

FTIR Study of Nanostructure Perovskite BaTiO₃ Doped with Both Fe³⁺ and Ni²⁺ Ions Prepared by Sol–Gel Technique

A. ABDEL AAL^a, T.R. HAMMAD^a, M. ZAWRAH^b, I.K. BATTISHA^{c,*} AND A.B. ABOU HAMMAD^c

^aHelwan University, Physics Department, Helwan, Cairo, Egypt

^bNational Research Center (NRC), Ceramic Department, Doky, Giza, Egypt

^cNational Research Center (NRC), Solid State Physics Department, Doky, Giza, Egypt

(Received November 10, 2012; in final form March 16, 2014)

Pure barium titanate BaTiO₃ (BT) and BT doped with two different transition elements Fe³⁺ and Ni²⁺ at 5 mol.% (BT5Fe and BT5Ni, respectively) as constant concentration in powder form have been prepared by sol-gel method using barium acetate, titanium(IV) *n*-butoxide, iron and nickel nitrates as precursor materials. The microstructure of BT and the influence of Fe and Ni dopants on it were investigated by X-ray diffraction and Fourier transform infrared spectroscopy. X-ray diffraction shows that tetragonal phase is dominant for pure BT sintered for 4 h at 800 °C. Scanning electron microscopy and transmission electron microscopy were used to study surface morphology and particle size distribution for BT5Fe and BT5Ni, respectively. The presence of hydroxyl defects were verified by Fourier transform infrared spectroscopy for (BaTi_{1-x}Fe_xO_{3-x/2}) (BT_xFe), where $x = 0.005, 0.01, 0.05,$ and 0.07 and (BaTi_{1-x}Ni_xO_{3-x/2}) (BT_xNi), where $x = 0.005, 0.01, 0.03, 0.05,$ and 0.07 .

DOI: [10.12693/APhysPolA.126.1318](https://doi.org/10.12693/APhysPolA.126.1318)

PACS: 81.20.Fw, 81.07.Bc, 81.20.Fw, 64.70.kg, 61.05.C-, 78.30.Ly, 81.10.Aj

1. Introduction

Ferroelectric BT belongs to the family of ABO₃ perovskite mineral (CaTiO₃) structures, in which A and B are metals [1–6]. The total charge of the positive ions A and B must be +6, A and B must be of quite different sizes; the smaller ion, with a larger charge, must be a transition metal. For BT, Ti is a 3*d* transition element and has the *d* orbital for electrons to form covalent bonds with its neighbors. The radius of Ti⁴⁺ ion is about 0.68 Å, and that of Ba²⁺ is about 1.35 Å. These ions form nice octahedral cages, with the O²⁻ ions held apart [7].

Doping of ferroelectric BT and BaSrTiO₃ (BST) based ceramics is of great importance in the fabrication of electric and electronic devices, where the intrinsic capability of the perovskite structure to host ions of different size and the large number of different dopants can be accommodated in the BT lattice. However, the effect of the specific impurity on the electrical conductivity depends on the substitution site (a trivalent ion behaves as an acceptor when substitution occurs at the Ti site or as a donor when it substitutes at the Ba site) as well as on the nature of the defect/electronic charge compensating defect. The ionic radius is the parameter which mainly determines the substitution site. Acceptor impurities of the first series of transition metals (Cr⁴⁺ (0.55 Å), Fe³⁺ (0.64 Å), Co³⁺ (0.63 Å), and Ni²⁺ (0.78 Å)) are incorporated at the Ti⁴⁺ (0.68 Å), as their size is incompatible with that of Ba²⁺ (1.35 Å), for the fabrication of multi-

layer ceramic capacitors to allow for the use of cheaper metal electrodes (i.e. Ni) [8].

In the present work, we have studied structural, morphology and Fourier transform infrared (FTIR) properties of BaTiO₃ and BaTiO₃-doped with two different transition elements Fe³⁺ and Ni²⁺ (BT5Fe and BT5Ni, respectively). The structural properties of BT powder were examined by X-ray diffraction (XRD) and the crystallite sizes were calculated using Scherrer's formula and FTIR. The morphology of the prepared samples was detected by scanning electron microscopy (SEM).

