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Low-sintering ceramic materials based on Bi_2O_3–ZnO–Nb_2O_5 compounds

E.A. Nenasheva[a,*], N.F. Kartenko[b]

[a] GIRICOND Research Institute, 10, Kurchatov str., Saint-Petersburg 194223, Russia
[b] A.F. Ioffe Physicotechnical Institute Russian Academy of Sciences, 26, Politechnicheskaya Str., Saint-Petersburg 194021, Russia

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Abstract

In this work, sintering behaviour of Bi_2O_3–ZnO–Nb_2O_5 compounds was investigated in order to develop LTCC materials with suitable microwave properties. Structure, dielectric properties and sintering were studied for ceramic dielectrics based on the system: $Bi_2ZnNb_2O_9$ with the pyrochlore structure and $ZnNb_2O_6$ with a columbite one. The work was carried out over a wide range of initial components concentration. Ceramic samples of these materials were prepared by the mixed oxide technique. The effect of adding glass to the materials have been discussed. The sintering behaviour, dielectric permittivity, quality factor and crystal structures have been characterized for ceramic samples depending on compositions. Low-temperature co-firable ceramic material with $\varepsilon \sim 30$, $\tau_\varepsilon = 0$ and $Q \times f = 3500$ GHz based on the above system was synthesized.

Keywords: C. Dielectric properties; D. TiO_2; Milling

1. Introduction

Low-temperature co-firable ceramic (LTCC) materials are the base materials for the development of multilayer components and devices operating at microwave frequencies. The developing LTCC processing requires the creation of new ceramic materials, which possess a wide range of dielectric permittivity (ε) values, small and close to zero values of the temperature coefficient of dielectric permittivity (τ_ε), small dielectric losses over a wide range of frequencies up to the microwaves region together with the low sintering temperature (~900 °C) and compatibility with Ag electrodes.

With this regard, of special interest are ceramic materials in the system including bismuth, zinc, and niobium oxides. A number of compositions of this system are well known and were studied by many authors.[1–4] Thus, the works[1,2] deal with the investigation of the systems of magnesium and zinc oxides together with bismuth and niobium oxides. The authors report about the composition that corresponds to a crystallographic formula $Bi_{1,5}[\,]_{0.5}(Mg_{1/3}Nb_{2/3})_2O_6O_{0,25}[\,]_{0.75}$, where [ ] is vacancy. It is a compound having the cubic pyrochlore structure with the unit cell parameter $a = 10.5775$ Å that corresponds to the ratio of initial oxides MgO:Bi_2O_3:Nb_2O_5 equal to 1:1,125:1. The work[2] describes ceramic materials in this system with low sintering temperatures with ε from 75–210 corresponding to a wide range of $\tau_\varepsilon = (+110 \ldots -750)$ ppm/°C. Dielectric loss tangent of these materials is equal to $\tan\delta = (5–10) \times 10^{-4}$.

In 1994, there was published the patent[5] with the priority from 1990 in which we declared the production of a series of compounds with the cubic pyrochlore structure that correspond to the compositions of oxides $1Bi_2O_3$:1MeO:$1Nb_2O_5$ where Me = Mg^{2+}, Zn^{2+}, and Ni^{2+}. The composition are describe in Table 1. We synthesized the composition in this group within the framework of investigation of the class of compounds with the so-called structural vacancies (denoted by square brackets in Table 1). We assign the compounds described in the patent to the same class of substances. Investigations of the chemical composition and density of the samples showed the proximity of the obtained analytical data to the ideal formula, proposed in the patent. The compounds have comparatively high values of the dielectric permittivity together with a lower absolute values of the temperature coefficient of this quantity as compared to the known high-frequency and microwave dielectrics-analogs (see Table 1). They also have very small dielectric losses, which in combination with a comparatively low sintering temperature places them among promising materials for the development of LTCC technologies on their basis.

* Corresponding author. Tel.: +7 812 55294 34; fax: +7 812 552 6057.
E-mail address: info@ceramics.sp.ru (E.A. Nenasheva).

