www.czasopisma.pan.pl PAN www.journals.pan.pl
POLSKA AKADEMIA NAUK

Arch. Metall. Mater. **65** (2020), 2, 817-821

DOI: 10.24425/amm.2020.132826

I. KUŹNIARSKA-BIERNACKA[1*], A. LISIŃSKA-CZEKAJ[2], D. CZEKAJ[2]

STUDY OF CuO AND V_2O_5 EFFECT ON IR SPECTRA OF POLYCRYSTALLINE BISMUTH NIOBATE

Bismuth niobate ($BiNbO_4$) ceramics were fabricated by mixed oxide method and sintered by presureless sintering method. $BiNbO_4$ ceramics doped with V_2O_5 additive in amount 0.125 wt%, 0.250 wt% and 1 wt% of was sintered at $T = 910°C$ whereas $BiNbO_4$ ceramics doped with 2 wt% of CuO additive was sintered at $T = 890°C$ and $T = 910°C$. It was found that V_2O_5 additive improved morphology of the ceramic samples. However, the chemical composition of $BiNbO_4$ ceramics in relation to bismuth oxide and niobium oxide manifested a tendency of lack of Bi_2O_3 component. Absorption bands for the $BiNbO_4$ compound were identified. FTIR band positions associated with NbO_6 octahedra suggested that the crystal structure changes after V_2O_5 incorporation.

Keywords: $BiNbO_4$, ceramics, SEM, FTIR spectroscopy

1. Introduction

Bismuth-based dielectric ceramics have been studied for application as piezoelectric materials and in multilayer ceramic capacitors [1]. The microwave properties of bismuth niobate ($BiNbO_4$) were also studied and it has been reported to be a promising microwave dielectric due to its high quality factor ($Q = 14000$), small temperature coefficient of resonance frequency (~50 ppm/°C), and relatively low dielectric constant (~45) [2]. Another but very important advantage of bismuth niobate as material for microwave technology is that it can be sintered at rather low temperatures ($T < 1000°C$). This in turn makes possible an integration of passive components (e.g. capacitors, resistors, inductors and line resonators with low loss and low melting point electrode such as Ag or Cu) into the substrate carrying the integrated circuits [3]. Such "passive integration" may be a substantial contribution to achieve further miniaturization of microwave devices.

It should be noted however, that $BiNbO_4$ ceramics is difficult to be densified without addition of low-melting oxide. It has been shown [4] that small amounts of V_2O_5 or CuO added in $BiNbO_4$ could improve sinterability of bismuth niobate ceramics. However, the effect of the amount of additives on optical properties in IR range of $BiNbO_4$ ceramics were not reported. It is interesting to clarify the relationship above. Therefore, in this paper, $BiNbO_4$ ceramics was fabricated with an addition of a small amount of CuO or V_2O_5 oxides and FTIR spectroscopy was utilized to study the effect of an oxide additive on vibrational response of $BiNbO_4$ compound.

2. Experimental

$BiNbO_4$ ceramics used in the present study was synthesized using solid state reaction method from the mixture of oxide powders (all reagents used were of 99.9% purity, from Sigma-Aldrich), viz. Bi_2O_3 and Nb_2O_5. An appropriate amount of oxide powders, were thoroughly weighted in stoichiometric amount to provide conditions for formation of the desired composition, given in Eq. (1):

$$Bi_2O_3 + Nb_2O_5 \rightarrow 2BiNbO_4 \tag{1}$$

Also, two sets of $BiNbO_4$ ceramic samples containing additives were fabricated. The one set of the samples contained an excess of CuO oxide (99.9% purity, Aldrich Chemical Co.) in amount of 2 wt%. The other set of the $BiNbO_4$ samples contained an excess of V_2O_5 oxide (99.9% purity, Aldrich Chemical Co.) in amount of 0.125 wt%, 0.250 wt% and 1.000 wt%. The mixture of oxides was ground with an agate mortar and pestle first. After that the chemicals were wet ground in polyamide

[1] REQUIMTE/LAQV, DEPARTAMENTO DE QUÍMICA E BIOQUÍMICA, FACULDADE DE CIÊNCIAS, UNIV. DO PORTO, RUA DO CAMPO ALEGRE S/N, 4169-007 PORTO, PORTUGAL
[2] GDAŃSK UNIVERSITY OF TECHNOLOGY, FACULTY OF MECHANICAL ENGINEERING, DEPARTMENT OF MATERIALS ENGINEERING AND WELDING, 11/12, NARUTOWICZA STR., 80-233 GDAŃSK, POLAND

