Available online at www.sciencedirect.com

Journal of the European Ceramic Society 26 (2006) 1965–1968

www.elsevier.com/locate/jeurceramsoc

Microwave properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Nb_{2/3})O_3$ and $Ba(Co_{1/3}Nb_{2/3})O_3$ ceramics revealed by Raman scattering

M.-Y. Chen[a], C.-T. Chia[a,*], I.-N. Lin[b], L.-J. Lin[c], C.-W. Ahn[d], Shan Nahm[d]

[a] *Department of Physics, National Taiwan Normal University, Taipei 116, Taiwan ROC*
[b] *Department of Physics, Tamkang University, Tamsui, Taipei 251, Taiwan ROC*
[c] *Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 310, Taiwan ROC*
[d] *Department of Materials Science and Engineering, Korea University, 1-5ka, Anam-dong, Sungbuk-ku, Seoul 136-701, Korea*

Available online 27 October 2005

Abstract

Five $Ba(Co_{1/3}Nb_{2/3})O_3$ samples sintered at different temperatures (form 1350 to 1550 °C), one $Ba(Mg_{1/3}Ta_{2/3})O_3$ and a $Ba(Mg_{1/3}Nb_{2/3})O_3$ sample were examined by Raman scattering to reveal the correlation of the 1:2 ordered perovskite structure with the microwave properties, such as dielectric constant and Q factors. The $Ba(Co_{1/3}Nb_{2/3})O_3$ sample sintered at 1400 °C, which possesses the highest microwave Q value and the lowest dielectric constant among five $Ba(Co_{1/3}Nb_{2/3})O_3$ samples, has the narrowest width and the highest frequency of the stretch mode of oxygen octahedron (i.e. $A_{1g}(O)$ near 800 cm^{-1}). We found that the dielectric constant is strongly correlated with the Raman shift of $A_{1g}(O)$ stretch modes, and the width of $A_{1g}(O)$ stretch mode reflects the quality factor $Q \times f$ value in the 1:2 ordered perovskite materials. This concludes that the oxygen octahedron play an important role of the material's microwave performance. Based on the results of $Q \times f$ values and the lineshapes of $A_{1g}(O)$ stretch mode, we found that the propagation of microwave energy in $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Nb_{2/3})O_3$ shows weak damping behavior, however, $Ba(Co_{1/3}Nb_{2/3})O_3$ samples sintered at different temperature exhibit heavily damped behavior.

© 2005 Elsevier Ltd. All rights reserved.

Keyword: Raman scattering; Dielectric properties; Optical properties; Perovskites

1. Introduction

The well known 1:2 ordered perovskite ceramics, such as $Ba(Co_{1/3}Nb_{2/3})O_3$, $Ba(Mg_{1/3}Nb_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$, have great potential for industrial application.[1–3] Due to the low dielectric loss and high Q value in the microwave region, there are several important applications in the communications industry, such as dielectric resonators (DRS), and microwave integrated circuits.[1] The search for high performance materials in microwave application is still in progress, and the crystal structures that affect the microwave properties are not fully investigated. Raman scattering is one of the powerful tools to investigate the crystal structure, and Raman studies of microwave material have many achievements.[3–5] However, the relation between atomic vibration and microwave properties of perovskite ceramics is not easy to elucidate. A recent optical study has shown that the 1:2 ordered structure-related phonon vibrations (the so-called 1:2 ordered phonons) have strong correlation with the microwave properties.[6,7] It is well understood that samples having a higher degree of 1:2 ordered structure possess higher Q factors,[8–13] therefore, the 1:2 ordered phonons are strongly correlated with the microwave properties of 1:2 ordered perovskite compounds. Though $A(B'_{1/3}B''_{2/3})O_3$ ceramic samples were prepared with 1:2 order, the intensities of 1:2 ordered phonons were too weak to detect in many cases.[6,7,14–16] A recent study shows that physical properties of the oxygen octahedral network in the 1:2 ordered structure plays an important role on the material microwave performance.[6,7] Therefore, the characteristics of the stretch modes of oxygen octahedra can give an indication of the material's microwave performance. One way to detect the structural properties of oxygen octahedra of microwave material is to analyze the stretch modes of the oxygen cages.

