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Influences of Mg and Mn doping on structure, B-site ordering and microwave dielectric properties of Ba(Co$_{1/3}$Nb$_{2/3}$)O$_3$ ceramics

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Abstract

Influence of Mg and Mn doping on structure and microwave dielectric properties of Ba(Co$_{1/3}$Nb$_{2/3}$)O$_3$ (BCN) ceramics with complex perovskite structure is investigated systematically. X-ray diffraction and Raman spectrum investigations show that doping Mg and Mn into BCN ceramics is helpful for improving the quality factor ($Q$ × $f$ value) resulted from enhanced B-site 1:2 ordering degree. Mg- doped samples show higher ordering degrees and larger $Q$ × $f$ values than Mn-doped counterparts. The sintering density, grain size, 1:2 B-site ordering structure and microwave dielectric properties of BCN ceramics show a strong dependence on Mg and Mn doping content. The sintering density of BCN ceramics can be increased significantly by doping a small amount of Mg and Mn. However, further increase in doping content results in the decrease of sintering density. $\tau_f$ value of BCN ceramics can be tailored by doping of Mg into Co sites. The near-zero $\tau_f$ value ($\sim$0.64 ppm °C$^{-1}$) is obtained when the Mg doping content is at $x$ = 0.1. The ordering degree and $Q$ × $f$ value of Mg- and Mn- doped BCN ceramics increase significantly with increasing annealing time.

1. Introduction

Rapid development in wireless communication technology has always been the driving force of microwave dielectric materials research [1–4]. Ba(B′$^{1/3}$B′′$^{2/3}$)$_3$O$_9$ (B′ = Co, Zn, Mg, Ni, B′′ = Ta, Nb) ceramics with complex perovskite structure have attracted considerable attentions due to their excellent microwave dielectric properties, especially extra-high quality factor ($Q$ × $f$ value) [5–7]. Despite the fact that the commercial Ta-based complex perovskite ceramics, like Ba(Zn$_{1/3}$Ta$_{2/3}$)$_3$O$_9$ (BZT) [8, 9] and Ba(Mg$_{1/3}$Ta$_{2/3}$)$_3$O$_9$ (BMT) ceramics [10], have been widely utilized as dielectric resonators and filters, high cost of Ta$_2$O$_5$ have still limited its wide applications. Especially, the building of next generation communication system is the culmination of intense preparation in which low cost ceramic resonators are always considered firstly. Therefore, more attention has been paid on Nb-based perovskite ceramics due to their significantly lower raw material costs and better sintering performance than Ta-based counterparts [10, 11].

Although Ba(Co$_{1/3}$Nb$_{2/3}$)O$_3$ (BCN) ceramics exhibit comparable microwave dielectric properties with Ta-based perovskite ceramics, their $Q$ × $f$ values are very sensitive to processing parameters during the sintering and annealing. It is believed it is ascribed to the evaporative Co and changeable valence of transition Co element. Li et al [12] have demonstrated that microwave loss due to the presence of P-type bulk phase is associated with the mixed presence of Co$^{2+}$ and Co$^{3+}$ on the B-site lattice. Sayyadi-Shahraki et al [13] further verified that polaron hopping between Co$^{2+}$ and Co$^{3+}$ cations also contributes to the dielectric loss in Ba(Co$_{1/3}$Nb$_{2/3}$)O$_3$ at cryogenic temperatures. It is well known that the excellent microwave properties of BCN complex perovskite ceramics are related to pores, secondary phases, impurities, grain boundaries and B-site 1:2 ordering [14–16]. B-site ordering results from the repeated arrangement of B′ layers and B′′ layers along the (111) directions of the parent cubic
perovskite cell [17–19]. Molodetsky et al. [20] have revealed that \( Q \cdot f \) value of BCN ceramics with 1:2 ordered arrangement in B-site (\( \sim 64400 \) GHz) is significantly higher than disordered variant (\( \sim 10800 \) GHz). The 1:2 ordered arrangement of B-site cations in Ba\((B'_{1/3}B''_{2/3})\)O\(_3\) ceramics is usually closely relevant to the difference in radius and charge between the cations in B-site [19].