* Corresponding author: iwonakb@fc.up.pt

© 2020. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution-NonCommercial License (CC BY-NC 4.0, https://creativecommons.org/licenses/by-nc/4.0/deed.en which permits the use, redistribution of the material in any medium or format, transforming and building upon the material, provided that the article is properly cited, the use is noncommercial, and no modifications or adaptations are made.

bottles to get proper mixing and surface active fine powder. The planetary ball mill was utilized for wet grinding of the powders. A small amount of ethyl alcohol and zirconia balls (of 10 mm in diameter) as grinding medium were used in the milling/homogenizing treatment that lasted for $t = 24$ h. For 50 g of oxides mixture 15 zirconia balls were used. After milling the powders were subjected for drying. Then the dried mixture of powders was compacted into pellets of 20 mm in diameter by pressing under pressure of $p = 30$ MPa in a stainless – steel die. The green bodies were then placed in an alumina crucible and fired with air at $T = 800$°C (the heating rate 5°C/min, the soaking time $t = 2$ h) to conduct the solid state reaction. After thermal treatment the pellets were crushed in a mortar and the synthesized material was subjected to wet milling and drying again. Before sintering the compacts were formed in a stainless – steel die of 10 mm in diameter. Sintering was performed by pressureless sintering under ambient air in a furnace. The samples ($BiNbO_4$ + 2 wt% CuO) were sintered at T_s = 890°C and T_s = 910°C whereas the sintering temperature of the ($BiNbO_4$ + x wt% V_2O_5; where $x = 0.125$, 0.250 and 1.000) samples was $T_s = 910$°C. The soaking time was $t = 2$ h. The fabricated $BiNbO_4$ + 2 wt% CuO ceramics as well as $BiNbO_4$ + x wt% V_2O_5; (x = 0.125, 0.250 and 1.000) ceramics were characterized in terms of morphology (SEM), chemical composition (EDS) and optical properties (FTIR).

Morphology of the samples was studied by Scanning Electron Microscopy (SEM) using scanning electron microscope HITACHI S-4700 type and chemical composition was checked by Energy Dispersive Spectroscopy (EDS) using NORAN Vantage EDS spectrometer. The SEM measurements were performed at magnification $M = 2k$, 5k and $10k$, on fractures of the ceramic samples. The EDS point measurements were performed at magnification $M = 2k$. Quantitative results for EDS were obtained according to the Thermo Fisher Scientific (algorithm/ procedure) using NSS Microanalysis System. The following parameters were used during the EDS spectra acquiring and analysis: acceleration voltage: 20.0 kV, take off angle: 30.3°; correction method: Proza (Phi-Rho-Z).

Room temperature Fourier Transform Infrared (FTIR) spectra of solid samples of diluted 4% in KBr pellets were measured using a Bomem MB104 spectrometer in the range 4000-500 cm^{-1} by averaging 32 scans at a maximum resolution of 4 cm^{-1}.

3. Results and discussion

SEM images of $BiNbO_4$ + x wt% V_2O_5 ceramics sintered at T_s = 910°C with an additive of V_2O_5 in amount of $x = 0.125$, 0.250 and 1.000 wt% are shown in Fig. 1a, Fig. 1b, and Fig. 1c, respectively. On the other hand, morphology of $BiNbO_4$ + 2 wt% CuO ceramics sintered at T_s = 890°C and T_s = 910°C are shown in Fig. 1d, and Fig. 1e, respectively.

One can see in from Fig. 1 that V_2O_5 additive substantially influences morphology of ceramic fractures. Application of a sintering aid in a form of V_2O_5 oxide caused a decrease in porosity of ceramic samples under study. On the other hand, visual inspection of the SEM images of $BiNbO_4$ + 2 wt% CuO ceramics shows rather negligible influence of the sintering temperature on porosity of the samples.

Composition of $BiNbO_4$ ceramics calulations performed on the base of the EDS measurements are given in Table 1.

