

Microwave Dielectric Properties Trends in a Solid Solution $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}, 0.0 \leq x \leq 0.2$) System

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The influence of La^{3+} and Nd^{3+} substitution for the Bi^{3+} cations in the low-firing $\text{Bi}_2\text{Mo}_2\text{O}_9$ system is considered in regard to the sintering behavior, density, phase composition, and microwave dielectric properties. All the compositions can be sintered to high densities in temperature range of $620^\circ\text{--}680^\circ\text{C}$. In $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics, when $x \leq 0.2$ the solid solution is within a monoclinic phase ($P2_1/n$) and the phase had an increase in melting temperature with the doping. In the La substitution case, the $(\text{Bi}_{0.8}\text{La}_{0.2})_2\text{Mo}_2\text{O}_9$ ceramics had the best microwave dielectric properties with a permittivity of 32.7, a Qf value ($f =$ resonant frequency, $Q = 1/\text{dielectric loss at } f$) of 13 490 GHz and a temperature coefficient of $-4.6 \text{ ppm}/^\circ\text{C}$. With the Nd-substituted samples, the $(\text{Bi}_{0.9}\text{Nd}_{0.1})_2\text{Mo}_2\text{O}_9$ ceramics had the best microwave dielectric properties with a permittivity of 33.9, a Qf value of 15 200 GHz and a temperature coefficient of $+8.05 \text{ ppm}/^\circ\text{C}$. The substitution of La and Nd can effectively modify the microwave dielectric properties of $\text{Bi}_2\text{Mo}_2\text{O}_9$ ceramic and in particular adjust the temperature coefficient to near zero. The $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics are very interesting new materials for an ultralow-temperature cofired ceramics technology that is compatible with Al metal electrodes.

I. Introduction

DIFFERENT kinds of microwave ceramic components are needed to meet the rapidly increasing demands of the telecommunication and satellite broadcasting industry. To achieve the miniaturization of microwave components for wireless communication, the multilayer cofired ceramic and low-temperature cofired ceramic technology will be used to the fabrication of band-pass filters, local oscillators, and other devices. In order to meet all the requirements, the material must have high dielectric permittivity, high Qf value ($f =$ resonant frequency, $Q = 1/\text{dielectric loss at } f$), a near zero temperature coefficient of resonant frequency, a low sintering temperature (below the melting points of common electrodes such as, silver, copper, gold, aluminum, etc.) and chemical compatibility with the metal electrodes.^{1–5}

Many of the high-performance microwave dielectric have high sintering temperatures (above 1000°C) and include materials such as the compositions $\text{ZnO-Nb}_2\text{O}_5$,^{6,7} $\text{Bi}(\text{Nb}, \text{Ta}, \text{Sb})\text{O}_4$,^{8–10} $\text{BaO-TiO}_2\text{-Nb}_2\text{O}_5$,¹¹ $\text{Li}_2\text{O-Nb}_2\text{O}_5\text{-TiO}_2$,¹² $(\text{Zr}, \text{Sn})\text{TiO}_4$,¹³ and the $(\text{A}_1\text{A}_2)(\text{B}_1\text{B}_2)\text{O}_3$ complex perovskite system.^{14,15} Low melting point oxides and glasses are usually added to lower

their sintering temperatures, but often have detrimental effects on the microwave dielectric properties. Currently there is a trend in the field to find ceramics with ultralow firing temperatures ($< 800^\circ\text{C}$), which include the following compositions: TeO_2 -rich compounds ($\text{Bi}_2\text{O}_3\text{-TeO}_2$, $\text{TiO}_2\text{-TeO}_2$, CaO-TeO_2 , BaO-TeO_2 , $\text{ZrO}_2\text{-TeO}_2$, MgO-TeO_2 , $\text{BaO-TiO}_2\text{-TeO}_2$),^{16–23} Bi_2O_3 -rich compounds ($\text{Bi}_2\text{W}_2\text{O}_9$, $\text{Bi}_{12}\text{MO}_{20}$ ($\text{M} = \text{Pb}, \text{Mn}$), BiVO_4 , BiPO_4 , and $\text{Bi}_2\text{Mo}_2\text{O}_9$),^{5,24–27} V_2O_5 -rich compounds ($\text{MgZn}_2(\text{VO}_4)_2$, $\text{Mg}_3(\text{VO}_4)_2$, $\text{Zn}_2\text{V}_2\text{O}_7$),^{28–30} MoO_3 -rich compounds,^{27,31,32} P_2O_5 -rich compounds,^{33–35} B_2O_3 -rich compounds,^{36–40} etc. However, the application of many of these ceramics are limited due to the chemical incompatibility with the most common electrode metal, silver.⁵ The low firing temperature of these ceramics could be attributed to the low melting points of the initial oxides TeO_2 , MoO_3 , Bi_2O_3 , B_2O_3 , P_2O_5 , SiO_2 , Li_2O , V_2O_5 , etc. In other words, the low melting points aid the low-temperature phase formation and densification. Among all the ceramics mentioned above, BaTe_4O_9 has the lowest sintering temperature about 550°C and it can be cofired with Al electrodes.²¹ However, the TeO_2 is rather expensive and toxic. Our recent research found that $\text{Bi}_2\text{Mo}_2\text{O}_9$ ceramic could be sintered well at around 620°C and it possessed very interesting microwave dielectric properties with the permittivity about 38, the Qf value about 12 500 GHz and temperature coefficient of resonant frequency (TCF) about $+31 \text{ ppm}/^\circ\text{C}$.²⁷ From the further study,⁴¹ we found that $\text{Bi}_2\text{Mo}_2\text{O}_9$ ceramic did not react with aluminum. So $\text{Bi}_2\text{Mo}_2\text{O}_9$ is a promising candidate for ultralow-temperature cofired ceramics technology. Considering the same charge (isovalent) and the similar size (ionic radii), the La^{3+} , Nd^{3+} along with other lanthanide ions can be substituted directly for the Bi^{3+} in many compounds.^{42,43} In the present work, La^{3+} and Nd^{3+} are used to substitute for the Bi^{3+} in the monoclinic phase of $\text{Bi}_2\text{Mo}_2\text{O}_9$. The objective of this work was to consider the structure–property–processing relations of the $\text{Bi}_2\text{Mo}_2\text{O}_9$ with lanthanide doping considering the sintering behavior, phase development, grain microstructure, and associated microwave dielectric properties.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 ($> 99\%$, Shu-Du Powders Co. Ltd., Chengdu, China), La_2O_3 , Nd_2O_3 ($> 99\%$, Guo-Yao Co. Ltd., Shanghai, China), and MoO_3 ($> 99\%$, Fuchen Chemical Reagents, Tianjin, China) were prepared according to the stoichiometric formulation $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ ($x = 0.0, 0.1, 0.2$, and noted with the nomenclature BM229, BM229La01, and BM229La02, respectively) compositions and $(\text{Bi}_{1-x}\text{Nd}_x)_2\text{Mo}_2\text{O}_9$ ($x = 0.0, 0.1, 0.2$, and they are named BM229, BM229Nd01, and BM229Nd02, respectively) compositions. 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.

