dielectric constant	Temperature Curie (°C)	Impedance (Ω)
FeBS0	7,214	300	147,370
FeBS1	12,037	400	139,280
FeBS2	7,185	30	146,500
FeBS3	5,975	200	145,320
FeBS4	12,029	300	142,770

The determination of the peaks in the diffraction pattern from the XRD results refers to the ICDD (International Center of Diffraction Data) database. $Bi_{0.5}Na_{0.5}TiO_3$ and $SrTiO_3$ phases were obtained from the XRD test results, which formed rhombohedral and cubic crystal structures in FeBS0 (codes 00-036-0340 and 00-040-1500). Furthermore, $SrTiO_3$, $FeBi_5Ti_3O_{15}$, and $Na_2Ti_3O_7$ phases appeared in FeBS1, FeBS2, FeBS3, and FeBS4 samples. The $SrTiO_3$, $FeBi_5Ti_3O_{15}$, and $Na_2Ti_3O_7$ phases are related to the cubic, orthorhombic, and monoclinic crystal structures (codes 00-040-1500, 00-038-1257, and 01-072-0148). The crystal size of each phase is calculated using the Debye-Scherner equation.

Furthermore, the sample's microstructure was characterized using a Scanning Electron Microscope (SEM). Material characterization using SEM is used to see the structure and particle size. Fig. 5 is the SEM result of $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ and Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ samples with a magnification of 3000 times.

Some parts of the Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ sample still contain a polymer structure which is thought to be polyvinyl alcohol which has not yet been combined with other particles. The Samples have different particle sizes which is obtained by comparing the particle length with the length of the reference line located at the bottom right of Fig. 5. The particle size of each sample is shown in Table 1 below.

