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VERSITA

A-site deficient perovskites $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$: microstructural attributes for a high quality factor*

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Slight A-site deficiency in ordered perovskites $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$(M – Co, Zn, Mg) is shown to promote the formation of single-phase dense ceramics, in which the microwave (MW) quality factor Q attains its maximum values. Any further decrease in the Ba concentration in $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ always results in the formation of a multiphase material containing secondary phase with the tetragonal tungsten bronze (TTB) structure. The amount of TTB phase in the perovskite matrix was found to depend on both the Ba concentration and the sintering temperature. The composition and properties of the TTB phase are discussed in terms of their effect on the MW dielectric parameters of $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ ceramics.

Keywords: *ordered perovskites, cation deficiency, microwave naterials, dielectric properties.*

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1. Introduction

Complex perovskites $Ba(B'_{1/3}B''_{2/3})O_3$ (B' = Mg, Co, Zn; B'' = Ta, Nb) have been extensively studied for the last three decades. The research interest derives from the exceptionally high microwave (MW) quality factor (Q = 1/tanδ) inherent to these compounds, together with suitable temperature coefficient of resonance frequency (τ_f) [1–5]. For instance, $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$, for which the product Qxf (where f is the sampling frequency) is much higher than 100 000 GHz, have found numerous applications as commercial, high-Q dielectric resonator materials [1–5]. The extremely high Q-factor of a perovskite $Ba(B'_{1/3}B''_{2/3})O_3$ is generally ascribed to the 1:2 cation ordering in its B-subblatice [2, 6]. In the ordered state the perovskite structure comprises single layers of B^{2+} cations alternating with double layers of B^{5+} cations perpendicular to the <111> direction of the pseudocubic cell [6, 7]. Depending on the composition, cation ordering of a $Ba(B'_{1/3}B''_{2/3})O_3$ requires high temperatures (typically 1300 – 1500 °C) and long-duration annealing (typically 20 to 50 hours), and is therefore an expensive and hard-to-control process.

However, several authors have recently shown that the ordering processes in $Ba(B'_{1/3}B''_{2/3})O_3$ can be significantly promoted through the local structural changes initiated by either aliovalent ions (for instance Zr^{4+}) introduced into the structure [6], or by a slight adjustment of the stoichiometric composition [8–10]. It has been shown that a slight deficiency at both the A-site and the B-site in $Ba(B'_{1/3}B''_{2/3})O_3$ can make a noticeable improvement to Q. At the same time, there is no common agreement about whether the degree of 1:2

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cation ordering is the main reason for the variation in Q, for the perovskites $Ba(B'_{1/3}B''_{2/3})O_3$. Many authors consider the Q-magnitude to be predominantly influenced by "extrinsic" factors, like densification, microstructural defects and secondary phase. Moreover, there are several studies which report on the strong correlation between the microstructure, ordering degree, and Q-factor of the materials, based on non-stoichiometric perovskites $Ba(B'_{1/3}B''_{2/3})O_3$ [8, 10–13]. This is especially relevant for the Nb-based ordered perovskites which, in comparison with their Ta-containing analogues, generally show a more pronounced dependence on the dielectric parameters on the composition and the processing regimes [10–13]. Therefore, in this paper we tried to summarize the common peculiarities of the microstructure observed in a specific case of a slight A-site deficiency in $Ba(B'_{1/3}Nb_{2/3})O_3$ for different B' (Co, Zn, Mg) as well as to discuss their effect on the microwave dielectric parameters of a ceramic material.

