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Effect of Nonstoichiometry on the Structure and Microwave Dielectric Properties of $Ba(Co_{1/3}Nb_{2/3})O_3$

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Abstract—Polycrystalline nonstoichiometric $Ba(Co_{1/3}Nb_{2/3})O_3$ (BCN) materials have been synthesized and investigated. Deviations from stoichiometry have been shown to lead to the formation of crystalline $Ba_6CoNb_9O_{30}$ (barium deficiency) and $Ba_8CoNb_6O_{24}$ (cobalt deficiency). The effect of phase composition on the microwave dielectric properties of BCN has been studied. The results demonstrate that the dielectric properties of BCN-based materials can be tuned by varying cobalt content. The materials obtained are high-Q microwave dielectrics with temperature-stable properties.

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INTRODUCTION

The technology of modern wireless communication systems requires ceramic materials with record low dielectric losses (high quality factor $Q = 1/\tan\delta$) in the microwave range. The use of high-Q materials in microwave devices makes it possible to improve the sensitivity and selectivity of communication channels and reduce the noise level, thereby ensuring high efficiency and reliability of data transfer [1, 2].

The highest Q values have been achieved in materials based on the $Ba(M^{2+}_{1/3}Ta^{5+}_{2/3})O_3$ (M = Mg, Co, Zn) mixed perovskites [1–4]. These compounds have a 1 : 2 ordered superstructure formed by stacking of one M^{2+} and two Ta^{5+} layers in the [111] direction of a pseudocubic cell [5]. B-site cation ordering in multicomponent perovskites may have a significant effect on their microwave Q [6–8]. For example, long-term high-temperature (1500–1600°C) annealing was reported to substantially raise the Q of $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) owing to B-site cation ordering [3–6]. However, the high cost of tantalum oxide and the necessity of prolonged (more than 20 h) high-temperature heat treatments limit potential applications of the $Ba(M^{2+}_{1/3}Ta_{2/3})O_3$ materials. This has led many researchers to focus on niobium-containing perovskites with the general formula $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$, which can be prepared under milder conditions and are noticeably less expensive than their tantalum analogues [7–9].

$Ba(Co_{1/3}Nb_{2/3})O_3$ (BCN) offers a particularly attractive combination of properties. Polycrystalline $Ba(Co_{1/3}Nb_{2/3})O_3$ has high dielectric permittivity ($\varepsilon = 32$) and $Qf = 40000$–60000 GHz [6–8]. At the same time, centimeter and millimeter wave applications require higher Q values. The properties of BCN are very weak functions of temperature. In particular, the temperature coefficient of its resonant frequency (τ_f) lies in the range −10 to −7 ppm/K, suggesting that it can be used in the production of high-Q/low-τ_f microwave materials [10–12]. The electrical properties of BCN, especially its Q (or its Qf product, where f is frequency), strongly depend on preparation conditions, in particular on the sintering temperature, heat-treatment time, and heating/cooling rate. For example, according to Endo et al. [10], increasing the sintering time to 20 h or subsequent annealing for 20–60 h increased the Qf of BCN to 40000 GHz, which was attributed to an increase in the degree of 1 : 2 cation order. The sintering temperature was reported to have an insignificant effect on the properties of the BCN. At the same time, Ahn et al. [11] obtained the highest Qf values, on the order of 60 000 GHz, in a very narrow range of sintering temperatures: 1440–1450°C.

The origin of such discrepancies is unclear, which may hinder reproducible production of materials with tailored properties. It is reasonable to assume that the observed variations in the properties of BCN are related to the ceramic microstructure evolution during the fabrication process, cation ordering, and lattice distortions. Such distortions can be produced in BCN via slight changes in its cation composition. This led us to study the effect of partial cation nonstoichiometry on the phase composition, microstructure, and electrical properties of BCN.

