Effect of Co and Y modification on structural, ferroelectric and magnetic properties of Bi$_5$Ti$_3$FeO$_{15}$ ceramics

Jelena D Bobic (jelenabobic@yahoo.com)  
Institute for Multidisciplinary Research, University of Belgrade  
https://orcid.org/0000-0002-9439-261X

Nikola Ilić  
Institute for Multidisciplinary Research

Vignaswaran Veerapandiyan  
Materials Center Leoben Forschung GmbH

Mirjana Vijatović Petrović  
Institute for multidisciplinary Research

Marco Deluca  
Materials Center Leoben Forschung GmbH

Adis Dzunuzovic  
Institute for Multidisciplinary Research

Jelena Vukmirovic  
Faculty of Technology Novi Sad

Kaijie Ning  
New York State College of Ceramics at Alfred University

Klaus Reichmann  
Graz University of Technology: Technische Universitat Graz

Steven Tidrow  
New York State College of Ceramics at Alfred University

Research Article

Keywords: Ceramics, Solid state reaction, Ferroelectric properties, Magnetic properties

Posted Date: February 16th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-228886/v1

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Abstract

The ferroelectric and magnetic properties of four-layered Aurivillius Bi$_5$Ti$_3$FeO$_{15}$ (BFT) compounds via partial substitution of Bi$^{3+}$ with Y$^{3+}$ and Fe$^{3+}$ with Co$^{2+}$ (according to formula: Bi$_{5-x}$Y$_x$Ti$_3$FeO$_{15}$, x = 0.1, 0.2, 0.3; Bi$_5$Ti$_3$Fe$_{1-y}$Co$_y$O$_{15}$, y = 0.1, 0.3, 0.5) were investigated. Polycrystalline ceramics of Co and Y substituted BFT were prepared by conventional solid-state reaction. Crystal structure and phase purity were confirmed via X-ray diffraction. Raman spectral signatures indicate that Y replaces Bi ions in the pseudo-perovskite layers and Co replaces Fe ions in the octahedral sites. SEM micrographs show a decrease in grain size for both chemically modified samples when compared to plate-like morphology for pure BFT with dimensions ranging from 3–5 µm in length and a thickness of ~ 0.5 µm. The decrease in grain size is more pronounced in Co substituted samples with plate-like grain dimensions of 1 µm in length and 0.1 µm in thickness. Ferroelectric measurements show unsaturated leaky hysteresis loops in both chemically modified samples until the maximum applied electric field. Magnetic measurements confirm the paramagnetic nature of pure and Y substituted BFT ceramics while Co substituted BFT ceramics exhibit a typical ferromagnetic $M-H$ loop. The largest remanent magnetization value of 0.084 emu/g at room temperature is recorded for the Co$^{2+}$ substituted sample with x = 0.30.

1. Introduction

Single-phase multiferroic materials that can exhibit a coupling of magnetic and ferroelectric properties have attracted profound interest due to their technological relevance and fundamental scientific challenges [1]. Among single phase multiferroics, the most frequently investigated materials such as BiFeO$_3$, BiMnO$_3$, LuFe$_2$O$_4$, CuFeO$_2$ etc. are not yet suitable for practical applications, either because the room temperature polarization and/or magnetization is negligible or exhibit a weak magnetoelectric effect [2]. Following single-phase multiferroics, a new class called Aurivillius compounds with a layered perovskite-like crystal structure that includes Bi$_5$Ti$_3$FeO$_{15}$, (BFT) has been identified as technologically relevant within magnetoelectric materials [3, 4]. The crystal structure of BFT consists of $n = 4$ perovskite-like layers ($A_{n-1}B_nO_{3n+1}$)$^{2-}$ stacked along the [001] direction and separated by fluorite-like (Bi$_2$O$_2$)$^{2+}$ layers. Based on the ionic radii, in perovskite layers, the A site can be occupied by Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Bi$^{3+}$, and Ln$^{3+}$ and the B site can accommodate Ti$^{4+}$, Nb$^{5+}$, and W$^{6+}$ [5–7]. Importantly, the B site can also accommodate magnetic elements, such as Fe, Mn, Co, and Ni, which will create the possibility of magnetic ordering while maintaining the intrinsic ferroelectric nature of perovskite layers due to off-centering of A and B site cations [8]. In BFT, Bi$^{3+}$ with a larger ionic-radius takes the 12-fold-coordinated A-site and Fe$^{3+}$ and Ti$^{4+}$ are small B site cations that are randomly distribute over two available octahedral sites (BO$_6$) in the perovskite block. The Bi$^{3+}$ cation is also located in the large cavity at the center of eight corner-sharing Fe/TiO$_6$ octahedra as well as in (Bi$_2$O$_2$)$^{2+}$ layers [7].