It should be stressed that the deviation of stoichiometry induced by the evaporation and changeable valence of transition Co subsequently could affect the structure and microstructure of BCN ceramics, which results in the instability of microwave properties. However, there are few investigations until now in clarifying the relationship between the structure and properties of Ba\((B'_{1/3}B''_{2/3})\)O\(_3\) ceramics with easily changeable valence transition element. Additionally, it has been reported that Mg and Mn doping could be effective to tailor 1:2 B-site ordered structure and microwave dielectric properties of Ba\((B'_{1/3}B''_{2/3})\)O\(_3\) ceramics [21–23].

Considering the difference of Mg (3s\(^2\)) and Mn (3d\(^4\)4s\(^2\)) in the electronic structure, the present paper aims to investigate the influence of Mg and Mn doping into B-site on the structure and microwave dielectric properties of BCN ceramics. Special attention has been paid on the sintering behavior and relationship between the B-site 1:2 ordering structure and microwave dielectric properties of BCN ceramics.

2. Experimental

Mg- and Mn- doped Ba\((Co_{1-y}Mg_y)_{3}B_2O_7\) (BCN) ceramics were synthesized by a conventional solid state reaction method aided by a high-energy milling technique. High-purity BaCO\(_3\) (99.95%), Co\(_3\)O\(_4\) (99.9%), Nb\(_2\)O\(_5\) (99.95%), MgO (99.97%) and MnO (99.99%) powders were used as raw materials. The starting powders weighed by stoichiometric ratio were mixed with ethanol as milling media at a rate of 300 rpm for 16 h to obtain homogeneous mixing raw materials. The slurry was dried and re-milled at a rate of 450 rpm for 10 h. Additionally, single-phase Co\(_3\)O\(_4\)-Mg\(_2\)Nb\(_2\)O\(_7\) (\( x = 0, 0.1, 0.2, 0.3, 0.4 \)) powders and Co\(_3\)O\(_4\)-Mn\(_2\)Nb\(_2\)O\(_7\) (\( y = 0.005, 0.01, 0.015, 0.02 \)) powders were synthesized by calcining at 1100 °C for 4 h and mixed with BaCO\(_3\) in a similar way as described above to obtain single phase Mg- and Mn- doped BCN powders. Those powders with 5wt% paraffin and 2wt% stearic acid as binder were further pressed into discs with 10 mm in diameter and 5 mm in height. The discs were sintered at 1380 °C in air for 6 h and annealed at 1300 °C for different time.

Sintering density, microstructure and elemental distribution of as-sintered BCN ceramics were measured by the Archimedes method and scanning electron microscopy (FEI Electro Optics B.V.) with energy dispersive spectrometry (EDS), respectively. The phase and crystal structure were identified by x-ray powder diffraction (Rigaku Ultima IV) with a Cu K\( \alpha \) source. For more detailed crystal structure investigation, Raman spectroscopy (Labram Aramis, Horiba Jobin) and Transmission Electron Microscopy (TEM) with spherical aberration correction (TECNAI G2 60-300, FEI) were applied. Microwave dielectric properties (\( \varepsilon_r \) and \( Qf \)) were determined by a network analyzer (N5230A, Agilent) using the Hakki-Coleman dielectric resonator method modified by Courtney. The temperature coefficient of resonance frequency (\( \tau_f \)) was determined in a temperature range from 25 °C to 85 °C, which was defined as follow [24, 25]:

\[
\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \times 10^6 (\text{ppm} \text{ °C}^{-1})
\]

Where \( f_{85} \) and \( f_{25} \) represent the resonant frequency determined at 25 °C and 85 °C, respectively.

3. Results and discussion

It is well known that high sintering density is a prerequisite to obtain excellent performance for Ba\((Co_{1-y}Mg_y)_{3}B_2O_7\) (BCN) ceramics. The dependence of relative density on Mg and Mn doping content for BCN ceramics sintered at 1380 °C for 6 h is shown in figures 1(a) and (b), respectively. As shown, BCN ceramics with high sintering density (>95%) have been synthesized successfully. It is further observed that the sintering density can be increased significantly by doping a small amount of Mg and Mn. Especially, BCN ceramics with Mg doping content \( x = 0.2 \) present highest sintering density (~97% of the theoretical density). However, it gradually decreases when Mg doping content is up to \( x = 0.4 \).