TABLE 1

Composition of $BiNbO_4$ ceramics calculated on the base of EDS measurements. The calculated stoichiometric values are given in parentheses

Ceramics	T_s, [°C]	Bi_2O_3, [wt%]	Nb_2O_5, [wt%]	V_2O_5/CuO; [wt%]
$BiNbO_4$ + 0.125wt%V_2O_5	910	61.03 (63.596)	38.97 (36.279)	0.00 (0.125)
$BiNbO_4$ + 0.250wt%V_2O_5	910	60.59 (63.517)	39.28 (36.233)	0.13 (0.249)
$BiNbO_4$ + 1.000wt%V_2O_5	910	60.46 (63.045)	38.04 (35.964)	1.49 (0.990)
$BiNbO_4$ + 2.000wt%CuO	890	59.54 (62.427)	39.68 (35.612)	0.78 (1.961)
$BiNbO_4$ + 2.000wt%CuO	910	59.49 (62.427)	39.08 (35.612)	1.43 (1.961)

One can see from Table 1 that the chemical composition of $BiNbO_4$ ceramics in relation to bismuth oxide and niobium oxide manifested a tendency of excess of Nb_2O_5 component. It is worth noting that theoretical stoichiometric composition of $BiNbO_4$ compound recalculated into constituting oxides is 36.32 wt% of Nb_2O_5 and 63.68 wt% of Bi_2O_3.

$BiNbO_4$ is known to have two polymorph phases, low-temperature orthorhombic a-phase and high temperature triclinic β-phase [1,5]. The triclinic β-$BiNbO_4$ structure consisting of pseudo layers of $[Bi_2O_2]$ units connected with each other and surrounded by sheets of formula $[NbO_4]_n$. Thus, the triclinic β-$BiNbO_4$ can be regarded as a layered structure, consisting of a $[Bi_2O_2]$ + $[NbO_4]$ + $[Bi_2O_2]$ + $[NbO_4]$ stacking sequence where the NbO_6 octahedra are joined at four vertices to form the sheets of formula $[NbO_4]_n$ with some distortion [6]. The orthorhombic α-$BiNbO_4$ structure consists of two bismuth layers and two separated NbO_6 octahedral layers with different distortions [7]. From this, we could expect vibrations related to the octahedral NbO_6 unit, bridged Nb-O-Nb and terminal Nb-O, as well as Bi-O and Bi-O-Bi vibrations [6] in FTIR spectra. The main difference of bismuth and oxygen arrangement in orthorhombic and triclinic phases is the formation of $[Bi_2O_2]$ layers in the triclinic crystals and it is the main reason for the slightly difference between the vibration bands associated to each polymorph. Thus by FTIR it is very difficult to distinguish between the α- and β-phase of $BiNbO_4$. The FTIR profile of $BiNbO_4$ ceramic powder is well known and it was presented in the literature [8,6]. The NbO_6 vibrations associated to Nb-O-Nb bonds are expected at 560 cm^{-1} and 600 cm^{-1} to 700 cm^{-1}, respectively [6,9,10]. Whereas the Nb-O symmetric stretching of the edge sharing oxygen atoms in the edge sharing NbO_6 group is observed at 840 cm^{-1} [11]. The bands usually observed from 810 to 850 cm^{-1} are related to symmetrical stretching vibrations of Bi-O-Bi [8].

