

# Order-disorder transition and its effect on microwave quality factor $Q$ in $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ system

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Received: 25 June 2005 / Revised: 10 February 2006 / Accepted: 5 June 2006  
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**Abstract** Influences of composition deviation from stoichiometry and heat treatment on crystal phases and  $Q$  factor in  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (BZN) were studied. The structural order and the crystal phases strongly depended on the slight composition deviation from stoichiometric BZN. The maximum  $Q$  factor was obtained at the vicinity of the stoichiometric BZN. In the other regions, non-stoichiometric disordered BZN or ordered BZN with secondary phase were formed, and their  $Q$  factors were found to be low. For the stoichiometric BZN, the order-disorder phase transition occurred between 1300 and 1400°C. The crystal-structural ordering of the stoichiometric BZN was improved by post-annealing at below its transition temperature, conserving the density and the grain size. However, no significant  $Q$  factor improvement was found. The  $Q$  factor of the stoichiometric BZN strongly depends on the density and grain size not on the crystal-structural order. These results suggest that the ceramic microstructure such as the pore and grain boundary, the secondary phase and lattice defect caused by non-stoichiometry affect the variation of the  $Q$  factor in BZN system than the crystal-structural ordering.

**Keywords** Dielectric properties · Perovskite · X-Ray methods ·  $Q$  factor · Ordering

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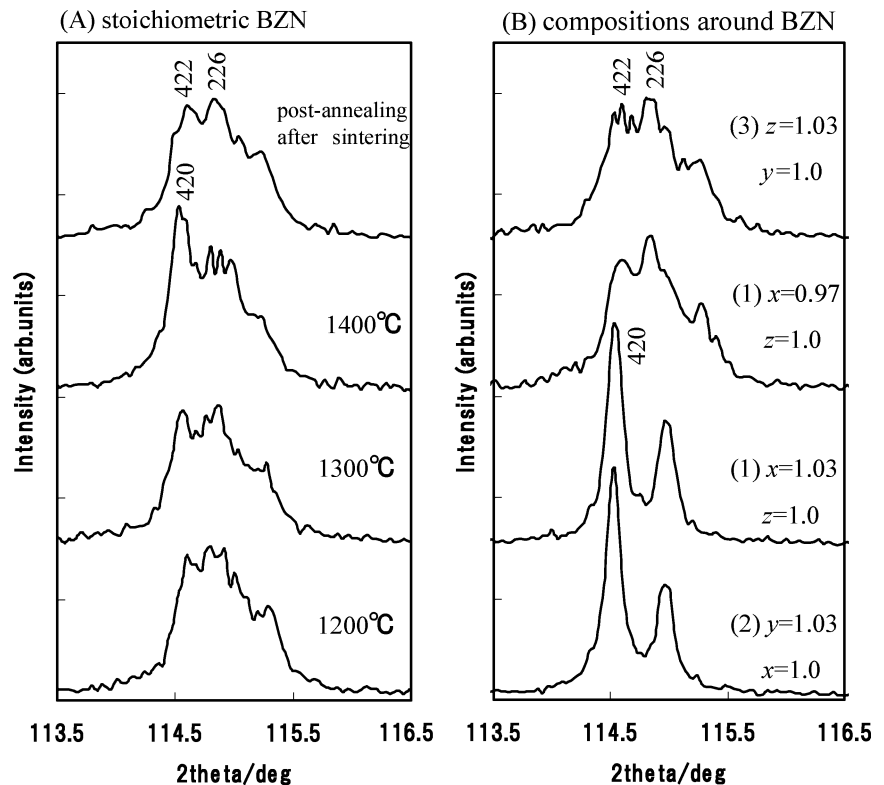
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## 1 Introduction