BFT exhibits ferroelectric as well as spin order at relatively high temperatures and shows a weak ferromagnetism (FM) and magnetoelectric (ME) coupling at relatively low magnetic field [6]. However, the
reported magneto-electric coefficient is still low for the bulk Bi$_5$Ti$_3$FeO$_{15}$ materials. It has been reported that the A and B-site cations in BFT structure can be partially substituted by different chemical species to improve both the ferroelectric and FM properties of the material. In this material class, A (Bi$^{3+}$) and B (Ti$^{4+}$) site are primary contributors of polarization while the magnetization comes only from the B (Fe$^{3+}$) site.

One main hindrance to the applicability of bismuth titanate based ceramics in devices is their high electrical conductivity, making it difficult to carry out ‘electrical poling’ and therefore making the material less functional. It is known that in Aurivillius compounds (Bi$_2$O$_2$)$^{2+}$ layers play an important role in space-charge compensation and hence improve the electrical properties by suppressing the leakage current [9]. Partial substitution of highly volatile Bi$^{3+}$ at the A-site can counteract the bismuth loss during the sintering process and thereby suppress the formation of point defects in addition to stabilizing the (Bi$_2$O$_2$)$^{2+}$ layer, where defects, such as oxygen vacancies can occur. The chemical stability of the perovskite layers against the formation of oxygen vacancies can also be drastically improved when volatile Bi-ions are partially substituted with more stable chemical species [10, 11].

There are many reports of aliovalent and isovalent modification on A-site (Bi ions) of BiFeO$_3$ [12–14] but not in Bi$_5$Ti$_3$FeO$_{15}$ based Aurivillius phase ceramics. Reports of isovalent substitution in bismuth ferrite at the A site have been controversial since a slight increase in ferroelectric polarization by partial elimination of Bi$^{3+}$ ions (with lone 6s$^2$ electron pair) was reported by some, while others reported higher leakage current densities which consequently suppress ferroelectric polarization [15, 16]. So far, La doped [17–19], Na/Ce co-doped [20] and rare-earth doping of BFT with Nd, Sm, Gd, Dy and Ho [14, 21–23] are reported in the literature. Isovalent substitution of Bi$^{3+}$ with Dy$^{3+}$ enhanced ferroelectricity, FM as well as ME properties [22]. Improved ME effect was recorded in Ho-Mn co-doped BFT films [24]. To the best of our knowledge, there are no reports about the influence of Y$^{3+}$ substitution on the ferroelectric and FM properties of BFT ceramics although many authors proved that leakage current is reduced after Y doping in bismuth ferrite ceramics [25, 26]. Smaller ionic radius of Y$^{3+}$ (1.02 Å) in comparison with Bi$^{3+}$ (1.17 Å) could facilitate higher solubility and larger reductions in Goldschmidt tolerance factor which can impact both magnetic and electrical properties of materials [12].

Most common magnetic elements substituted at the B-site (Fe ions) in BFT are Mn, Ni, Cr and Co [27–30]. In their crystalline phase Co and Ni are ferromagnetic, Cr is antiferromagnetic and Mn is ferromagnetic or antiferromagnetic depending on crystal structure [31]. Thus, partial replacement of Fe$^{3+}$ ions by aliovalent Co$^{2+}$ ions was selected in an attempt to increase magnetization of BFT ceramics. Although B-site modification can contribute to enhanced polarizability, other electrical properties might have to be compromised due to the multi-valent nature of the transition metals. To understand such effects, polarization and electrical measurements in addition to structural characterization by Raman spectroscopy are carried out. Our primary focus in this study is to investigate the influence of Y$^{3+}$ as an
isovalent substituent at the A-site and Co$^{2+}$ as an aliovalent substituent at the B-site on the multiferroic properties of BFT ceramics.