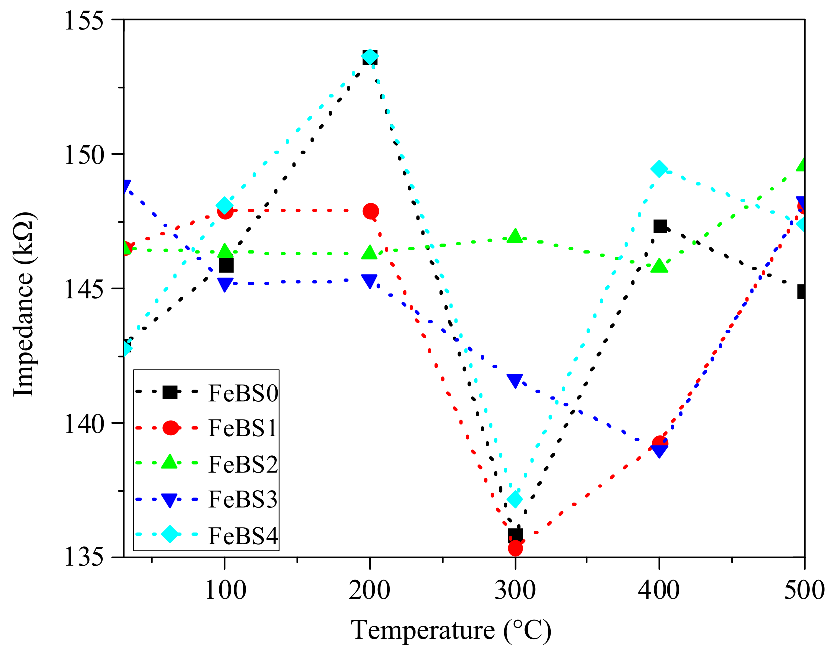

Fig. 2. Impedance of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$

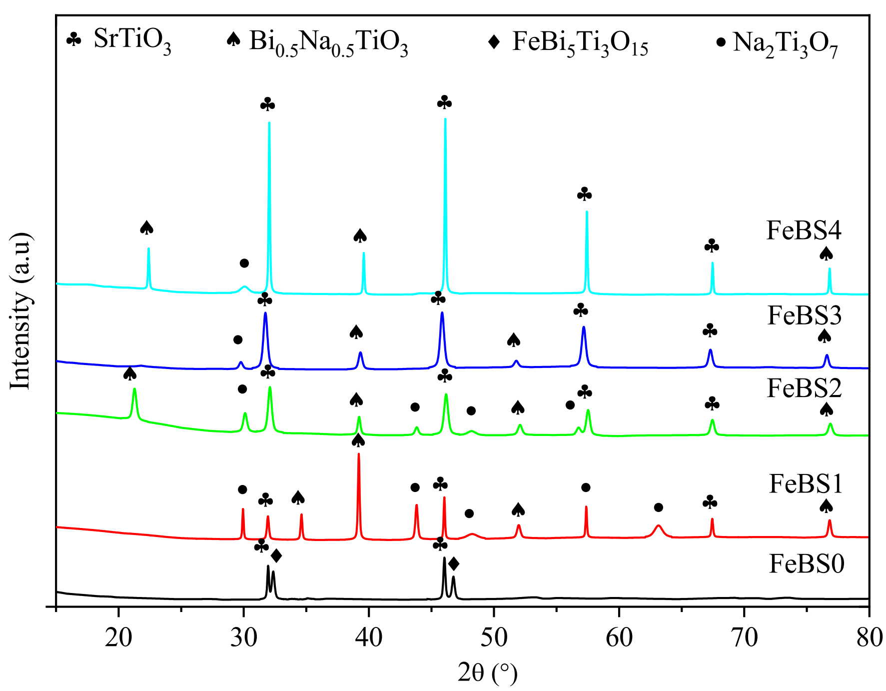

Fig. 3. Diffraction pattern of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$

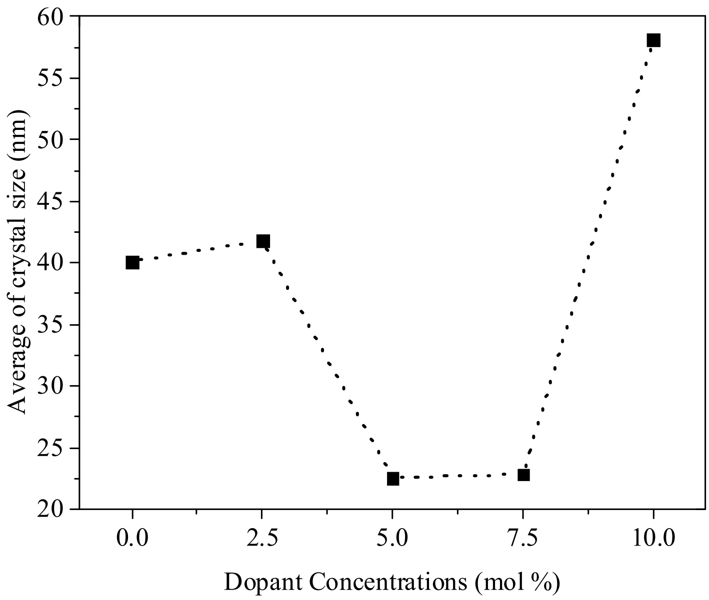

Fig. 4. Average crystal size of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$