The complex perovskite with the general formula  $A(\text{B}_{1/3}\text{B}_{2/3})\text{O}_3$  have an exceptionally high  $Q$  factor ( $Q \cdot f \approx 10 \times 10^4$  GHz) at microwave frequency, and have been used as dielectric resonator material for the mobile communication [1, 2]. The dielectric properties have been mainly discussed on the basis of the crystal structure [2–4]. The complex perovskite can form disordered-type with a cubic phase space group of  $Pm\bar{3}m$  or ordered-type with a trigonal space group of  $P3m1$  [5]. In case of  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (BZT) and  $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (BMT), depending on the synthesize conditions, both ordered and disordered-type were formed [2, 6]. Their  $Q$  factors are improved with the superlattice ordering enhancement by long-time sintering (e.g. around 100 h). Therefore, the structural order has been generally considered playing an important role in the  $Q$  factors improvement [2–4]. However, usually, a significant ceramic microstructure difference between the ordered and the disordered perovskite was found [7]. Dense ceramics (density  $\approx 7.76 \text{ g/cm}^3$ ) was obtained in the ordered perovskite with the relatively larger grain (1.0–1.5  $\mu\text{m}$ ). In contrast, the disordered perovskite has the lower density (density  $\approx 5.0 \text{ g/cm}^3$ ) with the smaller grain size (0.4–0.6  $\mu\text{m}$ ). Recently, author et al. reported that not only the crystal-structural ordering but also the ceramic microstructure strongly influenced the  $Q$  factor of BZT [7]. These two factors strongly related each other in the BZT system. Therefore, we could not discuss their influence on the  $Q$  factors separately. On the other hand, in the case of  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (BZN), much higher  $Q$  factor was found in the disordered phase sintered below 1350°C than the ordered-phase sintered above 1350°C [8]. The influence of the crystal-structural ordering and the microstructure on the high  $Q$  factor is far from fully understanding.

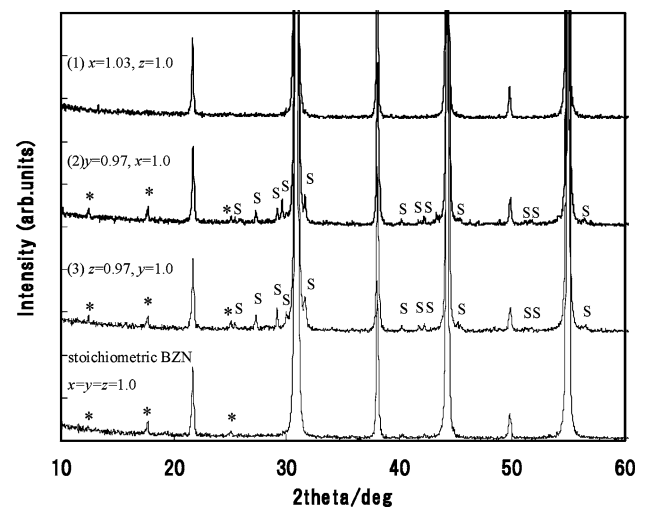
**Fig. 1** Powder XRD patterns ( $2\theta = 113.5$  to  $116.5/\text{deg}$ ) of (A) the stoichiometric BZN ( $x = y = z = 1.0$ ) sintered at various temperatures and annealed at  $1200^\circ\text{C}$  after sintering at  $1400^\circ\text{C}$ , and (B) composition deviations near BZN in  $x\text{BaO}-y1/3\text{ZnO}-z2/3\text{NbO}_{5/2}$  system ( $x + y + z = 3.0$ ) sintered at  $1300^\circ\text{C}$ , respectively



In this paper, we studied the influence of the crystal-structural ordering, microstructure, secondary phase and lattice defect on the high  $Q$  factor of the BZN, using series of the samples with their compositions near the stoichiometric BZN.