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Table 1
Electrical properties of samples with pyrochlore structure in comparison with analogs

No.	Compound	T_{sint} (°C)	Crystal structure, unit cell parameter (Å)	Permittivity (ε)	τ_ε (ppm/°C)
1	$(Bi_{2/3}[\,]_{1/3})_2\,(Mg_{1/3}Nb_{2/3})_2O_6[\,]_1$ [a]	1120	Pyrochlore $a = 10.557$	145	−342 ... −390
2	$(Bi_{2/3}[\,]_{1/3})_2\,(Zn_{1/3}Nb_{2/3})_2O_6[\,]_1$ [a]	1020	Pyrochlore $a = 10.560$	148	−410 ... −470
3	$(Bi_{2/3}[\,]_{1/3})_2(Ni_{1/3}Nb_{2/3})_2O_6[\,]_1$ [a]	1080	Pyrochlore $a = 10.542$	145	−346 ... −374
4	$Pb_2Nb_2O_7$	1200	Pyrochlore $a = 13.021$, $b = 7.483$, $c = 34.634$, $\beta = 125.18°$	140	−1500
5	$CaTiO_3$	1400	Perovskite	150	−1500
6	$(Ca,La)(Al,Ti)O_3$	1480	Perovskite	75	−330

[a] RU Patent 2021207, priority October 15, 1990.

Compound with Me = Zn has the lowest sintering temperature. This compound was selected to be used in our research work.

It should be noted that the later works in particular Ref.[6], confirmed the existence of the composition described in Table 1, $(Bi_{2/3}[\,]_{1/3})_2(Zn_{1/3}Nb_{2/3})_2O_6[\,]_1$(or $Bi_2ZnNb_6O_9$, in another notation), with the cubic pyrochlore structure, and reported about the research of the concentration range with an increased content of bismuth oxide. In addition this work describes a series of ceramic materials with $\varepsilon > 45$ that have low sintering temperatures. Meanwhile the purpose of this work was to produce low-temperature thermostable materials with low ε (less than 40) to be used as dielectrics in multilayer elements with silver-based electrodes.

Our previous investigations of the homogeneity region of the above described group of compounds[7–9] showed that in a wide range of the initial oxide concentrations: (0.9–1.3)Bi_2O_3, (0.8–1.0)Nb_2O_5 and (0.8–1.2)MeO, where Me = Mg, Zn, almost single-phase samples with the pyrochlore structure are formed with $\varepsilon = 120\ldots230$ and τ_ε from −330 to −650 ppm/°C, together with the low tan δ values. In the concentration range rich in the oxides of zinc and niobium, the second phase ($ZnNb_2O_6$) is formed with the columbite structure. As is known, $ZnNb_2O_6$ is a high-Q dielectric with $\varepsilon = 23$, $\tau_\varepsilon = +140$ ppm/°C, and, as our studies showed, it can have a comparatively low sintering temperature (≤1100 °C).

In accordance with all the above, it presented the interest to investigate the $Bi_2ZnNb_2O_9$–$ZnNb_2O_6$ system in the wide range of concentrations of the initial components for the purpose of the development of thermostable ceramic materials on its base with small dielectric losses in high-frequency and microwave ranges and low sintering temperature to be used for LTCC technology.

2. Samples preparation

Ceramic samples in the Bi_2O_3–ZnO–Nb_2O_5 system were prepared from preliminarily synthesized powders of bismuth zinc niobate $Bi_2ZnNb_2O_9$ and zinc niobate $ZnNb_2O_6$. These powders were prepared by the solid-phase synthesis technique from the oxides of niobium, bismuth and zinc at a temperature of synthesis equal to 900 °C. The samples of materials with the different ratio of initial components were obtained by mixing and grinding in a vibrating mill. Mixing of a ceramic powder with a glass-forming additive was carried out under wet grinding.

Disk samples of the size required for the electric measurements in the 10^5–10^6 Hz and (5–9 GHz) frequency bands were prepared by the hydraulic pressing technique. The samples were sintered at 740–1140 °C in an electric chamber furnace in air atmosphere until zero water absorption. X-ray study of the synthesized samples and the sintered samples was carried out with the DRON-3 X-ray diffractometer (Cu Kα radiation, Ni filter).

3. Results and discussion

Fig. 1 shows the X-ray patterns of the ceramic samples of initial compounds, namely phases of the pyrochlore and columbite types as well as their mixtures in various proportions. It is seen that with the increase of the zinc niobate concentration the phase composition of the samples presents itself a mechanical mixture of two initial crystalline phases. The volumetric content of the $ZnNb_2O_6$-type phase increases with an increase of its content in the initial mixture. In this case, no noticeable change