Figure 2 shows the SEM micrographs of Mg- and Mn- doped BCN ceramics sintered at 1380 °C for 6 h. As shown, all as-sintered samples present dense microstructure with few pores. This is well consistent with the high sintering density of as-sintered BCN ceramics. Further observations show that with increasing Mg doping content, the average grain sizes of Mg- doped BCN ceramics gradually decrease. Inhomogeneous and finer grains can be observed along the boundaries of coarse grains. It is believed they are related to the evaporation of CoO. Similar phenomenon has been reported for Mg- doped BCZN ceramics [21]. In contrast, the grain size distribution of Mn- doped BCN ceramics with doping content \( y \leq 0.015 \) is more homogeneous, although abnormal grain growth and the phenomenon of large grain surrounded small grains are observed when
$y = 0.02$, as shown in figure 2(h). The EDS results of grains with small and large size are summarized in table 1 and figure 3. As shown, they are of relatively homogeneous composition. It is believed that abnormal grain growth is attributed to large grain annexation of small grains, which results from the appearance of vacancies induced by the evaporation of CoO or the change of the valence of Co or Mn [12, 13]. It is well known that atom diffusion can be accelerated by vacancies that provide fast diffusion channel for mass.
Figures 4(a) and (b) illustrate the XRD spectra of Ba[(Co1−xMg)x1/3Nb2/3]O3 and (b) Ba[(Co1−yMn)y1/3Nb2/3]O3 ceramics, respectively. As shown, all samples exhibit hexagonal structure (space group P-3m1, PDF standard card 46-0997) without discernible secondary phases. As seen from the insets in figure 4, obvious superlattice peaks (2θ ≈ 17.7°) stemming from the B-site 1:2 ordering structure can be found in Mg- and Mn-doped BCN ceramics. It can be observed clearly that the intensity of superlattice reflection peaks of Mg- and Mn-doped BCN ceramics is higher than that of undoped counterparts. This indicates that doping Mg and Mn into BCN ceramics can promote the B-site 1:2 ordering. In order to further quantitatively analyze the B-site cation ordering degree, parameter (S) can be used, which is calculated by the integral intensities of (100) superlattice reflection and (110, 102) fundamental reflections using the following equation [26, 27]:

\[ S = \frac{(100)/(110, 012)_{\text{observation}}}{(100)/(110, 012)_{\text{calculation}}} \]  

(2)

The ordering degrees (S) of Ba[(Co1−xMg)x1/3Nb2/3]O3 and Ba[(Co1−yMn)y1/3Nb2/3]O3 ceramics sintered at 1380 °C for 6 h as a function of Mg and Mn doping content are summarized in figure 5. As shown in figure 5, when Mg doping content x increases, the ordering degree of Mg-doped BCN ceramics increases significantly as well. In contrast, the ordering degree decreases with increasing Mg doping content. Maximum ordering degree (∼37%) is obtained at x = 0.2. The change of ordering degrees of Mn-doped BCN ceramics with y increasing is similar to that of Mg-doped samples. The maximum ordering degree (∼25%) is achieved at y = 0.015. Overall, a strong dependence of the ordering degree on Mg- or Mn- doping content is observed, although Mg-doped BCN ceramics show relatively higher B-site 1:2 ordering degree than Mn-doped counterparts. Several reasons

| Element | Small grain (wt%) | Big grain (wt%) |
|---------|------------------|----------------|
| Ba      | 52.03            | 55.25          |
| Nb      | 34.33            | 29.02          |
| Co      | 06.56            | 08.07          |
| Mn      | 00.62            | 00.43          |
| O       | 06.47            | 07.22          |
can result in the enhanced B-site 1:2 ordering in Mg- or Mn- doped BCN ceramics. For example, Mg substantially doping into B-site could enhance the ordering-disordering transition temperature \[21, 22\]. Additionally, the increase in B-site ionic radius difference \(r_{\text{Co}^{2+}} - r_{\text{Nb}^{5+}} = 0.0105 \text{ nm}, r_{\text{Mn}^{2+}} - r_{\text{Nb}^{5+}} = 0.019 \text{ nm}\) is responsible for the increase of ordering degree of Mn- doped samples. The B-site ionic radius difference usually is considered as a strong indicator of the driving force for B-site 1:2 ordering arrangement \[19\].

