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Original Article

Microwave dielectric properties and structure of $ZnO–Nb_2O_5–TiO_2$ ceramics

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Abstract

Ceramic samples based on $ZnO–Nb_2O_5–TiO_2$ compositions have been prepared using solid state ceramic route. The work was carried out over a wide range of initial $ZnNb_2O_6$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ compounds concentration. The crystal structure and microstructure developments were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was shown that the phase compositions of the samples present itself a columbite type and mixture of two phases—solid solutions of columbite and rutile types.The sintering behavior, permittivity, its temperature coefficients and quality factor had been characterized for ceramic samples in depending on compositions. The permittivity of the samples in this system is within the limits from 24 to 80, τ_ε from 150 to −560 ppm/°C. For the samples with $\tau_\varepsilon \sim 0$, $\varepsilon_r \sim 43.8$ and $Q{\cdot}f = 35000$ GHz at $f = 9$ GHz. The comparatively low sintering temperature (≤1080 °C) and high dielectric properties in microwave range make these ceramics promising for application in electronics.

Keywords: Sintering; Microstructure; Electron microscopy; Dielectric properties; TiO_2

1. Introduction

Ceramic compositions in the $Nb_2O_5–TiO_2–ZnO$ oxide system have been studied in several works[1–3] with the aim of creating ceramic materials with high quality factor (Q), high permittivity (ε_r) and near-zero temperature coefficient of resonant frequency (τ_f) for use in microwave dielectric resonators and filters. Materials based on this system are characterized also by sufficiently low sintering temperatures, which makes them attractive for the development of LTCC for fabrication of miniature multilayer devices involving the co-firing of dielectric and highly conductive metal, such as silver and copper.[4–6] In these works samples of the $ZnNb_2O_6–TiO_2$ system have been studied together with compositions of the system with Cu, V, or B oxides as additives introduced to decrease the sintering temperature of ceramics to be used in LTCC technology.

In [2] samples were produced in the $(1-x)ZnNb_2O_6 - xTiO_2$ system at $x = 0.5$ with permittivity $\varepsilon_r = 34.3$, $Q{\cdot}f = 42{,}500$ GHz, but $\tau_f = -52$ ppm/°C. With x increasing to 0.58 τ_f of the samples reaches zero, but the quality factor decreases to $Q{\cdot}f = 6000$ GHz, which limits the use of the compositions in microwave devices.

In this work introduction of Ti into $ZnNb_2O_6$ is performed using the Ti-containing oxide with rutile structure $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ ($a = 4.6739$ Å, $c = 3.0214$ Å, $V = 66.00$ Å^3).[7] In this oxide Zn, Nb, and Ti are statistically distributed over cationic positions of rutile structure. The mean ionic radius of the cation, equal to 0.78 Å, coincides with the ionic radius of Nb^{+5}. These features of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ oxide can provide for the isomorphous entering of titanium into columbite structure.

It is known that cations Zn and Nb are ordered in octahedral positions in columbite structure alternating along the c axis, Zn–Nb–Nb–Zn. Substitution of Nb^{+5} with Ti^{+4} occurs according to the Scheme $2Nb^{+5} + Zn^{+2} \rightarrow 3Ti^{+4}$, which is not accompanied by the formation of vacancies. Isomorphous substitution of Nb^{+5} with Ti^{+4} is accompanied by the distortion of the order in the position of cations and, finally, leads to the statistical distribution

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of the cations over the structure. In this case ordered columbite ($b_0 \approx 14$ Å) becomes disordered ($b = b_0/3$).[1]

This work presents the results of studying samples in the $(1 - x)ZnNb_2O_6 - xZn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ system, within the range x = 0...1.0. Phase composition, structure, and dielectric properties of ceramic samples have been studied in this work in the microwave range depending on the composition and sintering temperature. All crystallographic parameters of the studied samples are reduced to the structures columbite.