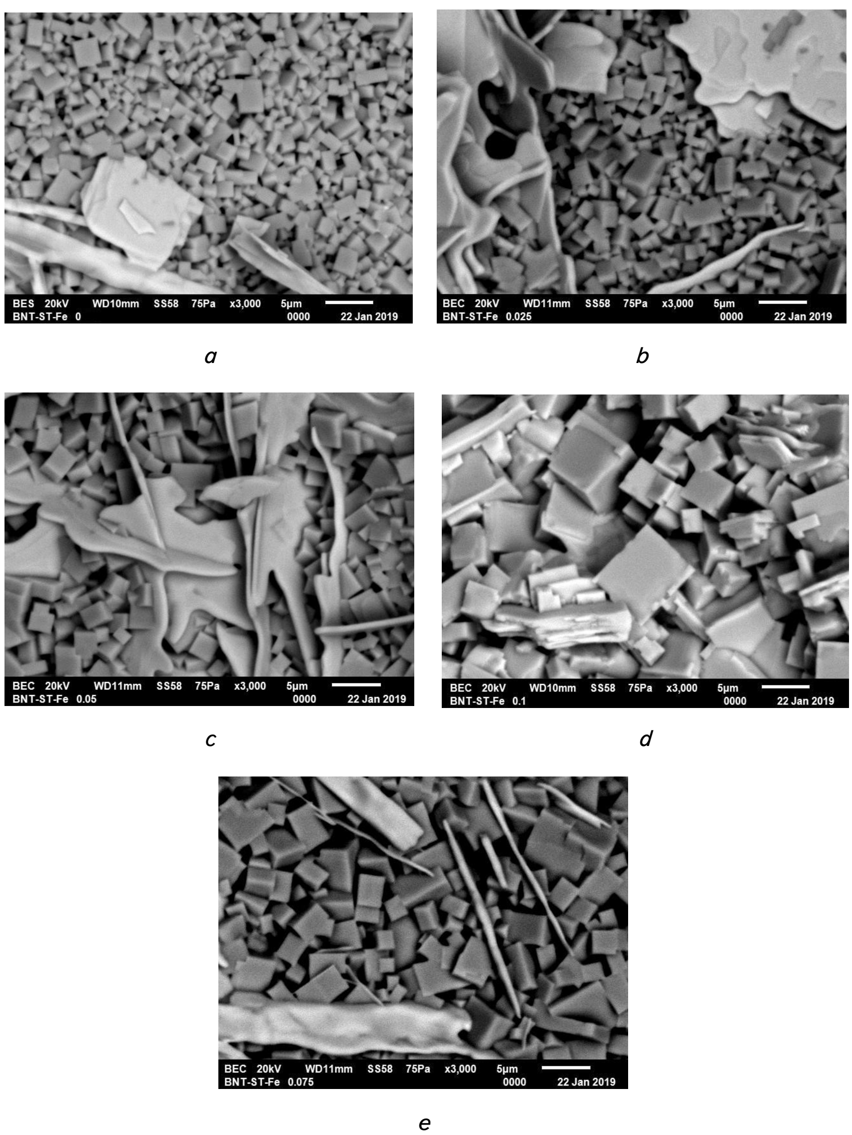

Fig. 5. Scanning Electron Microscopy images of samples: *a* – FeBS0; *b* – FeBS1; *c* – FeBS2; *d* – FeBS3; *e* – FeBS4

Table 2

Particle size of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$

Sample	Particle size (μm)
FeBS0	1.17–2.64
FeBS1	0.88–2.64
FeBS2	1.17–3.23
FeBS3	1.47–5.88
FeBS4	2.58–8.23

The particle size that forms a range for each sample concentration variation may be caused by inhomogeneous collisions during the shaking process in the PPF-UG Shaker Mill. The sample that has the smallest particle size is FeBS1, while the sample that has the largest particle size is FeBS4.

6. Discussion of the effect of the Fe_2O_3 concentration doping on the characteristics of the BNT-ST piezoelectric material

