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Synthesis and Microwave Dielectric Properties of $Zn_{1+x}Nb_2O_{6+x}$

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Abstract—We have studied the formation of zinc niobate, $ZnNb_2O_6$, with the columbite structure and the microstructure and microwave dielectric properties of $Zn_{1+x}Nb_2O_{6+x}$ ceramics. The results demonstrate that, in the range $0.005 \le x \le 0.03$, the excess zinc reduces the porosity of the material and increases its microwave quality factor Q. For $x \ge 0.03$, the Q of the ceramics decreases because of the formation of an additional, zinc-enriched phase. Sintering in an oxygen atmosphere is shown to improve the dielectric properties of stoichiometric $ZnNb_2O_6$.

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INTRODUCTION

MNb_2O_6 (M = Mg, Zn) columbite-structure niobates feature low dielectric losses in the microwave region and are, accordingly, of considerable scientific and technological interest for designing high-performance microwave dielectrics for advanced communication systems [1–5]. In the columbite family, the lowest microwave losses (the highest microwave quality factor, $Q = 1/\tan\delta$) are offered by zinc niobate, $ZnNb_2O_6$ [1–4]. Based on this compound, Pullar et al. [4] fabricated polycrystalline materials with a dielectric permittivity $\varepsilon = 23$ and Qf product of 84000 GHz. In addition to their superior dielectric properties, $ZnNb_2O_6$-based materials offer the lowest sintering temperature among the columbite niobates, ≃1100–1200°C [3, 4], and are, therefore, potentially attractive for the low-temperature cofired ceramic technology [5, 6]. In earlier studies, the dielectric properties of zinc-containing niobates, in particular their Qf product, were found to depend significantly on sintering conditions. Moreover, increasing the sintering time to 50 h and more was shown to raise the quality factor of the material [3]. Those changes in the properties of $ZnNb_2O_6$ were interpreted by Pullar et al. [4] in terms of structural defects, such as anion vacancies. In light of the above, it is reasonable to assume that the formation of structural defects in zinc-containing niobates is associated with deviations from the $ZnNb_2O_6$ stoichiometry through zinc losses at high sintering temperatures. One would also expect the sintering atmosphere, in particular the oxygen pressure, to have a significant effect on the structural perfection of the material and, hence, on its Qf.

The objective of this work was to investigate the effects of chemical composition and sintering atmosphere on the microstructure and microwave dielectric properties of $ZnNb_2O_6$.

EXPERIMENTAL

Polycrystalline $Zn_{1+x}Nb_2O_{6+x}$ materials were prepared by solid-state reactions, using ZnO (99.95% purity) and Nb_2O_5 (99.9%) as starting chemicals. Appropriate amounts of these oxides were mixed by grinding with water in a vibratory mill for 4 h. After drying, the powders were pressed into disks. To study phase changes preceding $ZnNb_2O_6$ formation, the green compacts were heat-treated for 4 h at temperatures of up to 1300°C. To obtain polycrystalline materials, the starting mixtures were preheat-treated at temperatures from 1100 to 1150°C, ground in a vibratory mill, and pressed. The compacts were then sintered in the range 1200–1300°C for 2–8 h in air and an oxygen atmosphere at a pressure of 1 MPa. Nonstoichiometric samples, $Zn_{1+x}Nb_2O_{6+x}$, were prepared in the composition range $0 < x \le 0.05$ with x varied in steps of 0.005.

The phase composition and structural parameters of heat-treated samples were determined by x-ray diffraction (XRD) with a DRON-3M powder diffractometer (CuK_α radiation). The microstructure and chemical composition of the synthesized phases were determined by scanning electron microscopy (SEM) on a JEOL JXA 840A equipped with an energy-dispersive x-ray