In this paper, we examine the microwave properties of $Ba(Co_{1/3}Nb_{2/3})O_3$ (BCN) sintered at different temperatures by using the Raman scattering method. For comparison, the Raman results of a $Ba(Mg_{1/3}Nb_{2/3})O_3$ sample (BMN) and a $Ba(Mg_{1/3}Ta_{2/3})O_3$ sample (BMT) from a previous study[6,7] are also presented. The sintering effect is known to be important

---

[*] Corresponding author.
E-mail address: chiact@phy.ntnu.edu.tw (C.-T. Chia).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.09.042

factor on the crystal structure, and we intended to study the correlation of sintering-temperature dependent octahedral structure with the microwave properties. On the other hand, we also distinguished the difference of microwave propagation in BCN, BMN and BMT ceramics, based on the properties of the stretch mode of the oxygen octahedra and the measured $Q \times f$ value.

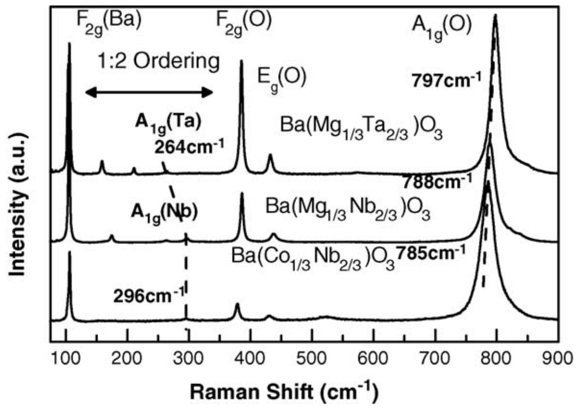

Fig. 1. The Raman spectra of BMT, BMN, and BCN sintered at 1400 °C, and four important features are marked: (1) the F_{2g}(Ba) phonon mode near 105 cm^{-1}, (2) the degenerate A_{1g}(O) and E_g(O) phonon modes near 375 cm^{-1}, (3) the E_g(O) phonon mode near 450 cm^{-1}, and (4) the stretch vibration of oxygen octahedra near 800 cm^{-1}.

2. Experiment

Ceramics of the composition Ba($Co_{1/3}Nb_{2/3}$)O_3 with sintering temperatures of 1350 °C, 1400 °C, 1420 °C, 1450 °C, and 1550 °C were prepared from the oxides of >99% purity by using conventional solid state synthesis.[17,18] Oxide compounds of $BaCO_3$, CoO and Nb_2O_5 were mixed for 24 h in a nylon jar with zirconia balls and then dried and calcined at 1100–1200 °C for 4 h. After remilling, the powder was dried and pressed into discs and sintered at 1300–1550 °C. The Ba($Mg_{1/3}Nb_{2/3}$)O_3 sample (BMN) and a Ba($Mg_{1/3}Ta_{2/3}$)O_3 samples are prepared by using HIP technique, and sintered at 1650 °C.[5,13] The microstructure of the specimen was studied by Raman spectroscopy. The Raman signal was collected at room temperature and recorded by a DILOR XY-800 triple-grating Raman spectrometer equipped with a liquid-nitrogen-cooled CCD. The 10 mW output of the 514.5 nm line of Ar$^+$ ion laser was used as the excitation source. The obtained Raman spectra exhibited a resolution approximately of 0.5 cm^{-1}. The microwave dielectric properties were