2. Experimental Procedure

Pure and modified BFT polycrystalline ceramics were synthesized using conventional solid-state reaction method. Appropriate analytically pure oxide precursors: TiO$_2$, Fe$_2$O$_3$, Bi$_2$O$_3$, Y$_2$O$_3$ and CoO (Alfa Aesar, p.a. 99%) were used. The starting materials were weighed in stoichiometric proportions and mixed by planetary ball mill (Pulverisette 5, Fritsch, Germany) in isopropanol medium for 24 h. Y and Co substituted BFT ceramics were prepared according to the following chemical formula: $\text{Bi}_{1-x} \text{Y}_x \text{Ti}_3 \text{FeO}_{15}$, $x = 0.1, 0.2, 0.3$ (BFTY1, BFTY2 and BFTY3) and $\text{BiTi}_3 \text{Fe}_{1-y} \text{Co}_y \text{O}_{15}$, $y = 0.1, 0.3, 0.5$ (BFTCo1, BFTCo3 and BFTCo5), respectively. The mixed powders were calcined at 700°C for 4 h with heating rate of 10°C/min. The calcined powders were ground and subsequently pressed into pellets (8 mm in diameter and 3 mm thick) under a uniaxial pressure of 100 MPa and sintered at 950°C for 2 h. The sintering was performed in a covered alumina crucible to avoid bismuth loss with a heating rate of 5°C/min and samples were left to cool naturally in air after sintering. The relative density of the fabricated ceramics was calculated geometrically by measuring the ceramics mass and dimensions and calculating from the equation $\rho = 4m/\pi d^2 h$ (where m is mass, $d$ – average diameter and $h$ – height of the sintered samples).

The morphology and microstructure of obtained ceramics were examined using scanning electron microscope (Model Vega TS5130MM, Tescan, Czech Republic). The phase purity and crystal structure of obtained ceramics was verified using a conventional X-ray diffractometer (Model XRD D5000, Siemens, Germany) with CuK$_\alpha$ radiation ($\lambda_{ka1} = 1.5405 \text{Å}$, $\lambda_{ka2} = 1.5443 \text{Å}$, $I_{ka1}/I_{ka2} = 0.5$), 2$\theta$ range between 20° and 60°, step size of 0.02° (2$\theta$), divergence slit = 0.5 mm, receiving slit = 0.3 mm. Silver electrodes (7095 Silver conductor paste, DuPont, USA) were painted on the polished surfaces of the ceramics as electrodes for electrical measurements. Temperature dependent resistivity of materials were measured from RT to 700°C using a picoammeter (6487, Keithley Instruments Gmbh, USA) and voltage source controlled using LabVIEW software with GUI. The polarization-electric field curves were measured with a Piezoelectric Evaluation System (aixPES, aixACCT system GmbH, Germany). Magnetic measurements of materials were carried out with a vibrating-sample magnetometer (7307 Series VSM, Lake Shore Cryotronics, USA). Raman measurements were carried out in a spectrometer (LabRAM 300, Horiba Jobin Yvon, France) using an excitation wavelength of $\lambda = 532 \text{ nm}$ in a backscattering geometry. Temperature dependent Raman measurements were carried out in a temperature-controlled stage (THMS600, Linkam, UK).

3. Results And Discussion

Figure 1. shows SEM micrograph of free surfaces (with inserted figures of fractured surfaces) of all investigated compositions. It is evident that the ceramics are dense (geometrical density more than 92% of theoretical value) and show well-developed laminar, randomly oriented grains typical of Aurivillius-type structures. The grain size of pure BFT is approximately 3–5 µm in length and 0.5 µm in thickness. With
both Y and Co incorporation, the grain size decreased and this reduction is more pronounced for Co substitution where the grain size decreased down to 1 µm in length and 0.2 µm in thickness. From this it can be concluded that both substituents suppress grain growth along \( a-b \) plane leading to smaller grain sizes and change of the aspect ratio.

