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Microwave Dielectric Properties of Low-Firing Li_2MO_3 (M = Ti, Zr, Sn) Ceramics with B_2O_3–CuO Addition

Li-Xia Pang†

Laboratory of Thin Film Techniques and Optical Test, Xi'an Technological University, Xi'an 710032, China

Di Zhou

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

In this work, the sintering behaviors, microwave dielectric properties, and chemical compatibility with silver of pure and B_2O_3–CuO addition Li_2MO_3 (M = Ti, Zr, Sn) ceramics were studied. The 1 wt% B_2O_3–CuO addition does not affect the phase composition of Li_2MO_3 (M = Ti, Zr, Sn) and no secondary phase could be observed from XRD analysis. The sintering temperatures can be lowered from above 1200°C to around 900°C by 1 wt% B_2O_3–CuO addition. XRD analysis of cofired ceramics indicates that the Li_2MO_3 (M = Ti, Zr, Sn) ceramics are chemically compatible with silver. With 1 wt% B_2O_3–CuO addition, both Li_2TiO_3 and Li_2SnO_3 ceramics can be sintered well and possess good microwave dielectric properties with a permittivity of ~19.67, a $Q \times f$ value of ~46 300 GHz, a temperature coefficient of resonant frequency (TCF) of ~+31.3 ppm/°C, and a permittivity of 13.73, a $Q \times f$ value of 36 400 GHz and a TCF about +27.4 ppm/°C, respectively.

I. Introduction

With the rapid development of mobile communication and satellite communication, low-temperature cofired ceramic technology (LTCC) becomes an important fabricating technology that can integrate the passive components within a monolithic bulk module with IC chips mounted on its surface. The microwave dielectric materials used in LTCC field must have a range of dielectric permittivity (ε_r), a high $Q \times f$ value (f = resonant frequency, Q = 1/dielectric loss at f, $Q \times f > 5000$ GHz), a near zero temperature coefficient of resonant frequency (TCF ≈ 0 ppm/°C), a low sintering temperature (below the melting points of common electrode metals, such as silver, copper, gold, aluminum, etc.), and chemical compatibility with the metal electrodes. Besides this, considering the environment and economic elements, people prefer to explore microwave dielectric ceramics with low price (not containing rare metal oxides) and without toxicity (at least lead free).[1–6]

The Li_2TiO_3 and its modification ceramics have attracted much attention because of its good microwave dielectric properties (relative permittivity ε_r = 22–24, $Q \times f$ value = 40 000–70 000 GHz, TCF = +20 ppm/°C).[7–9] Pure Li_2TiO_3 ceramics cannot be well densified below 1000°C and at high temperature the volatilization of Li becomes serious. Liang and Lu[9] successfully used ZnO–B_2O_3 frit to lower the sintering temperature to around 900°C, and the good microwave dielectric properties with an ε_r of ~23.06, a $Q \times f$ of ~32 275 GHz, a TCF of ~+35.79 ppm/°C were obtained for 2.5 wt% ZnO–B_2O_3 frit-doped Li_2TiO_3 ceramics sintered at 900°C for 2 h. The B_2O_3–CuO was usually used to lower the sintering temperature of microwave dielectric ceramics and it works well in the $Ba(Mg_{1/3}Nb_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$, and $BiSbO_4$ systems.[10–12] In the present work, the influence of B_2O_3–CuO addition on the sintering behaviors, phase compositions and microwave dielectric properties of Li_2MO_3 (M = Ti, Zr, Sn) ceramics were studied. To apply this system in the LTCC technology, the chemical compatibility between Li_2MO_3 (M = Ti, Zr, Sn) ceramics and silver was also studied.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of Li_2CO_3, TiO_2, ZrO_2, and SnO_2 (>99%, Guo-Yao Co. Ltd., Shanghai, China) were prepared according to the stoichiometric formulation Li_2MO_3 (M = Ti, Zr, Sn). Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with the yttria-stabilized zirconia (2 mm in diameter) milling media. The mixed oxides were then calcined at 1000°C for 4 h. Then some powders were re-milled to obtain homogeneous pure Li_2MO_3 (M = Ti, Zr, Sn) powders. The other powders were re-milled with 1 wt% B_2O_3–CuO addition (with 4:6 in mole ratio) for 5 h using the ZrO_2 milling media and deionized water. After drying, the powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die with 5 wt% PVA binder addition under a uniaxial pressure of 200 MPa. Samples were sintered in the temperature range of 1070°–1280°C and 825°–950°C for 2 h, respectively, for pure Li_2MO_3 and sample with B_2O_3–CuO addition. To investigate the chemical compatibility of Li_2MO_3 system with silver powder, 20 wt% Ag powders were mixed with the Li_2MO_3 samples with B_2O_3–CuO addition and held at 900°C for 4 h.