MOST WIEDZY Downloaded from mostwiedzy.pl

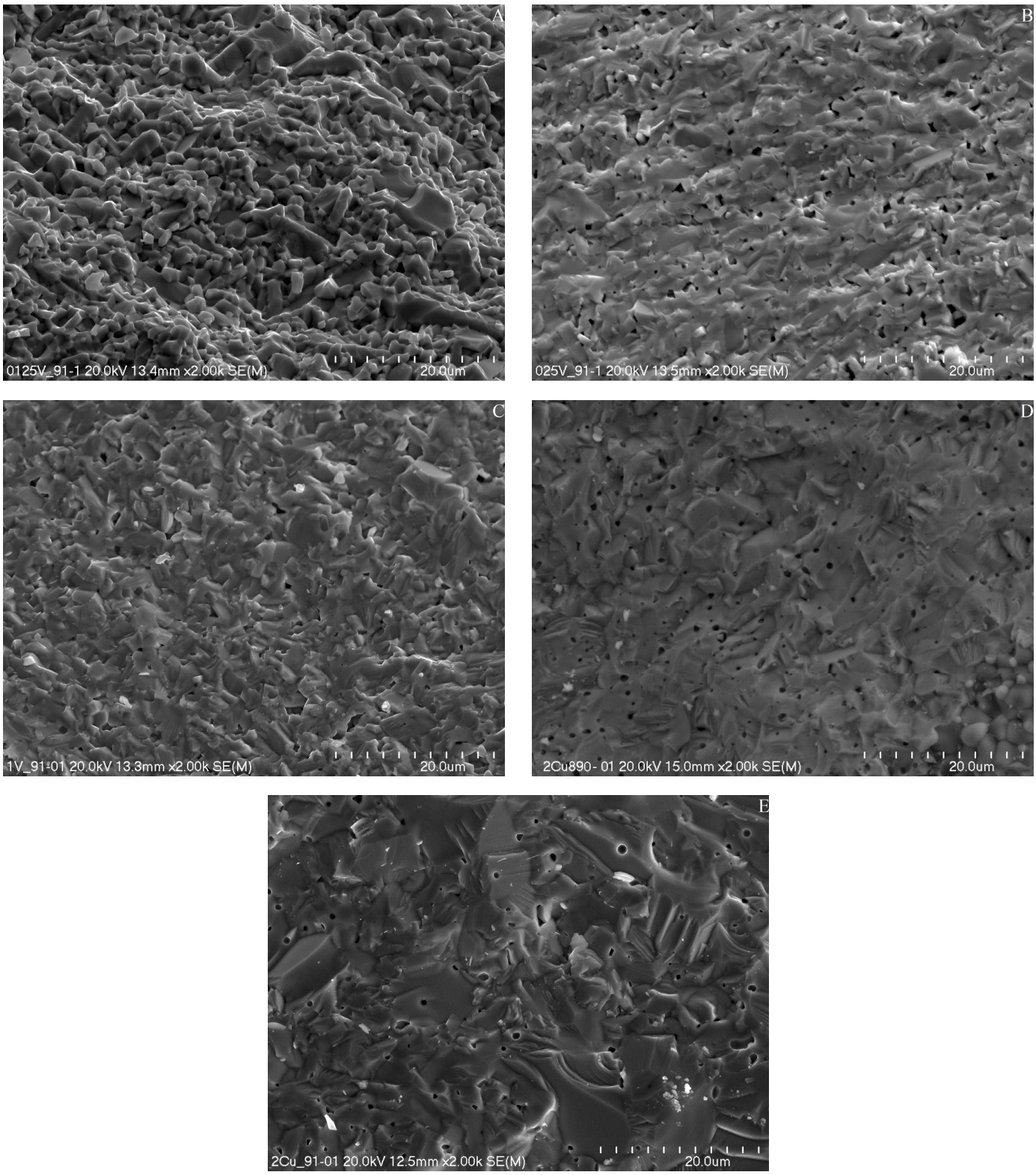

Fig. 1. Morphology of $BiNbO_4$ + x wt% V_2O_5 /CuO ceramics sintered at T_s: (a) T_s = 910°C; x = 0.125 wt% V_2O_5; (b) T_s = 910°C; x = 0.250 wt% V_2O_5; (c) T_s = 910°C; x = 1.000 wt% V_2O_5; (d) T_s = 890°C; x = 2.000 wt% CuO; (e) T_s = 910°C; x = 2.000 wt% CuO

The bands from 400 to 500 cm^{-1} are associated with the Bi-O stretching vibrations [11, 12]. While the band near 850 cm^{-1} seems to be associated to the β-$BiNbO_4$ phase, the 446 cm^{-1} vibration is related to α-$BiNbO_4$ phase [6]. Similar vibration bands were also observed for the orthorhombic polymorph by previous studies.

Comparison of the FITR spectra of $BiNbO_4$ ceramics doped with V_2O_5 with different wt% of vanadium (V) oxide sintered at T = 910°C are presented in Fig. 2. The FTIR spectra of all $BiNbO_4$-V_2O_5 ceramics sintered at T = 910°C characterises the very weak bands at 3475 cm^{-1} and 1647 cm^{-1} which are due to vibrational stretching and deformation bands of O-H groups [13]

MOST WIEDZY Downloaded from mostwiedzy.pl

and the bands in the region 2950-2850 cm^{-1}, which are attributed to the C-H stretching vibrations [8]. The weak band at 1450 cm^{-1} can be due to the presence of C = O groups [11] from incomplete decomposition of solvents/reagents used during the preparation of the samples. At low energy region it is possible to identify some known absorption bands for the $BiNbO_4$. The bands observed at 709-714 cm^{-1}, 640-645 cm^{-1} and 597-602 cm^{-1} for $BiNbO_4$-V_2O_5 ceramics can be associated with Nb-O stretching of the terminal oxygen atoms in NbO_6 group vibration of NbO_6 octahedra [11].