The x-ray diffractograms of all samples are shown in Fig. 2. All diffraction peaks can be indexed to the orthorhombic structure according to the JCPDS database (No.: 89-8545) with space group \( \text{A2}_1\text{am} \). There is no evidence of secondary phases or presence of unreacted oxides within the detection capability, which is consistent with the successful incorporation of Co and Y ions in the BFT lattice. Based on the available database, the (1 1 9) peak is the most intense peak for BFT ceramics with randomly oriented grains. However, for the fabricated pure BFT ceramics, besides the (1 1 9) peak, (0 0 10) and (0 0 18) are of equal intensity compared to (1 1 9) peak. Such intensities are due to the anisotropic structure of Aurivillius compounds, and such discrepancies in peak intensities can indicate a certain extent of texturing along the c-axis [32]. However, SEM micrographs, especially fractured surface images, indicate that grains are randomly oriented in all samples. A possible reason for intensity change could be the preferential grain growth at the surface. As grain size decreases with substitution concentration, the preferential grain growth is less pronounced and so would be the intensities of the (0 0 10) and (0 0 18) peaks, leading to improved peak matching.

Raman scattering is a sensitive technique for investigating lattice vibrational modes and can also provide information on the crystallographic positions of substitutional ions and its effect on the ferroelectric behavior primarily through the appearance of extra modes and/or peak positions [33, 34]. The Raman spectra for all ceramics were investigated in the Raman frequency shift range of 100–1000 cm\(^{-1}\). Figure 3. shows temperature-dependent spectra of pure BFT ceramics ranging from 25 °C to 600 °C where 11 Raman peaks are observed at room temperature. The overall spectral signature of pure BFT is unchanged as a function of temperature and is consistent with the available literature [35, 36]. Generally, Raman spectra of Aurivillius type materials can be divided into two segments: (1) below 200 cm\(^{-1}\) are the modes related to the motions of heavy Bi ions at the A-site; and, (2) above 200 cm\(^{-1}\) are the modes corresponding to the torsional bending and stretching of BO\(_6\) octahedral.

The soft Raman modes 1, 2 and 3 at \( \sim 100, \sim 120 \) and \( \sim 145 \) cm\(^{-1}\) are closely associated with the vibrations of the Bi\(^{3+}\) ions at the A-site positions of the perovskite-like slabs. The high frequency modes from O-Ti/Fe-O bending vibrations appear around 270 cm\(^{-1}\) (modes 4, 5 and 6). The mode 8 at \( \sim 544 \) cm\(^{-1}\) corresponds to the stretching vibrations of the TiO\(_6\) octahedra and the mode 9 at \( \sim 566 \) cm\(^{-1}\) is caused by the variation of bond distances between the Bi atoms within (Bi\(_2\)O\(_2\))\(^{2+}\) layers and the apical O atoms of the perovskite block. The mode 10 at \( \sim 700 \) cm\(^{-1}\) and mode 11 at \( \sim 862 \) cm\(^{-1}\) correspond to the torsion of the octahedra in the \( a-b \) plane and stretching of the octahedra along c-axis of BO\(_6\) octahedra, respectively [23, 36–38]. All pure BFT ceramics related modes are numbered from 1 to 11 and are consistent with other chemically modified BFT ceramics. Extra Raman modes specific to particular chemically modified system are highlighted and marked.
Figure 4. show the Raman spectra of pure and Y modified BFT samples observed at room temperature. It can be noticed that the modes 1, 2 and 3 are weakened by Y doping in comparison with pure BFT which is consistent with Y replacing Bi ions in the pseudo-perovskite layers. It is evident that the position and intensities of 3, 4 and 5 modes do not change upon Y substitution (as marked by arrows), which indicates that substitution does not affect the tilting distortion of TiO$_6$ octahedra. Modes 8 and 9 show interesting changes with varying Y$^{3+}$ substitution concentration. Y$^{3+}$ substitution at the A-site leads to structural disorder, which results in progressive shifting and merging of these two modes leading to a convolution, as highlighted by box. Such indicates that Y$^{3+}$ prefers to replace Bi$^{3+}$ ions in the pseudo-perovskite layers consequently affecting bond distances between (Bi$_2$O$_2$)$^{2+}$ layers and the apical O atoms of the perovskite block. The modes 10 and 11 which correspond to the FeO$_6$ and TiO$_6$ octahedra, respectively, are unaffected by Y$^{3+}$ modification as expected.