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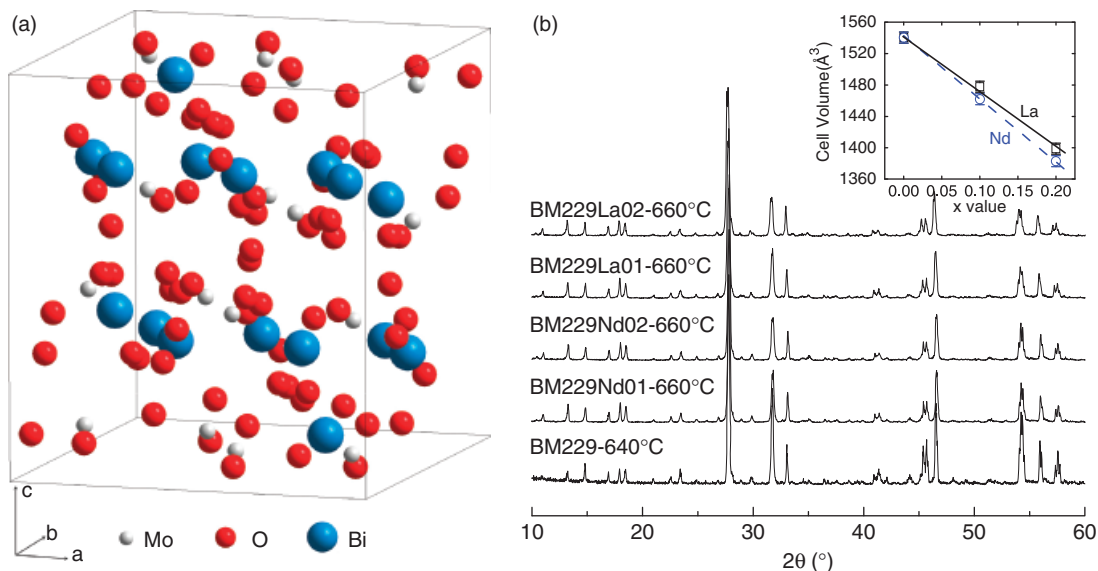


Fig. 1. (a) Schematic of the crystal structure, (b) X-ray diffraction results of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}, x = 0.1, 0.2$) ceramics sintered at 640°, 660°C and the linear variation of the cell volume with composition.

The mixed oxides were then calcined at 620°C for 4 h. After being crushed and remilled for 5 h using the ZrO_2 milling media and deionized water, powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die with 5wt% PVA binder addition under a uniaxial pressure of 200 MPa. Samples were sintered in the temperature range from 600° to 680°C for 2 h.

The crystalline structures of samples were investigated using X-ray diffraction with $\text{CuK}\alpha$ radiation (X-ray diffractometer, Rigaku D/MAX-2400 Tokyo, Japan). Microstructures of sintered ceramic were observed on the as-fired surface and fractured surfaces with scanning electron microscopy (SEM) (JSM-6460, Jeol, Tokyo, Japan). The apparent densities of sintered ceramics were measured by Archimedes' method. Dielectric behaviors at microwave frequency were measured with the TE_{018} shielded cavity method with 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:

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

where f_{85} and f_{25} were the TE_{018} resonant frequencies at 85° and 25°C, respectively.

III. Results and Discussion

Chen and Sleight⁴⁴ investigated the structure of $\text{Bi}_2\text{Mo}_2\text{O}_9$ using a single crystal and modeled the diffraction data with Patterson and Fourier techniques. It was determined that a significant structural feature is a Bi_2O_2 chains run parallel to the b -axis of the monoclinic phase. There are also Bi atoms bound only to MoO_4 tetrahedra. All the Mo atoms are in more or less ideal MoO_4 tetrahedral configurations and all four Bi atoms are eight-coordinated. The crystal structure is schematically represented in Fig. 1. The room temperature X-ray diffraction patterns for $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics sintered at different temperatures are also shown in Fig. 1. Only a single monoclinic phase can be indexed in $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics. As we discussed in our previous work,⁴¹ $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and Bi_2MoO_6 phases could appear as the secondary phases when sintering temperature approaches 650°C or higher. Egashira *et al.*⁴⁵ also pointed out that $\text{Bi}_2\text{Mo}_2\text{O}_9$ would partially decompose to Bi_2MoO_6 and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ phase at high temper-

atures. However, there was no secondary phase found in the $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}, x = 0.1, \text{ and } 0.2$) ceramics even when sintered at 660°C. It is clear that substitution of La^{3+} and Nd^{3+} with smaller ionic radii for Bi^{3+} ion in $\text{Bi}_2\text{Mo}_2\text{O}_9$ stabilizes the monoclinic phase and restrains the decomposition to higher temperatures. This may account for the increase in the densification and melting temperatures in $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ceramics, which will be discussed below.