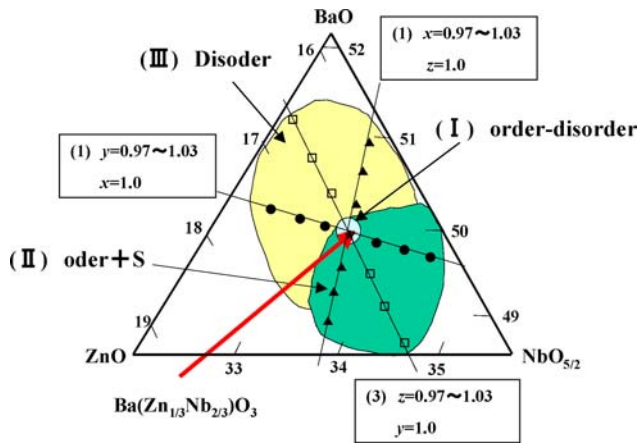
## 2 Experimental procedure

$\text{BaCO}_3$ ,  $\text{ZnO}$  and  $\text{Nb}_2\text{O}_5$  powders with purity of 99.9% or more were used as raw materials. These raw material powders were weighed as per the general formula  $x\text{BaO}-y1/3\text{ZnO}-z2/3\text{NbO}_{5/2}$  ( $x$ ,  $y$  and  $z = 0.97$  to  $1.03$ ,  $x + y + z = 3.00$ ) and ball milled in polyethylene bottles with zirconia balls ( $\varphi 5$  mm) and water for 20 h. The powder was calcined at  $1100^\circ\text{C}$  for 2 h. The calcined powder was milled for 20 h. After drying, the powders were granulated with organic binder by mesh screen. The powder was pressed into cylindrical shapes, and sintered at 1200, 1300 and  $1400^\circ\text{C}$  for 100 h in air. For the sample sintered at  $1400^\circ\text{C}$ , post-annealing was performed at  $1200^\circ\text{C}$  for 100 h. The crystal structure was examined by powder XRD. XRD measurements were performed using conventional XRD equipment with  $\text{CuK}\alpha$  radiation, and measuring condition: a step width of  $0.04^\circ$ , count time of 1 s per step and measuring range of  $10$  to  $150^\circ$  in  $2\theta$ . The density was calculated from sample weight and dimension. The grain size was measured by



**Fig. 2** Powder XRD patterns ( $2\theta = 10$  to  $60/\text{deg}$ ) of composition deviations near BZN in  $x\text{BaO}-y1/3\text{ZnO}-z2/3\text{NbO}_{5/2}$  system ( $x + y + z = 3.0$ ) sintered at  $1300^\circ\text{C}$ . S and \* in Fig. 2 show as follows: S: secondary phase peak, \*: superlattice peak indexed as the ordered perovskite, respectively

observation on surface of the sintered samples using scanning electron microscope (SEM). The dielectric properties were measured at 4 to 6 GHz using a network analyzer. The  $Q$  factor was determined by resonant cavity method in the  $\text{TE}_{018}$  mode.



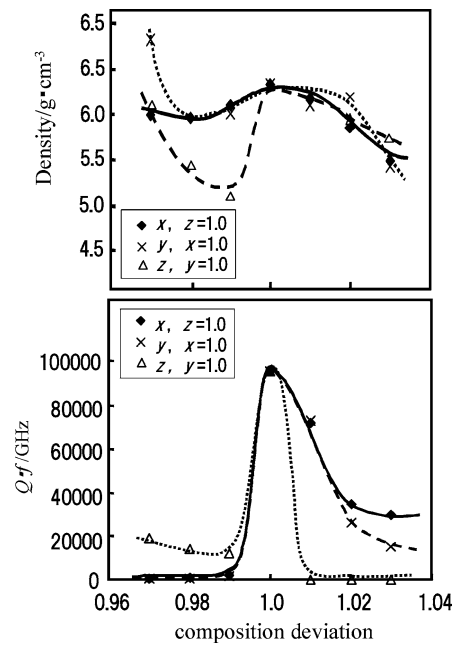
**Fig. 3** Partial ternary phase diagram near BZN in  $x\text{BaO}-y1/3\text{ZnO}-z2/3\text{NbO}_{5/2}$  system ( $x + y + z = 3.0$ ). S shows presence of secondary phase detected by XRD. Order: Ordered perovskite (trigonal), Disorder: Disordered perovskite (cubic)

