Characterizing $x\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3+(1-x)\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ microwave ceramics using extended x-ray absorption fine structure method

P.-J. Chang and C.-T. Chia[a)]
Department of Physics, National Taiwan Normal University, Taipei 116, Taiwan

I.-N. Lin
Department of Physics, Tamkang University, Tamsui 251, Taiwan

J.-F. Lee
National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

C. M. Lin
Department of Science Education, National Hsin-Chu Teachers College, Hsinchu 300, Taiwan

K. T. Wu
Department of Physics, Soochow University, Taipei 111, Taiwan

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The structures of TaO_6 and NbO_6 oxygen octahedra in $x\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3+(1-x)\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ perovskite ceramics with $x=0$, 0.25, 0.50, 0.75, and 1.0 were investigated by the extended x-ray absorption fine structure method. The decline in the microwave dielectric constant as x increases is caused mainly by the decrease of the mean volume of the oxygen octahedra, regardless of the 1:2 ordered structure and the distortion of the oxygen octahedron. The low Qf values of the TaO_6 and NbO_6 mixed samples are caused by not only the degrading of the 1:2 ordered structure but also the distortion of oxygen octahedral cages. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2213514]

$A(B'_{1/3}B''_{2/3})\mathrm{O}_3$ 1:2 ordered ceramics are well known for their potential applications in microwave communications and their high Qf value which can be exploited in microwave resonators.[1,2] B-site ordering and its relationship to microwave properties of the similar ceramics, as revealed by the Raman spectroscopy, infrared spectroscopy, and x-ray diffraction, have attracted substantial attention.[3–13] Recent studies have examined how the microwave properties of $A(B'_{1/3}B'')\mathrm{O}_3$ and phonon vibrations are related,[7–9] indicating that structural characteristics of the $B'\mathrm{O}_6$ oxygen octahedra in $A(B'_{1/3}B''_{2/3})\mathrm{O}_3$ ceramics are critical to the microwave performance. However, optical measurements, including those obtained by Raman spectroscopy or infrared spectroscopy, yield information that indirectly relates phonon vibrations to the microwave characteristics. The $B'\mathrm{O}_6$ local structure must be directly measured, such as by an extended x-ray absorption fine structure (EXAFS), to support the optical measurements.[14,15] Although the crystalline structure of $x\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Ta}_{2/3})\mathrm{O}_3+(1-x)\mathrm{Ba}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ [hereafter xBMT+$(1-x)$BMN] perovskite can be determined by powder x-ray diffraction, this approach cannot easily resolve the differences between the local surroundings of Ta and Nb core atoms. The interferencelike pattern embedded in the EXAFS spectrum yields quantitative information about the local structure near an absorbing atom with relatively sensitive to structural disorder.[12,13] However, discussion of EXAFS to elucidate the effect of B'' site on the microwave characteristics is rare. This work reports the EXAFS results of the Ta L_{III} edge and the Nb K edge of xBMT+$(1-x)$BMN ceramics, with $x=0$, 0.25, 0.50, 0.75, and 1.0. The structural factors that directly affect the microwave performance are elucidated.

The microwave dielectric properties of xBMT+$(1-x)$BMN ceramics were measured by the TE_{011} resonant cavity method using an HP 8722 network analyzer, around 6 GHz.[16,17] The dielectric constant declines linearly as the Ta concentration increases; BMN ($x=0$) has the highest dielectric constant of 31.4 and BMT ($x=1$) has the lowest dielectric constant of 23.5. The BMT sample also has the highest Qf value (141.6 kHz) as expected and the Qf value of BMN (121.1 kHz) is the second highest. The sample with the lowest Qf value (33.3 kHz) is that with $x=0.5$, primarily because the 1:2 ordered structure is degraded, if the Nb and Ta atoms are assumed to be evenly distributed. However, the Qf value of the $x=0.75$ sample (46.3 kHz) is two and a half times smaller than that of the $x=0.25$ sample (114.3 kHz), although they have similar B'' site ordered structure.

Ta L_{III}-edge and Nb K-edge EXAFS measurements were made in wiggler beamline BL17C and beamline BL01C, respectively, at the National Synchrotron Radiation Research Center of Taiwan. The absorption coefficient $\mu(E)$, converted from the fluorescence spectrum of the Ta L_{III} edge, was obtained between 9.68 and 10.88 keV. $\mu(E)$ of Nb K-edge spectra ranged from 18.7 to 20 keV. The absorption coefficient $\mu(E)$ raised at the absorption edge agrees with the expected growth and is proportional to the concentration of the absorbing atoms. The EXAFS results were interpreted using the FEFF-8 code which is based on real space full multiple scattering calculations;[18] the structural parameters of TaO_6 and NbO_6 can be determined to interpret the microwave dielectric characteristics of xBMT+$(1-x)$BMN.