2. Experimental procedure

2.1. Samples preparation

A sol-gel process was used to prepare pure BaTiO₃ and BT doped with iron (Fe³⁺) (BT_xFe) and nickel (Ni²⁺) (BT_xNi). Pure BT was prepared using barium acetate (Ba(CH₃COO)₂) 99% and titanium(IV) *n*-butoxide ((Ti(C₄H₉O)₄) as precursor materials. Barium acetate (Ba(CH₃COO)₂) (99%, Sisco Research Laboratories PVT.LTD, India) was dissolved in mixture of acetic acid (AcAc) (HAc)–H₂O mixture (96%, Adwic, Egypt) and distilled water. Titanium(IV) *n*-butoxide (Ti(C₄H₉O)₄), (97%, Sigma-Aldrich, Germany) was dissolved in acetyl acetone, (AcAc, C₅H₈O₂), (98%, Fluka, Switzerland), then those solutions were mixed together with the molar ratio (Ba:Ti = 1:1) to form pure BT, and then were stirred for 1 h at room temperature (RT).

For doped samples, barium acetate solution was added to titanium(IV) *n*-butoxide solution in different ratio (Ba/Ti > 1) then the appropriate amount of dopant solution was added to the host solution to achieve the chemical structure (BaTi_{1-x}Fe_xO_{3-x/2}) (BTFe) and

*corresponding author; e-mail:

szbasha@yahoo.com, ibattisha@gmail.com

TABLE I

Name and concentration of Fe³⁺ doped nanostructure BT powders.

Dopant [mol.%]	Sample abbreviations	Chemical formula	Oxygen vacancy
$x = 0.005$ (0.5%)	BT0.5Fe	BaTi _{0.995} Fe _{0.005} O _{2.9975}	$\Delta = 0.0025$
$x = 0.01$ (1%)	BT1Fe	BaTi _{0.99} Fe _{0.01} O _{2.995}	$\Delta = 0.005$
$x = 0.03$ (3%)	BT3Fe	BaTi _{0.97} Fe _{0.03} O _{2.985}	$\Delta = 0.015$
$x = 0.05$ (7%)	BT5Fe	BaTi _{0.95} Fe _{0.05} O _{2.975}	$\Delta = 0.025$
$x = 0.07$ (7%)	BT7Fe	BaTi _{0.93} Fe _{0.07} O _{2.965}	$\Delta = 0.035$

TABLE II

Name and concentration of Ni²⁺ doped nanostructure BT powders.

Dopant [mol.%]	Sample abbreviations	Chemical formula	Oxygen vacancy
$x = 0.005$ (0.5%)	BT0.5Ni	BaTi _{0.995} Ni _{0.005} O _{2.995}	$\Delta = 0.005$
$x = 0.01$ (1%)	BT1Ni	BaTi _{0.99} Ni _{0.01} O _{2.99}	$\Delta = 0.01$
$x = 0.05$ (5%)	BT5Ni	BaTi _{0.95} Ni _{0.05} O _{2.95}	$\Delta = 0.05$
$x = 0.07$ (7%)	BT7Ni	BaTi _{0.93} Ni _{0.07} O _{2.93}	$\Delta = 0.07$
$x = 0.1$ (10%)	BT10Ni	BaTi _{0.9} Ni _{0.1} O _{2.9}	$\Delta = 0.1$

(BaTi_{1-0.05}Ni_{0.05}O_{3-0.05}) (BTNi) for XRD and SEM analysis, while (BaTi_{1-x}Fe_xO_{3-x/2}) (BT_xFe), where $x = 0.005, 0.01, 0.05$ and 0.07 and (BaTi_{1-x}Ni_xO_{3-x/2}) (BT_xNi), where $x = 0.005, 0.01, 0.03, 0.05, \text{ and } 0.07$ for FTIR analysis, as shown in Tables I and II both kinds of samples were stirred for 1 h at RT. The dopant solutions were prepared using iron nitrate and nickel nitrate where they dissolved in water. The final resulted solutions were dried at 300 °C for 4 h in air. The dried gel for all samples was calcined in air for 4 h at 800 °C on Muffle furnace type Carbolite CWF to obtain polycrystalline (BT, BT_xFe and BT_xNi) powder.