The apparent densities of $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ ceramics and $(\text{Bi}_{1-x}\text{Nd}_x)_2\text{Mo}_2\text{O}_9$ ceramics as a function of the sintering temperature are shown in Figs. 2(a) and (b), respectively. As the x value increased from 0.0 to 0.2, the optimal sintering temperatures of $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ ceramics increased from 620° to 650°C and the densities decreased from 6.29 to 6.03 g/cm^3 due to the smaller atomic weight of La as compared with Bi. With the substitution of Nd for Bi there is a similar influence on the sintering behavior and density of $(\text{Bi}_{1-x}\text{Nd}_x)_2\text{Mo}_2\text{O}_9$ ceramics, whose densification temperatures were around 660°C as shown in Fig. 2(b).

SEM micrographs of both as-fired and fractured surfaces of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}, x = 0.1, 0.2$) ceramics sintered at 650°C are shown in Fig. 3. Homogeneous microstructures with almost no pores were revealed in $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$

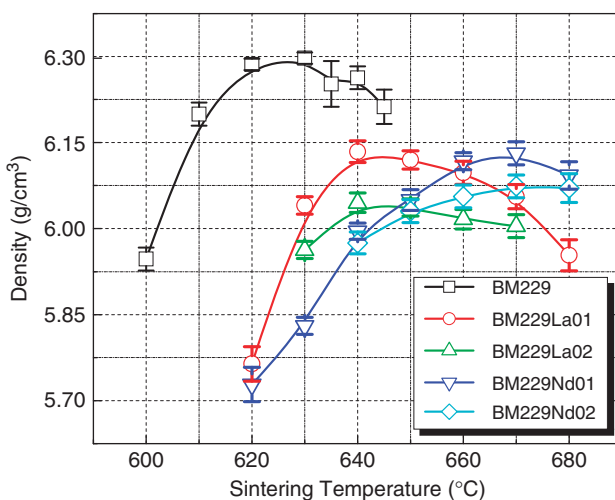


Fig. 2. Apparent densities of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ceramics as a function of sintering temperature for composition in the monoclinic phase.

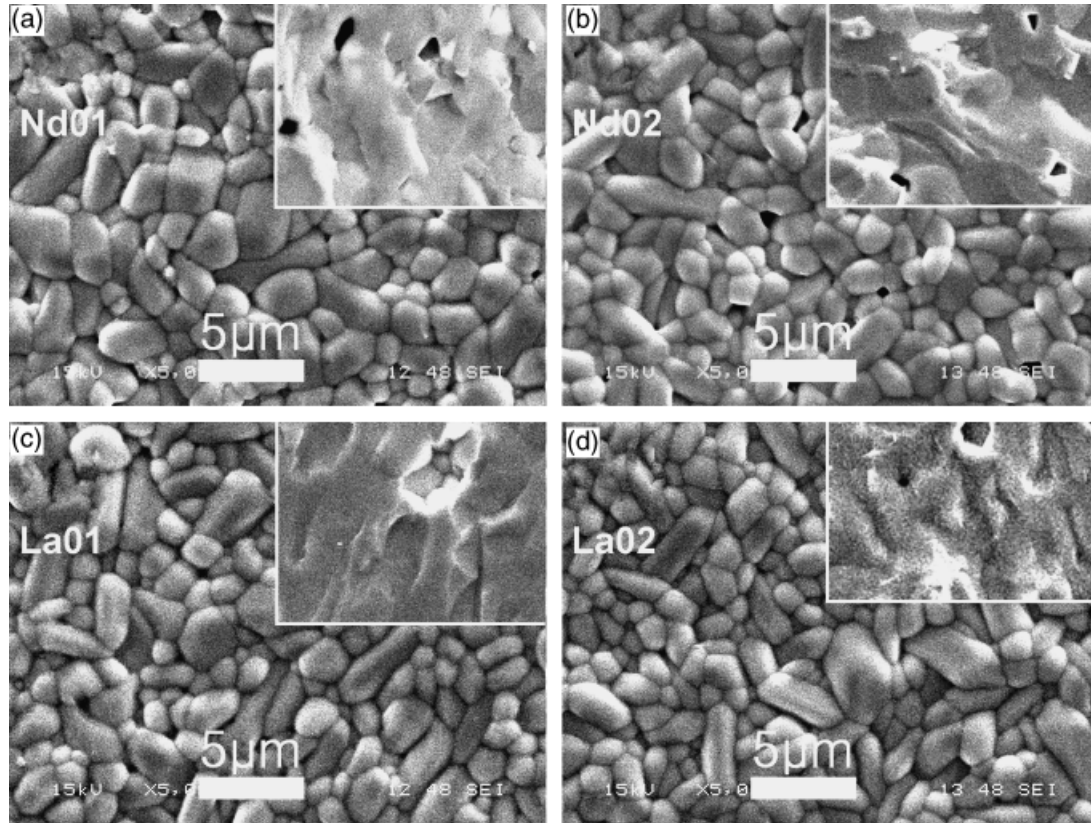


Fig. 3. Scanning electron microscopy micrographs of as-fired surface and fractured surface (inserts) of the (a) $(\text{Bi}_{0.9}\text{Nd}_{0.1})_2\text{Mo}_2\text{O}_9$ ceramic, (b) $(\text{Bi}_{0.8}\text{Nd}_{0.2})_2\text{Mo}_2\text{O}_9$ ceramic, (c) $(\text{Bi}_{0.9}\text{La}_{0.1})_2\text{Mo}_2\text{O}_9$ ceramic, and (d) $(\text{Bi}_{0.8}\text{La}_{0.2})_2\text{Mo}_2\text{O}_9$ ceramic all sintered at 650°C for 2 h.