2. Experimental

In this work A-site deficient perovskites $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ (M = Co, Zn, Mg) were studied. The ceramics were produced by the two-step mixed-oxide columbite route described elsewhere [14]. The starting reagents were extra pure (99.95%) ZnO, MgO, Co_3O_4 , Nb_2O_5, and $BaCO_3$. At the first stage the columbites $M_{1+x}Nb_2O_6$ were synthesized from the weighted mixtures of corresponding oxides by calcining them at 1100 – 1200 °C for 4 hours. At the second stage, the appropriate ratios of $BaCO_3$ and the corresponding columbite were ball milled again, and calcined at 1200 °C for another 4 hours. By contrast, the individual phases $Ba_9MNb_{14}O_{45}$ were produced from the same reagents by a single-step calcination procedure. The sintering was performed in air for 8 hours at temperatures in the 1350 – 1500 °C range. The phase composition and crystal lattice parameters of the sintered ceramics were examined by X-ray diffraction analysis (XRD) using CuKα - radiation (Model PW 1700, Philips, Eindhoven, The Netherlands). Microstructural analysis of the ceramic samples was performed by scanning electron microscopy (JEOL, JSM 5800, Tokyo, Japan) using energy dispersive X-ray spectroscopy (EDS) and the LINK software package (ISIS 3000, Oxford Instruments, Bucks, UK). The dielectric properties (ε and tan δ) of the ceramics were studied by means of a Solartron 1260 A Impedance Analyzer, whereas their low-temperature behavior was evaluated with an Agilent E4980 Precision LCR Meter in the 2.5 – 300 K temperature range, utilizing a home-made dielectric measurement probe coupled with a Physical Property Measurement System (Quantum Design, USA). The microwave dielectric characteristics of the materials (ε, Q, and τ_f) at frequencies around 10 GHz were examined using a cavity reflection method with the Network Analyser PNA-L Agilent N5230A.

3. Results and Discussion

3.1. Phase composition and ordering in the Ba-deficient perovskites $Ba(B'_{1/3}Nb_{2/3})O_3$

The studied Ba-deficient perovskites comprised $Ba_{1-x}(Co_{1/3}Nb_{2/3})O_{3-x}$ (BCN), $Ba_{1-x}(Zn_{1/3}Nb_{2/3})O_{3-x}$ (BZN), and $Ba_{1-x}(Mg_{1/3}Nb_{2/3})O_{3-x}$ (BMN). In all the studied systems, the compositions varied within the range of $0 \leq x \leq 0.1$. In the case of smaller x ($0 \leq x \leq 0.01$), the phase content of sintered ceramics differs, depending on the B^{2+} ion (Figs. 1-5).

Whereas well sintered BCN (relative density $\rho \geq 96\%$) has a single-phase composition at $x = 0$ only, BZN and BMN adopt Ba-deficiency up to $x = 0.01$. Unlike other materials, the phase content of BZN strongly depends on the sintering temperature: when the sintering temperature is increased from 1370 to 1450 °C, the stability region of the perovskite structure extends from $x = 0$ to $0 \leq x \leq 0.01$ (Figs. 3, 4). This phenomenon is most likely due to Zn losses, which are proportional to the temperature. As a consequence, at higher temperatures the system shifts towards a composition having a slight B-site deficiency ($Ba_{1-x}(Zn_{1/3}$-$\delta Nb_{2/3})O_{3-x}$-δ.

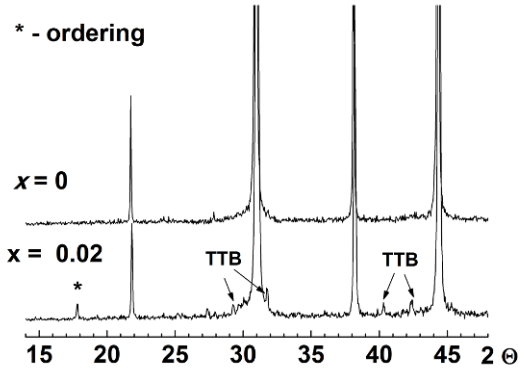


Fig. 1. XRD patterns collected on the crushed powder of the samples $Ba_{1-x}(Co_{1/3}Nb_{2/3})O_{3-x}$ sintered at 1470 °C for 8 hours. 1- $x = 0$; 2- $x = 0.02$; TTB - $Ba_9CoNb_{14}O_{45}$.