2.2. Characterizations

XRD was performed on the heat-treated powder for the doped and undoped BT in order to characterize their crystalline structure. The crystallinity of these samples was probed using Philips X-ray diffractometer using monochromatic CuK_{α1} radiation of wavelength $\lambda = 1.5418 \text{ \AA}$ from a fixed source operated at 40 kV and 30 mA. The crystallite size (G) is determined from the Scherrer equation $G = K\lambda/D \cos \theta$, where K is the Scherrer constant (0.9), λ is the wavelength and D is the full width (in radians) of the peak at half maximum (FWHM) intensity. The correction to the measured FWHM D_s for a sample peak was made to accommodate systemic instrumental broadening and utilized peak widths D_q measured from a diffraction scan, taken under identical conditions, from a strain-free powdered quartz sample, with crystallite size ranging between 5 and 10 μm . The corrected sample peak widths were calculated as $D = (D_s^2 - D_q^2)^{1/2}$. Micro-strain and crystallite size contributions to D were separated using the Win-Fit program, using standard samples for estimation of instrumental broadening. The final sample crystallite sizes G were obtained by the Fourier analysis, using the corrected profile. The diffraction peak used was the most intense diffraction peak, assigned to the (101) reflection from the BT powder phase.

Fourier transformation infrared was used to study the structure of the samples. The FTIR absorption spectra were measured at room temperature from wave number 4000 cm^{-1} to 400 cm^{-1} by the standard KBr pellet technique using a Fourier transform infrared spectrometer.

Microstructure and morphology for the BT5Ni was characterized by using the electron microscope of type JEOL transmission electron microscope (TEM) model: JEOL 1230 made in Japan magnification power up to 600 k \times Resolving power down to 0.2 nm. Accelerating voltage 100 kV, can reach 120 kV through steps.

3. Results and discussion

3.1. XRD patterns of BT5Fe and BT5Ni

Figure 1 a and b shows the XRD performed at RT for the BT5Fe and BT5Ni powders, calcined in air for 4 h at 800 °C. As can be seen in Fig. 1, the XRD data show no structure difference in both samples. Only the diffraction pattern of tetragonal BT was observed, indicating that they are crystallized in a tetragonal perovskite structure. The XRD data for both samples are completely matched with the tetragonal JCPDS file number 81-2201 [9]. No Bragg peak of other phases or FeO or NiO was found. Very weak line corresponding to the residual barium carbonate phase (BaCO₃) appeared at $2\theta^\circ$ equal to about 24° in the two figures.

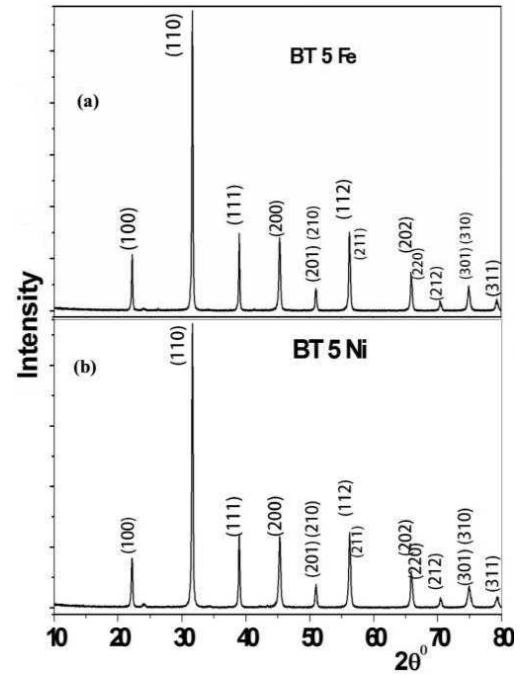


Fig. 1. XRD patterns of BT_xNi calcined in air for 4 h at 800 °C.

The figure shows sharp peaks corresponding to tetragonal BT. Therefore, it appears that Fe³⁺ and Ni²⁺ atoms have been incorporated into the BT matrix, and secondary phases are absent, which indicates that Fe³⁺ and

Ni^{2+} ions replace the Ti^{4+} ions in the B site of the perovskite structure ABO_3 due to its similar ionic radius, (the ionic radius of Fe^{3+} , Ni^{2+} , and Ti^{4+} are 0.64, 0.78, and 0.68 Å, respectively) [10].