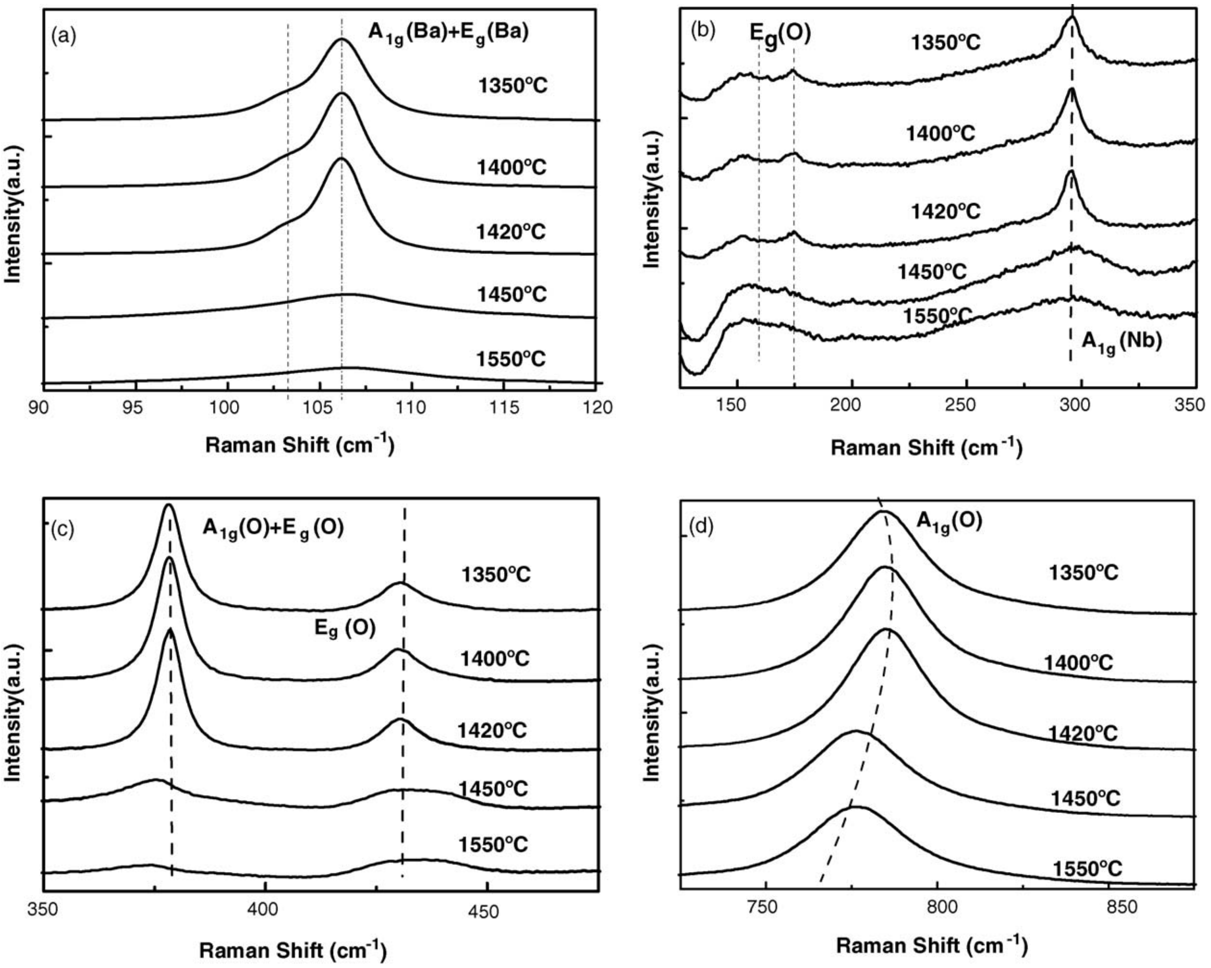

Fig. 2. The Raman spectra of BCN samples sintered at 1350 °C, 1400 °C, 1420 °C, 1450 °C, and 1550 °C. Vibration modes (a) related to the Ba atomic motion near 105 cm^{-1}; (b) the 1:2 ordering (c) related to the O atomic motion in between 350 and 450 cm^{-1}and (d) the oxygen-octahedron stretch modes.

measured by the TE_{011} resonant cavity method using an HP 8722 network analyzer, around 6 GHz.

3. Results and discussion

$A(B'_{1/3}B''_{2/3})O_3$ perovskite has a 1:2 ordered-structure and belongs to the $P-3m1(\equiv D_{3d}^3)$ space group. In Fig. 1, the typical Raman spectra of BCN, BMN and BMT are shown. There are four prominent peaks related to the ordered structure as found in the Raman spectra of 1:2 order pervoskite.[4] They are (1) the F_{2g}(Ba) phonon mode near 105 cm^{-1}, (2) the degenerate A_{1g}(O) and E_g(O) phonon modes near 375 cm^{-1}, (3) the E_g(O) phonon mode near 450 cm^{-1}, and (4) the stretch vibration of oxygen octahedra near 800 cm^{-1}. Besides these strong modes, three weak modes are also observed in the 150–300 cm^{-1} range. These weak phonon modes have been identified as the 1:2 ordered structure-related vibrations.[4,7] Apparently, the intensities of these modes can be used to determine the degree of 1:2 order. These 1:2 ordered phonon modes of BMT have the highest intensities among all samples, it also possesses the highest $Q\times f$ values. For the Raman spectrum of BCN sintered at 1400 °C shown in Fig. 1, the 1:2 ordered modes are almost immeasurable. This suggests that BCN has the lowest $Q\times f$ value among three samples, based on the measurement of the lineshapes of the 1:2 ordered phonons.