Figure 1(a) presents the typical momentum (k^3) weighted EXAFS signals of the Ta L_{III} edge (9.881 keV) and

a)Author to whom correspondence should be addressed; electronic mail: chiact@phy.ntnu.edu.tw

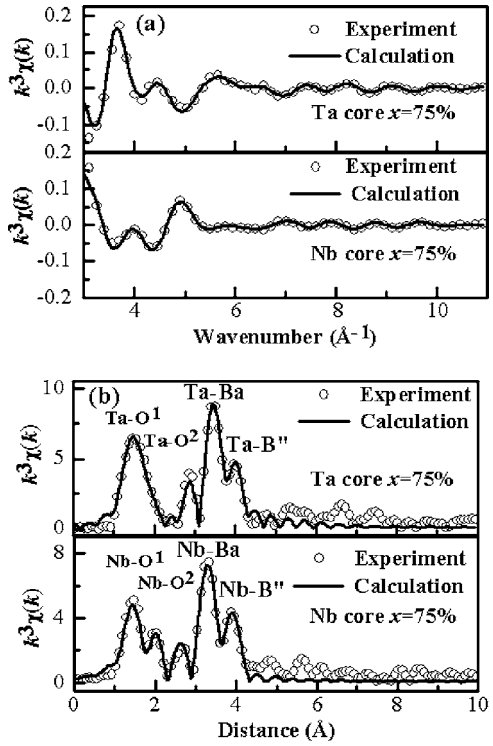

FIG. 1. EXAFS signal of 0.75BMT+0.25BMN. (a) k^3 weighted EXAFS signal of Ta L_{III} edge and Nb K edge in k space and (b) in R space. Hollow circles represent the experimental data and the solid lines represent the FEFF-8 fitting results.

Nb K edge (18.986 keV) in momentum (k) space for the 0.75BMT+0.25BMN sample after the background was removed using the AUTOBK program in FEFF-8.[18] The $\chi(k)$ denotes the EXAFS function. Figure 1(b) presents the EXAFS spectra with distance R measured from the absorbing core atoms at B'' lattice sites. The results presented in Fig. 1(b) were obtained by Fourier transform (FT) of the $k^3\chi(k)$ EXAFS signals shown in Fig. 1(a). The FTs were performed in the range of 3–11 Å^{-1} in k space. The hollow circles in Fig. 1 represent the experimental results, while the solid lines are the FEFF-8 fitting results. The solid lines in Fig. 1 are the FEFF-8 fitting data for the seven nearest neighboring atoms at 0.9–4.2 Å from the core atoms. The FEFF-8 analyses of the other samples are similar to that in Fig. 1, and the R factors of all fittings were under 0.003. The average distances of the three first nearest oxygen atoms in TaO_6 (denoted as Ta–O^1) are around 1.89(4), 1.87(1), 1.85(7), and 1.87(1) Å for x=0.25, x=0.5, x=0.75, and BMT samples, respectively, while the Nb–O^1 bonds in NbO_6 are slightly larger, at around 1.95(6), 1.94(8), 1.94(4), and 1.94(4) Å in the BMN, x=0.25, x=0.5, and x=0.75 samples, respectively. Similarly, the three second nearest three oxygen atoms in TaO_6, Ta–O^2, are around 2.09(0), 2.07(4), 2.07(3), and 2.07(2) Å in the x=0.25, x=0.5, x=0.75, and BMT samples, respectively, while those in NbO_6, Nb–O^2, are 2.11(4), 2.11(6), 2.11(8), and 2.12(4) Å for the BMN, x=0.25, x=0.5, and x=0.75 samples, respectively. The EXAFS results indicate that the mean volume of NbO_6 slightly exceeds that of TaO_6, mainly because of the large polarizability of Ta^{5+} ions, although the effective ion radii of Nb^{5+} and Ta^{5+} are about the same.[19–21] However, the polarizability of Mg^{2+} is much lower than those of Nb^{5+} and Ta^{5+}. Therefore, we expect that the microwave dielectric constants of xBMT+$(1-x)$BMN

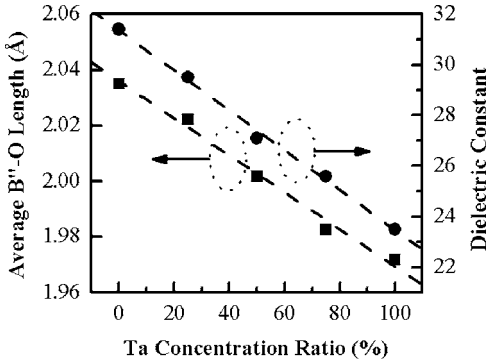

FIG. 2. Plot of the averaged B''–O bond length, determined using $[x\mathrm{TaO}^1+(1-x)\mathrm{NbO}^1+x\mathrm{TaO}^2+(1-x)\mathrm{NbO}^2]/2$, and dielectric constant of xBMT $+(1-x)$BMN ceramics vs Ta concentration.

are strongly related to the polarizability of the B''-site ion.