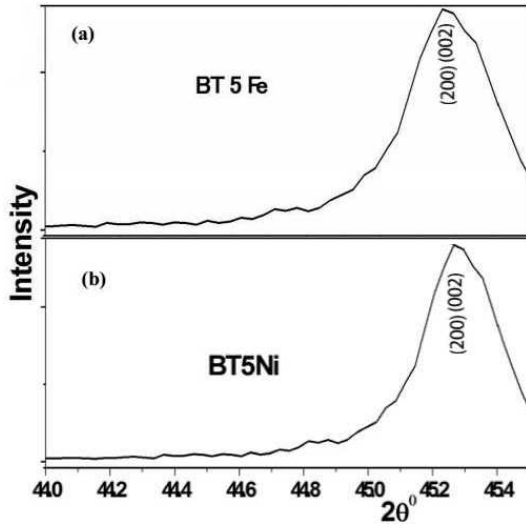


Fig. 2. The expansion of the $2\theta^\circ$ range between (a) 44.2° up to (b) 45.5° .

Figure 2a and b shows the expansion of the $2\theta^\circ$ ranging between 42.2° and 45.5° . The splitting of the characteristic peak at 2θ equal to about 45.4° appeared for both samples BT5Fe and BT5Ni, indicating the presence of the single tetragonal BT phase for both of them.

3.2. Scanning electron microscope of pure BT and doped ones BT5Fe and BT5Ni

SEM was used to study the surface morphology for the prepared powders. Figure 3a–c shows the SEM images for the pure and doped samples, BT, BT5Fe, and BT5Ni, calcined at 800°C for 4 h. As seen from SEM images all samples have high degree of crystallinity, homogeneous distribution shapes and particle size due to the high calcined temperature. The particles in all samples tend to aggregate in cluster due to its small size. On the other hand, in both dopants ions content there was induced a reduction in the grain size giving rise to nanograin sizes formation and an increase in the density of the doped samples and in the volume ratio of the grain boundary region.

Figures 4 and 5 show the FTIR absorption spectra of nanostructure pure BT sample and BT doped with different concentrations of both of Fe^{3+} and Ni^{2+} ions BT (0.5, 1, 3, 5, and 7)Fe and BT (0.5, 1, 3, 5, and 7)Ni, calcined for 4 h at 800°C . It is well known that two kinds of OH– groups, such as a surface adsorbed OH– and a lattice OH– group can be observed in BT. The broad low-intensity peak with the maximum around 3450 cm^{-1} has been assigned to O–H stretching modes of surface adsorbed water corresponding to the stretching vibrations of weakly bound water interacting with its environment via hydrogen bonding and to stretching vibrations

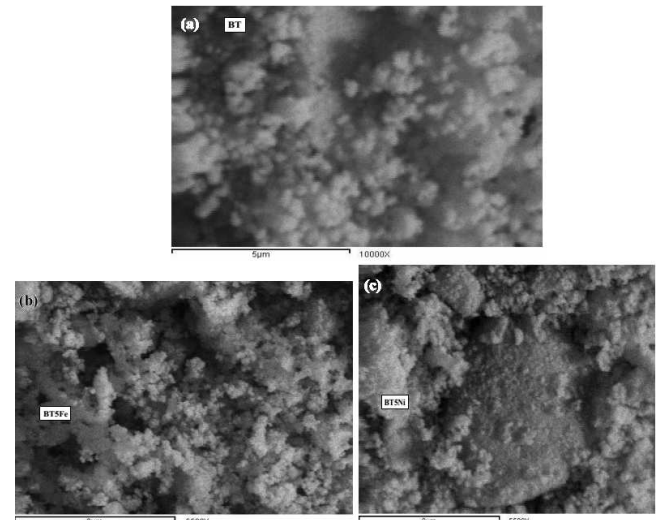


Fig. 3. SEM micrographs of BT (a), BT5Fe (b), and BT5Ni (c) samples calcined at 800°C for 4 h.

of hydrogen-bonded OH groups. The peaks at 2921.5 and 2853 cm^{-1} were assigned to the CH_3 and CH_2 symmetric, respectively. The 1642 cm^{-1} peak was due to the deformation mode of adsorbed H_2O molecules, assigned to the bending vibration [11–13].

