

I. KUŹNIARSKA-BIERNACKA<sup>1\*</sup>, A. LISIŃSKA-CZEKAJ<sup>2</sup>, D. CZEKAJ<sup>2</sup>STUDY OF CuO AND V<sub>2</sub>O<sub>5</sub> EFFECT ON IR SPECTRA OF POLYCRYSTALLINE BISMUTH NIOBATE

Bismuth niobate (BiNbO<sub>4</sub>) ceramics were fabricated by mixed oxide method and sintered by pressureless sintering method. BiNbO<sub>4</sub> ceramics doped with V<sub>2</sub>O<sub>5</sub> additive in amount 0.125 wt%, 0.250 wt% and 1 wt% of was sintered at  $T = 910^{\circ}\text{C}$  whereas BiNbO<sub>4</sub> ceramics doped with 2 wt% of CuO additive was sintered at  $T = 890^{\circ}\text{C}$  and  $T = 910^{\circ}\text{C}$ . It was found that V<sub>2</sub>O<sub>5</sub> additive improved morphology of the ceramic samples. However, the chemical composition of BiNbO<sub>4</sub> ceramics in relation to bismuth oxide and niobium oxide manifested a tendency of lack of Bi<sub>2</sub>O<sub>3</sub> component. Absorption bands for the BiNbO<sub>4</sub> compound were identified. FTIR band positions associated with NbO<sub>6</sub> octahedra suggested that the crystal structure changes after V<sub>2</sub>O<sub>5</sub> incorporation.

*Keywords:* BiNbO<sub>4</sub>, 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<sub>4</sub>) 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 ( $\sim 50$  ppm/ $^{\circ}\text{C}$ ), and relatively low dielectric constant ( $\sim 45$ ) [2]. Another but very important advantage of bismuth niobate as material for microwave technology is that it can be sintered at rather low temperatures ( $T < 1000^{\circ}\text{C}$ ). 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<sub>4</sub> ceramics is difficult to be densified without addition of low-melting oxide. It has been shown [4] that small amounts of V<sub>2</sub>O<sub>5</sub> or CuO added in BiNbO<sub>4</sub> could improve sinterability of bismuth niobate ceramics. However, the effect of the amount of additives on optical properties in IR range of BiNbO<sub>4</sub> ceramics were not reported. It is interesting to clarify the relationship above. Therefore, in

this paper, BiNbO<sub>4</sub> ceramics was fabricated with an addition of a small amount of CuO or V<sub>2</sub>O<sub>5</sub> oxides and FTIR spectroscopy was utilized to study the effect of an oxide additive on vibrational response of BiNbO<sub>4</sub> compound.

## 2. Experimental

BiNbO<sub>4</sub> 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<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub>. 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):



Also, two sets of BiNbO<sub>4</sub> 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<sub>4</sub> samples contained an excess of V<sub>2</sub>O<sub>5</sub> 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

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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  $T = 800^\circ\text{C}$  (the heating rate  $5^\circ\text{C}/\text{min}$ , 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 ( $\text{BiNbO}_4 + 2$  wt% CuO) were sintered at  $T_s = 890^\circ\text{C}$  and  $T_s = 910^\circ\text{C}$  whereas the sintering temperature of the ( $\text{BiNbO}_4 + x$  wt%  $\text{V}_2\text{O}_5$ ; where  $x = 0.125, 0.250$  and  $1.000$ ) samples was  $T_s = 910^\circ\text{C}$ . The soaking time was  $t = 2$  h. The fabricated  $\text{BiNbO}_4 + 2$  wt% CuO ceramics as well as  $\text{BiNbO}_4 + x$  wt%  $\text{V}_2\text{O}_5$ ; ( $x = 0.125, 0.250$  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:  $30.3^\circ$ ; 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  $4000\text{--}500\text{ cm}^{-1}$  by averaging 32 scans at a maximum resolution of  $4\text{ cm}^{-1}$ .

### 3. Results and discussion

SEM images of  $\text{BiNbO}_4 + x$  wt%  $\text{V}_2\text{O}_5$  ceramics sintered at  $T_s = 910^\circ\text{C}$  with an additive of  $\text{V}_2\text{O}_5$  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  $\text{BiNbO}_4 + 2$  wt% CuO ceramics sintered at  $T_s = 890^\circ\text{C}$  and  $T_s = 910^\circ\text{C}$  are shown in Fig. 1d, and Fig. 1e, respectively.