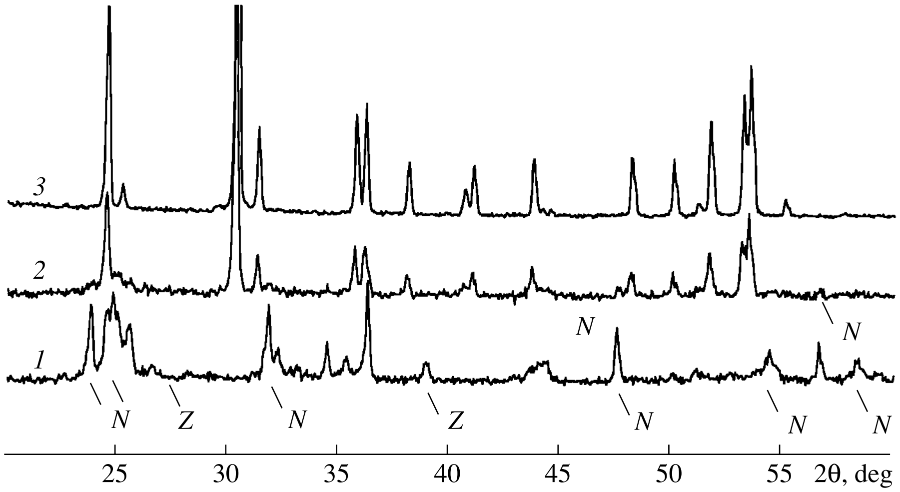

Fig. 1. Phase transformations in the ZnO–Nb_2O_5 system at (*1*) 500, (*2*) 700, and (*3*) 800°C; *Z* = ZnO (PDF, no. 21-1486), *N* = Nb_2O_5 (PDF, nos. 27-1003, 26-0885, 32-0711); synthesis in air for 4 h.

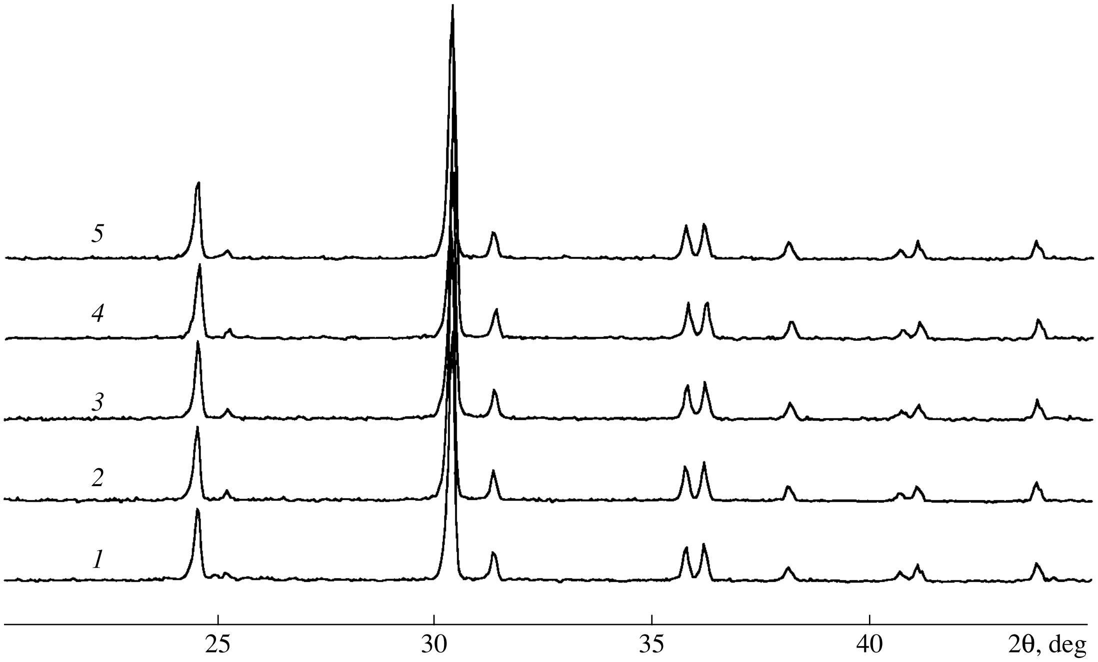

Fig. 2. XRD patterns of $Zn_{1+x}Nb_2O_{6+x}$ samples heat-treated at 1150°C for 4 h: x = (*1*) 0, (*2*) 0.005, (*3*) 0.01, (*4*) 0.03, (*5*) 0.04.

(EDX) spectrometer (Tracor Northern Series II x-ray microanalyzer system). The dielectric properties of the synthesized materials were studied at a frequency of 8–10 GHz by a dielectric resonator method using HP 8719C and Agilent PNA-L N5230A network analyzers.