($\text{Ln} = \text{La}, \text{Nd}, x = 0.1, 0.2$) ceramics sintered at the optimal sintering temperatures. The microstructure of as-fired surfaces and fractured surfaces agreed with each other. For both La and Nd substitution ceramics, the grain sizes and shapes are also similar from the surface images; the fractures are consistent with a transgranular fracture.

Microwave dielectric relative permittivity and Qf values of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}, x = 0.1, 0.2$) ceramics measured at ~ 6.8 GHz are shown in Fig. 4(a) as a function of sintering temperature. As the sintering temperature increases, microwave dielectric constant increases and then reaches a saturated value as there is an elimination of the pores. As the x value in $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ increased from 0.0 to 0.2, permittivity decreased linearly as shown in Fig. 4(b). In the microwave region, the polarizability is the sum of both ionic and electronic components.⁴⁶ Shannon⁴⁷ suggested that molecular polarizabilities of complex substances can be estimated by summing the polarizabilities of the constituent ions. Then the polarizabilities α_x of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$) could be obtained as follows:

$$\alpha_x = 2(1-x) \times \alpha_{\text{Bi}^{3+}} + 2x\alpha_{\text{Ln}^{3+}} + 2\alpha_{\text{Mo}^{6+}} + 9\alpha_{\text{O}^{2-}} \quad (2)$$

where $\alpha_{\text{Bi}^{3+}}, \alpha_{\text{Ln}^{3+}}, \alpha_{\text{Mo}^{6+}}, \alpha_{\text{O}^{2-}}$ are the respective polarizabilities of $\text{Bi}^{3+}, \text{Ln}^{3+}, \text{Mo}^{6+},$ and O^{2-} . Because of the smaller polarizabilities of La^{3+} and Nd^{3+} relative to Bi^{3+} ($\alpha_{\text{Bi}^{3+}} = 6.12 > \alpha_{\text{La}^{3+}} = 6.07 > \alpha_{\text{Nd}^{3+}} = 5.01 \text{ \AA}^3$, obtained from Shannon's results⁴⁷), the increasing of substitution of Ln^{3+} for Bi^{3+} in $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$) would decrease their dielectric permittivities linearly. There is a more significant decrease in the Nd^{3+} -doped system relative to the La^{3+} for a similar x . The trends can be accounted for but the relative differences in the doping types are not readily accounted for with this simple polarizability model. Using the Clausius–Mosotti relation, the molecular dielectric po-

larizability α_x and the molar volume V_x , the dielectric constant can be calculated as following:

$$\epsilon_x = \frac{3V_x + 8\pi\alpha_x}{3V_x - 4\pi\alpha_x} = 1 + \frac{12\pi\alpha_x}{3V_x - 4\pi\alpha_x} \quad (3)$$

where V_x is the cell volume and ϵ_x is the calculated dielectric permittivity. It is seen from Eq. (3) that the smaller cell volume can cause a larger dielectric constant if the total polarizability is similar. This could account for the major difference between the relative permittivities in the $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ and $(\text{Bi}_{1-x}\text{Nd}_x)_2\text{Mo}_2\text{O}_9$ ceramics. Using Eq. (2), we can get a relationship between $\alpha(\text{La}^{3+})$ and $\alpha(\text{Nd}^{3+})$ as following:

$$\alpha_{\text{La}^{3+}} - \alpha_{\text{Nd}^{3+}} = \frac{\alpha_x(\text{La}) - \alpha_x(\text{Nd})}{x} \quad (4)$$

where $\alpha_x(\text{Ln})$ are the molecular polarizabilities of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$). Using Eq. (3), data from Fig. 1(b) and data from Fig. 4(b), we can calculate $\alpha_x(\text{La})$ and $\alpha_x(\text{Nd})$ and then get the polarizability difference between La^{3+} and Nd^{3+} : $|\alpha_{\text{La}^{3+}} - \alpha_{\text{Nd}^{3+}}| = 1.9 \pm 0.4 \text{ \AA}^3$, which is a little bigger than that reported by Shannon.⁴⁷ This result proves the domination of cell volume in controlling the permittivity. Based on rare-earth aluminates system Feteira *et al.*⁴⁸ provided a series of revised dielectric polarizabilities for rare-earth lanthanides, which are smaller than that reported by Shannon.⁴⁷ As Feteira and colleagues correctly states, in noncubic systems the macroscopic polarizability is not a simple sum of ionic polarizabilities but also includes many additional terms related to the crystal structure and local anisotropy. In regard to the microwave dielectric loss there are in general two parts: the intrinsic loss and the extrinsic loss. Intrinsic losses are caused by absorptions of phonon oscillation within the lattice and extrinsic losses are caused by defects (impurities,

