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Journal of the European Ceramic Society 32 (2012) 2373–2380

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Effect of small amount of cobalt substitution on structure and microwave dielectric properties of barium magnesium niobate ceramics

Ching-Tien Chen[a], Chi-Yuen Huang[a,*], Hong-Jin Lin[a], Chun-Te Lee[b]

[a] *Department of Resources Engineering, National Cheng Kung University, Tainan, Taiwan*
[b] *R&D Technology Center, Yageo Corporation, Kaohsiung 811, Taiwan*

Received 31 October 2011; received in revised form 15 March 2012; accepted 18 March 2012
Available online 11 April 2012

Abstract

We investigated effects of substituting cobalt for magnesium on microstructures and microwave dielectric properties of $BaMg_{1/3}Nb_{2/3}O_3$ ceramics. Nucleation and growth of 1:2 ordered domains dominate microstructural variations for $Ba(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ ceramics. Microstructures such as grains sizes and domain sizes significantly dominate variations of $Q \times f$ value. Less ordered domains are nucleated when substituting small amount of cobalt ($x < 0.1$). Accordingly, domains and grains significantly grow with increased cobalt substitution. The 1:2 ordering degree is subsequently increased, and $Q \times f$ achieves a maximum value at $x = 0.05$. Nevertheless, while cobalt substitution exceeds $x = 0.1$, more ordered nuclei occur and consequently affect the domain growth and the grain growth. The $Q \times f$ value remarkably decreases at $x = 0.1$, and varies due to different ordering degrees and compositions. The $Q \times f$ value of specimens at $x = 0.05$ becomes as high as 43,000, and is similar to that of specimens at $x = 0.5$.

Keywords: C. Dielectric properties; D. Perovskites; D. Niobate; B. Electron microscopy; Ordered phase

1. Introduction

The complex perovskite compounds of $A(B'_{1/3}B''_{2/3})O_3$ ($A = Ba^{+2}$, Ca^{+2}; $B' = Mg^{+2}$, Zn^{+2}; $B'' = Nb^{+5}$, Ta^{+5}), which exhibit high relative permittivity (ε_r), good quality factor (Q), and a near-zero temperature coefficient of resonant frequency (τ_f), have been widely used to manufacture dielectric resonators for wireless telecommunication applications.

The $BaMg_{1/3}Nb_{2/3}O_3$ ceramics have excellent microwave dielectric properties, and the ordering degree of B-site cations has a significant effect on the quality factor.[1,2] Kawashima et al.[3] indicate that the quality factor increases when the ordering degree increases, and that they achieved a perfect hexagonal ordered structure within 120 h of the annealing process.

To avoid the need for firing in a long annealing process to achieve a high ordering degree, the effects of using minor additives or solid solutions of multi-perovskite have been studied. The effect of cobalt substitution on $Ba(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ ceramics has also been reported.[4,5]

However, many studies have reported that minor additives or the proportion of the solid solution would affect the domain growth and the volume of the domain boundaries,[6–9] significantly affecting the $Q \times f$ value. Davies et al.[6,7] reported the effect of the Zr concentration on the domain size and boundaries in both $BaZn_{1/3}Ta_{2/3}O_3$ and $BaMg_{1/3}Nb_{2/3}O_3$ systems, respectively, and that the Q factor was affected by the variation in the Zr concentration. Wu and Davies[8] also indicate that substitution with a small amount of tungsten additive ($0 \leq x \leq 0.02$) in the $Ba(Zn_{1-x})_{1/3}(Nb_{1-x}W_x)_{2/3}O_3$ system would cause Zn vacancies, which would increase the kinetics of the domain growth and subsequently lead to a high $Q \times f$ value (118,000). These studies have implied that there would be significant effects of domain size and domain boundaries on the $Q \times f$ value.

The domain boundary are regions that disrupt the long-range ordering arrangement. In addition, localized disordering arrangements of cations and anions further affect the results of localized charge imbalance and chemical non-stoichiometry. As mentioned in Hiroshi's report,[10] whereas the charge neutrality and chemical stoichiometry are no longer maintained in this region, it is expected that the dielectric loss tangents would increase and the $Q \times f$ value would be reduced.

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* Corresponding author at: Department of Resources Engineering, National Cheng Kung University, One University Road, Tainan 70101, Taiwan.
Tel.: +886 6 2754170; fax: +886 6 2380421.
E-mail address: cyhuang@mail.ncku.edu.tw (C.-Y. Huang).

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http://dx.doi.org/10.1016/j.jeurceramsoc.2012.03.025