In the LCR meter test results as shown in Table 1, the FeBS1 sample shows high piezoelectricity, characterized by the high dielectric constant. The high dielectric constant in the FeBS1 sample may be due to a higher number of sodium ions, which is characterized by a higher number of $Na_2Ti_3O_7$ phases and a higher intensity. Sodium-ion is an ion with an electrical storage ability similar to lithium [30, 31]. The FeBS2 sample still has an increase in the dielectric constant at temperatures of 100 °C and 200 °C, although the constant dielectric increase is not higher than the optimum condition of the FeBS2 sample. The small value of piezoelectricity, in the form of dielectric constant and Curie temperature, could be due to the crystal size of FeBS2, which is the sample with the smallest crystal size among other sample variations. Apart from that, the small value of the dielectric constant and Curie temperature is also possible because the large value of dielectric loss due to the addition of iron ions does not have a more significant effect on FeBS2 compared to other concentration variations. In addition to the dielectric constant, the LCR meter can also be used for impedance analysis of materials. The FeBS2 sample has a material impedance that tends to be stable, resulting in a small dielectric constant. An impedance is taken to represent the dissipative component of the dielectric response. Therefore, the higher the impedance of the material, the smaller the value of the dielectric constant.

From the XRD examination data, the addition of iron is thought to have restructured $Bi_{0.5}Na_{0.5}TiO_3$ into $FeBi_5Ti_3O_{15}$ and $Na_2Ti_3O_7$. This phenomenon is caused by the small binding force of Na atoms, as evidenced by the electronegativity value of Na atoms, which is 0.93. The electronegativity value of Na atoms is smaller than that of Bi, Ti, and Fe atoms, namely 2.02, 1.54, and 1.83, which causes the Bi atom to bond first with the Fe and Ti atoms so that there is no leftover to share electrons with the Na atom.

The addition of iron ions from Fe_2O_3 has succeeded in doping $Bi_{0.5}Na_{0.5}TiO_3$, as evidenced by the addition of Fe in $FeBi_5Ti_3O_{15}$. The ionic radius of iron (0.67 Å), which is smaller than titanium (0.88 Å), allows the occurrence of interstitials between the $Bi_{0.5}Na_{0.5}TiO_3$ lattice and breaks down $Bi_{0.5}Na_{0.5}TiO_3$ compounds. It is suspected that the doped iron species is Fe^{3+}. Meanwhile, the $SrTiO_3$ phase increased its peak intensity and did not undergo a phase change. The sintering treatment will make the ions in $SrTiO_3$ diffuse into the crystal structure without changing the oxidation number [32]. The more Fe_2O_3 doping concentration resulted in the decreasing intensity of the $Na_2Ti_3O_7$ phase and the increasing intensity of the $SrTiO_3$ and $FeBi_5Ti_3O_{15}$ phases. In the test results, the highest phase intensity was obtained in FeBS4.

FeBS0, FeBS1, FeBS2, FeBS3, and FeBS4 samples ideally produce larger crystal sizes as the doping composition increases. This is because the high-intensity value influences the magnitude of the FWHM value in each sample. The higher the intensity value, the smaller the FWHM value obtained because the width of the peak is getting smaller. Scherrer stated that the FWHM value is inversely proportional to the size of the crystal so a large crystal size is obtained for a small FWHM value. However, the crystal size in the sample composition of FeBS2 and FeBS3 tends to decrease more than the crystal size of FeBS1. FeBS2 and FeBS3 materials have an anomaly. This anomaly can be due to the bond in the sample is not homogeneous. In addition, the presence of the $Na_2Ti_3O_7$ phase, whose intensity decreases with some of the decreasing $FeBi_5Ti_3O_{15}$ phases, also can produce a small crystal size. However, there is also a $SrTiO_3$ phase and some other $FeBi_5Ti_3O_{15}$ phases whose intensity increases with doping.

All samples appear to have cavities or pores still, and some particles are fused. This structure indicates that the diffusion process in the sintering is not perfect, so the mechanical strength tends to be brittle. Some of the sides of the Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ sample still have a polymer structure which is suspected to be polyvinyl alcohol that has not been fused with other particles. The size of the particles as shown in Table 1, that make up the range for each variation of the sample concentration indicates an inhomogeneous collision during the shaking process in the PPF-UG Shaker Mill.