2. Experimental procedure

Ceramic samples in the $ZnO–Nb_2O_5–TiO_2$ system were prepared from preliminarily synthesized powders of zinc niobate $ZnNb_2O_6$ and zinc niobium–titanium oxides $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$. These powders were prepared by the solid-phase synthesis technique from high purity TiO_2 (99.95%), ZnO and Nb_2O_5 (99.9%) oxides. After milling in a vibration mill for 3 h the $ZnO–Nb_2O_5$ and $ZnO–Nb_2O_5–TiO_2$ mixtures were calcined in air at 900 °C for 4 h, and then the calcined powders were re-milled in a ball mill for 2 h to a grain size ≤ 1 μm. Pre-synthesized $ZnNb_2O_6$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ compositions were mixed in the desired relationship in a vibration mill for 2 h.

Disk samples of the required geometrical shape and size were prepared by hydraulic pressing; 10% solution of polyvinyl alcohol was taken as a binder. The prepared samples were sintered in air within the temperature range of 1060–1200 °C (3 h) in a chamber electric furnace. After sintering, density of the samples was determined and their electric properties were measured. The measurements of the relative permittivity, $\tan\delta$, quality factor Q ($1/\tan\delta$) and τ_f were performed at the frequency $f \sim 9$ GHz on disc samples 6.0 mm in diameter, correspondingly, and 2.0 mm thick. The τ_f was measured for test samples of the dielectric resonators within the temperature range −60 to +60 °C. The methods for the measurements electrical parameters at 9 GHz were described in [8,9]. Sintered samples were studied on a DRON-3 diffractometer with a Cu-K_α, Ni filter, recording mode $\Theta - 2\Theta$ ($2\Theta = 10–150°$). Ge was used as external standard. Unit cell parameters of the columbite and rutile phases were measured on all reflections of the every phase. Reflections with arbitrary intensity ≥3% were used only. Further measurements were made using a scanning electron microscope (SEM) JSM-6460LV (JEOL, Japan) and an EDS-spectrometer for X-ray microanalysis. BSE (back-scattering electrons) detector was used for SEM images.

3. Results and discussion

X-ray investigation of the samples in the system $(1 - x)ZnNb_2O_6 - xZn_{0.17}Nb_{0.33}Ti_{0.5}O_2$, sintered at an optimal temperature demonstrated that the increase of the concentration of complex oxide $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ with rutile structure in the initial composition up to 50 wt% keeps the samples single-phase with the structure close to columbite. Further increase of the oxide content in the initial composition results in the appearance of the second phase with rutile structure and the formation of a mixture of two crystalline phases with the structures of columbite and rutile. The increase of the oxide content in the initial mixture from $x = 0.5$ up to $x = 0.95$ is accompanied with the increase of its content in the phase composition of ceramic samples, which is confirmed by the data of X-ray analysis and electron microscopy presented at Fig. 1a and b. The phase with rutile structure is shown as darker crystalline formations at the electron micrograph (Fig. 1b). It is seen that the volume content of dark crystallites increases with the increase of the concentration (x) of the complex oxide with rutile structure in the initial composition. Average content of titanium on these phases from EDS data is presented in Fig. 2. It is seen that the increase of the content of the oxide in the samples up to $x = 0.5$ is accompanied by nearly linear increase of its content in the phase with columbite structure. Further increase of the oxide content in the initial composition results in the further increase of titanium content in the columbite phase though the rate of growth decreases, titanium content in the complex oxide phase remaining almost unchanged. These results are in good agreement with the XRD data. Cell parameters for the phases of the columbite solid solution are presented in Table 1 and are seen to decrease with the increase of the oxide content in the initial composition. Fig. 3a and b presents dependences of the elementary cell volume of the corresponding phases in ceramic samples on the composition in the $(1 - x)ZnNb_2O_6 - xZn_{0.17}Nb_{0.33}Ti_{0.5}O_2$. It is seen that the elementary cell of the columbite phase decreases almost linearly with the increase of the content of the oxide with rutile structure in the initial composition up to $x = 0.5$. Further increase of the concentration of the oxide in the composition up to $x = 0.8$ leads to slowing down of the decrease of the elementary cell volume of the phase with columbite structure. In the concentration range close to the pure oxide ($x \to 1$) the elementary cell volume of solid solutions with columbite structure sharply decreases again with the increase of the oxide concentration in the mixture. Besides, it is seen from Fig. 3b that the elementary cell volume of the phase with rutile structure almost does not change with sample composition within the entire investigated concentration range.