### 3 Results and discussion

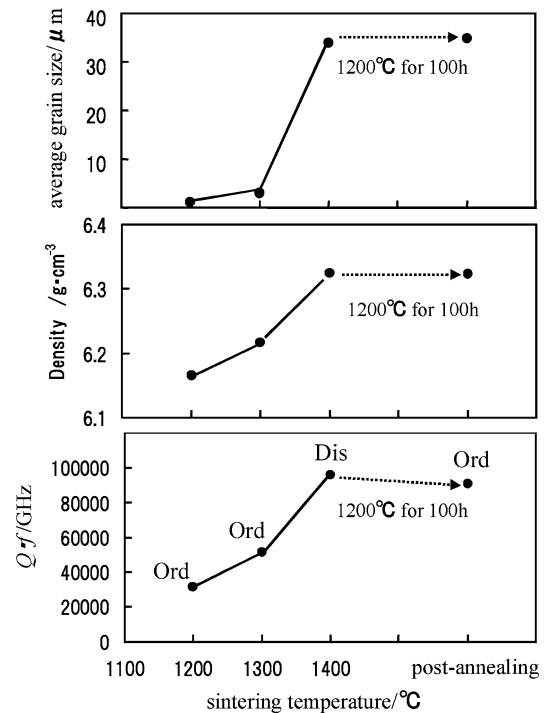
#### 3.1 Order-disorder transition in BZN system caused by slight composition deviation and heat treatment

By sintering at various temperatures and post-annealing, the crystal-structural phase in the BZN system was studied for three series of compositions: (1)  $x = 0.97$  to  $1.03 = (2 - y)$  at  $z = 1.0$ , (2)  $y = 0.97$  to  $1.03$  at  $x = 1.0$  and (3)  $z = 0.97$  to  $1.03$  at  $y = 1.0$ , respectively. The structural ordering is often estimated by the intensity of superlattice peak 100 and peak separation of 422 and 226 in XRD pattern. In case of BZN, the superlattice peak observation was difficult due to their extremely weak intensity. Therefore, we evaluated the ordering for BZN system by the peak separation in XRD patterns. Figure 1 shows XRD patterns ( $2\theta = 113$  to  $115^\circ$ ) of the stoichiometric BZN ( $x = y = z = 1.00$ ) sintered at various temperature and of several samples near BZN. Figure 2 shows XRD patterns ( $2\theta = 10$  to  $60^\circ$ ) for several samples near BZN sintered at  $1400^\circ\text{C}$ . The stoichiometric BZN sintered at  $1200$  and  $1300^\circ\text{C}$  showed the peak separation as indexed the ordered-type, whereas, at  $1400^\circ\text{C}$ , the peak separation was not found, the peak of 420 indexed as the disordered-type. This clearly showed the order-disorder phase transition occurred temperature between  $1300$  and  $1400^\circ\text{C}$ . This phase transition detected in our study agreed with former reported by electron diffraction pattern [8, 9].

In near stoichiometric BZN, both order and disorder phase was found. The ordered phase were found in the composition range of (1)  $x = 0.97$  to  $0.99$ , (2)  $y = 0.97$  to  $0.99$  and (3)  $z = 1.01$  to  $1.03$  in each composition series respectively. In these regions, the perovskite formed the ordered-type. Most of the ordered phase in this system were containing secondary phases. However, for the stoichiometric BZN, the secondary phase was not detected by XRD. The extra peaks by the