One can see in from Fig. 1 that  $\text{V}_2\text{O}_5$  additive substantially influences morphology of ceramic fractures. Application of a sintering aid in a form of  $\text{V}_2\text{O}_5$  oxide caused a decrease in porosity of ceramic samples under study. On the other hand, visual

inspection of the SEM images of  $\text{BiNbO}_4 + 2$  wt% CuO ceramics shows rather negligible influence of the sintering temperature on porosity of the samples.

Composition of  $\text{BiNbO}_4$  ceramics calculations performed on the base of the EDS measurements are given in Table 1.

TABLE 1

Composition of  $\text{BiNbO}_4$  ceramics calculated on the base of EDS measurements. The calculated stoichiometric values are given in parentheses

Ceramics	$T_s$ , [ $^\circ\text{C}$ ]	$\text{Bi}_2\text{O}_3$ , [wt%]	$\text{Nb}_2\text{O}_5$ , [wt%]	$\text{V}_2\text{O}_5/\text{CuO}$ ; [wt%]
$\text{BiNbO}_4 + 0.125\text{wt}\%\text{V}_2\text{O}_5$	910	61.03 (63.596)	38.97 (36.279)	0.00 (0.125)
$\text{BiNbO}_4 + 0.250\text{wt}\%\text{V}_2\text{O}_5$	910	60.59 (63.517)	39.28 (36.233)	0.13 (0.249)
$\text{BiNbO}_4 + 1.000\text{wt}\%\text{V}_2\text{O}_5$	910	60.46 (63.045)	38.04 (35.964)	1.49 (0.990)
$\text{BiNbO}_4 + 2.000\text{wt}\%\text{CuO}$	890	59.54 (62.427)	39.68 (35.612)	0.78 (1.961)
$\text{BiNbO}_4 + 2.000\text{wt}\%\text{CuO}$	910	59.49 (62.427)	39.08 (35.612)	1.43 (1.961)

One can see from Table 1 that the chemical composition of  $\text{BiNbO}_4$  ceramics in relation to bismuth oxide and niobium oxide manifested a tendency of excess of  $\text{Nb}_2\text{O}_5$  component. It is worth noting that theoretical stoichiometric composition of  $\text{BiNbO}_4$  compound recalculated into constituting oxides is 36.32 wt% of  $\text{Nb}_2\text{O}_5$  and 63.68 wt% of  $\text{Bi}_2\text{O}_3$ .

$\text{BiNbO}_4$  is known to have two polymorph phases, low-temperature orthorhombic  $\alpha$ -phase and high temperature triclinic  $\beta$ -phase [1,5]. The triclinic  $\beta$ - $\text{BiNbO}_4$  structure consisting of pseudo layers of  $[\text{Bi}_2\text{O}_2]$  units connected with each other and surrounded by sheets of formula  $[\text{NbO}_4]_n$ . Thus, the triclinic  $\beta$ - $\text{BiNbO}_4$  can be regarded as a layered structure, consisting of a  $[\text{Bi}_2\text{O}_2] + [\text{NbO}_4] + [\text{Bi}_2\text{O}_2] + [\text{NbO}_4]$  stacking sequence where the  $\text{NbO}_6$  octahedra are joined at four vertices to form the sheets of formula  $[\text{NbO}_4]_n$  with some distortion [6]. The orthorhombic  $\alpha$ - $\text{BiNbO}_4$  structure consists of two bismuth layers and two separated  $\text{NbO}_6$  octahedral layers with different distortions [7]. From this, we could expect vibrations related to the octahedral  $\text{NbO}_6$  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  $[\text{Bi}_2\text{O}_2]$  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  $\alpha$ - and  $\beta$ -phase of  $\text{BiNbO}_4$ . The FTIR profile of  $\text{BiNbO}_4$  ceramic powder is well known and it was presented in the literature [8,6]. The  $\text{NbO}_6$  vibrations associated to Nb-O-Nb bonds are expected at  $560\text{ cm}^{-1}$  and  $600\text{ cm}^{-1}$  to  $700\text{ cm}^{-1}$ , respectively [6,9,10]. Whereas the Nb-O symmetric stretching of the edge sharing oxygen atoms in the edge sharing  $\text{NbO}_6$  group is observed at  $840\text{ cm}^{-1}$  [11]. The bands usually observed from  $810$  to  $850\text{ cm}^{-1}$  are related to symmetrical stretching vibrations of Bi-O-Bi [8].