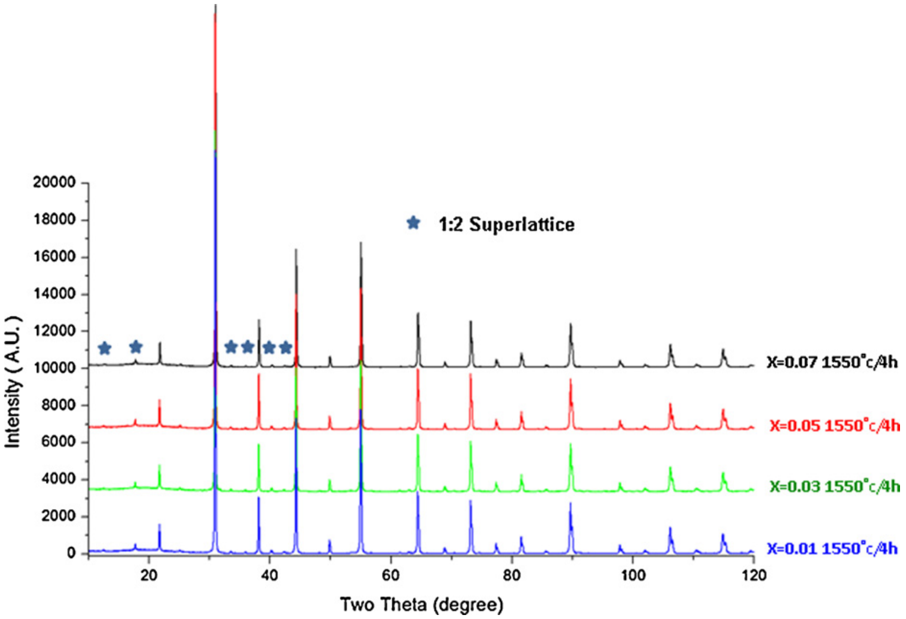

Fig. 1. XRD patterns of $Ba(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ sintered bulks.

It is expected that a relatively small amount of additive should lead to a decrease in the volume of anti-phase domain boundaries without the need for firing in a long annealing process. However, there are few studies that discuss the effect of substituting small amounts, and in some cases, the effect is very good. This is in contrast to general solid solutions where relatively large amounts are substituted.

In one study,[5] cobalt substitution was found to cause significant homogenous nucleation of ordered domains, and induces many anti-phase boundaries and smaller ordered domain sizes, which results in a smaller $Q \times f$ value than that obtained for BMN ceramics with an annealing treatment. Therefore, we substituted a small amount of cobalt to study the relationship between the microstructure and the dielectric properties in ordered $Ba(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ ceramics.

2. Experimental procedure

Sample powders of $Ba_3(Mg_{1-x}Co_x)Nb_2O_9$ (for $x = 0$, 0.01, 0.03, 0.05, 0.07, and 0.1) were prepared using the conventional solid-state reaction method beginning with $BaCO_3$, calcined MgO, $CoCO_3$, and Nb_2O_5 (all with 99.9% purity), which were ball-mill mixed in ethanol and with yttrium-stabilized zirconia media for 8 h. The slurry was dried and calcined at 1200 °C for 4 h in air. To achieve relative densities >95%, the calcined powder was again milled for 12 h, dried, sieved and compacted in cylinders, and sintered at 1350–1650 °C for 4 h based on the different compositions. A cooling rate of 120 °C/h was employed and all ceramics has >95% of theoretical density.

The phase composition was investigated by X-ray diffractometry (XRD; Siemens D5000) using graphite-filtered Cu $K_{\alpha 1}$ ($\lambda = 1.5406$ Å) radiation for $2\theta = 10$–$120°$, a step size of 0.02° 2θ/s and a sampling time of 8 s/step. The microstructures of the polished samples were investigated and analyzed using scanning electron microscopy (SEM; Hitachi S4100). The ordering domain configuration was observed and analyzed using the transmission electron microscopy (TEM).

The relative permittivity (ε_r) and quality factor (Q) at microwave frequencies (6.5–7.5 GHz) were measured by the Hakki-Coleman dielectric resonator method using a network analyser (Model: HP8757D, Agilent Technologies, Palo Alto, CA) and a sweep oscillator (Model: HP8350B, Agilent Technologies, Palo Alto, CA). The Q values were determined using a TE_{011} resonant peak, and the temperature coefficient of the resonant frequency (τ_f) was calculated after measuring the resonant frequency in the temperature range of +25–70 °C with

$$\tau_f = \frac{(f_2 - f_1)}{f_1(T_2 - T_1)} \qquad (2\text{-}1)$$

where f_1 and f_2 represent the resonant frequencies at temperatures T_1 and T_2, respectively. To compare the dielectric characteristics at microwave frequencies, the product of the quality factor and resonant frequency ($Q \times f$) were used.

3. Results

In a $BaMg_{1/3}Nb_{2/3}O_3$ system (BMN), the B-site cations undergo a 1:2 ordered to disordered arrangement, so a 1:2 ordered phase can be easily determined by monitoring the reflection peaks of the 1:2 ordered superlattice. However, the reflection peaks of the 1:2 ordered superlattice always exist in diffraction patterns of calcined powder of $Ba(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ (BMCN) ceramics for $x = 0$–0.1. That is, the ordered phase was formed in the early stage of synthesis. For sintered specimens, the reflection peaks of the 1:2 ordered superlattice were also observed in the XRD pattern (as shown in Fig. 1), and have greater intensities than that of calcined powders. Therefore, an increasing number of disordered phases have transitioned to the ordered phases, and the crystalline structure became hexagonal structure in nature.