Based on characterization data, both electrical properties data in the form of dielectric constant values and impedance values accompanied by curie temperature data; crystal phase and crystal size data as well as from the discussion presented, it appears that piezoelectric material doped with Fe_2O_3 in the amount of 0.025 mol % is the best composition for an alternative replacement for PZT.

The primary limitation of this study lies in the challenge of obtaining stable values with smaller temperature intervals when measuring the dielectric constant and Curie temperature using an LCR meter on materials within a furnace. Moreover, the inclusion of polyvinyl alcohol (PVA) during the grinding process appears to increase the pore area, consequently reducing the compactness of the ceramic samples. This observation is corroborated by the findings of [33], who demonstrated that the same method, with the addition of PVA as a binder incorporated differently, resulted in a smaller pore area and enhanced compactness. On the other hand, the disadvantage of this study is the increased porosity observed with higher concentrations of Fe_2O_3. A large area of porosity can limit the stability and strength of ceramic materials at high temperatures. When a material contains pores or voids, the overall volume of solid material contributing to the dielectric response is effectively reduced. The presence of air within the material creates regions with lower dielectric values. Porosity can be reduced by employing a fabrication method that includes higher sintering temperatures, increased compaction, and the incorporation of a lower concentration of PVA into the material. Furthermore, the results of this study indicate that, overall, the $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$-Fe_2O_3 exhibits excellent dielectric properties. The scope of this research is the relative dielectric constant with distance between two plates, air permittivity, and a fixed cross-sectional area which is maintained constant, was evaluated as the temperature increases at intervals of 100 °C. Whilst, the scope of application of the results of this study is the use of Fe_2O_3 doped BNT-ST material as a piezoelectric material to replace lead-based piezoelectric so that it is secure for the environment. The limitations of the conditions for the application of the results of this study are the permittivity value used when calculating the dielectric constant is the permittivity value of air, not the permittivity value of other materials. The use of Fe_2O_3 doped BNT-ST piezoelectric material resulting from this study which has an increased dielectric constant value is expected to provide an increase in electrical gain when applied. Therefore, the study could be further developed using different fabrication methods and evaluated to determine the ferroelectric properties of the material.

7. Conclusions

1. Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ had been successfully synthesized, resulting in a new compound in the form of $FeBi_5Ti_3O_{15}$-$Na_2Ti_3O_7$-$SrTiO_3$. The new compound has a crystal structure in cubic, orthorhombic, and monoclinic. The size of the crystallite tends to fluctuate with increasing concentration of Fe_2O_3, while the particle size starting from 0.88 µm tends to increase to 8.23 µm. The crystallite and particle size exhibited typical features of Fe^{3+} addition.

2. The more Fe_2O_3 doping concentration resulted in the decreasing intensity of the $Na_2Ti_3O_7$ phase and the increasing intensity of the $SrTiO_3$ and $FeBi_5Ti_3O_{15}$ phases. The optimum composition of Fe_2O_3 doped $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$ is with Fe_2O_3 doping of 0.025 mol % because it has the highest dielectric constant (ε_r) and Curie temperature (T_c), that is 12.037 at T_c=400 °C and the most negligible ma-

terial impedance (Z) is 135 kΩ. The obtained Curie temperature is significantly higher than that of the pure BNT. The results suggest that the synthesized material has the potential to exhibit superior piezoelectric properties compared to BNT.