EXPERIMENTAL

We studied the effect of nonstoichiometry in the A and B sublattices on the structure and properties of the

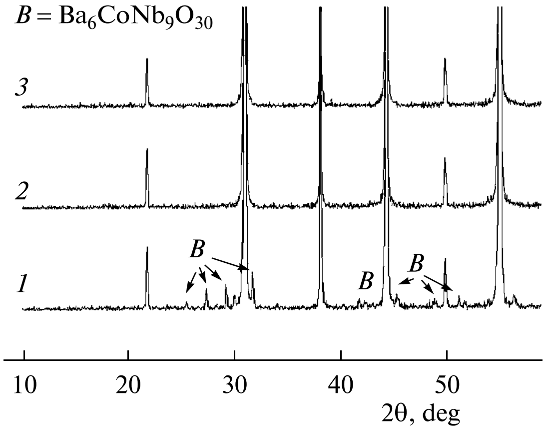

Fig. 1. XRD patterns of the $Ba_{3+3x}CoNb_2O_{9+3x}$ samples sintered at 1470°C for 8 h: x = (*1*) –0.1, (*2*) 0, (*3*) 0.01.

$Ba(Co_{1/3}Nb_{2/3})O_3$ niobate. To this end, we synthesized and investigated polycrystalline materials with the intended compositions $Ba_{3+3x}CoNb_2O_{9+3x}$ and $Ba_3Co_{1+y}Nb_2O_{9+y}$. The oxygen stoichiometry of the materials was not determined, so in what follows we use the above formulas.

The materials were prepared by solid-state reactions in two steps. The starting chemicals used were $BaCO_3$, Co_3O_4, and Nb_2O_5 (CERAC, USA). All of the chemicals were of extrapure grade (99.95%). Grinding and mixing were performed in a vibratory ball mill under water. In the first step, the cobalt and niobium oxides were reacted to give cobalt niobate, $CoNb_2O_6$. $Co_3O_4 + 3Nb_2O_5$ mixtures were preheat-treated for 4 h at temperatures from 1100 to 1200°C. In the second step, the resultant material was mixed with barium carbonate, $BaCO_3$, and the mixture was heat-treated in the range 1100–1200°C for 4 h. To synthesize polycrystalline materials, the heat-treated material was ground in a vibratory mill, the powder was pressed, and the green bodies were air-sintered for 8 h at temperatures from 1400 to 1500°C.

The phase composition and structural parameters of the heat-treated samples were determined by X-ray diffraction (XRD) on a DRON-3U diffractometer with CuK_α radiation. The microstructure and chemical composition of the synthesized crystalline phases were determined by scanning electron microscopy (SEM) on a JEOL JXA 840A equipped with an energy dispersive X-ray (EDX) spectrometer (Tracor Northern Series II X-ray microanalyzer system). Electron diffraction patterns of ceramic samples were obtained on a JEOL JEM-2000FX transmission electron microscope (TEM). The dielectric properties of the synthesized materials were studied at frequencies in the range 9–11 GHz by a dielectric resonator method using an Agilent N5230A PNA-L network analyzer.

RESULTS AND DISCUSSION

$Ba_{3+3x}CoNb_2O_{9+3x}$. The composition range studied in this system was $-0.1 \le x \le 0.01$. According to XRD data, the materials with x above zero ($0 \le x \le 0.01$)) were single-phase (Fig. 1, scans *2*, *3*). The same was evidenced by electron microscopy results (Figs. 2b, 2c). The samples with $x < 0$ contained an additional phase, which was identified by XRD as $Ba_6CoNb_9O_{30}$ (PDF no. 73-1879) (Fig. 1, scan *1*; Fig. 2a). EDX microanalysis of this phase in the samples with a considerable barium deficiency ($x = -0.1$) confirmed that its composition was $Ba_6CoNb_9O_{30}$. This compound was reported earlier to have the tetragonal tungsten bronze structure and to be in a ferroelectric state at room temperature [13]. $Ba_6CoNb_9O_{30}$ undergoes a broad phase transition around 360°C and shows hysteresis with a spontaneous polarization of $1.2(5) \times 10^{-2}$ cm^{-2} [13]. Note that, throughout the composition range studied, BCN has the cubic perovskite structure: no reflections attributable to 1 : 2 B-site cation ordering were detected (Fig. 1). Increasing the barium content leads to a monotonic increase in the relative density of the sintered samples and the corresponding slight increase in permittivity in the range $\varepsilon = 30$–33 in the single-phase region (Fig. 3a). Over the entire composition range studied, the temperature coefficient of resonant frequency, τ_f, varies little with barium content and lies in the range –20 to –7 ppm/K. At the same time, the quality factor Q drops sharply with increasing barium deficiency (x below zero) (Fig. 3b). This is due to the presence of the ferroelectric phase $Ba_6CoNb_9O_{30}$, which is characterized by considerable dielectric losses. Its content increases with decreasing x. Even the slight amount of this phase in the BCN sample with $x = -0.005$ leads to a considerable reduction in Q. It is of interest to note that, at x above zero (x ($0 \le x \le 0.01$)), where the BCN contains no $Ba_6CoNb_9O_{30}$, an increase in barium content within the single-phase region is accompanied by a reduction in Q (Fig. 3b). This may be due to the decrease in the density of the ceramics.