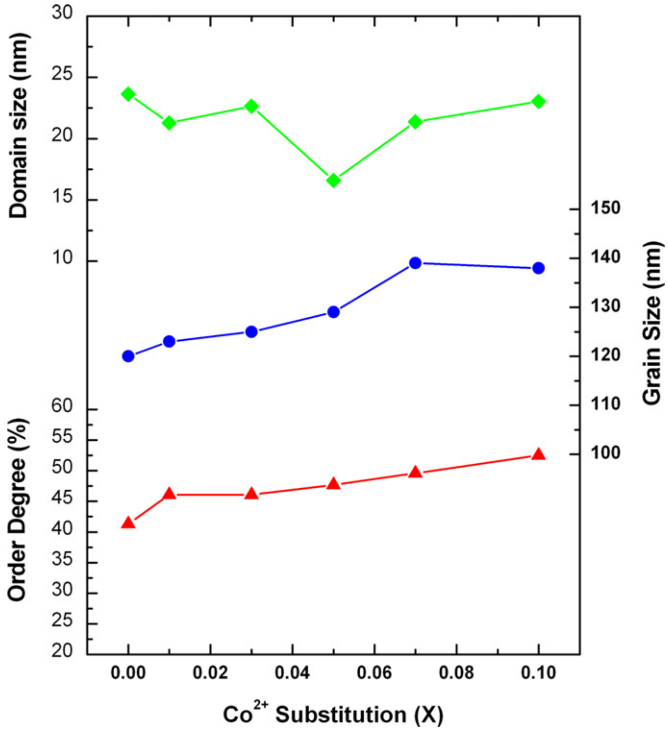

Fig. 2. Relationship between grain size, domain size, ordering degree, and the substitution rate of Co^{2+} cations in calcined powder of Ba$(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ ceramics. (For interpretation of the references to color in this text, the reader is referred to the web version of the article.)

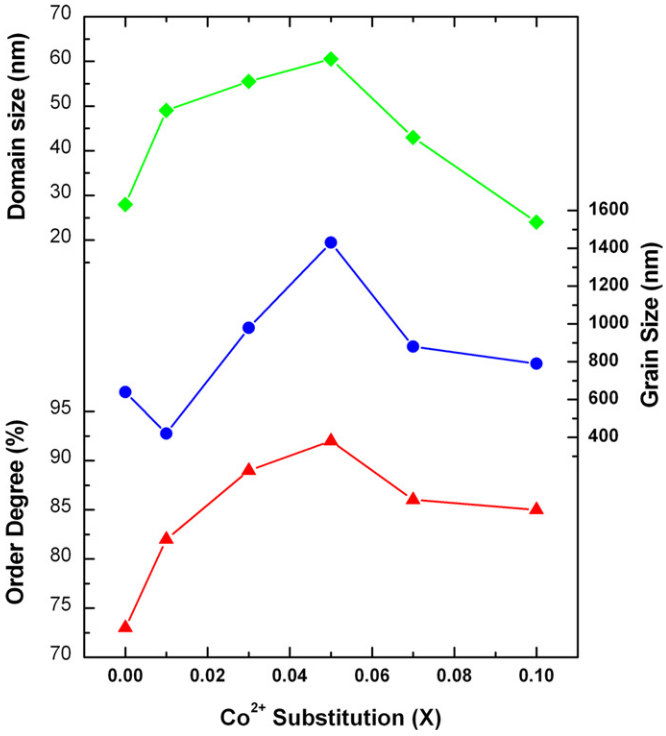

Fig. 3. Relationship between grain size, domain size, ordering degree, and the substitution rate of Co^{2+} cations in sintered specimens of Ba$(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ ceramics. (For interpretation of the references to color in this text, the reader is referred to the web version of the article.)

A quantitative calculation for the ordering degree was used to understand the transition between ordering and disordering structures. The ordering degree is estimated based on the XRD pattern. The ratio of the intensities ($I_{1\,0\,0}/I_{1\,1\,0,1\,0\,2,0\,1\,2}$) is used to deduce the ordering degree (S parameter) according to the following equation:

$$\left\{ S = \sqrt{\frac{(I_{1\,0\,0}/(I_{1\,1\,0}+I_{1\,0\,2}+I_{0\,1\,2}))_{\exp}}{(I_{1\,0\,0}/(I_{1\,1\,0}+I_{1\,0\,2}+I_{0\,1\,2}))_{cal,S=1}}} \right\}$$

The estimation result of the ordering degree for calcined powder is shown as the red line in Fig. 2, which indicates that the ordering degree of calcined powder increases with increasing ratio of cobalt substitution. The estimation result for the ordering degree of the sintered specimens is shown as the red line in Fig. 3, and is very different from the result for calcined powder. The ordering degree of the sintered specimen increases from 73% to 92% as the cobalt substitution increases from $x = 0$ to $x = 0.05$, but decreases from 92% to 85% as the cobalt substitution increases from $x = 0.05$ to $x = 0.1$. The highest ordering degree is achieved in the specimen at $x = 0.05$.

The ordered domain size is estimated according to the Scherrer formula, and the FWHM of the strongest reflection peak $1/3(1\,1\,1)_h$ for the 1:2 ordered superlattice in the XRD pattern was used in the calculations. The estimation result of the domain size for calcined powder is shown as the green line in Fig. 2, and indicates that ordered domains in the calcined powder at $x = 0$–0.1 are all small and maintain a similar value of ~20 nm. After sintering, the original domains in calcined powder will grow. The estimation result of the domain size for the sintered specimens is shown as the green line in Fig. 3. As the cobalt substitution ratio increases, the specimen at $x = 0.05$ achieves the largest domain size of 60 nm. However, the domain size decreases when the cobalt substitution exceeds $x = 0.05$. The domain size of the sintered specimen at $x = 0.1$ is 24 nm.