The sintering-temperature effect on the BCN samples was found by the Raman spectroscopy. In Fig. 2(a)–(d), the four Raman features of the BCN samples sintered at 1350 °C, 1400 °C, 1420 °C, 1450 °C and 1550 °C are shown. Fig. 2(a) shows vibration modes related to the Ba lattice site-related vibrations, and Fig. 2(b) shows the 1:2 ordering. In Fig. 2(c), the vibration modes related to oxygen layer are shown, and the stretch modes of the oxygen octahedra are shown in Fig. 2(d). For sintering temperatures above 1450 °C, broad and weak phonon lineshapes are observed in Fig. 2. This result indicates that degradation of microwave properties for samples sintered at temperatures above 1450 °C. The vibration modes of 1:2 ordering for all BCN samples shown in Fig. 2(b) are too broad and too weak to analyze. However, the stretch mode of the oxygen octahedra is the most prominent peak. This mode can be used to deduce the properties of the oxygen octahedra, therefore, the correlation with the microwave dielectric properties can be examined.

In Fig. 3, the correlation of the microwave properties with the lineshapes of A_{1g}(O) is shown. In Fig. 3(a), the Raman shift of stretch A_{1g}(O) modes and the dielectric constant are plotted as a function of sintering temperature. The dielectric constant reaches minimum and the A_{1g}(O) phonon energy reaches maximum for samples sintered at 1400 °C. At higher temperature the dielectric constant markedly increases while the phonon shift significantly decreases. The reverse trend of phonon width and the $Q\times f$ value is also found, as shown in Fig. 3(b). $Q\times f$ value reaches maximum at 1400 °C, while the FWHM of stretch mode shows minimum, as found in Fig. 3(b). It clearly indicates that the Raman shift is related to the rigidity of the oxygen octahedra, while the peak width is correlated with decay of microwave propagation. This result clearly indicates that the rigid oxygen octahedra correlate with low dielectric constant and high $Q\times f$ value. For rigid oxygen octahedra, the relative motion of Ba^{2+} cation to $B''O_6$ anions induced by microwave energy is small, and this is the reason for the smaller dielectric constant of BCN sample sintered at 1400 °C. The narrowed width of A_{1g}(O) mode indicates the highly ordered and rigid oxygen-cage structure; therefore, the decay time of the propagation of the microwave energy is longer, and this implies the material possesses high Q value in the microwave frequency region. Our results indicate that the physical properties of oxygen octahedra, which can be revealed by Raman A_{1g}(O) measurements, have strong influence on microwave performance. Similar arguments have been applied to xBMT + $(1-x)$BMN system.[6,7]

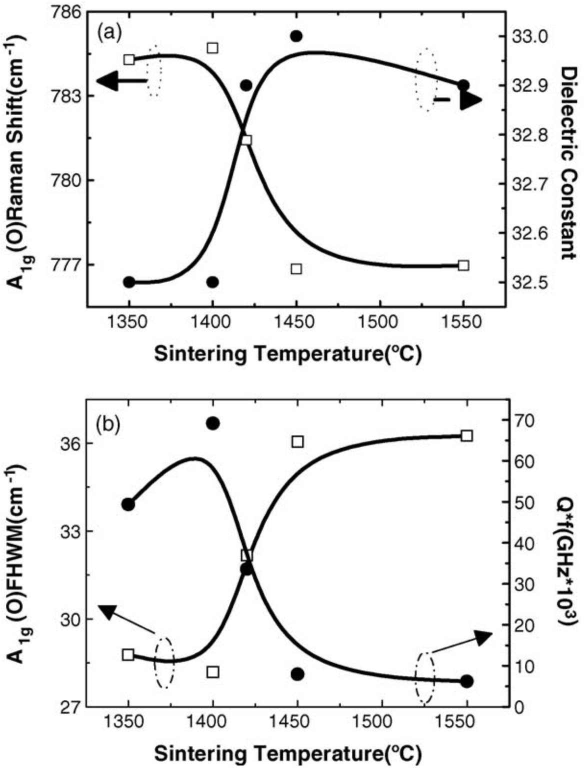

Fig. 3. Relationship between temperature characteristics of A_{1g}(O) phonon mode and the microwave properties for BCN material: (a) the correlation of Raman shift and the dielectric constant and (b) FWHM and the $Q\times f$ value.