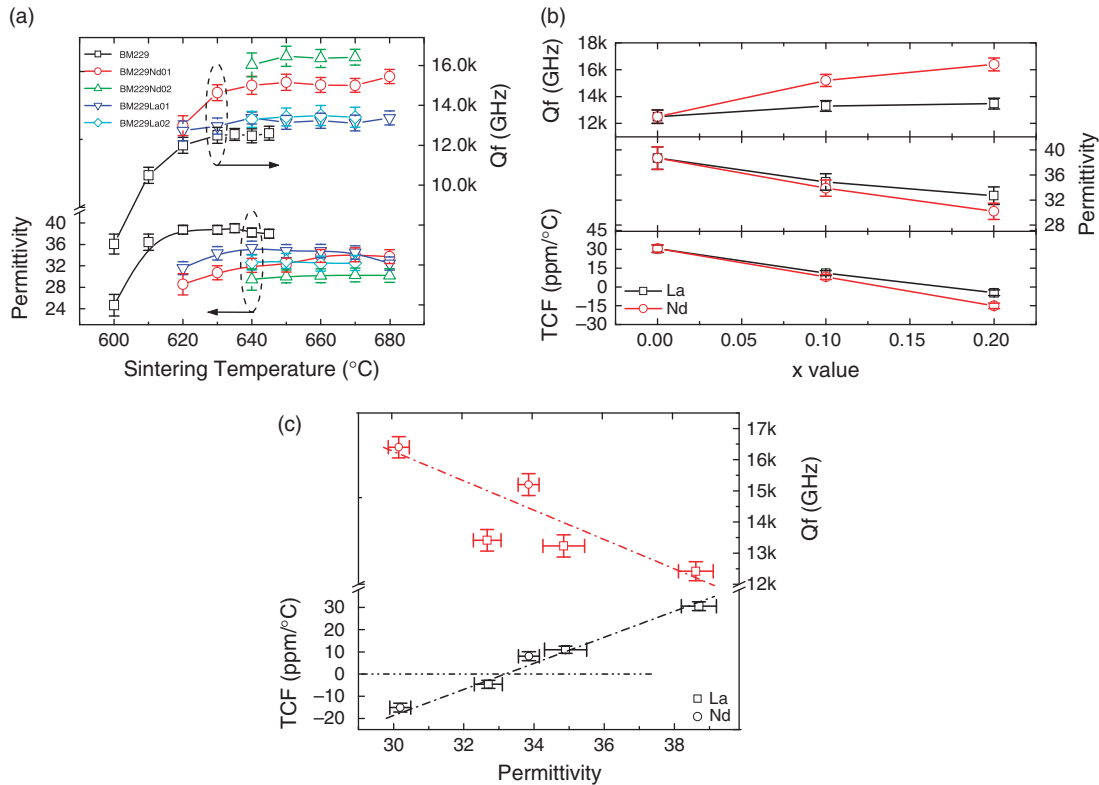


Fig. 4. Microwave dielectric constants and Qf values of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ceramics as a function of (a) sintering temperature, (b) as a function of x value, and (c) TCF and Qf values as a function of permittivity for the samples sintered for 2 h at 640°C , that are marked in (a).

substitution, grain boundaries, grain morphology and shape, secondary phase, pores, etc.).⁴⁹ Far-infrared spectroscopy methods is usually utilized to calculate the intrinsic losses.^{50–52} However, although the influence of porosity, grain size, grain boundary, etc. on the microwave dielectric loss have been studied in many good investigations,^{53–55} it is still difficult to accurately calculate the extrinsic losses in polycrystalline samples. Most dielectric materials possessing larger permittivities have smaller Qf values because of the increasing contribution from anharmonic terms from the large lattice displacements.⁵⁶ Both in $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ and $(\text{Bi}_{1-x}\text{Nd}_x)_2\text{Mo}_2\text{O}_9$ ceramics, the Qf values increased as the x values increased as shown in Fig. 4(b). This result can be qualitatively associated with the decrease of intrinsic loss caused by the substitution of La^{3+} and Nd^{3+} for Bi^{3+} . The La^{3+} and Nd^{3+} have smaller displacement polarization than Bi^{3+} and accordingly the dielectric loss caused by the ion oscillation would be less than that of Bi^{3+} . This observation in $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ is similar to trends in many other solid solution systems with different crystal structures.^{57–59}

The TCF values of $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ and $(\text{Bi}_{1-x}\text{Nd}_x)_2\text{Mo}_2\text{O}_9$ ceramics as a function of x value and permittivity are shown in Figs. 4(b) and (c), with errors estimated from the standard deviation of at least three samples. As the x value increased from 0.0 to 0.2, the TCF of $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ and $(\text{Bi}_{1-x}\text{Nd}_x)_2\text{Mo}_2\text{O}_9$ ceramics linearly shifted from $+30.6$ to -4.6 and -15.1 ppm/ $^\circ\text{C}$, respectively. The rate of decrease in TCF of $(\text{Bi}_{1-x}\text{Nd}_x)_2\text{Mo}_2\text{O}_9$ ceramics versus x value was larger than that of $(\text{Bi}_{1-x}\text{La}_x)_2\text{Mo}_2\text{O}_9$ ceramics. The temperature coefficients of resonant frequency, TCF, could be defined as following:

$$\text{TCF} = -\alpha_1 - \frac{1}{2}\tau_\epsilon \quad (5)$$

where α_1 is the linear thermal expansion coefficient and τ_ϵ is the temperature coefficient of permittivity. Because α_1 of microwave

dielectric is known to be in the range of 10 ppm/ $^\circ\text{C}$ and assuming that α_1 of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ceramic is independent on x value, TCF mainly depends on τ_ϵ . Using the Clausius–Mosotti equation, Bosman and Havinga⁶⁰ derived an expression for τ_ϵ at a constant pressure, as follows:

$$\begin{aligned} \tau_\epsilon &= \frac{1}{\epsilon} \left(\frac{\partial \epsilon}{\partial T} \right)_P = \frac{(\epsilon - 1)(\epsilon + 2)}{\epsilon} (A + B + C) \\ &= \left(\epsilon - \frac{2}{\epsilon} + 1 \right) (A + B + C) \\ A &= \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P, \quad B = \frac{1}{3\alpha_m} \left(\frac{\partial \alpha_m}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P, \\ C &= \frac{1}{3\alpha_m} \left(\frac{\partial \alpha_m}{\partial T} \right)_V \end{aligned} \quad (6)$$

The sum of the A and B terms is approximately 6 ± 1 ppm/ $^\circ\text{C}$. For term C , the suggested value is in the range of -1 to -10 ppm/ $^\circ\text{C}$. The term C represents the direct dependence of the polarizability on temperature. Plotting the trend of TCF values versus permittivity of $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics, it is found that TCF values decreased from $+30.6$ to -15.3 ppm/ $^\circ\text{C}$ linearly independent on the doping types (La or Nd) as permittivity decreased from 38.7 to 30.2. Hence, it is indicated that the TCF value has a linear relationship with the value of permittivity in monoclinic $\text{Bi}_2\text{Mo}_2\text{O}_9$ structured phase. The $(A+B+C)$ value could be extrapolated from Eqs. (3) and (4) and its value was about -10.95 ppm/ $^\circ\text{C}$. When $(A+B+C)$ value is negative, TCF value will increase with permittivity. When $(A+B+C)$ value is positive, TCF value will decrease with permittivity. Usually the absolute value of TCF will increase with permittivity. A near-zero TCF value -4.6 ppm/ $^\circ\text{C}$ was obtained in $(\text{Bi}_{0.8}\text{La}_{0.2})_2\text{Mo}_2\text{O}_9$ ceramic with a permittivity of 32.7 and Qf value of 13490 GHz. It is seen that a zero TCF can be obtained in $(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}$) ceramics if the x value is chosen precisely, with the appropriate sintering.