From the SEM micrographs of calcined powder, grains for all compositions of BMCN ceramics at $x = 0$–0.1 appear to range from 0.5 to 1 μm and many agglomerations are observed, as shown in Fig. 4(a). However, from the TEM micrograph observation, the grain size is around 100–300 nm, as shown in Fig. 4(b). The increase in cobalt substitution causes an insignificant increase in the grain size of calcined powder (of around 120–140 nm). The relationship between the cobalt substitution and the mean grain size in calcined powder is shown by the blue line in Fig. 2. However, after sintering, the grains also underwent significant growth. The sintered specimen at $x = 0.05$ also exhibits the largest grain size of 1.43 μm. The blue line in Fig. 3 shows the grain size in the sintered specimens for all compositions of BMCN ceramics.

The TEM selected area electron diffraction (SAED) pattern reveals the 1:2 ordered superlattice diffraction for calcined powder and the sintered specimens. Fig. 5(a) is the SAED pattern along the $1\,\bar{1}\,0$ zone axis from the calcined powder at $x = 0.05$, in which the 1:2 ordered superlattice $1/3(1\,1\,1)$ diffraction spot is not clear, but is observed as a white arrowhead. The TEM dark-field image from the same region is shown in Fig. 5(b), and the ordered domain is not easily to be observed. However, the ordered domain is revealed in Fig. 5(c), in which

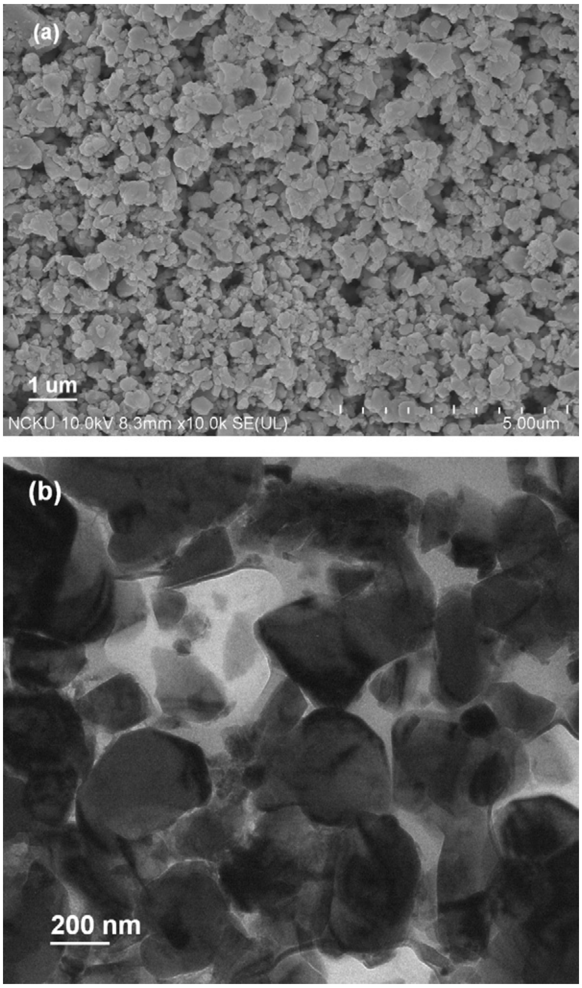

Fig. 4. Micrograph observation of $BaMg_{1/3}Nb_{2/3}O_3$ calcined powder at $x = 0.05$. (a) SEM photo and (b) TEM dark-field image.

the A and C areas illustrate disordering diffractions, while the B area shows an ordering diffraction. Moreover, the ordered area gradually becomes disordered without obvious boundaries. That is, 1:2 cation-ordered and -disordered structures coexist in calcined powder of $Ba(Mg_{0.95}Co_{0.05})_{1/3}Nb_{2/3}O_3$ ceramics. Fig. 6(a) shows the SAED pattern with a $1\,\bar{1}\,0$ one-axis for the sintered specimens at $x = 0.05$, which clearly displays the 1:2 ordered superlattice 1/3(1 1 1) diffraction blots. Fig. 6(b) is the TEM dark-field images from the same region, and it shows anti-phase boundaries and 1:2 ordered domains. In the image, the largest ordered domain has become larger than 100 nm, but the smallest one remains much smaller than 50 nm. Moreover, these ordered domains have intersected, and their morphologies are diverse and wormlike.

Fig. 7 shows the relationship between cobalt substitution and microwave dielectric properties for BMCN ceramics. The dielectric constant shows no significant variation with changes in the cobalt substitution, and has values between 31 and 32. The temperature coefficient of the resonant frequency has a linear function as the cobalt substitution increases, and it still behaves like the untilted field reported in Reaney's studies.[11–13] However, as the cobalt substitution increases, the $Q \times f$ value increases from 16,000 to 43,000 for $x = 0–0.05$, and decreases from 43,000 to 24,000 for $x = 0.05–0.1$. The maximum $Q \times f$ value (43,300) is achieved in the specimen of BMCN ceramics at $x = 0.05$.

4. Discussion

The reflection peaks of the 1:2 ordered superlattice in the XRD patterns and the TEM SAED pattern prove the existence of the 1:2 ordered arrangement of B-site cations in the perovskite structure, and indicate that the ordered phase has already existed in the early stage of synthesis for all compositions of BMCN solid solutions, including pure BMN compounds. Therefore, the starting ordered phase in calcined powder may become the nuclei for the formation of more ordered phases in the sintered specimen. The ordering degree of the calcined powder shows a linear relation with cobalt substitution. With the increase of the cobalt substitution, the ordering degree of the calcined powder increases, and calcined powder at $x = 0.1$ shows the highest ordering degree (52%), shown as the red line in Fig. 2. Therefore, greater cobalt substitution leads to the formation of more 1:2 ordered phases in calcined powder.