Raman spectra of pure and Co$^{2+}$ modified BFT ceramics are presented at Fig. 5. The mode that is primarily affected by Co-substitution is the mode 10. In addition to mode 10, a sharp extra Raman mode marked as I evolve with Co substitution concentration, which corresponds to the separate vibration of FeO$_6$ and CoO$_6$ octahedra, respectively [9, 30]. Such extra modes are commonly reported in other chemically modified systems. This result indicates that Co$^{2+}$ ions replace the Fe in FeO$_6$ based octahedral site in the BFT ceramics. The sharp appearance of mode I may indicate a possible ordering of Co ions, as sharp modes often refer to localized phonon vibrations. Additionally, mode 11 decreases in intensity with Co$^{2+}$ concentration, which indicates that the introduction of the Co$^{2+}$ ions into the bismuth-layered Aurivillius structure alters the local structural environment around BO$_6$ octahedra [38].

Figure 6 shows the polarization-electric field (P-E) hysteresis loops for all samples. P-E loops under high electric fields show a typical low-quality round-shaped hysteresis common to other multiferroic systems. Samples did not sustain high enough field to demonstrate saturated hysteresis loops. Therefore, it is not possible to compare the saturation polarization for different samples, however, comparison between the values at certain field strength can provide insight into developed ferroelectric properties of obtained ceramics. In BFT, polarization does not reach saturation even at relatively high electric fields (up to 130 kV/cm). When comparing the P-E loops of pure BFT with BFTY, the sustainable electric field strength was significantly increased with Y substitution (for BFTY3 electrical breakthrough occurred at field strength of 160 kV/cm). In the case of Co substitution, the electrical breakdown occurred at lower applied field strength (at 100 kV/cm) when compared to pure BFT (inset of Fig. 6b.). Discharge breakdown materials, which exhibit porosity and inhomogenous microstructures, typically found in ceramics, have been found to exhibit breakdown characteristics which are dominated by the presence of their internal voids and inclusions. Having in mind that porosity of all samples, pure and chemically modified, is very similar (varying for 6 to 8 %) reason for lower breakdown fields in Co modified samples in comparison with Y ones is probably localized porosity or presence of internal voids and inclusions in the bulk of BFTC samples.
From Fig. 6a it can be seen that the highest values of polarization at zero field were obtained for the pure BFT sample while the Y$^{3+}$ substituted samples showed sharper loops, which may indicate that chemically modified samples are less conductive due to the reduction of chemical defect, such as bismuth vacancies accompanied with oxygen vacancies that act as a space charge. This is consistent with I-E loops (Fig. 7a) where it can be seen that displacement current of BFTY samples are slightly decreased at low field in comparison with pure BFT while at high fields the difference is more pronounced. Even if the leakage current is slightly reduced in BFTY samples the improvements in ferroelectricity is not evident and ferroelectric switching induced current peaks were not observed. As already mentioned, ferroelectricity in Aurivillius Bi$_5$Ti$_3$FeO$_{15}$ compounds originates from the rotation and tilting of TiO$_6$/FeO$_6$ octahedra, the stereochemical activity of lone pair electrons of Bi$^{3+}$ ions and distorted (Bi$_2$O$_2$)$_{2+}$ layers [39]. The replacement of Bi$^{3+}$ with Y$^{3+}$ (which does not contain 6s$^2$ lone-pair electron) causes a reduction in orbital hybridization between Bi 6s and O 2s/2p orbitals and this contributes to the reduction in the observed saturation polarization with increasing Y$^{3+}$ concentration in comparison with pure BFT. Alternatively, a decrease in separation distances between positive and negative charge-centers due to the weakening of the hybridization generates smaller single electric dipole moments, leading to a decrease in electric polarization as a vector sum of all dipole moments.

In the case of Co substitution (Fig. 6.), the hysteresis shape and value of zero field polarization of BFTC1 sample remain almost the same in comparison with pure BFT while its increase in BFTC3 and BFTC5 samples is evident. Conductivity contribution in the current response of leaky ferroelectrics has a significant impact on the shape of the hysteresis curve. Increase leakage of hysteresis loops is consistent with I-E loops (Fig. 7.) where displacement current increased with higher content of Co (BFCT3 and BFCT5).