IV. Conclusions

$(\text{Bi}_{1-x}\text{Ln}_x)_2\text{Mo}_2\text{O}_9$ (Ln = La, Nd) ceramics were prepared by the solid-state reaction method and can be densified in a temperature range between 620° and 680°C. As the x value increased, the optimal sintering temperature increased. Substitution of La or Nd could stabilize the monoclinic phase and modify its microwave dielectric properties. The best microwave dielectric properties were obtained in $(\text{Bi}_{0.8}\text{La}_{0.2})_2\text{Mo}_2\text{O}_9$ ceramic with a permittivity of 32.7, Qf value of 13490 GHz and temperature coefficient about -4.6 ppm/°C. The TCF values of ceramics with monoclinic $\text{Bi}_2\text{Mo}_2\text{O}_9$ structure are shown to only depend on the permittivity.

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References

- T. K. Gupta and J. H. Jean, "Principles of the Development of a Silica Dielectric for Microelectronics," *J. Mater. Res.*, **11**, 243–63 (1996).
- H. Jantunen, R. Rautioaho, A. Uusimäki, and S. Leppavuori, "Compositions of MgTiO_3 - CaTiO_3 Ceramics with Two Borosilicate Glasses for LTCC Technology," *J. Eur. Ceram. Soc.*, **20**, 2331–6 (2000).
- M. T. Sebastian and H. Jantunen, "Low Loss Dielectric Materials for LTCC Applications: A Review," *Int. Mater. Rev.*, **53** [2] 57–90 (2008).
- A. K. Axelsson and N. M. Alford, "Bismuth Titanates Candidates for High Permittivity LTCC," *J. Eur. Ceram. Soc.*, **26**, 1933–6 (2006).
- 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).
- O. A. Shlyakhtin and Y. J. Oh, "Low Temperature Sintering of $\text{Zn}_3\text{Nb}_2\text{O}_8$ Ceramics from Fine Powders," *J. Am. Ceram. Soc.*, **89**, 3366–72 (2006).
- C. L. Huang, R. J. Lin, and J. H. Wang, "Effect of B_2O_3 Additives on Sintering and Microwave Dielectric Behaviors of CuO -Doped ZnNb_2O_6 Ceramics," *Jpn. J. Appl. Phys. Part1-Regular Papers Short Notes Rev. Papers*, **41**, 758–62 (2002).
- N. Wang, M. Y. Zhao, and Z. W. Yin, "Effects of Ta_2O_5 on Microwave Dielectric Properties of BiNbO_4 Ceramics," *Mater. Sci. Eng. B*, **99**, 238–42 (2003).
- C. L. Huang and M. H. Weng, "The Microwave Dielectric Properties and the Microstructures of $\text{Bi}(\text{Nb}, \text{Ta})\text{O}_4$ Ceramics," *Jpn. J. Appl. Phys. Part1-Regular Papers Short Notes Rev. Papers*, **38** [10] 5949–52 (1999).
- D. Zhou, H. Wang, X. Yao, and L. X. Pang, "Dielectric Behavior and Cofiring with Silver of Monoclinic BiSbO_4 Ceramic," *J. Am. Ceram. Soc.*, **91** [4] 1380–3 (2008).
- R. Ratheesh, H. Sreemoolanadhan, S. Suma, M. T. Sebastian, K. A. Jose, and P. Mohanan, "New High Permittivity and Low Loss Ceramics in the BaO - TiO_2 - Nb_2O_5 Composition," *J. Mater. Sci. Mater. Electron.*, **9**, 291–4 (1998).
- A. Y. Borisevich and P. K. Davies, "Crystalline Structure and Dielectric Properties of $\text{Li}_{1-x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4}\text{O}_3$ M-Phase Solid Solutions," *J. Am. Ceram. Soc.*, **85** [3] 573–8 (2002).
- C. L. Huang, C. S. Hsu, and R. J. Lin, "Improved High-Q Microwave Dielectric Resonator Using ZnO and WO_3 -Doped $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ Ceramics," *Mater. Res. Bull.*, **36**, 1985–93 (2001).
- H. J. Kim, S. Kucheiko, S. J. Yoon, and H. J. Jung, "Microwave Dielectrics in the $(\text{La}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ System," *J. Am. Ceram. Soc.*, **80** [5] 1316–8 (1997).
- M. S. Fu, X. Q. Liu, X. M. Chen, and Y. W. Zeng, "Microstructure and Microwave Dielectric Properties of $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3-x\text{CaTiO}_3$ Ceramics," *J. Am. Ceram. Soc.*, **91** [4] 1163–8 (2008).
- M. Udovic, M. Valant, and D. Suvorov, "Phase Formation and Dielectric Characterization of the Bi_2O_3 - TeO_2 System Prepared in an Oxygen Atmosphere," *J. Am. Ceram. Soc.*, **87**, 591–7 (2004).
- M. Udovic, M. Valant, and D. Suvorov, "Dielectric Characterisation of Ceramics from the TiO_2 - TeO_2 System," *J. Eur. Ceram. Soc.*, **21**, 1735–8 (2001).
- M. Valant and D. Suvorov, "Glass-Free Low-Temperature Co-Fired Ceramics: Calcium Germanates, Silicates and Tellurates," *J. Eur. Ceram. Soc.*, **24**, 1715–9 (2004).