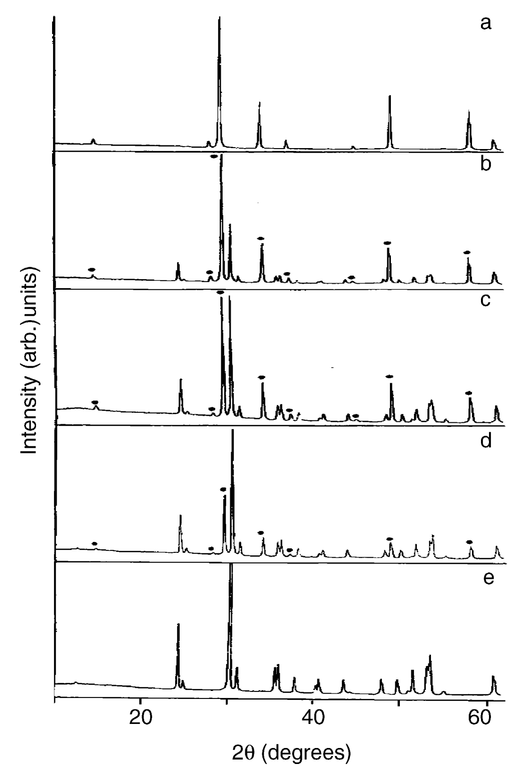

Fig. 1. X-ray patterns of ceramic samples of initial compounds—$Bi_2ZnNb_2O_9$—with pyrochlore structure (a), $ZnNb_2O_6$ with columbite structure (e) and their mixture in proportions: (b) 60 wt.% $Bi_2ZnNb_2O_9$–40 wt.% $ZnNb_2O_6$; (c) 40 wt.% $Bi_2ZnNb_2O_9$–60 wt.% $ZnNb_2O_6$; (d) 25 wt.% $Bi_2ZnNb_2O_9$–75 wt.% $ZnNb_2O_6$.

Table 2
Results of X-ray study of $Bi_2ZnNb_2O_9$–$ZnNb_2O_6$ ceramic samples ($T_{sint.}$—1100 °C)

Composition (wt.%)		Unit cell parameters of crystalline phases with structure			
$Bi_2ZnNb_2O_9$	$ZnNb_2O_6$	Pyrochlore	Columbite		
		a (Å)	*a* (Å)	*b* (Å)	*c* (Å)
100	0	10.557 (3)	–	–	–
95	5	10.556 (2)	–	–	–
90	10	10.557 (2)	5.029 (5)	14.191 (10)	5.720 (7)
80	20	10.557 (2)	5.032 (4)	14.200 (8)	5.721 (6)
60	40	10.556 (3)	5.035 (4)	14.197 (6)	5.725 (5)
40	60	10.554 (3)	5.033 (3)	14.185 (5)	5.723 (5)
25	75	10.553 (3)	5.036 (4)	14.187 (6)	5.723 (5)
5	95	10.552 (6)	5.036 (3)	14.191 (6)	5.722 (4)
–	100	–	5.032 (3)	14.192 (7)	5.722 (5)

was discovered in the unit cell parameters of the crystalline phases in the investigated concentration range of the mixture in comparison with the parameters of the initial phases, which is evident from the X-ray data of the $Bi_2ZnNb_2O_9$–$ZnNb_2O_6$ samples given in Table 2. Moreover, no additional phases (impurities) were discovered. This supposes the absence of the essential interaction of phases in the process of sample sintering, which occurs under comparatively low temperatures in the range 1000–1140 °C.

Fig. 2 shows the dependence of the dielectric permittivity and τ_ε on the composition of the samples in the studied system. It is seen, that with the increase of zinc niobate concentration in the samples, the negative τ_ε values characteristic for bismuth zinc-niobate are compensated by positive ones inherent to $ZnNb_2O_6$. In this case ε of the samples with the increased zinc niobate concentration decreases and corresponds to the values close to 30 at $\tau_\varepsilon \sim 0$. Dielectric losses of the samples in this case are very small (tan $\delta \sim 10^{-4} \ldots 10^{-5}$) at frequencies $\sim 10^6$ Hz. Measurments for the samples in the microwave region showed that an increase of zinc niobate content is accompanied by a certain increase in the product of quality-factor by frequency ($Q \times f$ increases from several hundreds for bismuth-zinc niobate to several thousands gigahertz for the compositions with an increased $ZnNb_2O_6$ content). $Q \times f$ of the pure Zn niobate was ∼90,000 GHz, while for the composition with $\tau_\varepsilon = 0$ and $\varepsilon = 30$, $Q \times f = 5000$ GHz. Sintering temperature for such compound is 1000 °C.