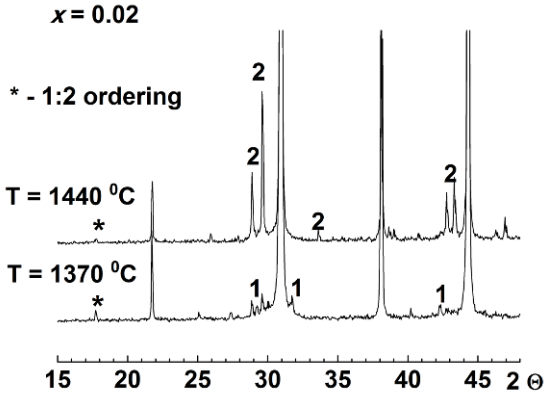
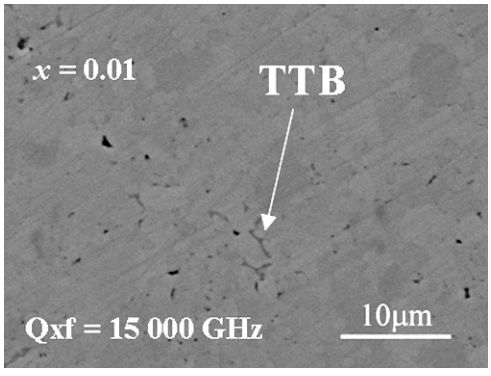
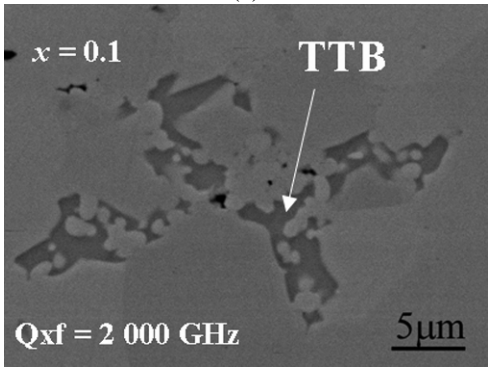


Fig. 3. XRD patterns collected on the crushed powder of the samples $Ba_{1-x}(Zn_{1/3}Nb_{2/3})O_{3-x}$ (x = 0.02) sintered at 1370 °C and 1440 °C for 8 hours. 1- $Ba_9ZnNb_{14}O_{45}$; 2- $Ba_5Nb_4O_{15}$.



(a)



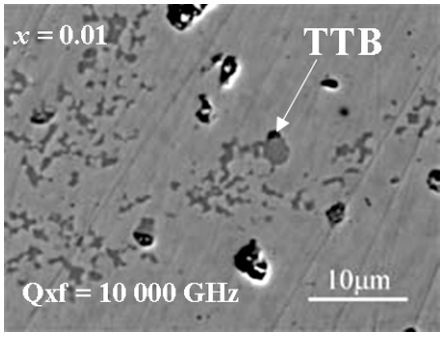
(b)

Fig. 2. SEM microphotographs of the polished surface of the ceramics $Ba_{1-x}(Co_{1/3}Nb_{2/3})O_{3-x}$ sintered at 1470 °C for 8 hours; (a) x = 0.01, (b) $x = 0.1$. TTB - $Ba_9CoNb_{14}O_{45}$.