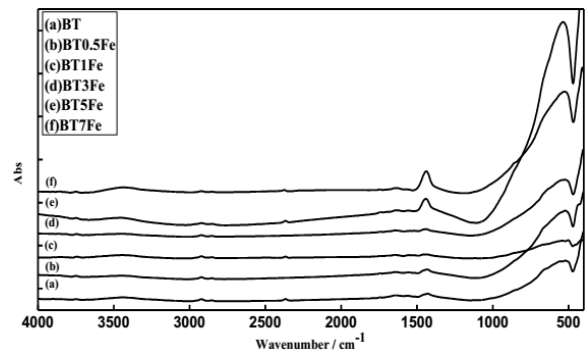


Fig. 4. FTIR spectra of nanostructure BT doped with Fe^{3+} calcined at 800°C for 4 h.

FTIR for pure BT sample shows that two strong peaks around 554 cm^{-1} and 520 cm^{-1} appeared, the former was assigned to TiO_6 stretching vibration that connected to the barium ion, which confirms that TiO_6 octahedral has been formed, while the later was assigned to Ti–O stretching vibration along the polar axis of spontaneous polarization in BT with tetragonal phase [16, 17].

FTIR spectra for BT doped with different concentrations of Fe^{3+} and Ni^{2+} ions have the same trend discussed for the pure sample in the previous paragraph. It was found that there are no new peaks appeared for the two dopants transition elements. The only change appeared in the band for Ti–O stretching vibration along the polar axis of spontaneous polarization at 520 cm^{-1} for pure BT. The mentioned band was shifted to 523, 541, 527,

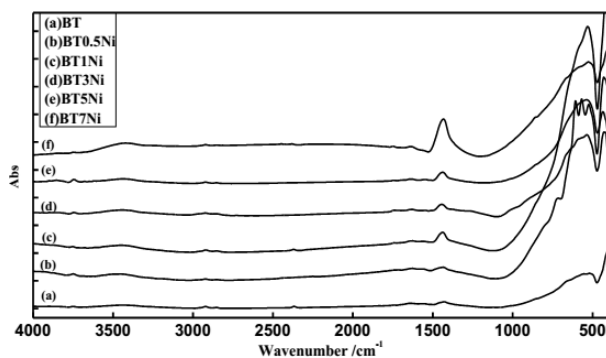


Fig. 5. FTIR spectra of nanostructure BT doped with Ni²⁺ calcined at 800 °C for 4 h.

537, and 528 cm⁻¹ for BT0.5Fe, BT1Fe, BT3Fe, BT5Fe and BT7Fe respectively and shifted to 525, 532, 537, 539, and 527 cm⁻¹ for BT0.5Ni, BT1Ni, BT3Ni, BT5Ni and BT7Ni, respectively which confirm that Fe³⁺ and Ni²⁺ ions completely substitute the Ti⁴⁺ ions in the B site of the perovskite structure ABO₃ as confirmed by the XRD obtained data.

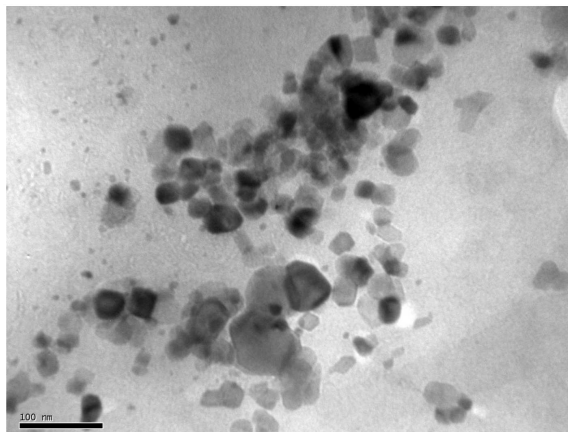


Fig. 6. TEM micrographs of BT5Ni sample calcined at 800 °C for 4 h.

Figure 6 shows the representative TEM micrograph of BT5Ni calcined in air for 4 h at 800 °C, it indicated that the doped sample is assigned to tetragonal perovskite phase. In addition, some degree of agglomerates were found in the clusters consisted of many small grains. The picture confirmed that BT5Ni powder is in good crystalline structure and has a bimodal size unit cell distribution with large particles 45.5 nm and smaller one 14 nm. This result refers to that the crystallite size obtained from TEM is in nanoscale as confirmed from XRD data.