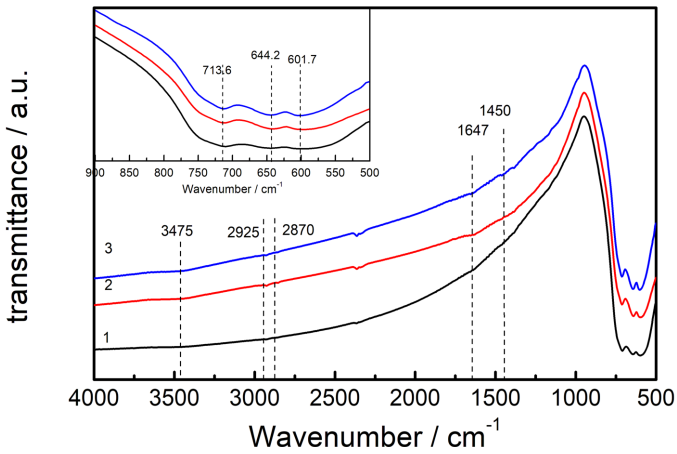

Fig. 2. The FTIR spectra of $BiNbO_4$ doped ceramics with 1-0.125 wt% V_2O_5, 2-0.25 wt% V_2O_5 and 3.000-1.000 wt% V_2O_5, sintered at T = 910ºC. Insert, enlarged of low energy region of FTIR spectra

The FTIR band positions associated with NbO_6 octahedra, observed for $BiNbO_4$-V_2O_5 ceramics, suggest that the crystal structure changes after dopant incorporation. It was observed that all FTIR bands are shifted to higher energy suggesting strong interaction/chemical bound formation between $BiNbO_4$ and V_2O_5. The comparison of FTIR spectra of $BiNbO_4$ presented in [9] and doped with V_2O_5 shows that bands at lower energy (597-602 cm^{-1}) observed for $BiNbO_4$-V_2O_5 ceramics are shifted to higher energy of 17.9 cm^{-1} for lower V_2O_5 content (0.125 and 0.250 wt%) and of 5.4 cm^{-1} for $BiNbO_4$ with 1 wt% V_2O_5. Moreover, the position of this band (597-602 cm^{-1}) is shifted to higher energy when the content of V_2O_5 increases (Fig. 3). This might suggest the partial substitution of Nb^{5+} by V^{5+} after doping [14]. Beside this, the other band (640-645 cm^{-1}) related to the Nb-O bridge stretching vibrations in NbO_6 group is slightly shifted to lower energy when the content of V_2O_5 increases from 0 to 0.250 wt% but increases to 644.2 cm^{-1} for $BiNbO_4$ with 1.000 wt% of V_2O_5. The band observed at 709.8 cm^{-1} for $BiNbO_4$ with 0.125 wt% of V_2O_5 is slightly shifted to higher energy when the content of V_2O_5 increases from 0 to 0.25 wt% and maintains at 713.6 cm^{-1} for the 1.00 wt% of V_2O_5 content (Fig. 3). This may be due to crystallinity changes in $BiNbO_4$-V_2O_5 ceramics. Anyway, the observed changes are very subtle and have to be confirmed by other characterisation methods.

The effect of the sintering temperature on FTIR spectra was also studied. The results show that position of the bands relate to