Conflict of interest

The authors declare that they have no conflict of interest concerning this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

All data are available in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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References

1. Gao, X., Wu, J., Yu, Y., Chu, Z., Shi, H., Dong, S. (2018). Giant Piezoelectric Coefficients in Relaxor Piezoelectric Ceramic PNN-PZT for Vibration Energy Harvesting. Advanced Functional Materials, 28 (30). https://doi.org/10.1002/adfm.201706895
2. Gao, B., Yao, Z., Lai, D., Guo, Q., Pan, W., Hao, H. et al. (2020). Unexpectedly high piezoelectric response in Sm-doped PZT ceramics beyond the morphotropic phase boundary region. Journal of Alloys and Compounds, 836, 155474. https://doi.org/10.1016/j.jallcom.2020.155474
3. Jain, A., K. J., P., Sharma, A. Kr., Jain, A., P. N, R. (2015). Dielectric and piezoelectric properties of PVDF/PZT composites: A review. Polymer Engineering & Science, 55 (7), 1589–1616. https://doi.org/10.1002/pen.24088
4. Song, R., Shan, X., Lv, F., Xie, T. (2015). A study of vortex-induced energy harvesting from water using PZT piezoelectric cantilever with cylindrical extension. Ceramics International, 41, S768–S773. https://doi.org/10.1016/j.ceramint.2015.03.262
5. Wang, G., Hong, Y.-H., Nguyen, H. T. K., Kim, B. W., Ahn, C. W., Han, H.-S., Lee, J.-S. (2019). High electromechanical strain properties in $SrTiO_3$-modified $Bi_{1/2}Na_{1/2}TiO_3$-$KTaO_3$ lead-free piezoelectric ceramics under low electric field. Sensors and Actuators A: Physical, 293, 1–6. https://doi.org/10.1016/j.sna.2019.04.016
6. Hong, C.-H., Kim, H.-P., Choi, B.-Y., Han, H.-S., Son, J. S., Ahn, C. W., Jo, W. (2016). Lead-free piezoceramics – Where to move on? Journal of Materiomics, 2 (1), 1–24. https://doi.org/10.1016/j.jmat.2015.12.002
7. Wu, S., Chen, P., Zhai, J., Shen, B., Li, P., Li, F. (2018). Enhanced piezoelectricity and energy storage performances of Fe-doped BNT–BKT–ST thin films. Ceramics International, 44 (17), 21289–21294. https://doi.org/10.1016/j.ceramint.2018.08.179
8. Zheng, H., Sun, E., Luo, H., Zhang, X., Yang, Y., Yang, B. et al. (2024). Comprehensive optimization of piezoelectric coefficient and depolarization temperature in Mn-doped $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$-$BaTiO^3$ lead-free piezoceramics. Journal of Materials Science & Technology, 172, 255–263. https://doi.org/10.1016/j.jmst.2023.06.043
9. Vuong, L. D., Gio, P. D. (2020). Enhancement in dielectric, ferroelectric, and piezoelectric properties of $BaTiO_3$-modified $Bi_{0.5}(Na_{0.4}K_{0.1})TiO_3$ lead-free ceramics. Journal of Alloys and Compounds, 817, 152790. https://doi.org/10.1016/j.jallcom.2019.152790
10. Maria Joseph Raj, N. P., Khandelwal, G., Kim, S.-J. (2021). 0.8BNT–0.2BKT ferroelectric-based multimode energy harvester for self-powered body motion sensors. Nano Energy, 83, 105848. https://doi.org/10.1016/j.nanoen.2021.105848
11. Nguyen, H. T. K., Duong, T. A., Erkinov, F., Kang, H., Kim, B. W., Ahn, C. W. et al. (2020). Effect of $SrTiO_3$ modification on dielectric, phase transition and piezoelectric properties of lead-free $Bi_{0.5}Na_{0.5}TiO_3$-$CaTiO_3$-$SrTiO_3$ piezoelectric ceramics. Journal of the Korean Ceramic Society, 57 (5), 570–577. https://doi.org/10.1007/s43207-020-00051-y
12. Nguyen, H. T. K., Duong, T. A., Erkinov, F., Ahn, C. W., Kim, B. W., Han, H.-S., Lee, J.-S. (2020). Large Electric Field-Induced Strain Response Under a Low Electric Field in Lead-Free $Bi_{1/2}Na_{1/2}TiO_3$-$SrTiO_3$-$BiAlO_3$ Ternary Piezoelectric Ceramics. Journal of Electronic Materials, 49 (11), 6677–6685. https://doi.org/10.1007/s11664-020-08436-9
13. Pattipaka, S., James, A. R., Dobbidi, P. (2018). Enhanced dielectric and piezoelectric properties of BNT-KNNG piezoelectric ceramics. Journal of Alloys and Compounds, 765, 1195–1208. https://doi.org/10.1016/j.jallcom.2018.06.138
14. Bai, W., Zheng, P., Wen, F., Zhang, J., Chen, D., Zhai, J., Ji, Z. (2017). Lead-free BNT-based composite materials: enhanced depolarization temperature and electromechanical behavior. Dalton Transactions, 46 (44), 15340–15353. https://doi.org/10.1039/c7dt02846f