- D. K. Kwon, M. T. Lanagan, and T. R. Shrout, "Microwave Dielectric Properties of BaO - TeO_2 Binary Compounds," *Mater. Lett.*, **61**, 1827–31 (2007).
- D. K. Kwon, M. T. Lanagan, and T. R. Shrout, "Synthesis of $\text{BaTiTe}_2\text{O}_9$ Ceramics for LTCC Application and its Dielectric Properties," *J. Ceram. Soc. Jpn.*, **113** [3] 216–9 (2005).
- D. K. Kwon, M. T. Lanagan, and T. R. Shrout, "Microwave Dielectric Properties and Low-Temperature Cofiring of BaTe_4O_9 with Aluminum Metal Electrode," *J. Am. Ceram. Soc.*, **88**, 3419–22 (2005).
- M. Maeda, T. Yamamura, and T. Ikeda, "Dielectric Characteristics of Several Complex Oxide Ceramics at Microwave-Frequencies," *Jpn. J. Appl. Phys.*, **26**, 76–9 (1987).
- G. Subodh, R. Ratheesh, M. V. Jacob, and M. T. Sebastian, "Microwave Dielectric Properties and Vibrational Spectroscopic Analysis of MgTe_2O_5 Ceramics," *J. Mater. Res.*, **23** [6] 1551–6 (2008).
- A. Feteira and D. C. Sinclair, "Microwave Dielectric Properties of Low Firing Temperature $\text{Bi}_2\text{W}_2\text{O}_9$ Ceramics," *J. Am. Ceram. Soc.*, **91**, 1338–41 (2008).
- M. Valant and D. Suvorov, "Processing and Dielectric Properties of Sillenite Compounds $\text{Bi}_2\text{MO}_{20}$ (M = Si, Ge, Ti, Pb, Mn, $\text{B}_{1/2}\text{P}_{1/2}$)," *J. Am. Ceram. Soc.*, **84**, 2900–4 (2001).
- I. S. Cho, J. R. Kim, D. W. Kim, and K. S. Hong, "Phase Transformation and Microwave Dielectric Properties of BiPO_4 Ceramics," *J. Electroceram.*, **16**, 379–83 (2006).
- D. Zhou, H. Wang, X. Yao, and L. X. Pang, "Microwave Dielectric Properties of Low Temperature Firing $\text{Bi}_2\text{Mo}_2\text{O}_9$ Ceramic," *J. Am. Ceram. Soc.*, **91** [10] 3419–22 (2008).
- H. Ogawa, A. Yokoi, R. Umemura, and A. Kan, "Microwave Dielectric Properties of $\text{Mg}_3(\text{VO}_4)_2-x\text{Ba}_3(\text{VO}_4)_2$ Ceramics for LTCC with Near Zero Temperature Coefficient of Resonant Frequency," *J. Eur. Ceram. Soc.*, **27**, 3099–104 (2007).
- R. Umemura, H. Ogawa, H. Ohsato, A. Kan, and A. Yokoi, "Microwave Dielectric Properties of Low-Temperature Sintered $\text{Mg}_3(\text{VO}_4)_2$ Ceramic," *J. Eur. Ceram. Soc.*, **25**, 2865–70 (2005).
- R. Umemura, H. Ogawa, and A. Kan, "Low Temperature Sintering and Microwave Dielectric Properties of $(\text{Mg}_{3-x}\text{Zn}_x)(\text{VO}_4)_2$ Ceramics," *J. Eur. Ceram. Soc.*, **26**, 2063–8 (2006).
- G. K. Choi, J. R. Kim, S. H. Yoon, and K. S. Hong, "Microwave Dielectric Properties of Scheelite (A = Ca, Sr, Ba) and Wolframite (A = Mg, Zn, Mn) AMoO_4 Compounds," *J. Eur. Ceram. Soc.*, **27**, 3063–7 (2007).
- G. K. Choi, S. Y. Cho, J. S. An, and K. S. Hong, "Microwave Dielectric Properties and Sintering Behaviors of Scheelite Compound CaMoO_4 ," *J. Eur. Ceram. Soc.*, **26**, 2011–5 (2006).
- J. J. Bian, D. W. Kim, and K. S. Hong, "Microwave Dielectric Properties of $\text{A}_2\text{P}_2\text{O}_7$ (A = Ca, Sr, Ba; Mg, Zn, Mn)," *Jpn. J. Appl. Phys.*, **43** [6A] 3521–5 (2004).
- J. J. Bian, D. W. Kim, and K. S. Hong, "Glass-Free LTCC Microwave Dielectric Ceramics," *Mater. Res. Bull.*, **40**, 2120–9 (2005).
- J. J. Bian, D. W. Kim, and K. S. Hong, "Microwave Dielectric Properties of $(\text{Zn}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$," *J. Mater. Sci.*, **40** [7] 1801–3 (2005).
- M. Ohashi, H. Ogawa, A. Kan, and E. Tanaka, "Microwave Dielectric Properties of Low-Temperature Sintered $\text{Li}_3\text{AlB}_2\text{O}_6$ Ceramic," *J. Eur. Ceram. Soc.*, **25**, 2877–81 (2005).
- T. Takada and K. Kageyama, "Synthesis and Microwave Dielectric Properties of $\text{La}_2\text{O}_3-x\text{B}_2\text{O}_3$ -Based Melt Mixtures for Low-Temperature Cofired Ceramics," *Jpn. J. Appl. Phys.*, **44**, 6629–35 (2005).
- I. S. Cho, D. W. Kim, J. R. Kim, and K. S. Hong, "Low-Temperature Sintering and Microwave Dielectric Properties of $\text{BaO}(\text{Nd}_{1-x}\text{Bi}_x)_2\text{O}_3-4\text{TiO}_2$ by the Glass Additions," *Ceram. Int.*, **30**, 1181–5 (2004).
- T. Takada, H. Yamamoto, and K. Kageyama, "Synthesis and Microwave Dielectric Properties of $x\text{Re}_2\text{O}_3-y\text{B}_2\text{O}_3$ (Re = La, Nd, Sm, Dy, Ho and Y) Compounds," *Jpn. J. Appl. Phys.*, **42**, 6162–7 (2003).