RESULTS AND DISCUSSION

XRD results showed that $ZnNb_2O_6$ was formed in the temperature range 500–800°C, with no reaction intermediates. At 800°C, we obtained phase-pure $ZnNb_2O_6$ (Fig. 1). At higher temperatures or longer heat-treatment times, no additional phases appeared, just as in the case of the columbite niobate $MgNb_2O_6$ [2]. This feature of $ZnNb_2O_6$ synthesis allows the starting mixture to be preheat-treated at relatively low temperatures, on the order of 800–1000°C, which insures its high reactivity during sintering.

XRD examination of the $Zn_{1+x}Nb_2O_{6+x}$ nonstoichiometric samples heat-treated for 4 h at 1150°C showed that the only phase present was $ZnNb_2O_6$ (Fig. 2), suggesting that $Zn_{1+x}Nb_2O_{6+x}$ (or $ZnNb_{2-y}O_{6-2.5y}$, where

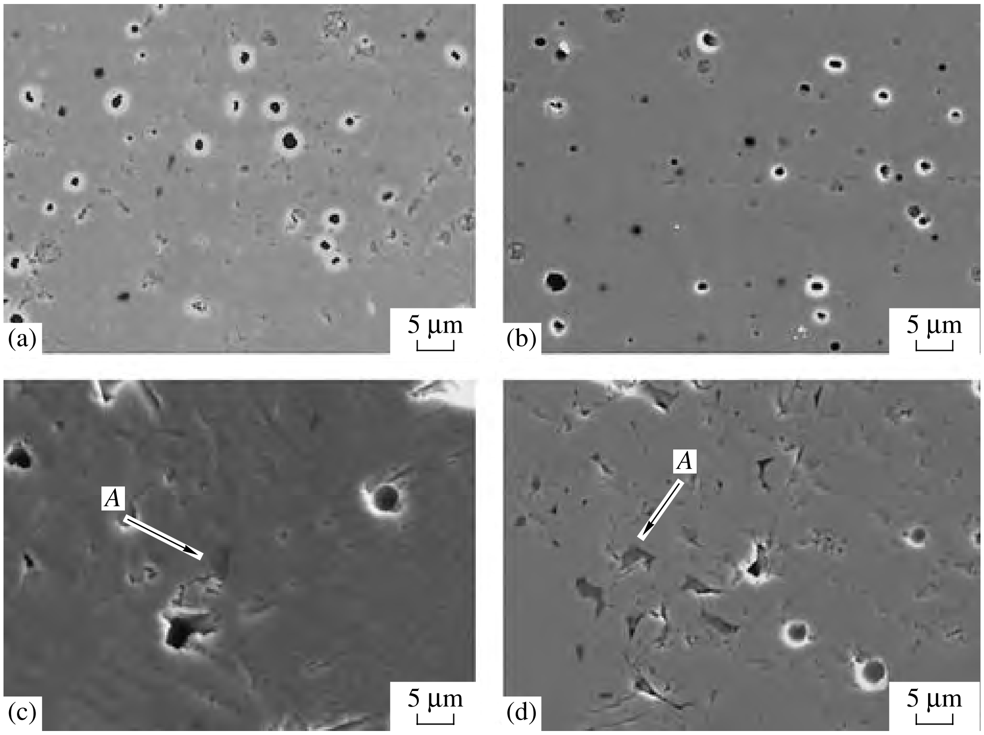

Fig. 3. SEM micrographs of polished $Zn_{1+x}Nb_2O_{6+x}$ samples sintered in air for 4 h: x = (a) 0, (b) 0.005, (c) 0.01, (d) 0.04; A = Zn-enriched phase.

$y = 2x/(x - 1)$) has a significant homogeneity range. This assumption is supported to some extent by SEM data: at $x = 0$ and 0.005, the ceramic samples contained no additional phases (Figs. 3a, 3b). At higher zinc contents ($0.005 \le x \le 0.04$), the sintered samples contained slight amounts of an additional, zinc-enriched phase. We failed to determine the chemical composition of that phase by EDX spectrometry. Its concentration was significant only at $x = 0.04$ (Fig. 3d). Microstructural analysis of the $Zn_{1+x}Nb_2O_{6+x}$ samples sintered at 1250°C indicates that the porosity of the ceramics decreases notably with increasing zinc content (Fig. 3b). The densest samples were obtained at $x = 0.01$ (Fig. 3c). It seems likely that the high porosity of the $Zn_{1+x}Nb_2O_{6+x}$ ceramics at low x values is the result of zinc vaporization and the associated deviations from stoichiometry, whereas the decrease in density for $0.01 \le x \le 0.04$ is due to the formation of the additional, zinc-enriched phase.