15. Liu, T. Y., Ma, Y., Yu, S. F., Shi, J., Xue, S. (2011). The effect of ball milling treatment on structure and porosity of maize starch granule. Innovative Food Science & Emerging Technologies, 12 (4), 586–593. https://doi.org/10.1016/j.ifset.2011.06.009
16. Eltouby, P., Shyha, I., Li, C., Khaliq, J. (2021). Factors affecting the piezoelectric performance of ceramic-polymer composites: A comprehensive review. Ceramics International, 47 (13), 17813–17825. https://doi.org/10.1016/j.ceramint.2021.03.126
17. Donnelly, N. J., Shrout, T. R., Randall, C. A. (2007). Addition of a Sr, K, Nb (SKN) Combination to PZT(53/47) for High Strain Applications. Journal of the American Ceramic Society, 90 (2), 490–495. https://doi.org/10.1111/j.1551-2916.2006.01450.x
18. Widanarto, W., Wulandari, R., Rahmawati, D., Cahyanto, W. T., Sari, K., Effendi, M. et al. (2024). Microwave irradiation-induced yield enhancement of coconut shell biomass-derived graphene-like material. Physica Scripta, 99 (6), 065949. https://doi.org/10.1088/1402-4896/ad4691
19. Mansouri, B., Rafiei, M., Ebrahimzadeh, I., Naeimi, F., Barekat, M. (2023). The effect of milling time and heat treatment on the synthesis of the Cr_2AlC MAX phase. Canadian Metallurgical Quarterly, 63 (3), 970–980. https://doi.org/10.1080/00084433.2023.2251210
20. Effendi, M., Solihah, E., Kurniawan, C., Cahyanto, W. T., Widanarto, W. (2020). Transformation of Structure, Magnetic Properties and Microwave Absorption Capability in Nd-Doped Strontium Hexaferrite. Key Engineering Materials, 855, 255–260. https://doi.org/10.4028/www.scientific.net/kem.855.255
21. Moya, B. R., Iglesias-Jaime, A. C., Silva, A. C., Peláiz-Barranco, A., Guerra, J. D. S. (2024). Structural and dielectric features of $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ lead-free ferroelectric ceramics: An approach to the phase diagram. Journal of Applied Physics, 135 (16). https://doi.org/10.1063/5.0191402
22. Pham, T. H. N., Hua, P. H., Ngo, Q. B., Ha, T. K., Nguyen, V. T., Nguyen, C. T., Pham, Q. A. (2024). The effect of carbon black percentage on mechanical properties and microstructure of polybutylene terephthalate/polyamide 6/carbon black blends. Eastern-European Journal of Enterprise Technologies, 1 (12 (127)), 20–26. https://doi.org/10.15587/1729-4061.2024.299067
23. Krauss, W., Schütz, D., Mautner, F. A., Feteira, A., Reichmann, K. (2010). Piezoelectric properties and phase transition temperatures of the solid solution of $(1-x)(Bi_{0.5}Na_{0.5})TiO_{3-x}SrTiO_3$. Journal of the European Ceramic Society, 30 (8), 1827–1832. https://doi.org/10.1016/j.jeurceramsoc.2010.02.001