Fig. 4 displays dependences of the permittivity (ε_r), its temperature coefficient (TK_ε), and $Q{\cdot}f$ measured in the microwave range on the composition of the samples of the studied system. In the concentration range up to $x = 0.5$, which corresponds to the range of formation of single-phase isomorphous solid solutions with columbite structure, the values of permittivity and its temperature coefficient smoothly increase. With further increase of x the samples become two-phase and a more sharp change of ε_r and TK_ε with composition is observed. In this case the increase of x results in the increase of the permittivity up to 80 (for $x = 1.0$), while TK_ε changes its sign and falls down to −560 ppm/°C. Meanwhile, it is seen from the picture that the increase of the oxide content in the batch within the isomorphism range and the corresponding permittivity increase are accompanied with the decrease of the quality factor level, the $Q{\cdot}f$ value remaining relatively high though. Further increase of the oxide content and the appearance of the second phase are accompanied with decrease of the quality factor to $Q{\cdot}f = 10{,}000 \div 11{,}000$ GHz, which corresponds to the sam-

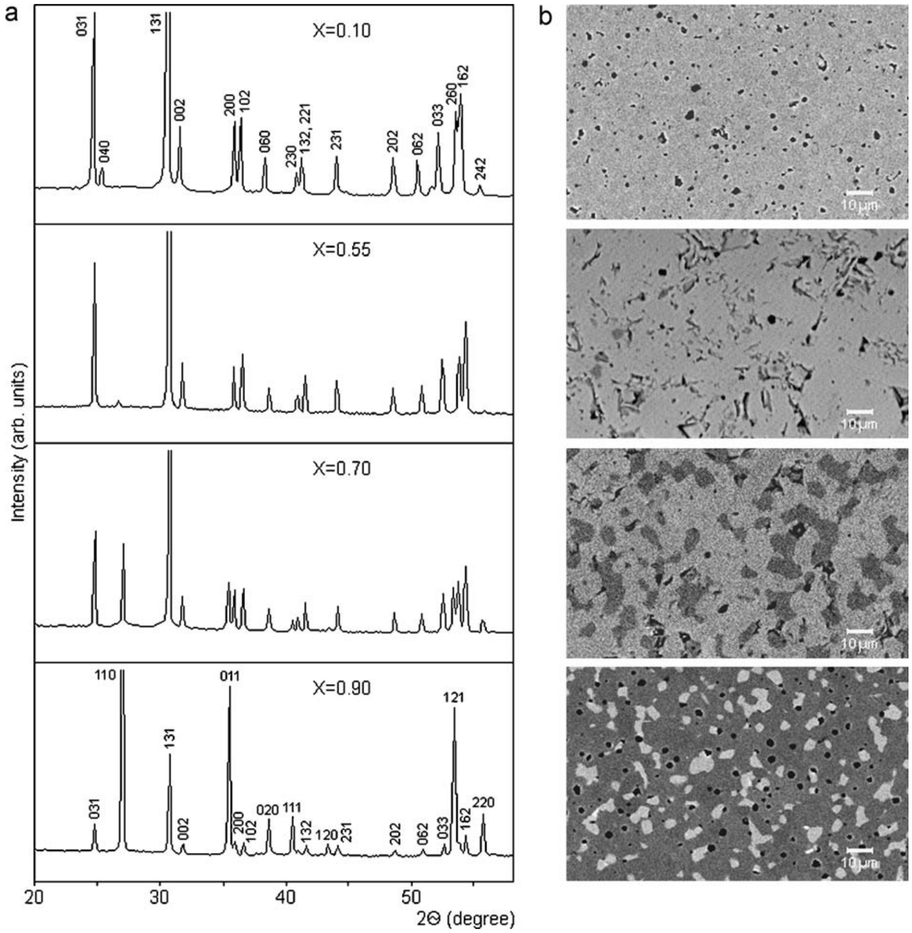

Fig. 1. X-ray patterns (a) and SEM images (b) of ceramic samples of the system $(1-x)\text{ZnNb}_2\text{O}_6-x\text{Z}_{0.17}\text{Nb}_{0.33}\text{Ti}_{0.5}\text{O}_2$ for different compositions.