The Y$^{3+}$ and Co$^{2+}$ dependence of the electrical resistivity was studied from 25–650 °C (Fig. 8). The results show that the resistivity decreases with temperature increase due to thermal activation of conducting species in all samples. In both cases, introduction of substituted ions did not significantly affect conductivity in all temperature range except in the case of minimum concentration of Co where conductivity was noticeable reduced. This reduction in conductivity of BFTC1 sample is unexpected and could be related with measurement problems (contact between sample and electrodes etc). Despite substitution of highly volatile Bi$^{3+}$ by more stable Y$^{3+}$ (probably because of the relatively small concentration of Y$^{3+}$) conductivity remained quite high so even Y$^{3+}$ substitution did not improve the electrical properties substantially. Figure 8. Temperature dependence of DC specific resistivity for a) Y modified and b) Co modified BFT samples

The magnetic hysteresis loops of all samples are displayed in Fig. 9. Linear $M$-$H$ loop of pure BFT samples at room temperature indicates the paramagnetic nature (Fig. 9a) of this material as was previously reported in the literature [40, 41, 4]. Because of the low concentration of Fe$^{3+}$ ions and their random occupancy of the octahedral B-sites [7, 40] the probability of long-range ordering of the iron spins in BFT is small, which makes the ferromagnetic exchange interaction practically impossible to be
achieved at room temperature [42]. Although long-range ordering of the Fe$^{3+}$ spins are small, the random distribution of Fe and Ti ions in the octahedral results in local Fe-O clusters. These clusters may thus favor the superparamagnetic (SPM) state at low temperature. In spite of this SMP state, the superchange of the Fe-O-Fe clusters still possibly favors the local AFM interaction which explains the reason why BFT shows the SPM behaviors with dominant AFM interaction background [27, 43].

At room temperature, the field dependence of the magnetization in Y substituted samples demonstrates a linear character, typical of paramagnets, indicating that the A-site Y substitution does not affect the magnetic state of the parent BFT phase. On the other hand, in recent years, researchers have adopted various chemical modification procedures to enhance the magnetic properties using elements such as Mn, Ni, Cr, Co etc. It is suggested that a possible coupling of Fe–O–M (M represents magnetic element but not Fe) octahedral clusters might contribute to the improvement of ferromagnetic characteristic in M-doped BFT [9, 42]. The FM properties in BFTCo originate from spin canting of the Fe- and Co-based sublattices via antisymmetric exchange interactions. It can be inferred that the best magnetic performance would be expected when the ratio of Fe$^{3+}$ to M$^{3+}$ is 1:1 because of the increased probability of adjacently appearing Fe–O and M–O octahedral and therefore the magnetic coupling [27]. In the present study, however, the best magnetic behavior appears in the BFTCo3 (Fe$^{3+}$: Co$^{2+}$ = 7:3) and not BFTCo5 where the ratio of Fe$^{3+}$ to Co$^{2+}$ is 1:1. This result agrees with previously reported Co modified BFT ceramics [44] inferring that there are other factors that might impact the magnetic performance. Occupancy of Fe ions is expected to randomly replace Ti ions in the perovskite-like layers while it is reported that Fe$^{3+}$ cations preferentially occupy the inner octahedral sites [7]. Accordingly, when the Co doping concentration (x) is 0.3, the ratio of Fe ions to Co ions located at the inner octahedral centers would be 1:1. As a consequence, the strongest direct Fe-O-Co antisymmetric exchange interactions occur in the inner octahedron which leads to the highest $M_r$ value of 0.084 emu/g. Values of saturation magnetization of BFTCo3 around 0.30 emu/g were also consistent with the work of Yu and co-authors [45]. When the Co substitution concentration (x) exceeded 0.3 the probability of formation of Co-O-Co and Fe-O-Co chains increased, and the AFM interaction was thus dominant, producing inferior hysteresis loops when compared to BFTCo3 [44, 46]. Additionally, with increasing Co substitution levels, the outer site occupation of the Co$^{2+}$ ions may also reduce the spin canting effects, which also weaken FM behavior and hence reduce the $M_r$ values to 0.040 emu/g for x = 0.5 of Co addition.