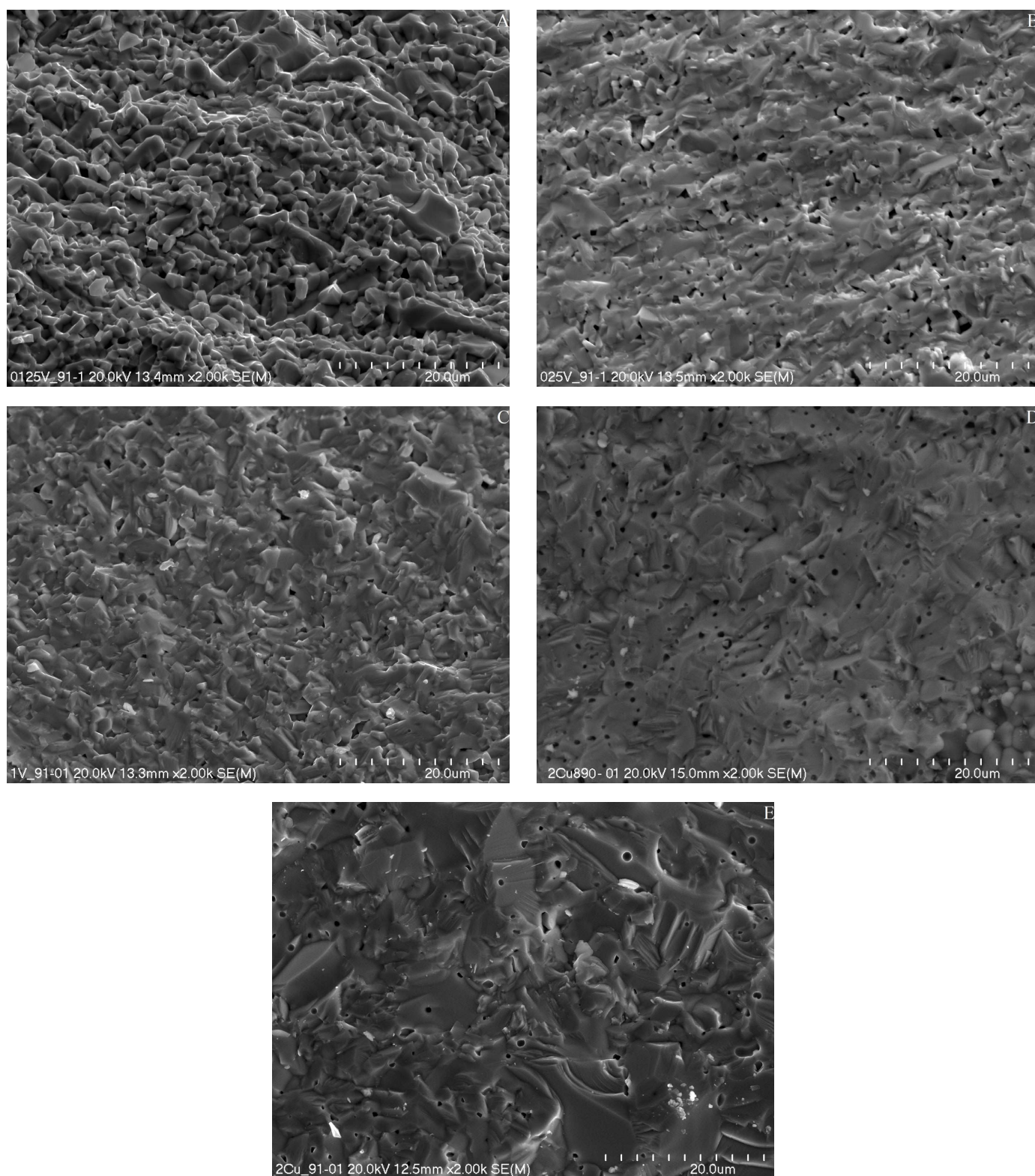


Fig. 1. Morphology of  $\text{BiNbO}_4 + x \text{ wt\% V}_2\text{O}_5 / \text{CuO}$  ceramics sintered at  $T_s$ : (a)  $T_s = 910^\circ\text{C}$ ;  $x = 0.125 \text{ wt\% V}_2\text{O}_5$ ; (b)  $T_s = 910^\circ\text{C}$ ;  $x = 0.250 \text{ wt\% V}_2\text{O}_5$ ; (c)  $T_s = 910^\circ\text{C}$ ;  $x = 1.000 \text{ wt\% V}_2\text{O}_5$ ; (d)  $T_s = 890^\circ\text{C}$ ;  $x = 2.000 \text{ wt\% CuO}$ ; (e)  $T_s = 910^\circ\text{C}$ ;  $x = 2.000 \text{ wt\% CuO}$