Figure 6 shows the XRD spectra of as-sintered \(\text{Ba}[(\text{Co}_{0.8}\text{Mg}_{0.2})_{1/3}\text{Nb}_{2/3}]\text{O}_3\) and \(\text{Ba}[(\text{Co}_{0.985}\text{Mn}_{0.015})_{1/3}\text{Nb}_{2/3}]\text{O}_3\) ceramics annealed at 1300 °C in air for 24 h, respectively. It is clear that all samples are still of 1:2 ordered hexagonal structure (space group P-\(3m_1\), PDF standard card 46-0997) and the peaks for second phase are not observed within the sensitivity of XRD. The inset in figure 6 shows that the intensity of superlattice reflection peaks of as-annealed \(\text{Ba}[(\text{Co}_{0.8}\text{Mg}_{0.2})_{1/3}\text{Nb}_{2/3}]\text{O}_3\) and \(\text{Ba}[(\text{Co}_{0.985}\text{Mn}_{0.015})_{1/3}\text{Nb}_{2/3}]\text{O}_3\) ceramics significantly higher than that of unannealed counterparts. Table 2 summarizes ordering degrees and \(Q\cdot f\) values of \(\text{Ba}[(\text{Co}_{0.8}\text{Mg}_{0.2})_{1/3}\text{Nb}_{2/3}]\text{O}_3\) and \(\text{Ba}[(\text{Co}_{0.985}\text{Mn}_{0.015})_{1/3}\text{Nb}_{2/3}]\text{O}_3\) ceramics sintered at 1380 °C for 6 h and annealed at 1300 °C in air for different time. As expected, the ordering degrees of both Mg- and Mn- doped BCN ceramics can be increased by annealing treatment. The ordering degree of Mn- doped BCN ceramics increases to 46% from 25% after annealing treatment. In contrast, Mg- doped BCN ceramics show highest ordering degree (∼90%). We would like to mention that the splitting of the reflections (422) and (226) usually is a strong evidence to trace the appearance of B-site 1:2 ordering in \(\text{Ba}(B'_1/B'_2/3)\text{O}_3\) ceramics with complex perovskite structure \[28\]. It is interesting that the splitting of the reflections (422) and (226) at \(2\theta \approx 114°–116°\), which results in the broadening of the peak, is observed clearly in as-annealed
Ba$[\text{Co}_{0.8}\text{Mg}_{0.2}\text{Nb}_{2/3}]\text{O}_3$ ceramics, due to lattice distortion induced by B site 1:2 ordered arrangement. The occurrence of splitting of the reflections $(422)$ and $(226)$ further demonstrates that Mg-doped BCN ceramics attain higher ordering degree after annealing.

Given the importance of B-site 1:2 ordering on the $Q \cdot f$ value of Ba$[\text{B}')_{1/3}\text{B}'_2/3]\text{O}_3$ ceramics, the 1:2 ordering structure of B-site of Mg- and Mn-doped BCN ceramics is further investigated by Raman spectroscopy and TEM. Raman patterns of Ba$[\text{Co}_{1-x}\text{Mg}_x\text{Nb}_{2/3}]\text{O}_3$ and Ba$[\text{Co}_{1-y}\text{Mn}_y\text{Nb}_{2/3}]\text{O}_3$ ceramics sintered at 1380 °C for 6 h are shown in Figure 7. Similar to the Raman patterns of Ba$[\text{Mg}_{1/3}\text{Nb}_{2/3}]\text{O}_3$ ceramics with B-site 1:2 ordering structure [29–31], four obvious peaks in as-sintered BCN ceramics are observed. They include $F_{2g}(\text{Ba})$ mode centered at $\sim 105$ cm$^{-1}$ related to Ba lattice site-related vibrations, $F_{2g}(\text{O})$ modes centered at $\sim 375$ cm$^{-1}$ and 450 cm$^{-1}$ related to oxygen layers, and $A_{1g}(\text{O})$ mode centered $\sim 800$ cm$^{-1}$ correlated with stretch vibration of oxygen octahedra. Additionally, three weak peaks in the range of 150–300 cm$^{-1}$ are observed, which are closely related to B-site 1:2 ordering. They are $E_g(\text{O})$ mode centered at 175 cm$^{-1}$, $E_f(\text{Nb/Ta})$ mode centered at 263 cm$^{-1}$, and $A_{1g}(\text{Nb})$ mode centered at $\sim 296$ cm$^{-1}$, respectively [32].