$Ba_3Co_{1+y}Nb_2O_{9+y}$. In this system, we studied the composition range $-0.15 \le y \le 0.03$. According to XRD data, the materials with $-0.05 \le y \le 0.03$ were single-phase (Fig. 4). As in the $Ba_{3+x}CoNb_2O_{9+x}$ system, no reflections attributable to 1 : 2 ordering were detected in the XRD patterns of the $Ba_3Co_{1+y}Nb_2O_{9+y}$ materials (Fig. 4). The BCN had the cubic perovskite structure.

At higher cobalt deficiencies ($y < -0.05$), the samples contained an additional phase (Figs. 2, 4). The positions and relative intensities of its XRD peaks were similar to those for the Zn-containing hexagonal perovskite $Ba_8ZnTa_6O_{24}$ (PDF no. 45-307) reported by Abakumov et al. [14]. Given this, the most likely composition of the phase in question is $Ba_8CoNb_6O_{24}$ [15]. The same is evidenced by EDX microanalysis of the samples with the largest deviation from stoichiometry

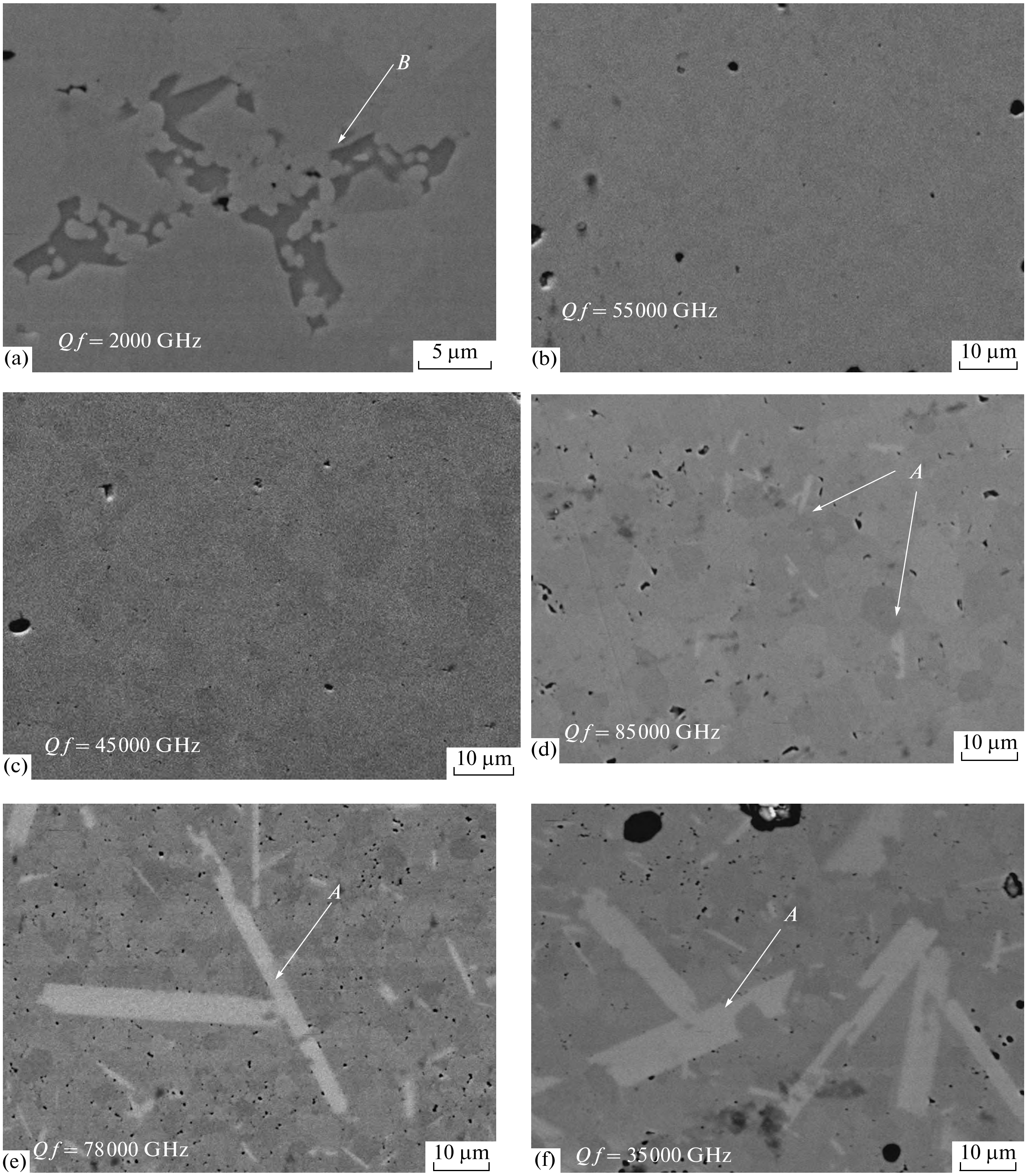