The bands from  $400$  to  $500 \text{ cm}^{-1}$  are associated with the Bi-O stretching vibrations [11, 12]. While the band near  $850 \text{ cm}^{-1}$  seems to be associated to the  $\beta\text{-BiNbO}_4$  phase, the  $446 \text{ cm}^{-1}$  vibration is related to  $\alpha\text{-BiNbO}_4$  phase [6]. Similar vibration bands were also observed for the orthorhombic polymorph by previous studies.

Comparison of the FITR spectra of  $\text{BiNbO}_4$  ceramics doped with  $\text{V}_2\text{O}_5$  with different wt% of vanadium (V) oxide sintered at  $T = 910^\circ\text{C}$  are presented in Fig. 2. The FTIR spectra of all  $\text{BiNbO}_4\text{-V}_2\text{O}_5$  ceramics sintered at  $T = 910^\circ\text{C}$  characterises the very weak bands at  $3475 \text{ cm}^{-1}$  and  $1647 \text{ cm}^{-1}$  which are due to vibrational stretching and deformation bands of O-H groups [13]

and the bands in the region  $2950\text{--}2850\text{ cm}^{-1}$ , which are attributed to the C-H stretching vibrations [8]. The weak band at  $1450\text{ cm}^{-1}$  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  $\text{BiNbO}_4$ . The bands observed at  $709\text{--}714\text{ cm}^{-1}$ ,  $640\text{--}645\text{ cm}^{-1}$  and  $597\text{--}602\text{ cm}^{-1}$  for  $\text{BiNbO}_4\text{--V}_2\text{O}_5$  ceramics can be associated with Nb-O stretching of the terminal oxygen atoms in  $\text{NbO}_6$  group vibration of  $\text{NbO}_6$  octahedra [11].

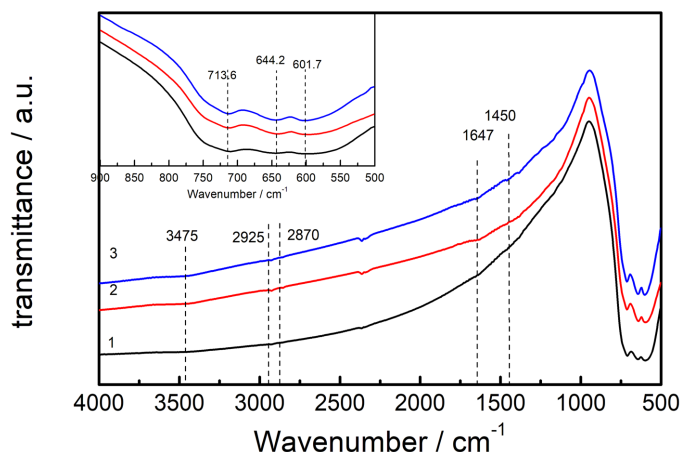


Fig. 2. The FTIR spectra of  $\text{BiNbO}_4$  doped ceramics with 1-0.125 wt%  $\text{V}_2\text{O}_5$ , 2-0.25 wt%  $\text{V}_2\text{O}_5$  and 3-0.000-1.000 wt%  $\text{V}_2\text{O}_5$ , sintered at  $T = 910^\circ\text{C}$ . Insert, enlarged of low energy region of FTIR spectra