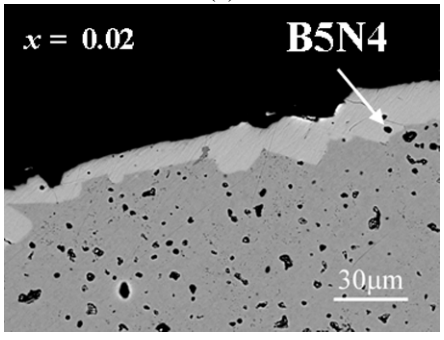
This fact is evident from the detailed examination of the sample edges, which contain Zn-deficient phase (Fig. 4b,d). According to the EDS analysis, the composition of this phase is close to $Ba_5Nb_4O_{15}$ – a 5-layered perovskite-derivative. This compound contains ordered layers of cation vacancies, and is known to form as a secondary phase in the B-site deficient perovskites $Ba(B'_{1/3}Nb_{2/3})O_3$. The area of this phase is distributed at the edges of the samples, and extends when there is a rise in temperature, and attains a depth of 100–200 μm (Fig. 4d). Therefore, in a strict sense, BZN samples are never single-phase compositions, because they always contain a small amount of secondary $Ba_5Nb_4O_{15}$ on the surface.

According to the X-ray diffraction analysis of sintered BZN and BMN samples, we do not see any noticeable improvement to the 1:2 cation ordering with the Ba-deficiency: the intensities of the corresponding X-ray peaks vary only slightly with the composition (Figs. 3, 5).

However, in the case of BCN a significant increase in the intensity of the (100) ordering peak is observed in the multiphase materials (Fig. 1). Apparently, according to the obtained results, one may expect the 1:2 cation ordering to have a much weaker (when compared with other factors) in-



(a)



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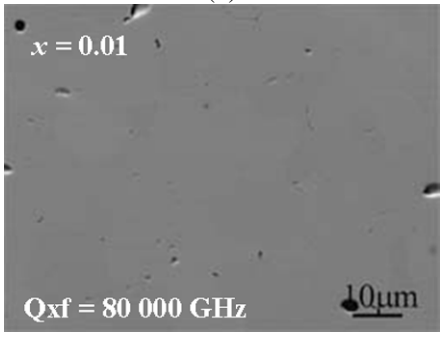

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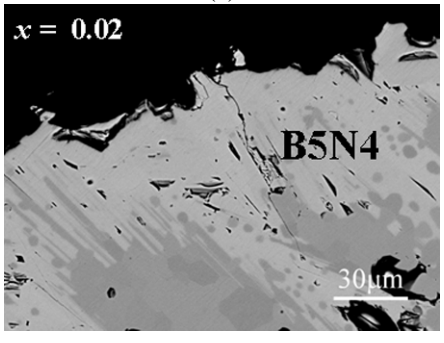


(d)

Fig. 4. SEM microphotographs of the polished surface of the ceramics $Ba_{1-x}(Zn_{1/3}Nb_{2/3})O_{3-x}$ sintered at 1370 °C (a,b) and 1450 °C (c,d) for 8 hours; (b) and (d) represent the Zn-free areas on the samples' edges. B5N4 - $Ba_5Nb_4O_{15}$; TTB - $Ba_9ZnNb_{14}O_{45}$

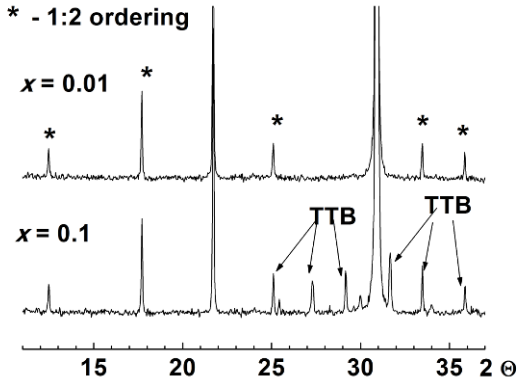


Fig. 5. XRD patterns collected on the crushed powder of the samples $Ba_{1-x}(Mg_{1/3}Nb_{2/3})O_{3-x}$ sintered at 1550 °C for 8 hours. TTB-$Ba_9MgNb_{14}O_{45}$