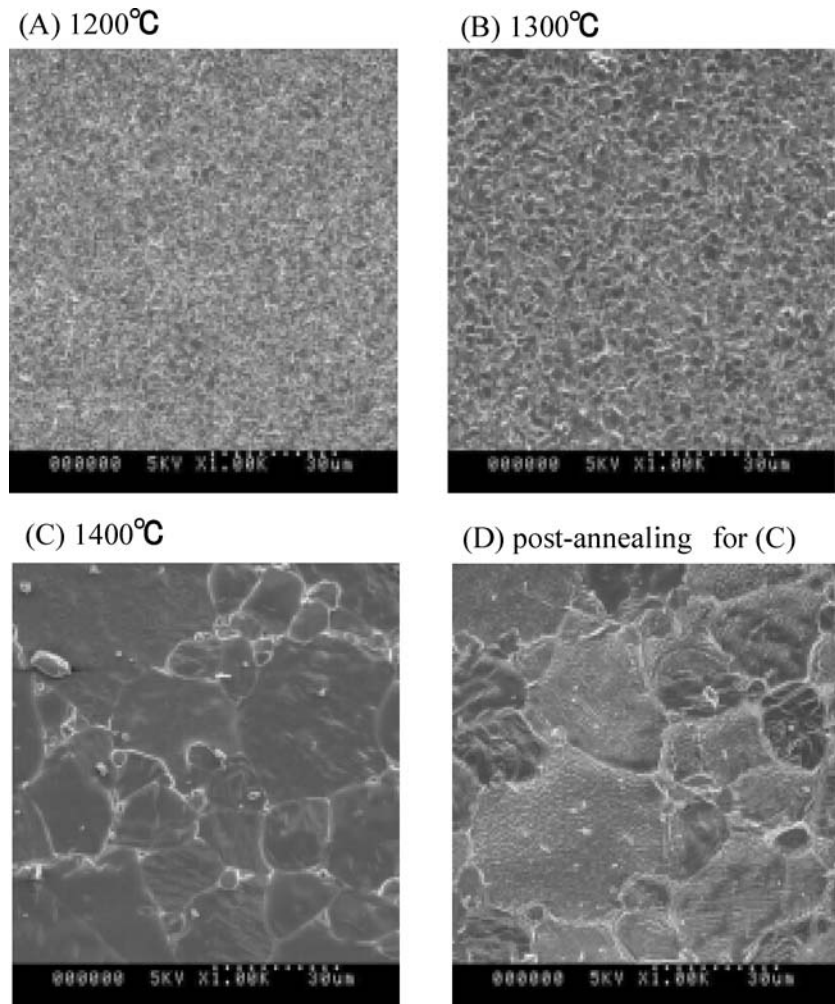
**Fig. 4**  $Q \cdot f$  and density dependence of composition deviations near BZN in  $x\text{BaO}-y1/3\text{ZnO}-z2/3\text{NbO}_{5/2}$  system ( $x + y + z = 3.0$ ) sintered at  $1400^\circ\text{C}$



**Fig. 5**  $Q \cdot f$ , density and average grain size dependence of the stoichiometric BZN as functions of various heat treatments. Ord: Ordered perovskite (trigonal), Dis: Disordered perovskite (cubic)

secondary phase situated around  $2\theta = 25$  to  $60^\circ$  mainly appeared in the ordered phase region. On the other hand, in the composition range of (1)  $x = 1.01$  to  $1.03$ , (2)  $y = 1.01$  to  $1.03$  and (3)  $z = 0.97$  to  $0.99$ , formed the disordered phase, since the peak of 420 reflection from cubic phase was only

**Fig. 6** SEM images from the free surface (each sample in Fig. 5) of the stoichiometric BZN as functions of various heat treatments



observed. In this region, no secondary phase was found by XRD. Therefore, the single phase of the non-stoichiometric disordered BZN can be formed, which may have the lattice defect caused by slight non-stoichiometry in the crystal.

To confirm the phase transition for the stoichiometric BZN, we performed the post-annealing for the stoichiometric disordered BZN at 1200°C for 100 h. This temperature was chosen in the sintering temperature range of the formation of the ordered-type. This result is shown in Fig. 1. The phase transition from disorder phase to order phase occurred by the post-annealing. Thus, the post-annealing at well below transition temperature for the disordered stoichiometric BZN was found to be effective for improvement of the crystal-structural ordering.

From these results, crystal-structural phase diagram near the stoichiometric BZN is shown in Fig. 3. The crystal-structural phases of the BZN system are distinguished into three parts as follows: (I) single phase ordered-disordered perovskite (vicinity of the stoichiometric BZN), the structural order depends on the heat treatment conditions. (II) ordered perovskite with the secondary phase (Nb-rich region)

and (III) non-stoichiometric disordered perovskite (Ba-rich or Nb-poor region). This crystal structural phase diagram was similar to that of BZT reported by author et al. [10, 11].