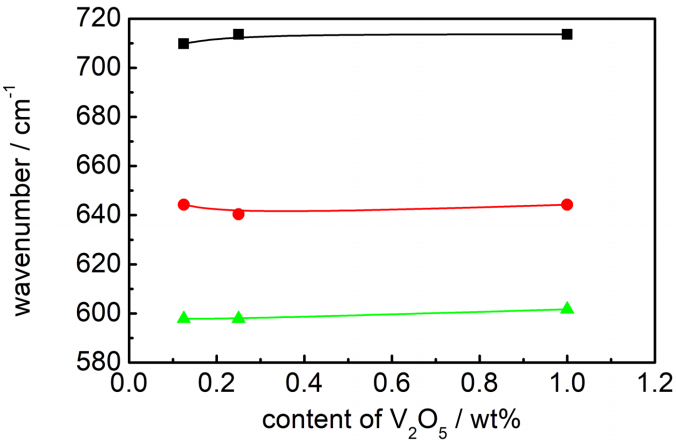

Fig. 3. The effect of V_2O_5 content on the wavenumbers of NiO_6 octahedra vibration of $BiNbO_4$-V_2O_5 sintered at T = 910°C

the $BiNbO_4$ structure (from 1000 cm^{-1}-500 cm^{-1}) maintain for each set of $BiNbO_4$-V_2O_5 ceramics. This suggests no structural and chemical changes induced by sintering conditions. Thus the changes are mainly induced by amount of dopant used.

Similar studies were performed for $BiNbO_4$ ceramics doped with CuO. Fig. 4 shows the FTIR spectra of $BiNbO_4$ doped ceramics with 2.000 wt% of CuO sintered at T = 890°C and T = 910°C. Similarly to $BiNbO_4$ ceramics doped with V_2O_5, both FTIR spectra of $BiNbO_4$ doped with CuO characterises the very weak bands at 3472 cm^{-1} and 1639 cm^{-1} and they are usually associated with vibrational stretching and deformation bands of O-H groups [13] and the band at 2931 cm^{-1}, which is usually attributed to the C-H stretching vibrations [8]. Other weak bands observed in the region 1465-1390 cm^{-1} (Fig. 4) can be due to the presence of some organic groups from incomplete decomposition of solvents/reagents used during the samples preparation.

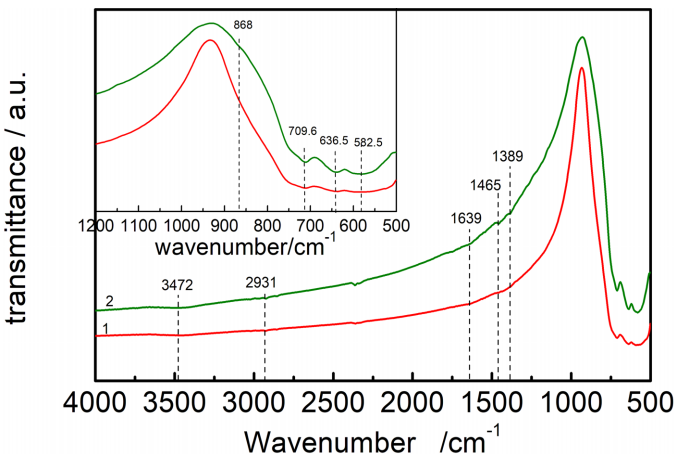

Fig. 4. The FTIR spectra of $BiNbO_4$ doped ceramics with 2.000 wt% of CuO sintered at T = 890ºC (1) and T = 910ºC (2). Insert, enlarged of low energy region of FTIR spectra

The FTIR bands observed at low energy region (1000-500 cm^{-1}) for $BiNbO_4$-CuO ceramics are related to the vibrations in the $BiNbO_4$ lattice [6,9-12]. The bands observed at 709.6,

MOST WIEDZY Downloaded from mostwiedzy.pl

636.5 and 582.5 cm^{-1} for both $BiNbO_4$-CuO ceramics can be associated with Nb-O stretching of the terminal oxygen atoms in NbO_6 group vibration of NbO_6 octahedra [11]. The positions of these bands maintain for both $BiNbO_4$-CuO ceramics suggesting no structural and chemical changes induced by sintering conditions. However the band position regarded to Nb-O-Nb group for $BiNbO_4$-CuO doped ceramics are slightly shifted (the highest shift of 6.4 cm^{-1} was observed for the band at 709.6 cm^{-1}) in comparison with pure $BiNbO_4$. The shoulder at 868 cm^{-1} more pronounced for $BiNbO_4$-CuO ceramics sintered at $T = 910°C$ (Fig. 4) may be due to symmetrical stretching vibrations of Bi-O-Bi or/and symmetric stretching of the edge sharing oxygen atoms in the edge sharing NbO_6 group shifted to lower energy. This indicates some structural changes of $BiNbO_4$ and may suggests the substitution of Cu^{2+} for Bi^{3+} [1]. As the substitution of Bi^{3+} by Cu^{2+} with lower electrovalency and smaller ionic radius than that of Bi^{3+} caused the lattice distortion [1] and also induces chemical changes.