- W. Huang, K. S. Liu, L. W. Chu, G. H. Hsue, and I. N. Lin, "Microwave Dielectric Properties of LTCC Materials Consisting of Glass- $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ Composites," *J. Eur. Ceram. Soc.*, **23**, 2559–64 (2003).
- D. Zhou, H. Wang, L. X. Pang, C. A. Randall, and X. Yao, " Bi_2O_3 - MoO_3 Binary System: An Alternative Ultra Low Sintering Temperature Microwave Dielectric," *J. Am. Ceram. Soc.*, doi: 10.1111/j.1551-2916.2009.03185.x
- H. Wang, D. S. Zhang, and X. L. Wang, "Effect of La_2O_3 Substitutions on Structure and Dielectric Properties of Bi_2O_3 - ZnO - Nb_2O_5 -Based Pyrochlore Ceramics," *J. Mater. Res.*, **14** [2] 546–8 (1999).
- W. Choi, K. Y. Kim, M. R. Moon, and K. S. Bae, "Effects of Nd_2O_3 on the Microwave Dielectric Properties of BiNbO_4 Ceramics," *J. Mater. Res.*, **13** [10] 2945–9 (1998).
- H. Y. Chen and A. W. Sleight, "Crystal Structure of $\text{Bi}_2\text{Mo}_2\text{O}_9$: A Selective Oxidation Catalyst," *J. Solid State Chem.*, **63**, 70–5 (1986).
- M. Egashira, K. Matsuo, S. Kagawa, and T. Seiyama, "Phase Diagram of the System Bi_2O_3 - MoO_3 ," *J. Catal.*, **58**, 409–18 (1979).
- A. Heydweiller, "Dichte, Dielektrizitätskonstante und Refraktion fester Salze," *Z. Phys.*, **3**, 308–17 (1920).
- R. D. Shannon, "Dielectric Polarizabilities of Ions in Oxides and Fluorides," *J. Appl. Phys.*, **73**, 348–66 (1993).
- A. Feteira, D. C. Sinclair, and M. T. Lanagan, "Structural and Electrical Characterization of CeAlO_3 Ceramics," *J. Appl. Phys.*, **101** [6] 064110, 7pp (2007).
- H. Tamura, "Microwave Loss Quality of $(\text{Zr}_{0.8}\text{Sn}_{0.2})\text{TiO}_4$," *Am. Ceram. Soc. Bull.*, **73**, 92–5 (1994).
- R. Kudesia, A. E. McHale, R. A. Condrate, and R. L. Snyder, "Microwave Characteristics and Far-Infrared Reflection Spectra of Zirconium Tin Titanate Dielectrics," *J. Mater. Sci.*, **28**, 5569–75 (1993).
- K. Fukuda and R. Kitoh, "Far-Infrared Reflection Spectra of Dielectric Ceramics for Microwave Applications," *J. Am. Ceram. Soc.*, **77**, 149–54 (1994).
- R. Zurmühlen, J. Petzelt, S. Kamba, V. V. Voitsekhovskii, E. Colla, and N. Setter, "Dielectric Spectroscopy of $\text{Ba}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$ Complex Perovskite Ceramics: Correlations between Ionic Parameters and Microwave Dielectric Properties. I. Infrared Reflectivity Study (10^{12} – 10^{14} Hz)," *J. Appl. Phys.*, **77**, 5341–50 (1995).
- N. M. Alford, J. Breeze, X. Wang, S. J. Penn, S. Dalla, S. J. Webb, N. Ljepojevic, and X. Aupi, "Dielectric Loss of Oxide Single Crystals and Polycrystalline Analogues from 10 to 320 K," *J. Eur. Ceram. Soc.*, **21**, 2605–11 (2001).
- S. J. Penn, N. M. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, and K. Schrapel, "Effect of Porosity and Grain Size on the Microwave Dielectric Properties of Sintered Alumina," *J. Am. Ceram. Soc.*, **80** [7] 1885–8 (1997).
- W. Wersing, "Microwave Ceramics for Resonators and Filters," *Curr. Opin. Solid State Mater. Sci.*, **1**, 715–31 (1996).
- H. Tamura, "Microwave Dielectric Losses Caused by Lattice Defects," *J. Eur. Ceram. Soc.*, **26**, 1775–80 (2006).

⁵⁷D. Zhou, H. Wang, X. Yao, and L. X. Pang, "Sintering Behavior and Microwave Dielectric Properties of $\text{Bi}_3(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_7$ Solid Solutions," *Mater. Chem. Phys.*, **110**, 212–5 (2008).

⁵⁸D. Zhou, H. Wang, X. Yao, and L. X. Pang, "Sintering Behavior, Phase Evolution, and Microwave Dielectric Properties of $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$ Ceramics," *J. Am. Ceram. Soc.*, **91** [7] 2228–31 (2008).

⁵⁹D. Zhou, H. Wang, X. Yao, L. X. Pang, and Y. H. Chen, "Sintering Behavior, Phase Evolution and Microwave Dielectric Properties of $\text{Bi}(\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x)\text{O}_4$ Ceramics," *Mater. Chem. Phys.*, **113**, 265–8 (2009).

⁶⁰A. J. Bosman and E. E. Havinga, "Temperature Dependence of Dielectric Constants of Cubic Ionic Compounds," *Phys. Rev.*, **129**, 1593–600 (1963). □