Figure 2 plots the mean length of B''–O bond in $B''O_6$ oxygen octahedra and the dielectric constant of the xBMT $+(1-x)$BMN ceramics versus Ta concentration ratio x. The averaged B''–O bond lengths of $B''O_6$ were determined using the formula $[x\mathrm{TaO}^1+(1x)\mathrm{NbO}^1+x\mathrm{TaO}^2+(1-x)\mathrm{NbO}^2]/2$, in which the superscripts 1 and 2 refer to the first and second nearest oxygen atoms in the $b''O_6$ octahedra, respectively. The mean bond length of the $B''O_6$ octahedra decreases linearly as the Ta concentration increases, as presented in Fig. 2, indicating that the mean volume of the $B''O_6$ octahedra declined linearly as the Ta concentration was increased. Although cation Nb^{5+} (0.67 Å) is slightly smaller than Ta^{5+} ion (0.68 Å) by EXAFS fitting, the large mean Nb–O bond length provides more space for Nb^{5+} ions than the Ta–O bond does for Ta^{5+} ions. Based on the above discussion, when an external electric field is applied to xBMT+$(1-x)$BMN ceramics, the displacement of Nb^{5+} against the oxygen cage exceeds that of Ta^{5+}. Hence, polarization the NbO_6^- caused by microwave propagation exceeds that of TaO_6^-. Consequently, the linear drop of the microwave dielectric constant as the Ta concentration increases is caused mainly by the smallness of the TaO_6.

The size homogeneity of $B''O_6$ is another cause for why the Qf values of the BMT and BMN exceed those of the TaO_6 and NbO_6 mixed samples, i.e., x=0.25, x=0.5, and x =0.75 samples. However, the smallest Ta–O bond length in the BMT sample, presented in Fig. 2, shows that the TaO_6-octahedral cages of BMT are the most rigid, and the fact that BMT has a higher Qf value than BMN is unsurprising, since denser materials are generally expected to have higher Qf values. However, the x=0.25 and x=0.75 samples have similar ordering characteristics, which is inconsistent with the above prediction; rather, the Qf value of the 0.75BMT+0.25BMN sample is around two and a half times smaller than that of the 0.25BMT+0.75BMN sample. Apparently, a factor other than the 1:2 ordered structure affects the microwave performance. The distortion of the oxygen octahedron is commonly considered to reduce the Qf values, although the definition of distorted oxygen octahedron is not well determined in such a case.

The deformation of the oxygen octahedral cages can be determined from the difference between the Ta–O^{1,2} and Nb–O^{1,2} bond lengths, $\Delta(\mathrm{Nb-O}^{1,2},\mathrm{Ta-O}^{1,2})$. Figure 3 plots the difference between the mean B''–O bond lengths of the first nearest oxygen atoms, $\Delta(\mathrm{Nb-O}^1,\mathrm{Ta-O}^1)$; difference

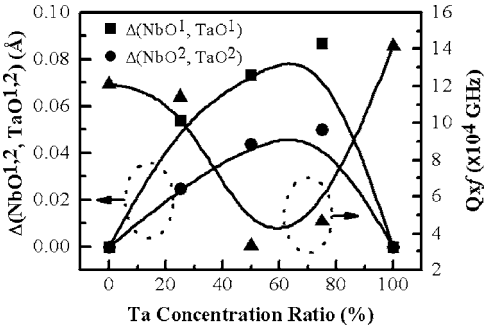

FIG. 3. Correlation of $\Delta(NbO^{1,2}-TaO^{1,2})$ with Qf value.