fluence on the microwave dielectric properties of Ba-deficient perovskite niobates. This fact is more than evident in the case of higher levels of Ba-deficiency, when the formation of secondary phases is observed. Regardless of the B^{2+} cation, these additional phases have similar structures, and correspond to the $Ba_9B^{2+}Nb_{14}O_{45}$ compounds that been further confirmed by the EDS analysis. The 9:1:7 phases $Ba_9B^{2+}Nb_{14}O_{45}$ have been synthesized before, and studied by Zhang et al. for B^{2+} = Co and Zn [15, 16]. These compounds have the tetragonal tungsten bronze (TTB) structure, for which very similar lattice parameters have been reported. However, the dielectric parameters of these TTB phases are not yet known, excepting one recent work in which strong frequency dependence together with high dielectric loss of $Ba_9MgNb_{14}O_{45}$ were measured [17]. Therefore, in order to elucidate the effect of the TTB phases in Ba-deficient BCN, BZN, and BMN, we isolated the corresponding compounds and measured their dielectric properties.

3.2. Properties of $Ba_9B^{2+}Nb_{14}O_{45}$ TTB phase

According to both the XRD patterns (Fig. 6) and the SEM data, single phase $Ba_9B^{2+}Nb_{14}O_{45}$ materials are formed for all of the B^{2+} (Co, Zn,

Mg). Only in the case when B^{2+} = Zn, the TTB matrix then also contains a negligible amount of $Ba_5Nb_4O_{15}$,which probably derives from the ZnO evaporation. It should be noted that all of the sintered TTB phases exhibit a low melting temperature of around 1400 – 1450 °C, which is comparable with the sintering temperature of the corresponding perovskite. Therefore, the TTBs act as liquid phases during the sintering of BCN, BZN, and BMN, and are uniformly distributed between the grains of perovskite matrix.

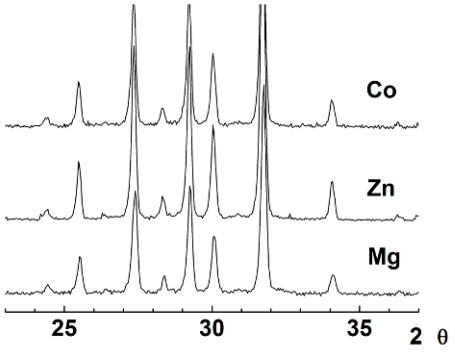
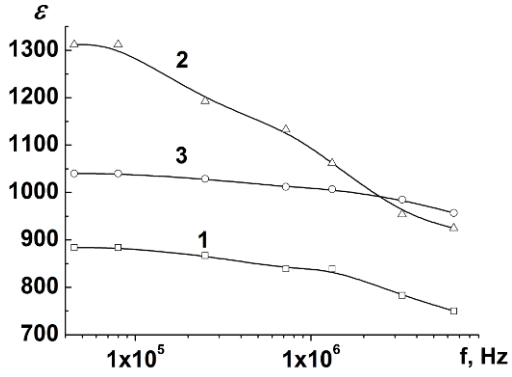


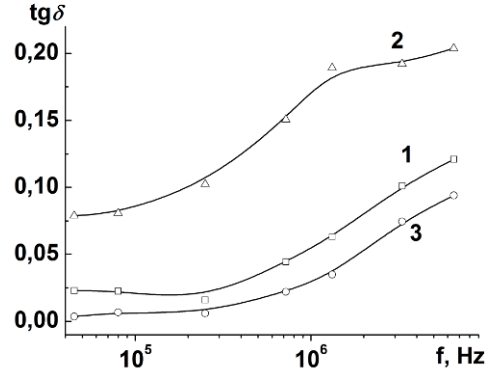
Fig. 6. XRD patterns collected on the crushed powder of sintered samples $Ba_9B^{2+}Nb_{14}O_{45}$ (B^{2+} = Co, Zn, Mg).

All the studied 9:1:7 TTB phases possess high permittivity, lying in the range ε = 700 – 1000, at frequencies of 1 – 6 MHz. These permittivities increase slightly with the ionic radii of the B^{2+} (Fig. 7a). Also, the TTB phases demonstrate strong frequency dispersion of permittivity, which is the most pronounced in the case of $Ba^9ZnNb_{14}O_{45}$. The observed dispersion of permittivity is accompanied by a monotonic rise in the dielectric loss (Fig. 7b).