4. Conclusions

Bismuth niobate ($BiNbO_4$) is known as a low-fired ceramics exhibiting promising microwave application potential especially as (i) multilayer ceramics capacitors or (ii) dielectric resonators within the multilayered integrated circuits. Low-fired ceramics like $BiNbO_4$ can meet the requirements for miniaturizations of the terminals for mobile communication systems – what is pointed out as the important subject focused on wide utilization of the microwave as a communication media. In the present studies $BiNbO_4$ compound was synthesized by solid state reaction of the stoichiometric mixture of powders with an addition of small amount (0.125 wt%, 0.250 wt% and 1.000 wt%) of the sintering aid namely, V_2O_5 or CuO (2.000 wt%). Ceramics were sintered by pressureless sintering method at relatively low temperature ranging from $T = 890°C$ to $T = 910°C$. It was found that V_2O_5 additive used improved morphology of the ceramic samples. However, the chemical composition of $BiNbO_4$ ceramics in relation to bismuth oxide and niobium oxide manifested a tendency of lack of Bi_2O_3 component. The effect of V_2O_5 or CuO additive on FTIR spectra of $BiNbO_4$ ceramics was studied. The absorption bands were identified and it was stated that no structural or chemical changes were induced by the sintering conditions. All the changes were mainly induced by amount of the dopant used. It was found that FTIR band positions associated with NbO_6 octahedra observed for $BiNbO_4$-V_2O_5 ceramics suggest that the crystal structure changes after V_2O_5 incorporation: all the bands are shifted to higher energy suggesting strong interaction/chemical bound formation between $BiNbO_4$ and V_2O_5. However, the observed changes are very subtle and have to be confirmed by other characterisation methods.

Acknowledgement

The present research has been supported by Polish National Science Centre (NCN) as a research project N N507 218540. The work was supported by UIDB/50006/2020 with funding from FCT/MCTES through national funds.

REFERENCES

[1] Di Zhou, Hong Wang, Xi Yao, Materials Chemistry and Physics **104**, 397-402 (2007).
[2] Yi-Cheng Liou, Wen-Chou Tsai, Hong-Meng Chen, Ceram. Int. **35**, 2119-2122 (2009).
[3] W. Wersing, Current Opinion in Solid State and Materials Science **1**, 5, 715-731 (1996).
[4] H. Kagata, T. Inoue, J. Kato, I. Kameyama, Jpn. J. Appl. Phys. **31**, 3152-3155 (1992).
[5] D. Czekaj, A. Lisińska-Czekaj, Advances in Materials Science **18**, 35(2018).
[6] M.L. Alcântara, J.S. da Silva, R.O. Soares, H.M.C. Andrade, L.A. da Silva, A.J.S. Mascarenhas, Materials Research Bulletin **103**, 166 (2018).
[7] H.-F. Zhai, X. Qian, J.-Z. Kong, A.-D. Li, Y.-P. Gong, H. Li, D. Wu, Journal of Alloys and Compounds **509**, 10230 (2011).
[8] K.S. Rao, S. Buddhudu, Ferroelectrics Letters **37**, 101 (2010).
[9] P. Ayyub, M.S. Multani, V.R. Palkar, R. Vijayaraghavan, Phys. Rev. B **34**, 8137 (1986).
[10] K.C. Mathai, S. Vidya, A. John, S. Solomon, J.K. Thomas, Advances in Condensed Matter Physics, **6** (2014).
[11] M. Verma, A. Tanwar, K. Sreenivas, J. Therm. Anal. Calorim. **135**, 2077 (2019).
[12] A. Acosta-Rangel, M. Sánchez-Polo, A.M.S. Polo, J. Rivera-Utrilla, M.S. Berber-Mendoza, Chemical Engineering Journal **344**, 21 (2018).
[13] I. Kuźniarska-Biernacka, A.R. Silva, A.P. Carvalho, J. Pires, C. Freire, Langmuir **21**, 10825 (2005).
[14] L. Zhang, X. Yao, H. Wang, D. Zhou, Journal of Electroceramics **21**, 465 (2008).

MOST WIEDZY Downloaded from mostwiedzy.pl