24. Lin, D., Kwok, K. W. (2010). Effect of Li-substitution on piezoelectric and ferroelectric properties of $(Bi_{0.92}Na_{0.92-x}Li_x)_{0.5}Ba_{0.06}Sr_{0.02}TiO_3$ lead-free ceramics. Current Applied Physics, 10 (4), 1196–1202. https://doi.org/10.1016/j.cap.2010.02.009
25. Widanarto, W., Effendi, M., Cahyanto, W. T., Ghoshal, S. K., Kurniawan, C., Handoko, E., Alaydrus, M. (2023). Enhanced Microwave Absorption Quality of Bio-Silica-Barium-Ferrite Composites: Interplay of Fe^{3+} and Si^{4+}. Molekul, 18 (2), 266. https://doi.org/10.20884/1.jm.2023.18.2.7326
26. Bongkarn, T., Chootin, S., Pinitsoontorn, S., Maensiri, S. (2016). Excellent piezoelectric and ferroelectric properties of KNLNTS ceramics with Fe2O3 doping synthesized by the solid state combustion technique. Journal of Alloys and Compounds, 682, 14–21. https://doi.org/10.1016/j.jallcom.2016.04.285
27. Yang, Y., Lin, C.-S., Chen, J.-F., Hu, L., Cheng, W.-D. (2014). Magnetoelectric effects at the interfaces between nonmagnetic perovskites: Ab initio prediction. EPL (Europhysics Letters), 105 (2), 27002. https://doi.org/10.1209/0295-5075/105/27002
28. Widanarto, W., Sahar, M. R., Ghoshal, S. K., Arifin, R., Rohani, M. S., Effendi, M. (2013). Thermal, structural and magnetic properties of zinc-tellurite glasses containing natural ferrite oxide. Materials Letters, 108, 289–292. https://doi.org/10.1016/j.matlet.2013.06.109
29. Widanarto, W., Rahayu, F. M., Ghoshal, S. K., Effendi, M., Cahyanto, W. T. (2015). Impact of ZnO substitution on magnetic response and microwave absorption capability of strontium-natural nanoferrites. Results in Physics, 5, 253–256. https://doi.org/10.1016/j.rinp.2015.09.002
30. Cech, O., Castkova, K., Chladil, L., Dohnal, P., Cudek, P., Libich, J., Vanysek, P. (2017). Synthesis and characterization of $Na_2Ti_6O_{13}$ and $Na_2Ti_6O_{13}/Na_2Ti_3O_7$ sodium titanates with nanorod-like structure as negative electrode materials for sodium-ion batteries. Journal of Energy Storage, 14, 391–398. https://doi.org/10.1016/j.est.2017.07.008
31. Libich, J., Minda, J., Sedlaříková, M., Vondrák, J., Máca, J., Fíbek, M. et al. (2020). Sodium-ion batteries: Electrochemical properties of sodium titanate as negative electrode. Journal of Energy Storage, 27, 101150. https://doi.org/10.1016/j.est.2019.101150
32. Husin, H., Pontas, K., Yuliana Sy, Y. S., Syawaliah, S., Saisa, S. (2014). Synthesis of Nanocrystalline of Lanthanum Doped $NaTaO_3$ and Photocatalytic Activity for Hydrogen Production. Journal of Engineering and Technological Sciences, 46 (3), 318–327. https://doi.org/10.5614/j.eng.technol.sci.2014.46.3.6
33. Huang, N., Liu, H., Hao, H., Yao, Z., Cao, M., Xie, J. (2019). Energy storage properties of MgO-doped $0.5Bi_0{\cdot}5Na_0{\cdot}5TiO_3$-$0.5SrTiO_3$ ceramics. Ceramics International, 45 (12), 14921–14927. https://doi.org/10.1016/j.ceramint.2019.04.227