ples of the pure $\text{Zn}_{0.17}\text{Nb}_{0.33}\text{Ti}_{0.5}\text{O}_2$. For the samples containing 66 wt% of the oxide in the initial composition with zinc niobate $\text{Zn}_2\text{Nb}_2\text{O}_6$, $\text{TK}_\varepsilon \sim 0$ and $Q{\cdot}f = 35{,}000$ GHz, the permittivity being 43.8.

Fig. 5a shows the results of the investigation of the electric properties of ceramics depending on the sintering temperature for the samples of the composition $0.34\text{ZnNb}_2\text{O}_6-0.66\text{Zn}_{0.17}\text{Nb}_{0.33}\text{Ti}_{0.5}\text{O}_2$. It is seen that the

Table 1
Cell parameters of $(1-x)\text{ZnNb}_2\text{O}_6-x\text{Z}_{0.17}\text{Nb}_{0.33}\text{Ti}_{0.5}\text{O}_2$ ceramics.

x	Ordering	Columbite phase			Rutile phase	
		a, Å	b, Å	c, Å	a, Å	c, Å
0	+	5.027(1)	14.184(6)	5.719(2)	–	–
0.05	+	5.033(2)	14.164(6)	5.701(2)	–	–
0.10	+	5.024(2)	14.143(5)	5.705(2)	–	–
0.17	+	5.019(2)	14.120(6)	5.701(2)	–	–
0.20	+	5.014(2)	14.085(6)	5.694(2)	–	–
0.30	+	5.024(2)	14.010(6)	5.669(3)	–	–
0.40	+	5.022(2)	14.070(5)	5.676(2)	Small	–
0.50	–	5.019(3)	14.029(8)	5.659(2)	4.680(2)	3.026(2)
0.55	–	5.014(2)	14.016(10)	5.660(3)	4.673(2)	3.019(2)
0.65	–	5.008(2)	14.002(8)	5.676(2)	4.676(2)	3.026(2)
0.70	–	5.014(2)	14.020(10)	5.652(2)	4.672(2)	3.018(1)
0.75	–	5.022(2)	14.015(10)	5.642(2)	4.675(1)	3.027(1)
0.80	–	5.014(2)	14.020(10)	5.645(2)	4.678(2)	3.025(2)
0.85	–	5.014(2)	14.029(8)	5.645(2)	4.677(2)	3.022(2)
0.90	–	5.003(2)	14.002(8)	5.645(2)	4.672(3)	3.022(2)
0.95	–	4.994(3)	13.990(10)	5.628(3)	4.678(2)	3.024(2)
1.00		–	–	–	4.677(1)	3.024(1)