Low-temperature measurements of the dielectric spectra of $Ba_9B^{2+}Nb_{14}O_{45}$ revealed all the studied TTB compounds exhibited typical relaxor behavior. The broad maxima for the temperature dependencies of ε and tan δ were found around -150 – -100 °C in the case of B^{2+} = Co, Mg, and around -100 – 0 °C in the case of B^{2+} = Zn. This fact explains why $Ba_9ZnNb_{14}O_{45}$ was observed to



(a)



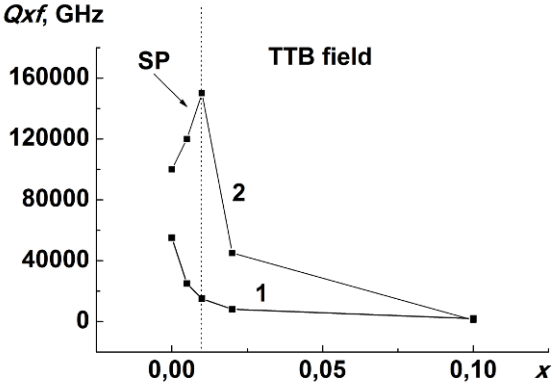
(b)

Fig. 7. Frequency dependencies of the dielectric permittivity (a) and dielectric loss (b) of sintered $Ba_9B^{2+}Nb_{14}O_{45}$;B^{2+} = Co (1), Zn (2), Mg (3).

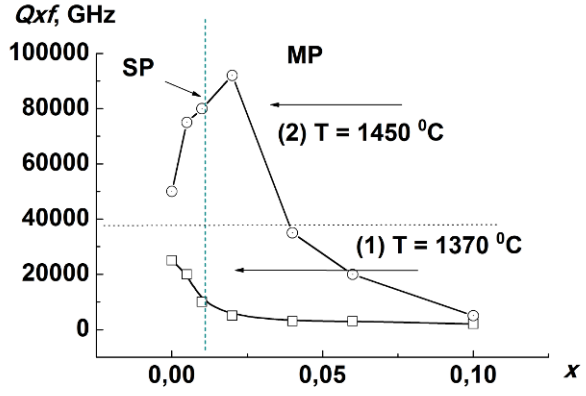
have the highest dielectric loss (tan δ = 0.1 – 0.2 at several MHz). Summarizing the obtained results, one may expect an even higher loss level in the microwave range. However, this requires further investigation.

3.3. Microwave dielectric properties of Ba-deficient perovskites $Ba(B'_{1/3}Nb_{2/3})O_3$

According to the measured data, the presence of $Ba_9B^{2+}Nb_{14}O_{45}$ secondary phase ought to make a prominent effect on the dielectric properties of the sintered materials. But in fact, apart from a slight deviation in the stoichiometric composition $Ba(B'_{1/3}Nb_{2/3})O_3$, the amount of $Ba_9B^{2+}Nb_{14}O_{45}$ is negligible, and the permittivity of the sintered

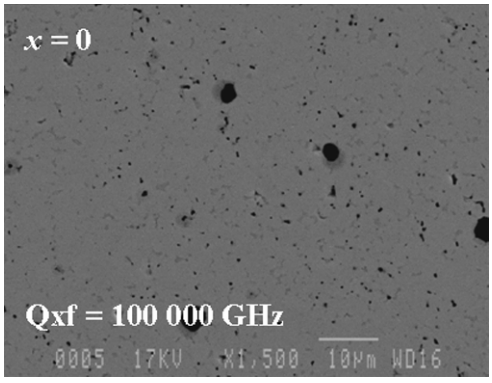


(a)