The FTIR band positions associated with  $\text{NbO}_6$  octahedra, observed for  $\text{BiNbO}_4\text{--V}_2\text{O}_5$  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 bond formation between  $\text{BiNbO}_4$  and  $\text{V}_2\text{O}_5$ . The comparison of FTIR spectra of  $\text{BiNbO}_4$  presented in [9] and doped with  $\text{V}_2\text{O}_5$  shows that bands at lower energy ( $597\text{--}602\text{ cm}^{-1}$ ) observed for  $\text{BiNbO}_4\text{--V}_2\text{O}_5$  ceramics are shifted to higher energy of  $17.9\text{ cm}^{-1}$  for lower  $\text{V}_2\text{O}_5$  content (0.125 and 0.250 wt%) and of  $5.4\text{ cm}^{-1}$  for  $\text{BiNbO}_4$  with 1 wt%  $\text{V}_2\text{O}_5$ . Moreover, the position of this band ( $597\text{--}602\text{ cm}^{-1}$ ) is shifted to higher energy when the content of  $\text{V}_2\text{O}_5$  increases (Fig. 3). This might suggest the partial substitution of  $\text{Nb}^{5+}$  by  $\text{V}^{5+}$  after doping [14]. Beside this, the other band ( $640\text{--}645\text{ cm}^{-1}$ ) related to the Nb-O bridge stretching vibrations in  $\text{NbO}_6$  group is slightly shifted to lower energy when the content of  $\text{V}_2\text{O}_5$  increases from 0 to 0.250 wt% but increases to  $644.2\text{ cm}^{-1}$  for  $\text{BiNbO}_4$  with 1.000 wt% of  $\text{V}_2\text{O}_5$ . The band observed at  $709.8\text{ cm}^{-1}$  for  $\text{BiNbO}_4$  with 0.125 wt% of  $\text{V}_2\text{O}_5$  is slightly shifted to higher energy when the content of  $\text{V}_2\text{O}_5$  increases from 0 to 0.25 wt% and maintains at  $713.6\text{ cm}^{-1}$  for the 1.00 wt% of  $\text{V}_2\text{O}_5$  content (Fig. 3). This may be due to crystallinity changes in  $\text{BiNbO}_4\text{--V}_2\text{O}_5$  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

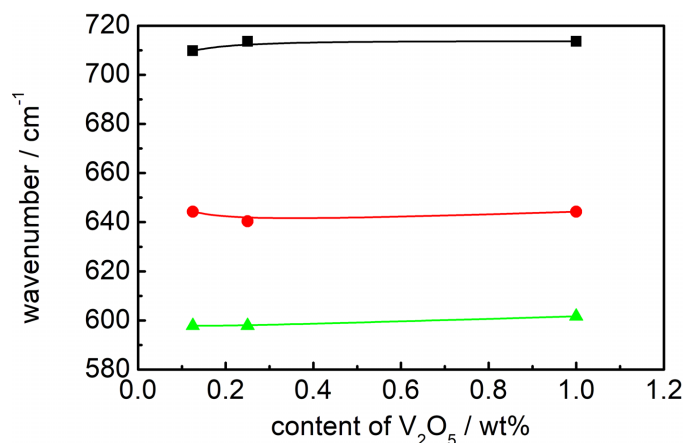


Fig. 3. The effect of  $\text{V}_2\text{O}_5$  content on the wavenumbers of  $\text{NiO}_6$  octahedra vibration of  $\text{BiNbO}_4\text{--V}_2\text{O}_5$  sintered at  $T = 910^\circ\text{C}$

the  $\text{BiNbO}_4$  structure (from  $1000\text{ cm}^{-1}\text{--}500\text{ cm}^{-1}$ ) maintain for each set of  $\text{BiNbO}_4\text{--V}_2\text{O}_5$  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  $\text{BiNbO}_4$  ceramics doped with  $\text{CuO}$ . Fig. 4 shows the FTIR spectra of  $\text{BiNbO}_4$  doped ceramics with 2.000 wt% of  $\text{CuO}$  sintered at  $T = 890^\circ\text{C}$  and  $T = 910^\circ\text{C}$ . Similarly to  $\text{BiNbO}_4$  ceramics doped with  $\text{V}_2\text{O}_5$ , both FTIR spectra of  $\text{BiNbO}_4$  doped with  $\text{CuO}$  characterises the very weak bands at  $3472\text{ cm}^{-1}$  and  $1639\text{ cm}^{-1}$  and they are usually associated with vibrational stretching and deformation bands of O-H groups [13] and the band at  $2931\text{ cm}^{-1}$ , which is usually attributed to the C-H stretching vibrations [8]. Other weak bands observed in the region  $1465\text{--}1390\text{ cm}^{-1}$  (Fig. 4) can be due to the presence of some organic groups from incomplete decomposition of solvents/reagents used during the samples preparation.