Further observations show specific peaks including $E_g(\text{O})$ mode and $A_{1g}(\text{Nb})$ mode are noticeable in Mg-doped BCN ceramics. However, only $A_{1g}(\text{Nb})$ mode is observed in Mn-doped BCN ceramics. Especially, the intensity of $E_g(\text{O})$ mode and $A_{1g}(\text{Nb})$ mode in undoped BCN ceramic is so weak that those could not be observed. Combining with the results from XRD and Raman spectra, it is clear doping Mg and Mn can be helpful for enhancing the B-site 1:2 ordering of BCN ceramics. The effect of Mg doping on the ordering degree of BCN ceramics is stronger than that of Mn doping. Figure 8 further shows Raman patterns of Ba$[\text{Co}_{0.9}\text{Mg}_{0.1}\text{Nb}_{2/3}]\text{O}_3$ and Ba$[\text{Co}_{0.98}\text{Mn}_{0.02}\text{Nb}_{2/3}]\text{O}_3$ ceramics annealed at 1300 °C in air for 24 h, respectively. It is observed that the Raman patterns of annealed BCN ceramics is similar to unannealed ceramics, but the weakest $E_g(\text{Nb/Ta})$ mode strongly related to B-site 1:2 ordering is clearly visible in as-annealed Mg-doped BCN ceramics. It is stressed that this $E_g(\text{Nb/Ta})$ mode does not appear in unannealed and Mn doped...
BCN ceramics annealed at 1300 °C in air for 24 h. Again, this result implies that higher B-site 1:2 ordering can be achieved in annealed Mg-doped BCN ceramics. This is well consistent with the XRD results.

In order to further explore the subtle difference in B-site 1:2 ordering structural of as-annealed Mg-doped BCN ceramics, TEM is applied. Figures 9(a) and (b) show the selected area electron diffraction patterns of different areas of Ba[(Co0.8Mg0.2)1/3Nb2/3]O3 ceramics annealed at 1300 °C in air.

Table 2. Ordering degrees (S) and Q - f values of Ba[(Co0.8Mg0.2)1/3Nb2/3]O3 and Ba[(Co0.985Mn0.015)1/3Nb2/3]O3 ceramics sintered at 1380 °C for 6 h and annealed at 1300 °C in air for different time.

| t (h) | S (%) | Q - f (GHz) | S (%) | Q - f (GHz) |
|------|-------|-------------|-------|-------------|
| 0    | 37    | 40405       | 25    | 37729       |
| 24   | 90    | 63161       | 46    | 51245       |

BCN ceramics annealed at 1300 °C in air for 24 h. Again, this result implies that higher B-site 1:2 ordering can be achieved in annealed Mg-doped BCN ceramics. This is well consistent with the XRD results.

In order to further explore the subtle difference in B-site 1:2 ordering structural of as-annealed Mg-doped BCN ceramics, TEM is applied. Figures 9(a) and (b) show the selected area electron diffraction patterns of different areas of Ba[(Co0.8Mg0.2)1/3Nb2/3]O3 ceramics annealed at 1300 °C in air for 24 h along the [110] crystal
zone axes, which are indexed by reference to the reciprocal lattice of pseudocubic perovskite sub-cell. As shown in figure 9(a), the superlattice diffraction used to characterize the 1:2 ordering structure with a hexagonal symmetry is visible at positions of $(h\pm 1/3, k\pm 1/3, l\pm 1/3)$ away from the fundamental reflections for pseudocubic perovskite structure [33]. Evidence for ordering is also found in XRD and Raman spectra, as discussed earlier. On the contrary, as shown in figure 9(b), the electron diffraction pattern collected from another area in the same Ba[$(Co_{0.8}Mg_{0.2})_{1/3}Nb_{2/3}]O_3$ sample do not observe superlattice reflection. These results indicate that the disordering and B-site 1:2 ordering co-exist in Ba[$(Co_{1-x}Mg_x)_{1/3}Nb_{2/3}]O_3$ ceramics annealed at 1300 °C in air for 24 h.