The crystalline structures of samples were investigated using X-ray diffraction with Cu$K\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of sintered ceramic were observed on the as-fired surfaces with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). The apparent densities of sintered ceramics were measured by the Archimedes' method. Dielectric behaviors at microwave frequency were measured with the $TE_{01\delta}$ shielded cavity method using a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The TCF (τ_f) was calculated with the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \quad (1)$$

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†Author to whom correspondence should be addressed. e-mail: plx1982@gmail.com

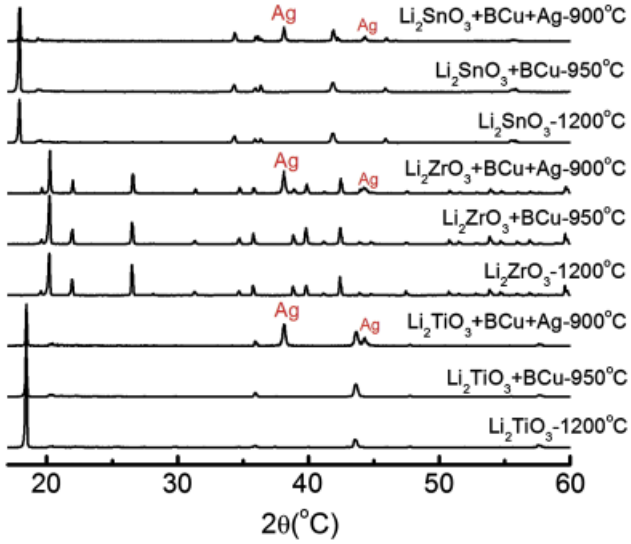

Fig. 1. XRD results of pure Li_2MO_3 (M = Ti, Zr, Sn) ceramics sintered at 1200°C/2 h, samples with 1 wt% B_2O_3–CuO addition sintered at 950°C/2 h, and cofired samples with 20 wt% Ag addition sintered at 900°C/4 h.

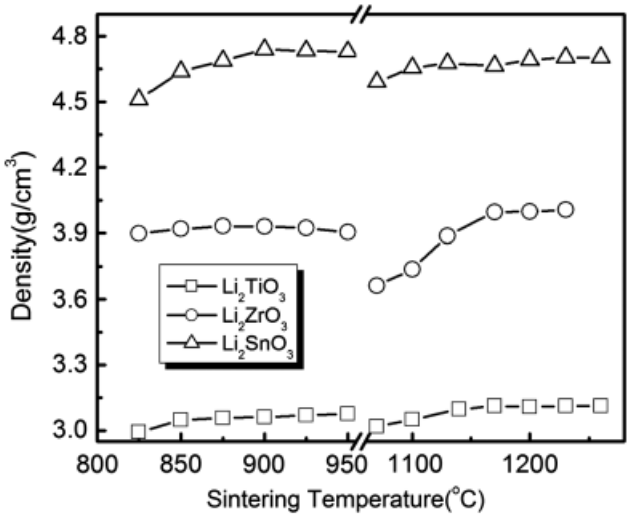

Fig. 2. Apparent density of both pure Li_2MO_3 (M = Ti, Zr, Sn) ceramics and samples with 1 wt% B_2O_3–CuO addition as a function of sintering temperature.

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85° and 25°C, respectively.