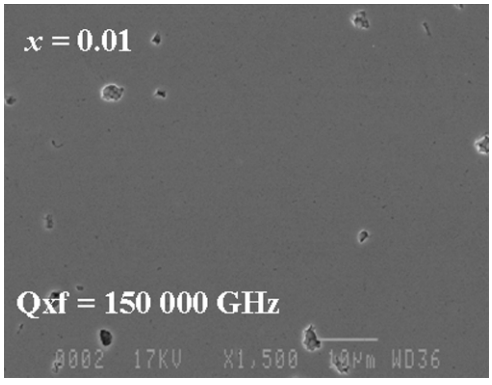


(b)

Fig. 8. *Qxf* product (measured at 10 GHz) of the samples (a) $Ba_{1-x}(Co_{1/3}Nb_{2/3})O_{3-x}$ (1) and $Ba_{1-x}(Mg_{1/3}Nb_{2/3})O_{3-x}$ (2) and (b) $Ba_{1-x}(Zn_{1/3}Nb_{2/3})O_{3-x}$ as a function of Ba content; MP- multiphase region, SP- single-phase region



(a)



(b)

Fig. 10. SEM microphotographs of the polished surface of the ceramics $Ba_{1-x}(Mg_{1/3}Nb_{2/3})O_{3-x}$ sintered at 1550 °C for 8 hours; (a) $x = 0$; (b) $x = 0.01$.

materials varies only slightly within the range of $\varepsilon = 30 - 33$ (for BCN and BMN) and $\varepsilon = 39 - 41$ (for BZN). At the same time, depending on the B^{2+}, the magnitude of the *Q*-factor appears strongly correlated with the level of Ba-deficiency (Fig. 8). For instance, small stoichiometric change in the Ba-deficient BCN induces a significant decrease in the *Q*-factor (see Fig. 8a, curve 1). By contrast, the *Q*-factor of Ba-deficient BMN passes through a maximum at $x = 0.01$, when the composition is still single-phase, and decreases for higher values of x, i.e. in the stoichiometric region corresponding to TTB phase (Fig. 8a, curve 2). According to the data measurements, one can see that in all cases the rapid drop in the *Q*-factor always correlates with the amount of TTB phase present in the material. Similar behavior is observed in the *Q*-factor associated with Ba-deficient BZN sintered at a lower temperature ($x > 0$) and at higher temperature ($x > 0.02$) (Fig. 8b). What this means, exactly, is that the presence of the 9:1:7 TTB phase, even if it is added in small quantities, is the most dominant factor affecting dielectric loss in Ba-deficient perovskites.

At the same time, when no TTB phase is detectable in the ceramics, even a slight deviation in the stoichiometry can significantly increase the *Q*-factor magnitude, both for Ba-deficient BZN as well as for BMN (see Fig. 8) . The observed maxima of the *Q*-factor, occurring at $x = 0.02$ (for

BZN) and x = 0.01 (for BMN), cannot be ascribed to the effect of the 1:2 cation ordering, since no noticeable increase in the intensities of superstructural XRD peaks was detected. It is most likely that changes in the Q-factor magnitude are due to the improved sintering of the ceramics; ceramics having slightly Ba-deficient compositions have demonstrably less porous microstructures (see Figs. 4 and 9).

4. Conclusions

On the basis of the results obtained, it is now possible to identify the main factors responsible for the variation in the Q-factor associated with the A-site deficient perovskites $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$ (where M = Co, Zn, or Mg). These factors include: (a) improvement to the microstructure of the ceramics, in the case of slight Ba-deficiency, and; (b) formation of a high-loss relaxor 9:1:7 TTB secondary phase $Ba_9M^{2+}Nb_{14}O_{45}$, which significantly lowers the Q-factor magnitude of the multiphase material. As a consequence, extremely high Q-factors were attained for the Ba-deficient BZN (Qxf = 100 000 GHz) and BMN (Qxf = 150 000 GHz) under relatively "soft" conditions, without requiring additional, long-duration annealing.

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