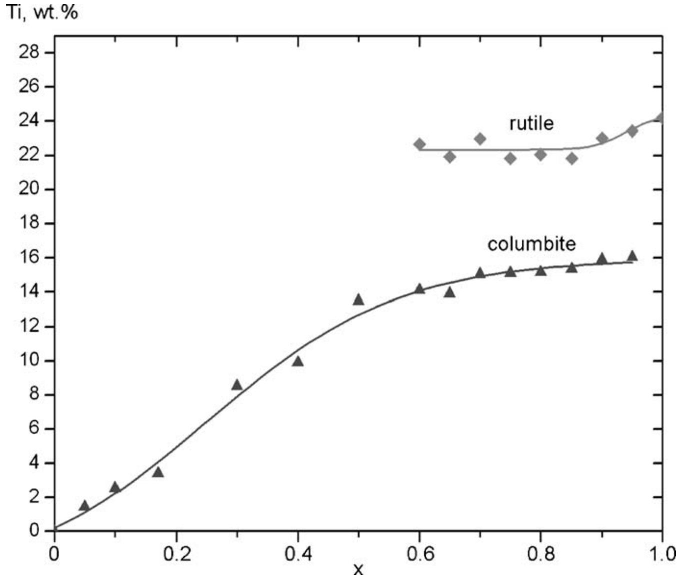

Fig. 2. Titanium content in crystalline phases with columbite and rutile structure by EDS data for the samples in the system $(1-x)ZnNb_2O_6-xZ_{0.17}Nb_{0.33}Ti_{0.5}O_2$, depending on the content of the oxide $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (x) in the initial composition.

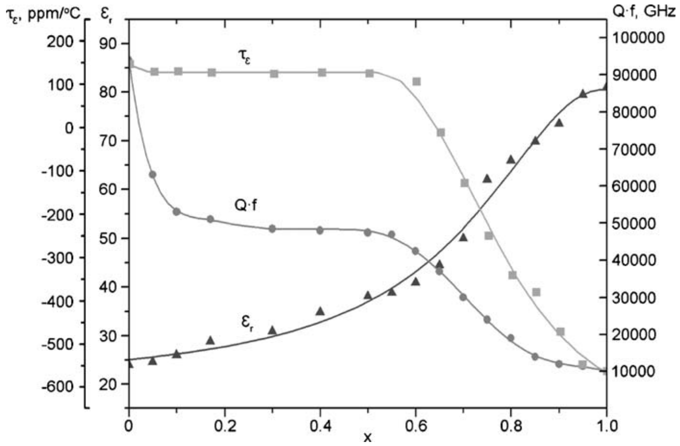

Fig. 4. Dependence of the permittivity ε', temperature coefficient of permittivity and $Q{\cdot}f$ of ceramic samples of the system $(1-x)ZnNb_2O_6-xZ_{0.17}Nb_{0.33}Ti_{0.5}O_2$ on the content of the oxide $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (x) in the initial composition.

increase of the sintering temperature from 1060 to 1200 °C results in the increase of the permittivity by 10 units. With the increase in temperature the $Q{\cdot}f$ value passes through a maximum. Meanwhile, data on the density of the samples of this composition sintered within a wide range of temperatures from 1060 to 1200 °C presented in Fig. 5b show that starting from 1080 °C experimentally determined density of the samples almost equals to the X-ray density (5.201 g/cm^3) and almost does not depend on the sintering temperature. Thus, the samples of the given composition are characterized by a sufficiently low sintering temperature and wide (more than 100°) sintering range. Meanwhile, X-ray and electron microscopy data (Fig. 6a and b) show that the phase composition of the samples sintered at different temperatures is different. Our studies showed that the increase of the sintering temperature leads to the increase of the content of dark crystallites (phase with rutile structure) in the composition of the samples. It can be seen in Fig. 6a that presents XRD data for the samples $0.34ZnNb_2O_6-0.66Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ sintered at different temperatures and in Fig. 6b that shows data on the microstructure of the corresponding samples. The presented data closely resemble the data in Fig. 1 with X-ray patterns and SEM images of ceramic samples for different compositions.