For all compositions of BMCN ceramics, the ordered domain size in calcined powder is approximately 20 nm, as shown by the green line in Fig. 2. The observation of TEM micrographs also indicates this size, as shown in Fig. 5(b). As discussed previously, for all compositions, the ordering degrees in calcined powder are different and increase with increasing cobalt substitution. That is, increased cobalt substitution would not cause an increase in the ordered domain size, but would result in the formation of a larger quantity of ordered domains in the calcined powders.

Having undergone an ordering-disordering phase transition during the sintering treatment, the ordering degree of the sintered specimens is higher than that of calcined powder. As shown in Fig. 1, the specimens for all compositions after sintering exhibit 1:2 superlattice intensities that are relatively stronger than that of calcined powder. However, as shown by the red line in Fig. 3, the ordering degree of sintered specimens does not show a linear relation with the cobalt substitution. The sintered specimens at $x = 0.05$ shows the highest ordering degree of 92%. In other words, BMCN ceramics having different degrees of cobalt substitution exhibit different increases in the ordered degree from calcined powder to sintered specimens. Fig. 8 describes the increase in the ordering degree caused during the sintering treatment for all cobalt substitutions with $x = 0–0.1$. The sintered specimen at $x = 0.05$ exhibits the largest increase in ordering degree, but specimens with other compositions do not show such a large increase in ordering degree. Therefore, there are mechanisms which have different effects on the growth rate of the ordered domain for different compositions.

After sintering, the ordered domain grew accordingly, and even the specimen at $x = 0.05$ achieved a sizes >100 nm, as shown in Fig. 6(a), which is much larger than that in calcined powder. Sintered specimens for $x = 0.01–0.07$ all exhibit significant increases in domain size. However, the domains in the specimen at $x = 0$ and 0.1 have no significant growth, even if the ordering

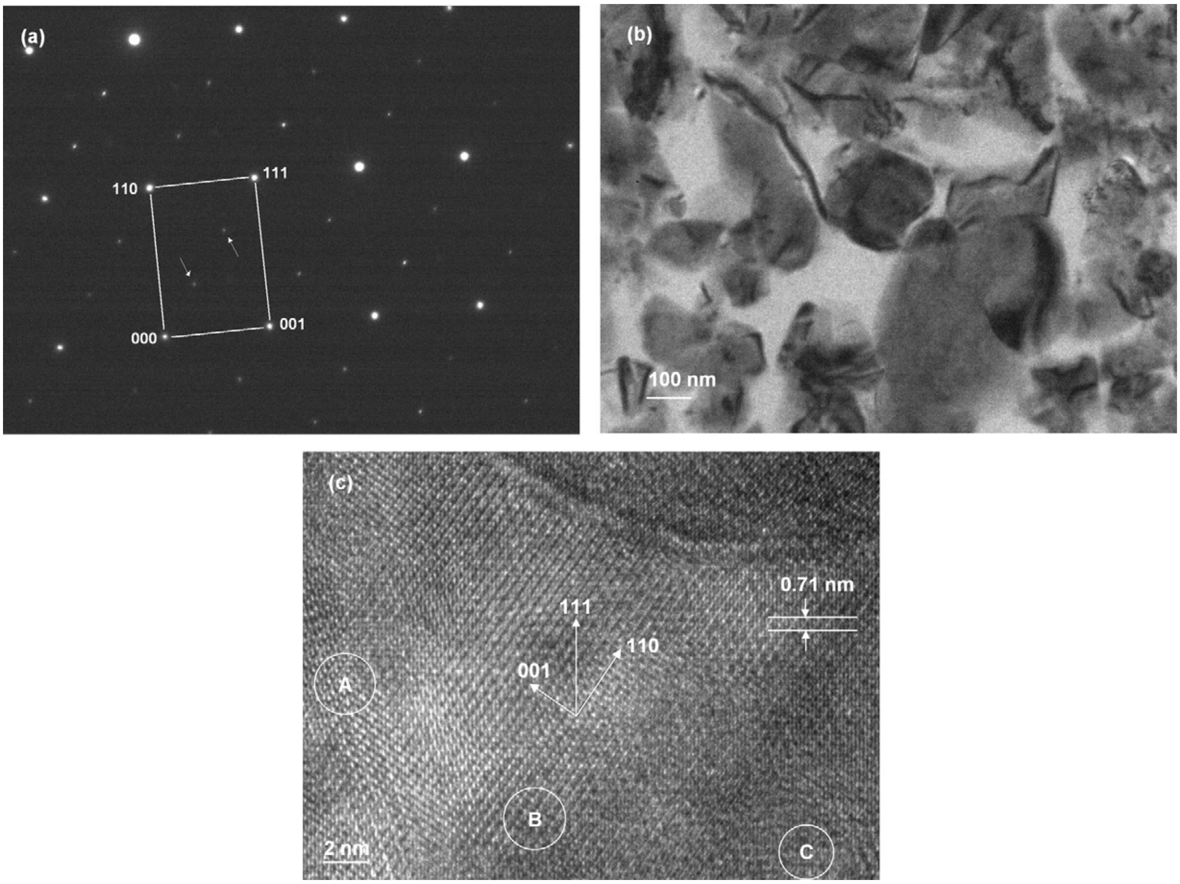

Fig. 5. TEM observation of $BaMg_{1/3}Nb_{2/3}O_3$ calcined powder at $x = 0.05$. (a) The SAED pattern, (b) the dark-field image, and (c) the lattice image.