Fig. 2. Micrographs of polished sections of (a–c) $Ba_{3+3x}CoNb_2O_{9+3x}$ and (d–f) $Ba_3Co_{1+y}Nb_2O_{9+y}$ ceramics: x = (a) –0.1, (b) 0, (c) 0.01; y = (d) –0.07, (e) –0.1, (f) –0.15. $B = Ba_6CoNb_9O_{30}$, $A = Ba_8CoNb_6O_{24}$.

($y = -0.15$), in which the second-phase inclusions (phase A in Figs. 2d–2f) were larger than 20 μm in size.

Increasing the cobalt content in this system leads to a monotonic increase in relative density and the corresponding slight increase in permittivity ε in the range 32 to 34 (Fig. 5a). In the range $-0.15 \le y \le 0.03$, the quality factor varies nonlinearly, with a maximum at $-0.1 \le y \le -0.05$. The Qf product exceeds that of stoichiometric BCN by 30–50%, reaching 80000–85000 GHz (Fig. 5b).

Electron diffraction data for the $Ba_3Co_{1+y}Nb_2O_{9+y}$ samples indicates that cobalt deficiencies in the range

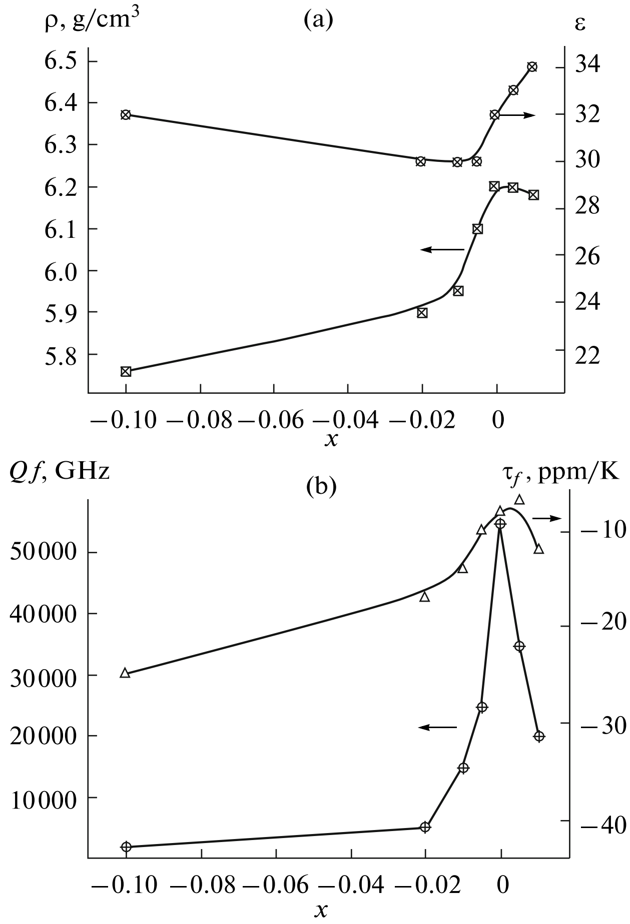

Fig. 3. Composition dependences of the (a) apparent density (ρ), permittivity (ε), (b) *Qf* product, and temperature coefficient of resonant frequency (τ_f) for $Ba_{3+3x}CoNb_2O_{9+3x}$ materials; measurements at 10 GHz.