Based on the previous result, the damping characteristics of the BMT, BMN and the five BCN samples can be revealed by Raman measurements. Therefore, the difference of the microwave propagation in these materials can be detected. In Fig. 4, the measured $Q\times f$ values are plotted against the inverse of the A_{1g}(O) peak width. In weak damping case, the quality factor is inversely proportional to the width. In our case, the $Q\times f$ values are determined by the microwave resonance, and microwave resonance width can be determined from the Q factor measurement. The lineshape of oxygen-octahedral stretching phonon, i.e. A_{1g}(O) near 800 cm^{-1}, reflects the structure properties of the O-cages, which has strong effect on the microwave properties of 1:2 ordered perovskite. Therefore, we think that the microwave resonance width and the A_{1g}(O) phonon width

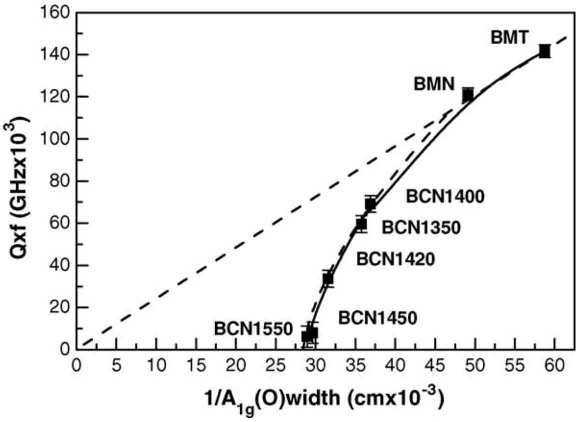

Fig. 4. Plot of $Q \times f$ value vs. 1/(FWHM) of the stretch A_{1g}(O) modes of a BMT, a BMN, and five BCN samples.

are linearly correlated, if the extrinsic effects of samples is negligible. As shown in Fig. 4, the $Q \times f$ values of BMT and BMN are linearly proportional to the 1/FWHM, and this indicates the weak damping character of the BMT and BMN for microwave propagation. The five BCNs show heavily damped behavior for microwave propagation, due to the parabolic curve found in the $Q \times f$ value and width. Fig. 4 clearly expresses the intrinsic difference of microwave propagation in BMT, BMN and BCN 1:2 ordered perovskite ceramics.

4. Conclusion

In this paper, the BCN samples sintered at different temperatures were examined by Raman scattering. The microwave dielectric properties show strong correlation with the characters of Raman lineshapes, including Raman shift, phonon width, and intensity. Especially, the lineshapes of 1:2 ordered phonons of BMT, BMN and BCN samples are found to have strong correlation with the microwave dielectric properties, as shown in Fig. 1. However, 1:2 ordered modes of BCN samples sintered at high temperature were too weak to realize. The Raman shift of the A_{1g}(O) stretch mode of oxygen octahedra reflects the property of dielectric constant, and the linewidth of stretch mode is related to the $Q \times f$ value. The rigid oxygen octahedra revealed by high frequency of A_{1g}(O) mode are related to the low dielectric constant in microwave region. The sample with narrowed linewidth of the A_{1g}(O) possesses high $Q \times f$ value. Based on the result of Raman phonon analysis, we also found that BMT and BMN samples show weak damping behavior of microwave propagation, whereas all BCN samples exhibit heavy damped character.

Acknowledgement

Financial support of this work from the National Science Council of Taiwan, ROC, under the Contract Nos. NSC 92-2112-M-003-017 and NSC 93-2112-M-003-012 is acknowledged.