III. Results and Discussions

Figure 1 shows the XRD patterns of Li_2MO_3 (M = Ti, Zr, Sn) ceramics sintered at 1200°C/2 h, samples with 1 wt% B_2O_3–CuO addition sintered at 950°C/2 h and cofired samples with 20 wt% Ag addition sintered at 900°C/4 h. Pure single phase could be revealed in all Li_2MO_3 (M = Ti, Zr, Sn) ceramics and samples with B_2O_3–CuO addition. The 1 wt% B_2O_3–CuO addition does not affect the phase composition of Li_2MO_3 and no secondary phase could be observed from XRD analysis. Both Li_2TiO_3 and Li_2SnO_3 crystallize in a monoclinic structure with a space group number C2/c (15) as reported by Dorrian and Newnham[13] and Hodeau *et al.*[14] The cell parameters calculated from XRD patterns are $a = 5.040(2)$, $b = 8.792(4)$, and $c = 9.715(4)$ for Li_2TiO_3 and $a = 5.290(4)$, $b = 9.183(2)$, $c = 10.029(5)$ for Li_2SnO_3, and $a = 5.420(2)$, $b = 9.019(4)$, $c = 5.417(4)$ for Li_2ZrO_3, which are similar to the literature's reports. For the cofired samples, only pure Li_2MO_3 (M = Ti, Zr, Sn) and silver phases were identified inferring that there were no chemical interactions. Although this is a brief and preliminary investigation of the chemical compatibility, it indicates the application possibility of Li_2MO_3 (M = Ti, Zr, Sn) ceramics for LTCC technology.

Densities of both pure Li_2MO_3 (M = Ti, Zr, Sn) ceramics and samples with 1 wt% B_2O_3–CuO addition as a function of sintering temperature are shown in Fig. 2. During the sintering course, the grains grow big while pores shrink as the sintering temperature increases. After most pores being eliminated from ceramics, the densities of samples will reach their saturated values and well-densified ceramics are obtained. All pure Li_2MO_3 (M = Ti, Zr, Sn) ceramics would not be well sintered until temperature was above 1100°C as shown in Fig. 2. The relative densities are not very large as shown in Table I and this might be caused by the volatilization of lithium. Addition of 1 wt% B_2O_3–CuO significantly lowered the sintering temperature of Li_2MO_3 (M = Ti, Zr, Sn) ceramics from above 1100°C to around 900°C and made them possible for application in LTCC. There is a eutectic point below 900°C at the composition of $0.6CuO–0.4B_2O_3$ in the B_2O_3–CuO binary system.[15] This eutectic compound is responsible for the low-temperature densification of Li_2MO_3 ceramics here. It might be a liquid sintering mechanism for this system.