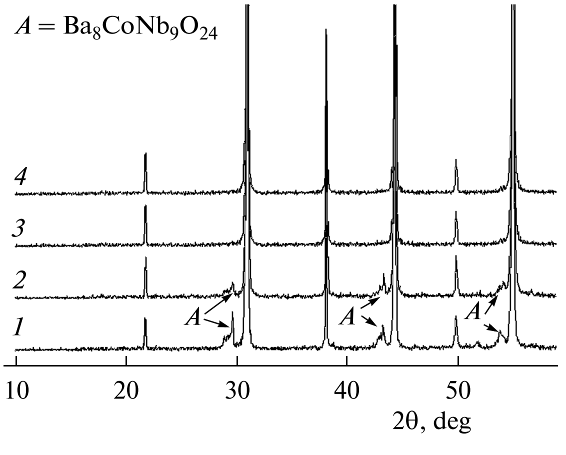

Fig. 4. XRD patterns of the $Ba_3Co_{1+y}Nb_2O_{9+y}$ samples sintered at 1470°C for 8 h: y = (*1*) −0.15, (*2*) −0.1, (*3*) 0, (*4*) 0.03.

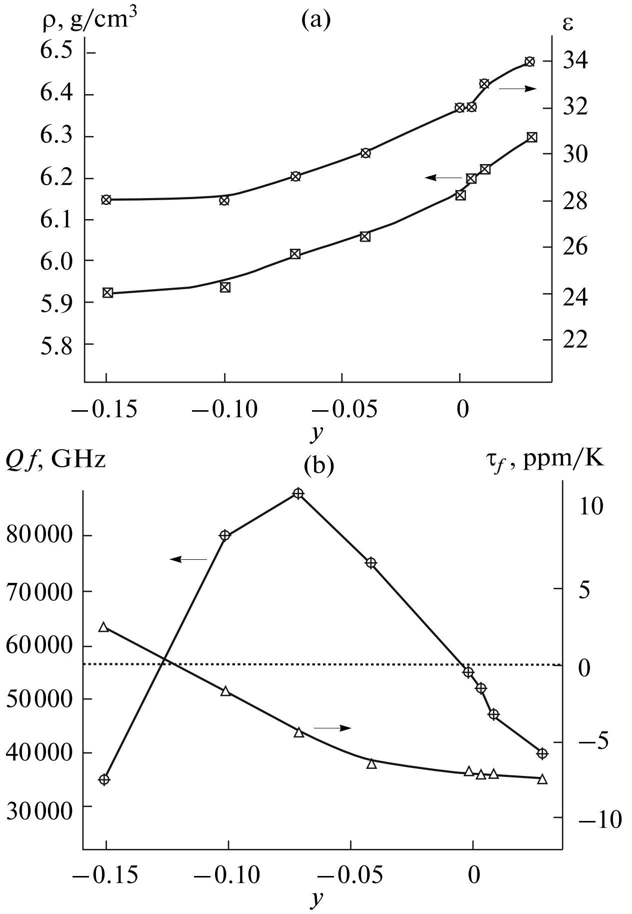

Fig. 5. Composition dependences of the (a) apparent density (ρ), permittivity (ε), (b) *Qf* product, and temperature coefficient of resonant frequency (τ_f) for $Ba_3Co_{1+y}Nb_2O_{9+y}$ materials; measurements at 10 GHz.

$-0.1 \le y \le -0.05$ are favorable for 1 : 2 B-site cation ordering in the cobalt-containing perovskite (Fig. 6). As mentioned above, cation ordering is accompanied by an increase in quality factor, as observed in this system (Fig. 5b). The reduction in quality factor at large deviations from stoichiometry ($y < -0.1$) is due to the presence of a significant amount of $Ba_8CoNb_6O_{24}$.