In order to decrease the sintering temperature of the samples in the investigated system down to ∼900 °C without worsening their electrical parameters, we studied electrical properties and sintering of the samples with the introduction of glass-forming additive in the amount up 5 wt.%. For this purpose, we selected the glass containing PbO, Bi_2O_3, B_2O_3, ZnO and TiO_2 as a suitable additive, i.e., the system compatible with the basic composition of the ceramics by the presented elements. With the increase of the amount of the glass in the composition of the ceramics up to 3 wt.% (Fig. 3), the sintering temperature of the samples with $\tau_\varepsilon \sim 0$ decreases down to 900 °C. Further increase in the content of glass does not lead to a noticeable effect. The

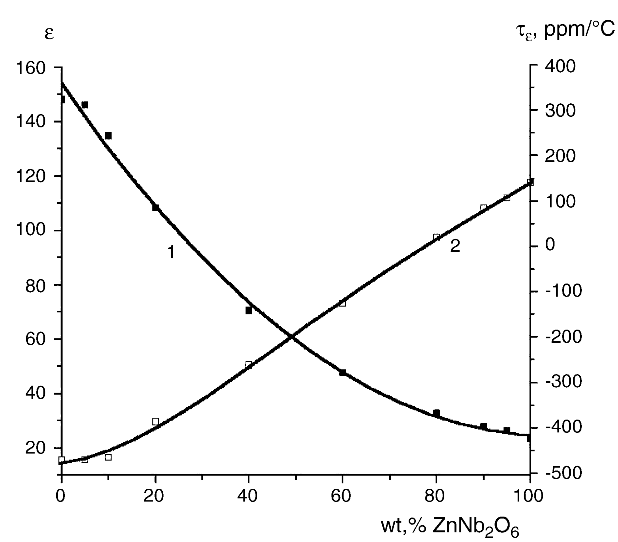

Fig. 2. The composition dependence of the dielectric permittivity ε (1) and its temperature coefficient τ_ε (2) of the samples in the system $Bi_2ZnNb_2O_9$–$ZnNb_2O_6$.

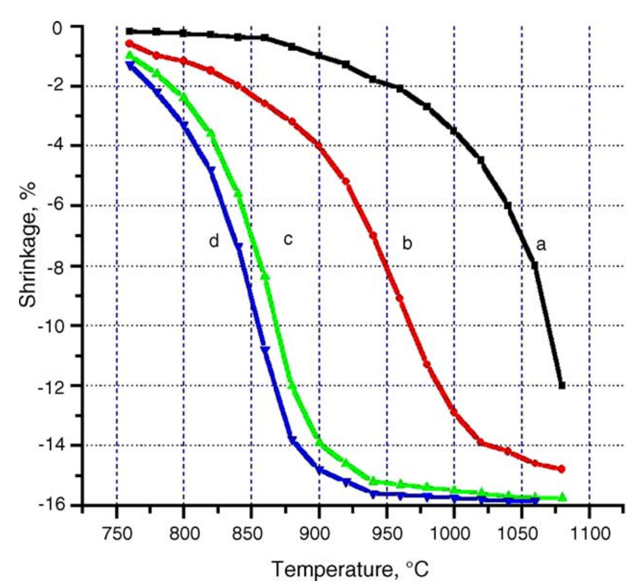

Fig. 3. The thermal shrinkage of ceramic samples based on mixture in proportion 80 wt.% $Bi_2ZnNb_2O_9$–20 wt.% $ZnNb_2O_6$ added with following amount of glass: (a) 0 wt.%, (b) 1.5 wt.%, (c) 3 wt.%, (d) 5 wt.%.

introduction of 3% of glass is accompanied by the insignificant change in the dielectric properties, ε decreases by 1–2 units and τ_ε shifts by 30–40 units towords the positive values. The composition with $\tau_\varepsilon \sim 0$ has $\varepsilon = 28–29$, $Q \times f = 3500$ GHz at $f = 5–9$ GHz.

4. Conclusions

Structure, dielectric properties, and sintering were studied for the ceramic dielectrics on the basis of the $Bi_2ZnNb_2O_9$ compounds with the pyrochlor structure and $ZnNb_2O_6$ compounds with the columbite structure. It is shown that in the investigated concentration range the mechanical mixture of two crystalline phases is formed; the unit cell parameters of the phases correspond to the parameters of the initial compounds. The dielectric constant of the samples in this system is within the limits from 23 to ∼150 for τ_ε from (140 to −460 ppm/°C. For the samples with $\tau_\varepsilon \sim 0$, $\varepsilon = 30$ and $Q \times f = 5000$ GHz at $f = 5–9$ GHz. Sintering temperature for the samples in the investigated system is 1000–1100 °C. Introduction of a glass on the base of oxides of Pb, Ti, B, Bi, and Zn into the composition of the ceramics in the amount of 3 wt.% leads to the decrease of sintering temperature to ∼900 °C almost without changing ε, $Q \times f$ being 3500 GHz at $f = 5–9$ GHz. The materials are promising for the use in the LTCC technology as the dielectrics of the multilayer ceramic capacitors with the electrodes on the basis of silver.

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