Fig. 7 shows the results of measurements of the temperature coefficient of the resonance frequency τ_f ($\tau_f=-\tau_\varepsilon/2-\alpha$, where α is the linear expansion coefficient of the ceramics) for the

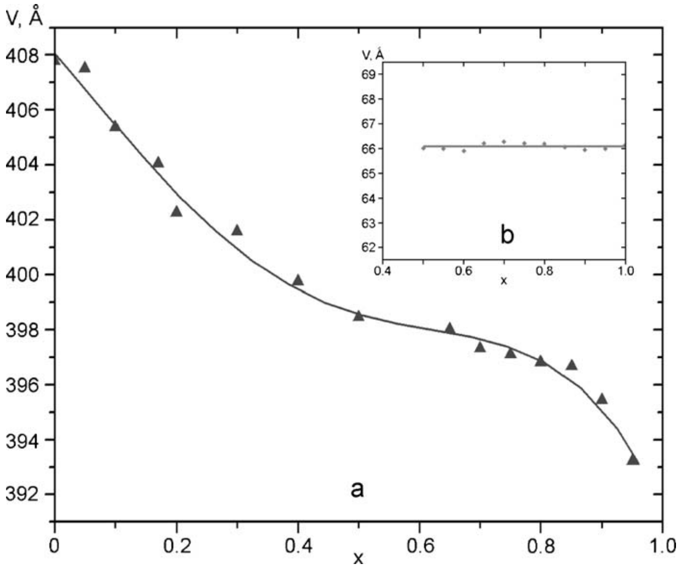

Fig. 3. Dependence of the elementary cell volume of the crystalline phases with columbite (a) and rutile (b) structure in the phase composition of ceramic samples in the system $(1-x)ZnNb_2O_6-xZ_{0.17}Nb_{0.33}Ti_{0.5}O_2$ on the content of the oxide $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (x) in the initial composition.

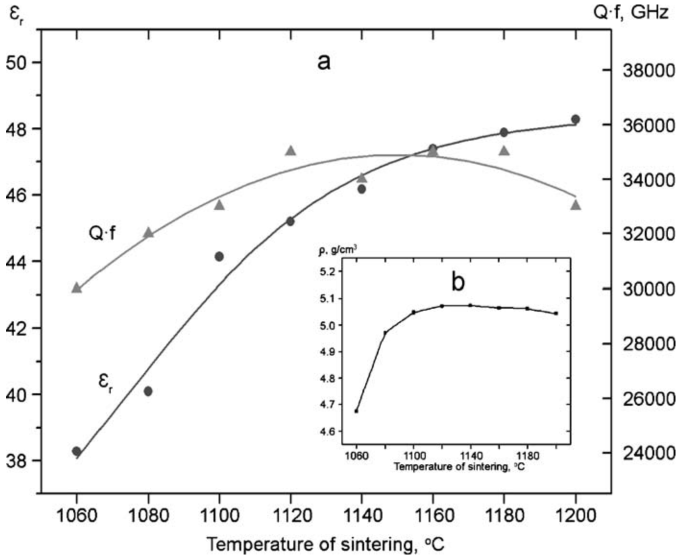

Fig. 5. Dependence of the permittivity ε' and $Q{\cdot}f$ (a) as well as density (b) of ceramic samples of the composition $0.34ZnNb_2O_6-0.66Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ on the sintering temperature.