Figure 10 illustrates the dependence of microwave dielectric properties of BCN ceramics sintered at 1380 °C for 6 h on the Mg and Mn doping content. It is obvious that the $Q \cdot f$ values are sensitive to doping content. As shown in figure 10(a), the $Q \cdot f$ values of Ba[$(Co_{1-x}Mg_x)_{1/3}Nb_{2/3}]O_3$ ceramics increase significantly after Mg doping, up to $\sim 40405$ GHz at $x = 0.2$. When the Mg doping content increases, the $Q \cdot f$ values decreases gradually. Similarly, as shown in figure 10(d), the $Q \cdot f$ values of Ba[$(Co_{1-y}Mn_y)_{1/3}Nb_{2/3}]O_3$ ceramics can be enhanced by doping Mn. The maximum $Q \cdot f$ values ($\sim 31729$ GHz) is achieved at $y = 0.015$. Again, it decreases
when Mn doping content further increases. Overall, the $Q \cdot f$ values of Mg- and Mn-doped samples are higher than that of pure BCN ceramics and the $Q \cdot f$ values of Ba[$(Co_{1-x}Mg_x)_{1/3}Nb_{2/3}$]O$_3$ ceramics are higher slightly than Mn-doped counterpart. As discussed above, the change tendency of B-site 1:2 ordering degree in Mg- and Mn-doped BCN ceramics is in a good consistency with that of $Q \cdot f$ values, indicating the increase of $Q \cdot f$ value is attributed to the enhanced B-site 1:2 ordering degree. Moreover, as shown in table 2, the highest ordering degree ($\sim 90\%$) is obtained in Ba[$(Co_{0.8}Mg_{0.2})_{1/3}Nb_{2/3}$]O$_3$ ceramics annealed at 1300 $^\circ$C in air for 24 h, which is of the largest $Q \cdot f$ value ($\sim 63161$ GHz) as well.

The dependence of $\tau_f$ values of Mg- and Mn-doped BCN ceramics on Mg and Mn doping content is shown in figures 10(b) and (e), respectively. As shown, the $\tau_f$ values of Ba[$(Co_{1-x}Mg_x)_{1/3}Nb_{2/3}$]O$_3$ ceramics increase monotonically from a negative value to a positive value with increasing $x$. It is expected since the $\tau_f$ values of Ba[$Mg_{1/3}Nb_{2/3}$]O$_3$ is positive and the $\tau_f$ value of Ba[$Co_{1/3}Nb_{2/3}$]O$_3$ ceramics is negative [34]. The near-zero $\tau_f$ values ($\sim 0.64$ ppm $^\circ$C$^{-1}$) is achieved at $x = 0.1$. Although $\tau_f$ value of Ba[$Mn_{1/3}Nb_{2/3}$]O$_3$ ceramics is also positive [35], the change of the $\tau_f$ values of Mn-doped BCN ceramics is not obvious. It is likely attribute to the less Mn doping content. Similarly, the effect of Mn doping on the dielectric constant is not significant.

Figure 8. Raman patterns of (a) Ba[$(Co_{0.8}Mg_{0.2})_{1/3}Nb_{2/3}$]O$_3$ and (b) Ba[$(Co_{0.985}Mn_{0.015})_{1/3}Nb_{2/3}$]O$_3$ ceramics annealed at 1300 $^\circ$C in air.
as well, shown in figure 10(f). The dependence of dielectric constant of Mg- doped BCN ceramics on Mg doping content is shown in figure 10(c). The decrease of dielectric constant of Mg- doped BCN ceramics with increasing x is observed. It may result from the smaller polarizability of Mg than Co. By optimizing the sintering and annealing processing parameters, the optimum microwave dielectric properties is exhibited in Ba[(Co0.8Mg0.2)1/3Nb2/3]O3 ceramics annealed at 1380 °C for 6 h as a function of Mg and Mn doping content.
4. Conclusion

Mg and Mn doping has a significant influence on sintering density, grain size, B-site 1:2 ordering and microwave dielectric properties of BCN ceramics with complex perovskite structure. X-ray diffraction and Raman spectroscopy investigations show doping Mg and Mn into BCN ceramics is helpful for improving the Q · f values resulted from the enhanced B-site 1:2 ordering degree. However, Mg-doped samples show higher ordering degrees and larger Q · f values than Mn-doped counterparts. The near-zero $\tau_f$ value ($\sim 0.64$ ppm °C$^{-1}$) is obtained when the Mg doping content is at $x = 0.1$. After annealing, the ordering degree and Q · f value of doped samples increase obviously and the highest ordering degree ($\sim 90\%$) is observed in Ba[(Co$_{0.8}$Mg$_{0.2}$)$_{1-x}$Nb$_{2/3}$]O$_3$ ceramics annealed at 1300 °C for 24 h.

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