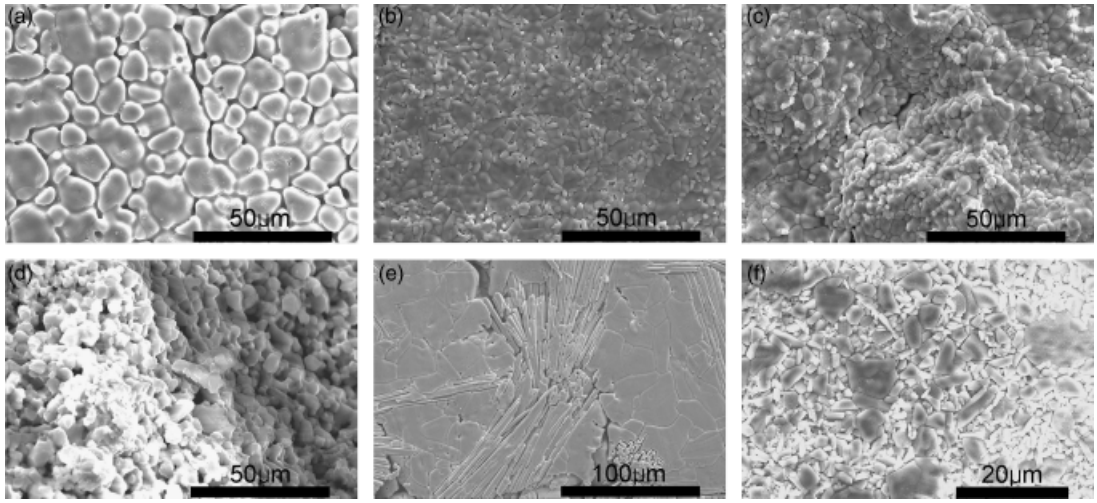

Fig. 3. Scanning electron micrographs of as-fired surfaces of (a) pure Li_2TiO_3 ceramics sintered at 1200°C/2 h, (b) Li_2TiO_3 ceramics with B_2O_3–CuO addition sintered at 875°C/2 h, (c) pure Li_2ZrO_3 ceramics sintered at 1200°C/2 h, (d) Li_2ZrO_3 ceramics with B_2O_3–CuO addition sintered at 875°C/2 h, (e) pure Li_2SnO_3 ceramics sintered at 1200°C/2 h, and (f) Li_2SnO_3 ceramics with B_2O_3–CuO addition sintered at 875°C/2 h.

Table I. Density and Microwave Dielectric Behavior of Li_2MO_3 (M = Ti, Zr, Sn) Ceramics

Sample	ST (°C)	Density (g/cm^3)	Relative density	Permittivity	$Q \times f$ (GHz)	TCF (ppm/°C)
Li_2TiO_3	1230	3.112	90.7%	19.75	23 600	+38.5
Li_2ZrO_3	1200	3.998	96.3%	14.10	17 640	+39.3
Li_2SnO_3	1230	4.702	94.2%	12.82	20 800	+26.9
Li_2TiO_3+BCu	900	3.062	—	19.67	46 300	+31.3
Li_2ZrO_3+BCu	900	3.930	—	17.75	4300	+12.5
Li_2SnO_3+BCu	900	4.738	—	13.73	36 400	+27.4

ST, sintering temperature; TCF, temperature coefficient of resonant frequency.

SEM micrographs of as-fired surfaces of pure Li_2MO_3 (M = Ti, Zr, Sn) ceramics sintered at 1200°C/2 h and samples with 1 wt% B_2O_3–CuO addition sintered at 875°C/2 h are shown in Fig. 3. The grain size of pure Li_2TiO_3 ceramics sintered at 1200°C/2 h lies in the range of 8–15 μm and its microstructure does not look very dense. For Li_2TiO_3 ceramics with B_2O_3–CuO addition sintered at 875°C/2 h, dense and fine microstructure is observed as shown in Fig. 3(b). The grain size is about 3–6 μm, which is much smaller than the pure Li_2TiO_3 ceramics. This result indicates that the addition of B_2O_3–CuO effectively accelerated the sintering course, lowered the sintering temperature, and helped to obtain the small grain size of Li_2TiO_3 ceramics. Similar results are obtained for Li_2SnO_3 ceramics. The grain size of pure Li_2SnO_3 ceramics is about 20–40 μm and it is bigger than that of the sample with B_2O_3–CuO addition around 3–10 μm. However, the grain sizes of both pure Li_2ZrO_3 ceramics and samples with B_2O_3–CuO addition have a very similar value of about 3–6 μm.