degree in the specimen at $x = 0.1$ has achieved 85%. Observation of the TEM micrographs shown in Fig. 6(a) reveals that the ordered domains of the sintered specimen at $x = 0.05$ are relative as large as the estimation from the XRD pattern, but many of them have grown to encounter each other and have to stop growing. Therefore, the limitation to the growth of an ordered domain is realized when it encounters another domain or a grain boundary. In other words, the grain size and the quantity of the ordered domain in calcined powder are key factors to the enhancement of the domain size and ordering degree during sintering. Furthermore, as previously discussed, there is a linear relation between the quantity of the ordered domain and the cobalt substitution at $x = 0$–0.1. Therefore, although an increase in the cobalt substitution would induce a greater number of ordered domains in calcined powder, this subsequent increase may cause limit of domain growth during sintering treatment. The cobalt substitution at $x = 0.05$ is therefore required to avoid limiting the domain growth. Hence, the ordered domain size and the ordering degree of the specimen at $x = 0.07$–0.1 are significantly lower than that of the specimen at $x = 0.05$.

Fig. 8 also shows the increase in domain size from calcined powder to sintered specimens for all cobalt substitution ratios ranging from $x = 0$ to 0.1. It is observed that the increased domain size is consistent with that of the ordering degree. The increased domain size mainly dominates the increase in the ordering degree for $x = 0$–0.1, and the difference in the increases observed for different cobalt substitutions is caused by the ‘limits of domain growth’.

Nevertheless, the grain size also increases with the increased cobalt substitution and achieves a maximum at $x = 0.05$. Apparently, increased cobalt substitution simultaneously causes significant grain growth and domain growth. However, as discussed previously, a smaller grain would impede the domain growth. Oppositely, a greater number of ordered domains would need more energy to grow and consequently affect the grain growth. Therefore, the grain growth and the domain growth interact with each other and simultaneously achieve maxima at $x = 0.05$. The ordering degree consequently reaches the maximum value of 92%.

We now summarize about the nucleating and growing of the 1:2 ordered domain from calcined powder to a sintered specimen for BMCN ceramics for $x = 0$–0.1. At the beginning of compounds synthesis, ordered domains were formed after calcinations. The domain sizes are small and similar for all compositions, and the calcined powder with greater cobalt substitution comprises more ordered domains and consequently higher ordering degrees. The grain and domains grew after undergoing sintering treatment. However, due to the grain size and the quantity of ordered domains, the limiting factors for domain growth are different for different substitution ratios, and the eventual domain sizes in sintered specimens differ significantly.

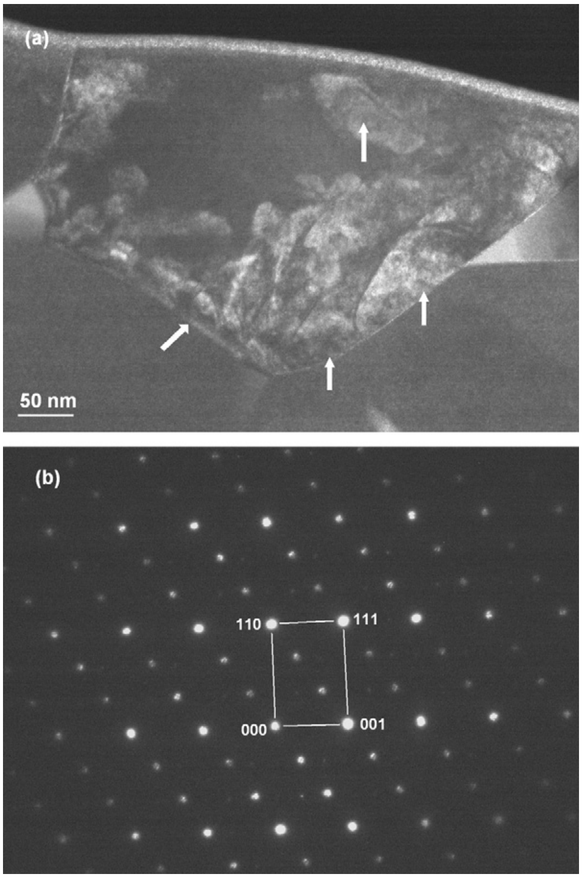

Fig. 6. TEM dark-field image and SAED pattern of Ba$(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ specimen at $x=0.05$. (a) The ordered domain is shown as the white arrowheads. (b) SAED pattern along the ⟨1 1 0⟩ zone axis.