References

1. You, C.-C., Huang, C.-L., Wei, C.-C. and Hang, J.-W., Improved High-*Q* dielectric resonator sintered at low firing temperature. *Jpn. J. Appl. Phys.*, 1995, **34**, 1911–1915.
2. Nomura, S., Toyama, K. and Kaneta, K., $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with temperature-stable high dielectric constant and low microwave loss. *Jpn. J. Appl. Phys.*, 1982, **21**, 624–626.
3. Moreira, R. L., Matinaga, F. M. and Dias, A., Raman-spectroscopic evaluation of the long-range order in $Ba(B'_{1/3}B''_{2/3})O_3$ ceramics. *Appl. Phys. Lett.*, 2001, **78**, 428–430.
4. Siny, I. G., Tao, R. W., Katiyar, R. S., Guo, R. A. and Bhalla, A. S., Raman spectroscopy of MG-TA order–disorder in $BAMG_{1/3}TA_{2/3}O_3$. *J. Phys. Chem. Solids*, 1998, **59**, 181–195.
5. Lin, I-N., Chia, C.-T., Liu, H.-L., Chen, Y.-C., Cheng, H.-F. and Chi, C.-C., High frequency dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ complex perovskite ceramics. *J. Eur. Ceram. Soc.*, 2003, **23**, 2633–2637.
6. Chen, Y.-C., Huang, H.-F., Lin, H.-L., Chia, C.-T. and Lin, I.-N., Correlation of microwave dielectric properties and normal vibration modes of $Ba(Mg_{1/3}Ta_{2/3}O_3–(1-x)\ Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics: II. Infrared spectroscopy. *J. Appl. Phys.*, 2003, **94**, 3365–3369.
7. Chia, C.-T., Chen, Y.-C. and Cheng, H.-F., Correlation of microwave dielectric properties and normal vibration modes of $Ba(Mg_{1/3}Ta_{2/3}O_3–(1-x)Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics: I. Raman spectroscopy. *J. Appl. Phys.*, 2003, **94**, 3360–3364.
8. Nomura, S., Toyama, K. and Kaneta, K., $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with temperature-stable high dielectric constant and low microwave loss. *Jpn. J. Appl. Phys.*, 1982, **21**, 624–626.
9. Guo, R., Shalla, A. S. and Cross, L. E., $Ba(Mg_{1/3}Ta_{2/3})O_3$ single crystal fiber grown by the laser heated pedestal growth technique. *J. Appl. Phys.*, 1994, **75**, 4704.
10. Iwata, M., Hoshino, H., Orihara, H., Ohwa, H., Yasuda, N. and Ishibashi, Y., Raman scattering in $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3–xPbTiO_3$ mixed crystal system. *Jpn. J. Appl. Phys.*, 2000, **39**, 5961–5966.
11. Sugiyama, M. and Nagai, T., Anomaly of dielectric-constant of (BA1-XSRX)$(MG_{1/3}TA_{2/3})O_3$ solid-solution and its relation to structural-change. *Jpn. J. Appl. Phys. Part 1*, 1993, **32**, 4360.
12. Lin, I. N., Chia, C. T., Liu, H. L., Cheng, H. F. and Chi, C. C., Dielectric properties of $xBa(Mg_{1/3}Ta_{2/3})O_3–(1-x)Ba(M_{g1/3}Nb_{2/3})O_3$ complex perovskite ceramics. *Jpn. J. Appl. Phys. Part 1*, 2002, **41**, 6952–6956.
13. Idink, H. and William, B., White Raman spectroscopic study of order–disorder in lead magnesium niobate. *J. Appl. Phys.*, 1994, **76**, 1789–1793.
14. Dias, A., Ciminelli, V. S. T., Matinagaa, F. M. and Moreira, R. L., Raman scattering and X-ray diffraction investigations on hydrothermal barium magnesium niobate ceramics. *J. Eur. Cream. Soc.*, 2001, **21**, 2739.
15. Jiang, F., Kojima, S., Zhao, C. and Feng, C., Chemical ordering in lanthanum-doped lead magnesium niobate relaxor ferroelectrics probed by A_{1g} Raman mode. *Appl. Phys. Lett.*, 2001, **79**, 3938–3940.
16. Ahn, C.-W., Jang, H.-J., Nahm, S., Park, H.-M. and Lee, H.-J., Effects of microstructure on the microwave dielectric properties of $Ba(Co_{1/3}Nb_{2/3})O_3$ and $(1-x)Ba(Co_{1/3}Nb_{2/3})O_3–xBa(Zn_{1/3}Nb_{2/3})O_3$. *J. Eur. Ceram. Soc.*, 2003, **23**, 2473–2478.
17. Ahn, C.-W., Nahm, S., Lim, Y.-S., Choi, W., Park, H.-M. and Lee, H.-J., Microstructure and microwave dielectric properties of $Ba(Co_{1/3}Nb_{2/3})O_3$ ceramics. *Jpn. J. Appl. Phys.*, 2002, **41**, 5277–5280.
18. Lin, I.-N., Chia, C.-T., Liu, H.-L., Cheng, H.-F. and Chi, C.-C., Dielectric Properties of $xBa(Mg_{1/3}Ta_{2/3})O_3–(1-x)Ba(Mg_{1/3}Nb_{2/3})O_3$ complex perovskite ceramics. *Jpn. J. Appl. Phys.*, 2002, **41**, 6952–6956.