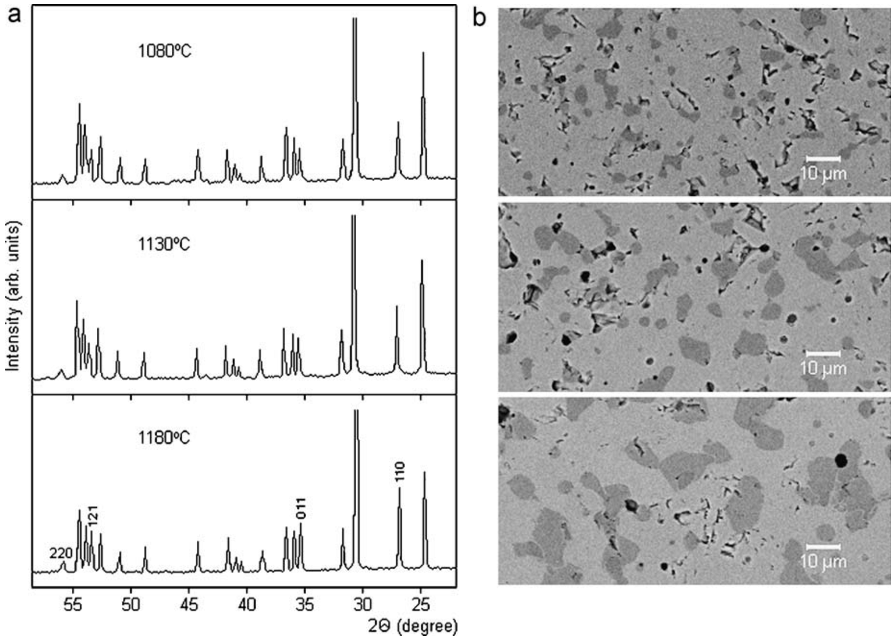

Fig. 6. X-ray patterns (a) and SEM images (b) of ceramic samples $0.34ZnNb_2O_6 - 0.66Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$, synthesized at different sintering temperatures.

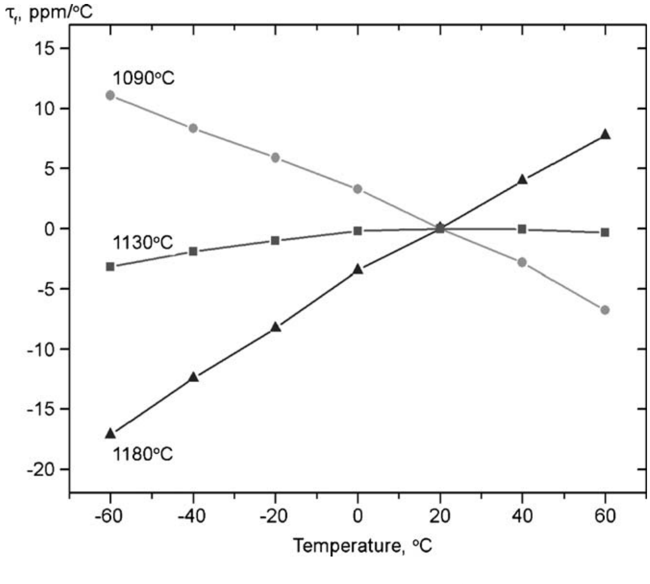

Fig. 7. Results of measurement of the temperature coefficient of the resonance frequency of the samples $0.34ZnNb_2O_6 - 0.66Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$, synthesized at different sintering temperatures.

samples $0.34ZnNb_2O_6 - 0.66Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$, synthesized at different sintering temperatures. It is seen that the increase of the sintering temperature and the corresponding increase of the content of the phase with rutile structure in the samples parameter τ_f effectively increases.

Thus, selection of the $(1-x)ZnNb_2O_6 - xZn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ system enabled us to significantly increase the range of isomorphism of the columbite phase and provided for the increase of the quality factor level of the samples in the wide concentration range under smooth changing of ε_r and τ_ε (τ_f).

4. Conclusions

Structure, dielectric properties and sintering behavior were studied for the ceramic dielectrics on the basis of the $ZnO–Nb_2O_5–TiO_2$ compositions with the columbite and rutile structures. The work was carried out over a wide range of initial $ZnNb_2O_6$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ compounds concentrations. The existence of wide range of the columbite phase isomorphism was discovered. It is shown that in investigated concentration range in the system $(1-x)ZnNb_2O_6 - xZn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ with the increasing of x from $x=0$ up to $x=0.5$ the phase composition of the samples presents itself a columbite structure. But the mechanical mixture of two crystalline phases namely columbite and rutile is formed with the increasing of x from $x=0.5$ up to $x=0.95$. The permittivity of the samples in this system is within the limits from 24 to 80, τ_ε from150 to -560 ppm/°C. For the samples with $\tau_\varepsilon \sim 0$, $\varepsilon_r \sim 43.8$ and $Q{\cdot}f = 35{,}000$ GHz at $f = 9$ GHz. The comparatively low sintering temperature (~1080 °C) and high dielectric properties in microwave range make these ceramics promising for application in microwave electronics.

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