### 3.2 Relationship the $Q$ factor and order-disorder transition in BZN system

Figure 4 shows the  $Q$  factor and the density dependence of composition deviations near BZN sintered at 1400°C. The  $Q \cdot f$  and the density showed large variation depending on their compositions. The high  $Q$  factors were only obtained in the vicinity of the stoichiometric BZN shown as (I) in Fig. 3. In the other regions, despite of the similar high density to that of the stoichiometric BZN, the  $Q$  factors were low. The  $Q$  factors were not improved by higher sintering temperature at 1400°C. Both ordered BZN with the secondary phases and non-stoichiometric disordered BZN showed the lower  $Q$  factor. This indicates that the decrease of the  $Q$  factors in the ordered BZN with the secondary phase can attribute to presence of the small amount of the secondary phase, the lower  $Q$  factors in the non-stoichiometric disordered BZN

may be a cause of the presence of lattice defects, which were formed by excessive Ba and poor Nb concentration than the stoichiometric BZN.

Figure 5 shows the  $Q$  factor, the density and the average grain size as functions of various heat treatment conditions. The  $Q$  factor of the stoichiometric BZN increased with increasing of sintering temperature. The significant  $Q$  factor improvement was found in the sintering temperature between 1200 to 1400°C. Thus, the stoichiometric disordered BZN sintered at 1400°C showed the higher  $Q$  factor ( $Q \cdot f = 95,700$  GHz) than the stoichiometric ordered BZN obtained by sintering at 1200 and 1300°C.

In order to examine the effect of the  $Q$  factor improvement of the stoichiometric BZN, we examined the ceramic microstructure analysis at the various heat treatments. Figure 6 shows SEM images from the free surface of the each sample in Fig. 5. The samples sintered at 1200 and 1300°C with the lower  $Q$  factor had the average grain size of 1.2 and 2.6  $\mu\text{m}$  and the density of 6.166 and 6.216  $\text{g}/\text{cm}^3$ , respectively. When the stoichiometric BZN was sintered at 1400°C, the disordered perovskite was formed and the drastic increase of  $Q$  factor, density and grain size with the ceramics densification were found. The average grain size and density of the sample sintered at 1400°C was about 34  $\mu\text{m}$  and 6.324  $\text{g}/\text{cm}^3$ . The improvement of the  $Q$  factor with increase in the sintering temperature well corresponds to the grain growth and the densification. By the post annealing at 1200°C for the disordered stoichiometric BZN, the ordered perovskite was obtained with the same grain size and density before the annealing. Therefore, comparing these samples, an effect of the ordering on the  $Q$  factor with the similar microstructure can be evaluated. These results are also shown in Figs. 5 and 6. No significant  $Q$  factor improvement was found by the crystal-structural ordering enhancement by the post-annealing. From this result, we can conclude the crystal-structural ordering in ceramics BZN system has no significant effect on the  $Q$  factor improvement. The  $Q$  factor of the stoichiometric BZN strongly depends on the density and grain size but not on the crystal-structural order. The large  $Q$  factor improvement for the stoichiometric BZN can be attributed to the drastic densification mainly. Therefore, ceramics microstructure, such as, pore and the grain boundary around the crystal grain should play a major role in the variation of the  $Q$  factor of stoichiometric BZN. To reveal the variation of the  $Q$  factors thoroughly, further studies to determine their effects on the  $Q$  factors are required.

## 4 Conclusions

Influences of composition deviations from the stoichiometry and the heat treatments on the crystal phases and the  $Q$  factor in the BZN system were studied. Our findings are listed below. (1) The structural order and the crystal phases depend on the slight composition deviation from the stoichiometric BZN and on the heat treatment. (2) For the stoichiometric BZN, the order-disorder phase transition occurred between 1300 and 1400°C. (3) Regardless the crystal-structural ordering the stoichiometric BZN with high density and large grain size exhibited the significant high  $Q$  factors ( $Q \cdot f \sim 9 \sim 10 \times 10^4$  GHz). This result suggests that the pore and grain boundary around the crystal grain should affects the variation of the  $Q$  factor than the crystal-structural ordering. (4) In the other regions, by the slight composition deviation from stoichiometry, the ordered BZN with the secondary phase or the non-stoichiometric disordered BZN with low density were formed. Since the  $Q$  factors were found to be low, the presence of the secondary phases, the lattice defect and low density were considered to be causes of the decrease of the  $Q$  factors in this system. From these results for BZN system, the highly dense ceramics with large grain size in the microstructure and the suppressions of the secondary phase and of the lattice defect by strict composition control would provide the further  $Q$  factor improvements in BZN system.

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