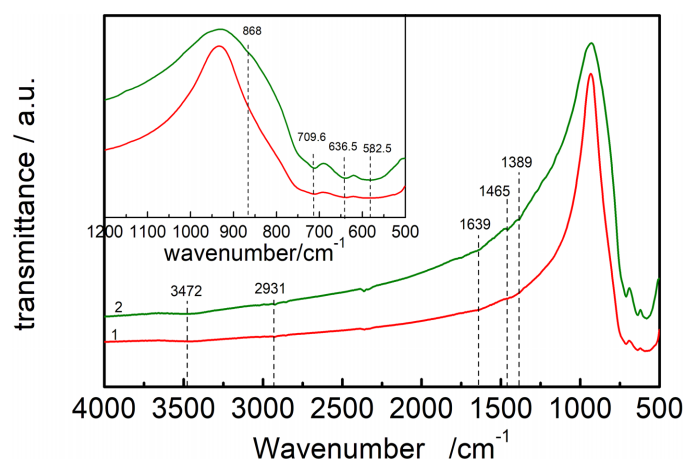


Fig. 4. The FTIR spectra of  $\text{BiNbO}_4$  doped ceramics with 2.000 wt% of  $\text{CuO}$  sintered at  $T = 890^\circ\text{C}$  (1) and  $T = 910^\circ\text{C}$  (2). Insert, enlarged of low energy region of FTIR spectra

The FTIR bands observed at low energy region ( $1000\text{--}500\text{ cm}^{-1}$ ) for  $\text{BiNbO}_4\text{--CuO}$  ceramics are related to the vibrations in the  $\text{BiNbO}_4$  lattice [6,9-12]. The bands observed at  $709.6$ ,

636.5 and 582.5  $\text{cm}^{-1}$  for both  $\text{BiNbO}_4\text{-CuO}$  ceramics can be associated with Nb-O stretching of the terminal oxygen atoms in  $\text{NbO}_6$  group vibration of  $\text{NbO}_6$  octahedra [11]. The positions of these bands maintain for both  $\text{BiNbO}_4\text{-CuO}$  ceramics suggesting no structural and chemical changes induced by sintering conditions. However the band position regarded to Nb-O-Nb group for  $\text{BiNbO}_4\text{-CuO}$  doped ceramics are slightly shifted (the highest shift of 6.4  $\text{cm}^{-1}$  was observed for the band at 709.6  $\text{cm}^{-1}$ ) in comparison with pure  $\text{BiNbO}_4$ . The shoulder at 868  $\text{cm}^{-1}$  more pronounced for  $\text{BiNbO}_4\text{-CuO}$  ceramics sintered at  $T = 910^\circ\text{C}$  (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  $\text{NbO}_6$  group shifted to lower energy. This indicates some structural changes of  $\text{BiNbO}_4$  and may suggests the substitution of  $\text{Cu}^{2+}$  for  $\text{Bi}^{3+}$  [1]. As the substitution of  $\text{Bi}^{3+}$  by  $\text{Cu}^{2+}$  with lower electrovalency and smaller ionic radius than that of  $\text{Bi}^{3+}$  caused the lattice distortion [1] and also induces chemical changes.

#### 4. Conclusions

Bismuth niobate ( $\text{BiNbO}_4$ ) 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  $\text{BiNbO}_4$  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  $\text{BiNbO}_4$  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,  $\text{V}_2\text{O}_5$  or  $\text{CuO}$  (2.000 wt%). Ceramics were sintered by pressureless sintering method at relatively low temperature ranging from  $T = 890^\circ\text{C}$  to  $T = 910^\circ\text{C}$ . It was found that  $\text{V}_2\text{O}_5$  additive used improved morphology of the ceramic samples. However, the chemical composition of  $\text{BiNbO}_4$  ceramics in relation to bismuth oxide and niobium oxide manifested a tendency of lack of  $\text{Bi}_2\text{O}_3$  component. The effect of  $\text{V}_2\text{O}_5$  or  $\text{CuO}$  additive on FTIR spectra of  $\text{BiNbO}_4$  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  $\text{NbO}_6$  octahedra observed for  $\text{BiNbO}_4\text{-V}_2\text{O}_5$  ceramics suggest that the

crystal structure changes after  $\text{V}_2\text{O}_5$  incorporation: all the bands are shifted to higher energy suggesting strong interaction/chemical bond formation between  $\text{BiNbO}_4$  and  $\text{V}_2\text{O}_5$ . However, the observed changes are very subtle and have to be confirmed by other characterisation methods.

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