Microwave dielectric properties of pure Li_2MO_3 (M = Ti, Zr, Sn) ceramics and samples with B_2O_3–CuO addition as a function of sintering temperature are presented in Fig. 4. The permittivity at microwave region is affected mainly by the pores in ceramics. Hence, the permittivity trend versus sintering temperature is very similar to that of density. The saturated permittivity of pure Li_2MO_3 (M = Ti, Zr, Sn) ceramics could be obtained at above 1100°C and the samples with B_2O_3–CuO addition reached their saturated values at around 900°C. Microwave dielectric loss includes two parts: intrinsic loss and extrinsic loss. Intrinsic losses are caused by absorptions of phonon oscillation and extrinsic losses are caused by lattice defect (impurity, cavity, substitution, grain boundaries, size and shapes of grains, second phase, pores, etc.).[16] In ceramics, the grain boundaries, related to the sizes and shapes of grains and pores, interrupt the perfect symmetry of the crystal and act as two-dimensional defects, contributing significantly into extrinsic dielectric loss.[17] In other words, the grain sizes, grain shapes, and the pores would significantly affect the dielectric loss at microwave region. The $Q \times f$ values of pure Li_2TiO_3, Li_2ZrO_3 and Li_2SnO_3 ceramics sintered at around 1230°C are about 23 600, 17 640, and 20 800 GHz, respectively, as shown in Fig. 4(b). For samples with B_2O_3–CuO addition, the $Q \times f$ values of Li_2TiO_3 and Li_2SnO_3 ceramics increased to 46 300 and 36 400 GHz, respectively, but the $Q \times f$ value of Li_2ZrO_3 ceramics decreased to about 4300 GHz. The density and microwave dielectric behavior of well-densified Li_2MO_3 (M = Ti, Zr, Sn) ceramics are shown in Table I. The TCF values are not sensitive to the sintering temperature and remain stable at various temperatures. Besides Li_2ZrO_3 samples, the B_2O_3–CuO addition effectively lowered the sintering temperature of Li_2TiO_3 and Li_2SnO_3 ceramics to around 900°C without deterioration of microwave dielectric properties.

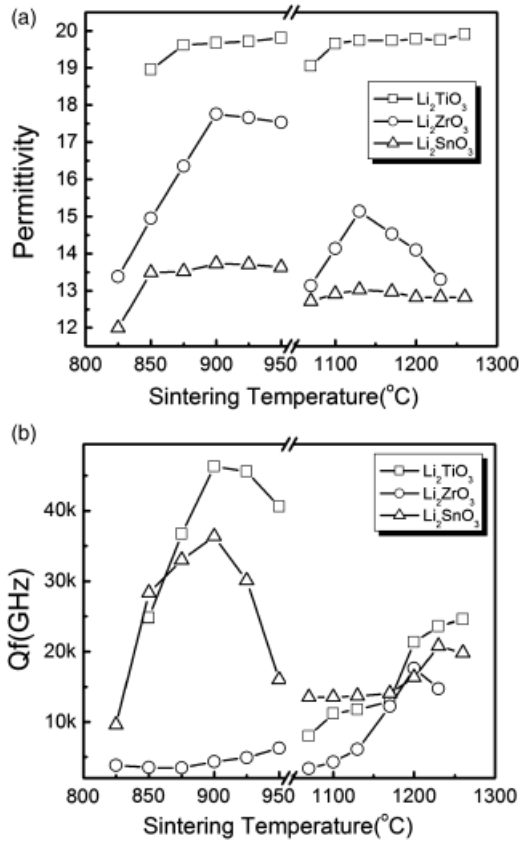

Fig. 4. (a) Microwave dielectric constant and (b) $Q \times f$ values of both pure Li_2MO_3 (M = Ti, Zr, Sn) ceramics and samples with 1 wt% B_2O_3–CuO addition as a function of sintering temperature.

IV. Conclusions

The sintering temperature of all the Li_2MO_3 (M = Ti, Zr, Sn) ceramics can be lowered from around 1200° to 900°C by addition of 1 wt% B_2O_3–CuO (with 4:6 in mole ratio). From the XRD analysis of cofired samples, the Li_2MO_3 (M = Ti, Zr, Sn) ceramics are chemically compatible with silver at 900°C. With 1 wt% B_2O_3–CuO addition, good microwave dielectric properties with a permittivity of ~19.67, a $Q \times f$ value of ~46 300 GHz, and a TCF of ~+31.3 ppm/°C were obtained in 900°C-sintered Li_2TiO_3 ceramics and Li_2SnO_3 ceramics sintered at 900°C obtained a permittivity of 13.73, a $Q \times f$ value of 36 400 GHz, and a TCF of about +27.4 ppm/°C.