The microwave dielectric properties of our samples are summarized in the table. Analysis of our data indicates that, independent of the sintering atmosphere, the dielectric permittivity of the ceramics is a weak function of zinc content and lies in the range $\varepsilon = 22–24$. The temperature coefficient of resonant frequency (TCF), related to the temperature coefficient of permittivity (TCP) by $\text{TCF} = -\text{TCP}/2 - \alpha_L$ (where α_L is the linear

10-GHz dielectric properties of $Zn_{1+x}Nb_2O_{6+x}$ ceramics

x	ε	TCF, ppm/K	Qf, GHz	ε	TCF, ppm/K	Qf, GHz
	sintering in air			sintering in oxygen atmosphere		
0	23.9	–74	60000	23.46	–68	108000
0.005	22.5	–75	102000	22.50	–71	101000
0.01	23.8	–73	120000	23.68	–71	98000
0.03	23.0	–71	92000	23.76	–71	110000
0.04	23.7	–72	87500	23.99	–72	92000

Note: TCF = temperature coefficient of resonant frequency.

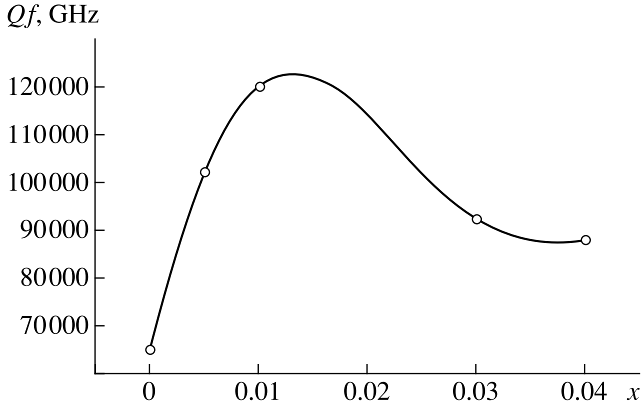

Fig. 4. Composition dependence of Qf ($\simeq$10 GHz) for air-sintered $Zn_{1+x}Nb_2O_{6+x}$ ceramics.

thermal expansion coefficient), is independent of zinc content.

At the same time, the Q of the air-sintered materials passes through a maximum at $x = 0.01$ (Fig. 4). The observed rise in Q in the composition range $0 \leq x \leq 0.01$ may be due to the increase in the density of the ceramics, whereas the drop in Q for $x \geq 0.01$ is attributable to the influence of the additional, zinc-enriched phase. The Q of the samples sintered in an oxygen atmosphere is a weak function of zinc content in the range $0 \leq x \leq 0.03$ and decreases slightly as x increases to 0.04 (the material contains a significant amount of the additional phase). The effect of the sintering atmosphere on the Q of our samples seems to be associated with the slower zinc vaporization at a higher oxygen pressure. The largest increase in Q (by as much as 80%) in going from air to oxygen sintering was observed for stoichiometric $ZnNb_2O_6$. With increasing zinc content, the effect of sintering atmosphere on Q becomes notably weaker. These findings suggest that a major contribution to dielectric losses in our samples comes from the structural defects related to zinc deficiency in $ZnNb_2O_6$, whereas an excess of zinc does not impair the dielectric properties of the samples in the composition range studied. Note, however, that the Q of the air-sintered $x = 0.01$ material is somewhat higher than that of the oxygen-sintered one. It is reasonable to assume that partial zinc vaporization from slightly zinc-enriched samples has a favorable effect on the sintering behavior of the material, thereby improving its microstructure and raising its Q.

CONCLUSIONS

The present results suggest that the excess zinc enhances the sinterability of $Zn_{1+x}Nb_2O_{6+x}$, thereby raising the Q of the resulting ceramics. The Q of stoichiometric $ZnNb_2O_6$ sintered in an oxygen atmosphere is found to be notably higher than that of air-sintered $ZnNb_2O_6$, which is attributable to the lower density of defects resulting from zinc vaporization.

In the composition range $0.01 \leq x \leq 0.04$, the formation of an additional crystalline phase enriched in zinc impairs the dielectric properties of $Zn_{1+x}Nb_2O_{6+x}$. Some of the dielectric materials synthesized here offer record high microwave quality factors.

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