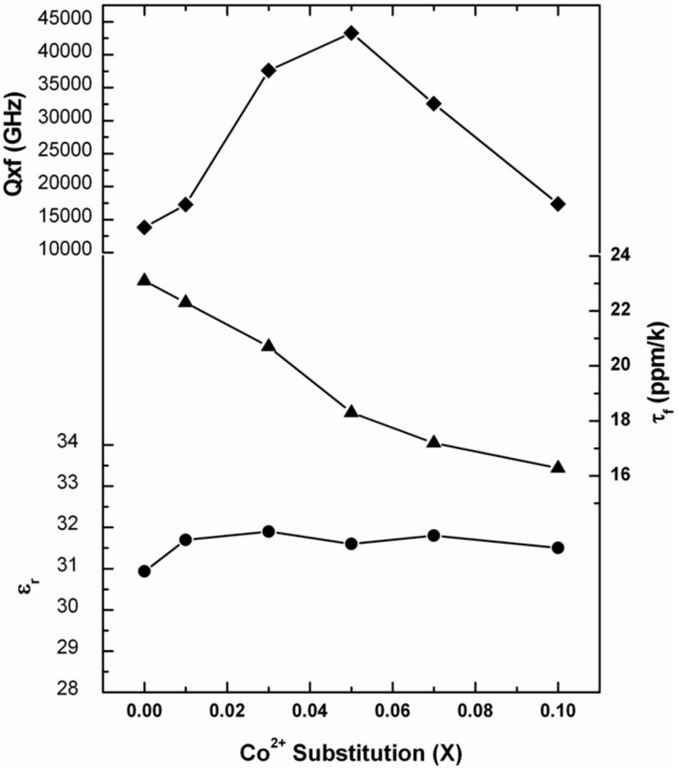

Fig. 7. Variation of dielectric constant, quality factor and τ_f of Ba$(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ ceramics at $x=0$–0.1.

Fig. 7 displays the dielectric properties for sintered specimens when $x=0$–0.1. The dielectric constant does not exhibit any obvious variation as the cobalt substitution changes. The temperature coefficient of the resonant frequency has a linear variation as the cobalt substitution increases. However, the $Q\times f$ value exhibits a maximum (43,300) at $x=0.05$. This result is consistent with previous microstructure analyses. The specimen at $x=0.05$ has the largest domain size and the largest grain size, and consequently results in the highest ordering degree. Therefore, a maximum value of $Q\times f$ can be attributed to the microstructural result. Moreover, although the $Q\times f$ value varies with changes in the ordering degree, the $Q\times f$ values for specimens at $x=0.01$ and 0.1 exhibit an unexpected drop. The ordering degree for specimens at $x=0.07$ and 0.01 are 86% and 85%, respectively. Moreover, the grain size for specimens at $x=0.07$ and 0.01 are 0.88 μm and 0.77 μm respectively. There is no significant difference in the ordering degree and in the grain size. Nevertheless, the domain sizes for specimens at $x=0.07$ and 0.1 are 60 nm and 24 nm; respectively, which are very different. This difference implies that the specimens at $x=0.07$ and 0.1 would have a greater number of ordered domains and must comprise many more anti-phase boundaries. This means that the increase in anti-phase boundaries is more than the increase in the ordering degree, which leads to a large decrease in the value of $Q\times f$. Therefore, the ordering degree of specimens at $x=0.07$ and 0.1 are 33,000 and 24,000, respectively. For the specimen at $x=0.01$, although the ordering degree reaches as high as 82%, the $Q\times f$ value is just 17,000 because of the smaller grain sizes and domain sizes.

While integrating the former data regarding sintered specimens at $x=0.3$–1, the $Q\times f$ value exhibited a significant

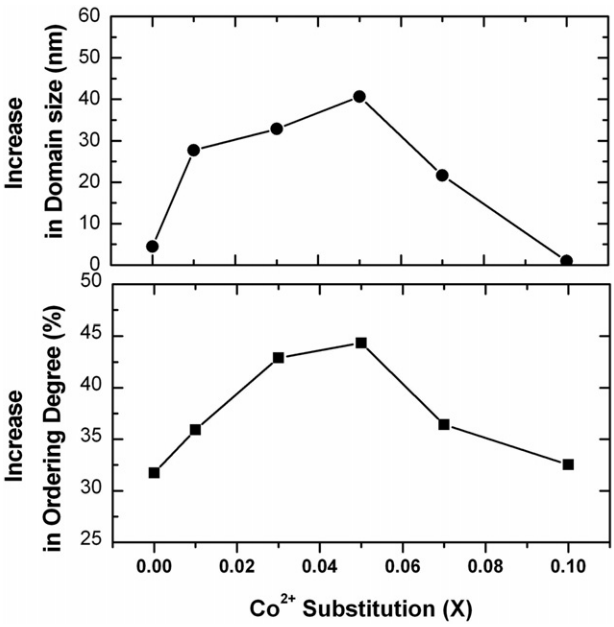

Fig. 8. Increase in the ordering degree and the domain size from calcined powder to a sintered specimen for all cobalt substitution ratios, $x=0$–0.1.

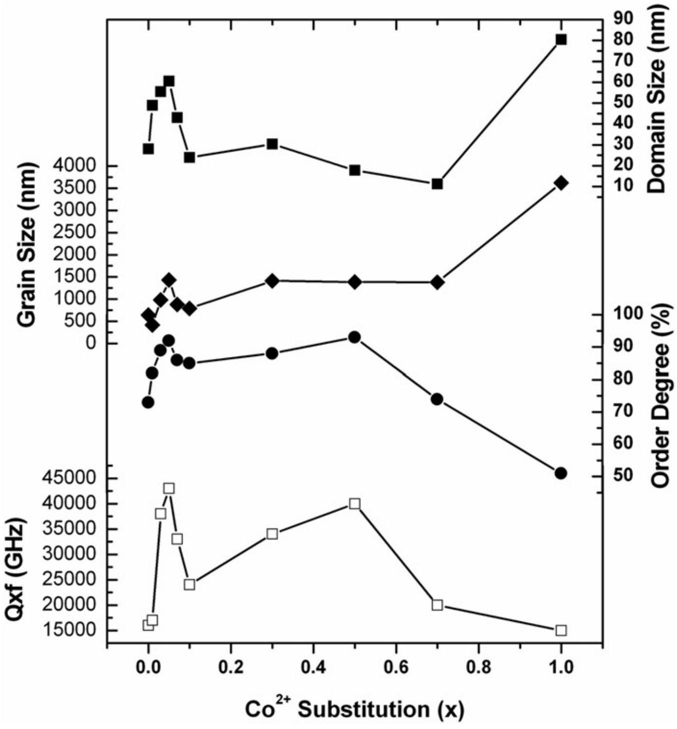

Fig. 9. Relationship between grain size, domain size, ordering degree, quality factor, and the substitution rate of Co^{2+} cations in sintered specimens of $Ba(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ ceramics at $x = 0–1$.