The increase in $Ba_8CoNb_6O_{24}$ content with increasing cobalt deficiency ($y < 0$) leads to a result of practical interest: the temperature coefficient of resonant frequency switches sign (Fig. 5b). The reason for this is that $Ba_3CoNb_2O_9$ and $Ba_8CoNb_6O_{24}$ differ in the sign of τ_f: −7 and +16 ppm/K, respectively [11, 15]. Because of this, the $Ba_3Co_{1+y}Nb_2O_{9+y}$ materials exhibit a temperature compensation effect, whose magnitude can be tuned by varying the cobalt content. The present results, therefore, suggest that cobalt-deficient $Ba(Co_{1/3}Nb_{2/3})O_3$ is an attractive host for engineering advanced temperature-stable microwave dielectric materials with *Qf* on the order of 80000–90000 GHz and $\tau_f = -2$ to +3 ppm/K.

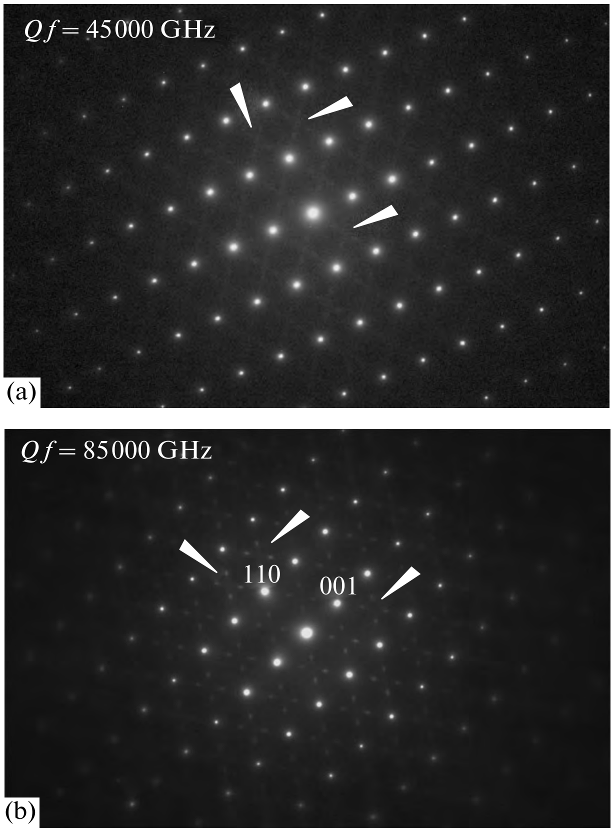

Fig. 6. [110] electron diffraction patterns of the $Ba_3Co_{1+y}Nb_2O_{9+y}$ samples with y = (a) –0.07 and (b) 0. The arrows mark superlattice reflections.

CONCLUSIONS

We studied the phase composition, microstructure, and dielectric properties of $Ba(Co_{1/3}Nb_{2/3})O_3$ with partial cation nonstoichiometry. The results indicate the formation of BCN-based solid solutions at slight barium or cobalt excesses. Barium-deficient BCN contains ferroelectric $Ba_6CoNb_9O_{30}$ (tetragonal tungsten bronze structure) as an impurity phase, which sharply reduces the quality factor Q of the material. The cobalt-deficient materials have two general tendencies. On the other hand, the presence of the hexagonal perovskite $Ba_8CoNb_6O_{24}$ reduces Q. On the other hand, cobalt deficiency is favorable for Co^{2+} and Nb^{5+} ordering, which increases Q. The competition between these tendencies results in a maximum in Q as a function of cobalt deficiency. At the same time, with an increase in the $Ba_8CoNb_6O_{24}$ content of nonstoichiometric BCN the temperature coefficient of its resonant frequency, τ_f, switches sign, while Q remains high.

We conclude that cobalt-deficient $Ba(Co_{1/3}Nb_{2/3})O_3$ is an attractive host for engineering advanced temperature-stable high-Qf microwave dielectric materials with Qf on the order of 80000–90000 GHz and $\tau_f = -2$ to +3 ppm/K.

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