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References

[1]T. K. Gupta and J. H. Jean, "Principles of the Development of a Silica Dielectric for Microelectronics," *J. Mater. Res.*, **11**, 243–63 (1996).
[2]M. T. Sebastian and H. Jantunen, "Low Loss Dielectric Materials for LTCC Applications: A Review," *Int. Mater. Rev.*, **53**, 57–90 (2008).
[3]A. K. Axelsson and N. M. Alford, "Bismuth Titanates Candidates for High Permittivity LTCC," *J. Eur. Ceram. Soc.*, **26**, 1933–6 (2006).
[4]D. Zhou, C. Randall, H. Wang, L. X. Pang, and X. Yao, "Microwave Dielectric Ceramics in Li_2O–Bi_2O_3–MoO_3 System with Ultra-Low Sintering Temperatures," *J. Am. Ceram. Soc.*, **93**, 1096–100 (2010).

[5]D. Zhou, H. Wang, L. X. Pang, C. Randall, and X. Yao, "Bi_2O_3–MoO_3 Binary System: An Alternative Ultralow Sintering Temperature Microwave Dielectric," *J. Am. Ceram. Soc.*, **92**, 2242–6 (2009).

[6]M. Valant and D. Suvorov, "Chemical Compatibility Between Silver Electrodes and Low-Firing Binary-Oxide Compounds: Conceptual Study," *J. Am. Ceram. Soc.*, **83**, 2721–9 (2000).

[7]Q. Zeng, W. Li, J. Shi, J. Guo, M. Zuo, and W. Wu, "A New Microwave Dielectric Ceramic for LTCC Applications," *J. Am. Ceram. Soc.*, **89**, 1733–5 (2006).

[8]J. J. Bian and Y. F. Dong, "New High Q Microwave Dielectric Ceramics with Rock Salt Structures: $(1-x)Li_2TiO_3+xMgO$ System $(0 \le x \le 0.5)$," *J. Eur. Ceram. Soc.*, **30**, 325–30 (2010).

[9]J. Liang and W. Z. Lu, "Microwave Dielectric Properties of Li_2TiO_3 Ceramics Doped with ZnO–B_2O_3 Frit," *J. Am. Ceram. Soc.*, **92** [4] 952–4 (2009).

[10]J. B. Lim, D. H. Kim, S. Nahm, J. H. Paik, and H. J. Lee, "Effect of B_2O_3 and CuO Additives on the Sintering Temperature and Microwave Dielectric Properties of $Ba(Mg_{1/3}Nb_{2/3})O_3$ Ceramics," *Mater. Res. Bull.*, **41**, 1199–205 (2006).

[11]M. H. Kim, Y. H. Jeong, S. Nahm, H. T. Kim, and H. J. Lee, "Effect of B_2O_3 and CuO Additives on the Sintering Temperature and Microwave Dielectric Properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ Ceramics," *J. Eur. Ceram. Soc.*, **26**, 2139–42 (2006).

[12]D. Zhou, H. Wang, L. X. Pang, X. Yao, and X. G. Wu, "Low Temperature Firing of $BiSbO_4$ Microwave Dielectric Ceramic with B_2O_3–CuO Addition," *J. Eur. Ceram. Soc.*, **29**, 1543–6 (2009).

[13]J. F. Dorrian and R. E. Newnham, "Refinement of the Structure of Li_2TiO_3," *Mater. Res. Bull.*, **4**, 179–83 (1969).

[14]J. L. Hodeau, M. Marezio, A. Santoro, and R. S. Roth, "Neutron Profile Refinement of the Structures of Li_2SnO_3 and Li_2ZrO_3," *J. Solid State Chem.*, **45**, 170–9 (1982).

[15]G. K. Abdulleav, P. F. Rza-Zade, and K. S. Mamedov, "Physicochemical Study of a Lithium Oxide–Copper(II) Oxide–Boron Oxide Ternary System," *Russ. J. Inorg. Chem. (English Translation)*, **27** [7] 1037–40 (1982).

[16]H. Tamura, "Microwave Loss Quality of $(Zr_{0.8}Sn_{0.2})TiO_4$," *Am. Ceram. Soc. Bull.*, **73**, 92–5 (1994).

[17]N. Ichinose and T. Shimada, "Effect of Grain Size and Secondary Phase on Microwave Dielectric Properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba([Mg,Zn]_{1/3}Ta_{2/3})O_3$ Systems," *J. Eur. Ceram. Soc.*, **26**, 1755–9 (2006). □