| Samples | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ (Oe) | $M_r/M_s$ (%) |
|---------|--------------|--------------|------------|---------------|
| BFTC1   | 0.08         | 0.023        | 287        | 28.7          |
| BFTC3   | 0.31         | 0.084        | 186        | 27.1          |
| BFTC5   | 0.09         | 0.040        | 345        | 44.4          |

### 4. Conclusions
In this work the main focus was to enhance ferroelectric and magnetic properties of BFT ceramics by chemical modification in order to improve multiferroic properties. Both A and B sites of BFT were modified separately with different ions according to the formula: Bi$_{1-x}$Y$_x$Ti$_3$FeO$_{15}$, $x = 0.1$, $0.2$, $0.3$; and, BiTi$_3$Fe$_{1-y}$Co$_y$O$_{15}$, $y = 0.1$, $0.3$, $0.5$, respectively. Dense single-phase polycrystalline ceramics were successfully synthesized by solid state reaction and analyzed for structural (XRD/Raman) and electric/magnetic properties, in order to elucidate the changes that occur by substitution at different length scales. Raman spectra analysis confirmed that Y$^{3+}$ replaces Bi$^{3+}$ ions in the pseudo-perovskite layers while Co ions occupy the FeO$_6$ based octahedral sites.

In all samples polarization saturation was not achieved because of the electrical breakdown at relatively lower fields (because of microstructural defects). Results show no improvement in the ferroelectric properties with Y$^{3+}$ modification despite the observed reduction of leakage current. Polarization at zero field decreased with increase in Y$^{3+}$ concentration, because of the replacement of Bi$^{3+}$ with Y$^{3+}$ (which does not contain 6s$^2$ lone-pair electron) changing the bonding environment and limiting the orbital hybridization between Bi 6s and O 2s/2p orbitals. In the case of Co substitution, polarization at zero field increased in comparison with pure BFT due to conductivity contributions in the current response. Magnetic measurements confirm the paramagnetic nature of pure and Y$^{3+}$ modified BFT ceramics while Co$^{2+}$ substitution enhanced the magnetic response of BFT. The largest $M_r$ value is recorded in BiTi$_3$Fe$_{0.7}$Co$_{0.3}$O$_{15}$ samples ($M_r$ of 0.084 emu/g and $H_c$ of 287 Oe), when the ratio of Fe ions to Co ions located at the inner octahedral centers is expected to be 1:1.

**Declarations**

**Acknowledgments:**

The authors gratefully acknowledge to financial support given through mobility on bilateral project “Lead free Aurivillius-based materials: close-line between Raman spectroscopy and ferro/multiferroic properties” of Ministry of Education, Science and Technological development Republic of Serbia (project code in SR 451-03-02141/2017-09/46) and OeAD-Austrian Agency for International Cooperation in Education and Research (project code in AT: SRB 04/2018). Also, the authors gratefully acknowledge to financial support of project program 451-03-68/2020-14/200053 given by the Ministry of Education, Science and Technological development Republic of Serbia as well as Austrian Science Found (FWF): Projects P29563-N36 and I4581-N. Special thanks to Dr Sašo Gyergyek from the Jožef Stefan Institute, Ljubljana, Slovenia, for magnetic measurements and Prof. Biljana Stojanovic from Institute for Multidisciplinary Research, University of Belgrade.

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Figures
Figure 1

SEM analysis of free surface (with inserted cross section) of all samples

Figure 2

XRD patterns of pure BFT ceramics and Y3+ (left) and Co2+ (right) modified BFT with different substitution concentrations
Figure 3

Temperature-dependent Raman spectra of the BFT ranging from 25 °C to 600 °C
Figure 4

Raman spectra of pure and Y modified BFT ceramics at room temperature
Figure 5

Raman spectra of pure and Co modified BFT ceramics at room temperature
Figure 6

Ferroelectric hysteresis loops of a) Y modified and b) Co modified BFT samples at RT

Figure 7

Current loops of a) Y modified and b) Co modified BFT samples
Figure 8

Temperature dependence of DC specific resistivity for a) Y modified and b) Co modified BFT samples

Figure 9

Magnetic hysteresis of a) Y modified and b) Co modified BFT samples measured at room temperature