between those of the second nearest oxygen atoms in the NbO_6 and TaO_6 octahedra, $\Delta(Nb-O^2,Ta-O^2)$; and Qf values versus the Ta concentration. $\Delta(Nb-O^1,Ta-O^1)$ and $\Delta(Nb-O^2,Ta-O^2)$ for BMT and BMN samples are both zero, because only TaO_6 or NbO_6 is present in the BMT or BMN sample. Figure 3 shows that $\Delta(Nb-O^1,Ta-O^1)$ is in the range of 0.05–0.09 Å and $\Delta(Nb-O^2,Ta-O^2)$ is around 0.02–0.05 Å for the $x=0.25$, 0.5, and 0.75 samples. Both $\Delta(Nb-O^1,Ta-O^1)$ and $\Delta(Nb-O^2,Ta-O^2)$ for the 0.75BMT+0.25BMN sample are significantly higher, and the values are about double those of the 0.25BMT +0.75BMN sample. Randomly mixed TaO_6 and NbO_6 with large $\Delta(Nb-O^1,Ta-O^1)$ and $\Delta(Nb-O^2,Ta-O^2)$ clearly affects the chemical bonding among the oxygen octahedra. Therefore, the oxygen octahedra are expected to become slightly distorted and to twist, dampening the microwave propagation, and yielding low Qf values. The 0.75BMT +0.25BMN sample has a similar B''-site ordered structure like the 0.25BMT+0.75BMN, but the lack of homogeneity of the sizes of the $B''O_6$ octahedra further degrade Qf value.

In summary, EXAFS measurements of 1:2 ordered xBMT+$(1-x)$BMN ceramics were made and the microwave dielectric properties explained by the structural properties of the $B''O_6$ octahedra thus identified. The size of the $B''O_6$ oxygen cage strongly affects the dielectric constant. The short bond length of the Ta–O causes the dielectric constant to decline, as the Ta concentration rises. The perovskite 1:2 ordered structure is responsible for the high Qf values of the BMT and BMN ceramics. However, the nonuniformity of the sizes of the $B''O_6$ is critical to reducing the Qf value of $x=0.75$ sample. The mean volume of the $B''O_6$ octahedra strongly affects the dielectric constant of the xBMT+$(1-x)$BMN. However, the nonhomogeneity of the size and the distortion of the oxygen octahedra strongly degrade the Qf value.

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[1]S. Nomura, K. Toyama, and K. Kaneta, Jpn. J. Appl. Phys., Part 2 **21**, L642 (1982).
[2]R. Guo, A. S. Shalla, and L. E. Cross, J. Appl. Phys. **75**, 4704 (1994).
[3]R. L. Moreira, F. M. Matinaga, and A. Dias, Appl. Phys. Lett. **78**, 428 (2001).
[4]A. Dias, V. S. T. Ciminelli, F. M. Matinaga, and R. L. Moreira, J. Eur. Ceram. Soc. **21**, 2739 (2001).
[5]Y. Fang, A. Hu, S. Ouyang, and J. J. Oh, J. Eur. Ceram. Soc. **21**, 2745 (2001).
[6]I. G. Siny, R. W. Tao, R. S. Katiyar, R. A. Guo, and A. S. Bhalla, J. Phys. Chem. Solids **59**, 181 (1998).
[7]C.-T. Chia, Y.-C. Chen, H.-F. Cheng, and I.-N. Lin, J. Appl. Phys. **94**, 3360 (2003).
[8]Y.-C. Chen, H.-Fung Cheng, H.-L. Liu, C.-T. Chia, and I.-N. Lin, J. Appl. Phys. **94**, 3365 (2003).
[9]S. Janaswamy, G. S. Murthy, E. D. Dias, and V. R. K. Murthy, Mater. Lett. **55**, 414 (2002).
[10]T. Nagai, T. Inuauka, and M. Sugiyama, Jpn. J. Appl. Phys., Part 1 **31**, 3132 (1992).
[11]M. Sugiyama and T. Nagai, Jpn. J. Appl. Phys., Part 1 **32**, 4360 (1993).
[12]T. Nagai, M. Sugiyama, M. Sando, and K. Niihara, Jpn. J. Appl. Phys., Part 1 **36**, 1146 (1997).
[13]T. Nagai, M. Sugiyama, M. Sando, and K. Niihara, Jpn. J. Appl. Phys., Part 1 **35**, 5163 (1996).
[14]J. J. Rehr and R. C. Albers, Rev. Mod. Phys. **72**, 621 (2000).
[15]R. Prins and D. C. Koningsberger, *X-Ray Absorption Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* (Wiley, New York, 1988), Chaps. 1 and 6.
[16]I. N. Lin, C. T. Chia, H. L. Liu, H. F. Cheng, and C. C. Chi, Jpn. J. Appl. Phys., Part 1 **41**, 6952 (2002).
[17]D. Kajfez and P. Guillon, *Dielectric Resonators* (Artech House, Norwood, MA, 1986), Chap. 6.
[18]A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, Phys. Rev. B **58**, 7565 (1998).
[19]R. D. Shannon, J. Appl. Phys. **73**, 348 (1993).
[20]N. W. Grimesy and R. W. Grimesz, J. Phys.: Condens. Matter **9**, 6737 (1997).
[21]N. W. Grimesy and R. W. Grimesz, J. Phys.: Condens. Matter **10**, 3029 (1998).