variation as the cobalt substitution increased, and displays two maximum values that are higher than 40,000 at $x = 0.05$ and 0.5. In other words, specimens with a small amount of cobalt substitution ($x = 0–0.1$) show almost similar variations in the $Q \times f$ value when compared to that of specimens with cobalt substitutions ranging from $x = 0$ to 1. However, the relationship between the ordering degree and the $Q \times f$ value is not consistent, as shown in Fig. 9. The $Q \times f$ value of the specimen at $x = 0.1$ sharply decreased to 24,000, but the ordering degree decreased only to 85%. As previously discussed, it is obvious that the domain size mainly affect the $Q \times f$ value at $x = 0.1$. Nevertheless, while cobalt substitution exceeds $x = 0.1$, the domain size remains small or becomes smaller, but the grain size and the ordering degree continue to increase. Therefore, the $Q \times f$ value increases and reaches 40,000 in the specimen at $x = 0.5$. A smaller domain size, a larger grain size, and higher ordering degree in the specimen at $x = 0.5$ implies the simultaneous presence of many more anti-phase boundaries and fewer disordering matrices. Fig. 10 shows the TEM dark-field image for the specimen at $x = 0.5$, and it clearly indicates that the domain size is limited to be < 20 nm and the grain is full of ordered domains.

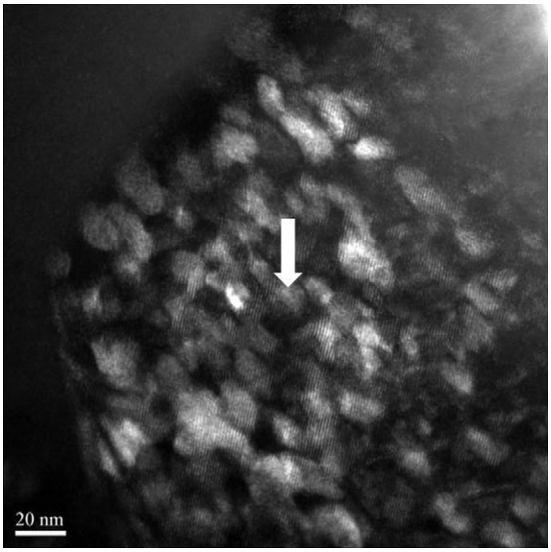

Fig. 10. TEM dark-field image of $Ba(Mg_{1-x}Co_x)_{1/3}Nb_{2/3}O_3$ specimen at $x = 0.5$.

5. Conclusions

The mechanism affecting the $Q \times f$ value for substitution of small amounts ($x = 0–0.1$) of cobalt in BMCN ceramics is very different from that for BMCN ceramics at $x > 0.1$.

In the BMCN ceramics for $x = 0–0.1$, as the degree of cobalt substitution increases, an increasing number of ordered domains would nucleate in the calcined powder in the early stage of synthesis. Moreover, these nuclei (ordered domain) would maintain a smaller size of ∼20 nm for all compositions of BMCN ceramics. After sintering treatment, ordered domains and grains would grow. Increased cobalt substitution simultaneously causes significant grain growth and domain growth, but which interact with each other and simultaneously achieve maxima at $x = 0.05$. The ordering degree of the specimen at $x = 0.05$ consequently reaches the maximum value of 92%. In addition to the grain size, the initial quantity of ordered domains would become another limitation to the domain growth. The final domain sizes in sintered specimens differ among specimens with different degree of cobalt substitution, and the maximum domain size is 60 nm in the specimen at $x = 0.05$.

The domain size and the grain size mostly dominate the variation of the $Q \times f$ value for BMCN ceramics for $x = 0–0.1$. As the domain and grain grow, the ordering degree and the $Q \times f$ value accordingly increase. However, the volume of anti-phase boundaries would increase with a greater number of ordered domains. Therefore, as cobalt substitution increases, both the ordered domains and the anti-phase boundaries increase, but the domain size and the grain size accordingly decrease as cobalt substitution exceeds $x = 0.05$. The $Q \times f$ value also decreases accordingly.

The $Q \times f$ value increases from 14,000 to 43,000 for $x = 0–0.05$ and decreases from 43,000 to 24,000 for $x = 0.05–0.1$. The specimen at $x = 0.05$ shows the highest $Q \times f$ value of 43,000.

When cobalt substitution exceeds $x = 0.1$, the domain size remains small, but the grain size and the ordering degree continues to increase due to the transition in disordered phase. Consequently, the $Q \times f$ value continues to increase to the second maximum of 40,000 in the specimen at $x = 0.5$.

Acknowledgement

This work was supported by the National Science Council of Taiwan under grant No. NSC 98-2221-E-006-078-MY2.

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