4. Conclusion

Nanostructure pure BT and doped with Fe³⁺ and Ni²⁺ ions BT_xFe and BT_xNi were successfully prepared by sol-gel technique. In addition a well defined perovskite

phase with nanocrystallite sizes for BT5Fe and BT5Ni equal to 46 and 35 nm, respectively, were achieved from XRD study. The TEM confirmed the nanoscale presence in BT5Ni sample.

Two kinds of OH⁻ groups, such as a surface adsorbed OH⁻ and a lattice OH⁻ group can be observed in pure BT. The broad low-intensity peak with the maximum around 3450 cm⁻¹ has been assigned to O-H stretching modes of surface adsorbed water. The peaks at 2921.5 and 2853 cm⁻¹ were assigned to the CH₃ symmetric and CH₂ symmetric, respectively. FTIR spectra for BT doped with transition elements have the same trend discussed for the pure sample. It was found that there are no new peaks appearing for the dopants (Fe³⁺ and Ni²⁺) and the only change appeared in the band for Ti-O stretching vibration at 520 cm⁻¹ for pure BT, in which it was shifted to 523, 541, 527, 537, and 528 cm⁻¹ for BT0.5Fe, BT1Fe, BT3Fe, BT5Fe, and BT7Fe respectively, and shifted to 525, 532, 537, 539, and 527 cm⁻¹ for BT0.5Ni, BT1Ni, BT3Ni, BT5Ni, and BT7Ni, respectively, confirming that Fe³⁺ and Ni²⁺ ions completely substitute Ti⁴⁺ ions in the B site of the perovskite structure ABO₃.

References

- [1] L. Bocher, A. Gloter, A. Crassous, V. Garcia, K. March, A. Zobelli, S. Valencia, S. Enouz-Vedrenne, X. Moya, N. D. Marthur, C. Deranlot, S. Fusil, K. Bouzehouane, M. Bibes, A. Barthélémy, C. Colliex, O. Stéphan, *Nano Lett.* **12**, 376 (2012).
- [2] K.C. Huang, T.C. Huang, W.F. Hsieh, *Inorg. Chem.* **48**, 9180 (2009).
- [3] V.C. Flores, D. Bueno-Baqués, R.F. Ziolo, *Acta Materialia* **58**, 764 (2010).
- [4] N. Bao, L. Shen, A. Gupta, A. Tatarenko, G. Srinivasan, K. Yanagisawa, *Appl. Phys. Lett.* **94**, 253109 (2009).
- [5] D. Chen, H. Zhang, R. Chen, X. Deng, J. Li, G. Zhang, L. Wang, *Phys. Status Solidi (a)* **209**, 714 (2012).
- [6] A.V. Polotai, A.V. Ragulya, C.A. Randal, *Ferroelectrics* **288**, 93 (2003).
- [7] M. Tyunina, B. Malic, M. Plekh, M. Kosec, *J. Am. Ceram. Soc.* **95**, 1333 (2012).
- [8] M. Willander, O. Nur, M.Q. Israr, A.B. Abou Hamad, F.G. Abd El Maksoud, M.A. Salem, I.K. Battisha, *J. Cryst. Proc. Techn. (JCPT)* **2**, 1 (2012).
- [9] JCPDS X-ray Powder Diffraction files, 812201, Tetragonal BaTiO₃.
- [10] I.K. Battisha, A.B. Abou Hamad, R.M. Mahani, *Physica B* **404**, 2274 (2009).
- [11] B.D. Stojanovic, A.Z. Simoes, C.O. Paiva-Santos, C. Jovalekic, V.V. Mitic, J.A. Varela, *J. Europ. Ceram. Soc.* **25**, 1985 (2005).
- [12] M. Cernea, O. Monnereau, P. Llewellyn, L. Tortet, C. Galassi, *J. Europ. Ceram. Soc.* **26**, 3241 (2006).
- [13] S. Keshri (Shaw), L. Joshi, S.K. Rout, *J. Alloys Comp.* **485**, 501 (2009).