Received: 23 October 2017 | Accepted: 12 December 2017
DOI: 10.1111/jace.15388

RAPID COMMUNICATION

Journal of the American Ceramic Society

Temperature stable $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ microwave dielectrics ceramics with ultra-low sintering temperature

Li-Xia Pang[1,2] | Di Zhou[2,3] | Da-Wei Wang[2] | Jin-Xiong Zhao[4] | Wei-Guo Liu[1] | Zhen-Xing Yue[5] | Ian M. Reaney[2]

[1]Micro-optoelectronic Systems Laboratories, Xi'an Technological University, Xi'an, Shaanxi, China
[2]Materials Science and Engineering, University of Sheffield, Sheffield, UK
[3]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an, Shaanxi, China
[4]State Grid Gansu Electric Power Research Institute, Lanzhou, China
[5]State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing, China

Correspondence
Di Zhou and Ian M. Reaney, Materials Science and Engineering, University of Sheffield, Sheffield, UK.
Emails: zhoudi1220@gmail.com and i.m.reaney@sheffield.ac.uk

Funding information
National Key Research and Development Program of China, Grant/Award Number: 2017YFB0406301; the Young Star Project of Science and Technology of Shaanxi Province, Grant/Award Number: 2015KJXX-39, XAGDXJJ1401; Headmaster Foundation of Xi'an Technological University, Grant/Award Number: 2015KJXX-39, XAGDXJJ1401; Fundamental Research Funds for the Central University; State Key Laboratory of New Ceramic and Fine Processing Tsinghua University

Abstract

$K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ($0.2 \leq x \leq 0.7$) ceramics were prepared via the solid-state reaction method. All ceramics densified below 720°C with a uniform microstructure. As x increased from 0.2 to 0.7, relative permittivity (ε_r) increased from 13.6 to 26.2 commensurate with an increase in temperature coefficient of resonant frequency (TCF) from – 31 ppm/°C to + 60 ppm/°C and a decrease in Qf value (Q = quality factor; f = resonant frequency) from 23 400 to 8620 GHz. Optimum TCF was obtained for x = 0.3 (−15 ppm/°C) and 0.4 (+4 ppm/°C) sintered at 660 and 620°C with ε_r ~15.4, Q_f ~19 650 GHz, and ε_r ~17.3, Q_f ~13 050 GHz, respectively. Ceramics in this novel solid solution are a candidate for ultra low temperature co-fired ceramic (ULTCC) technology.

KEYWORDS
electroceramics, LTCC, microwaves

1 | INTRODUCTION

Due to the requirements of miniaturization and integration, low temperature co-fired ceramic (LTCC) technology plays an important role in the fabrication of modern electronic components. For LTCC technology, microwave dielectric ceramics/composites are required whose sintering temperatures are lower than the melting point (M.P.) of the internal electrode. Silver is the most commonly used internal electrode with M.P. ~961°C.[1-6] The search for microwave dielectrics with low intrinsic sintering temperature has attracted much attention and the subject is now referred to ultra-low temperature co-fired ceramics (ULTCC). As densification temperature is strongly related to M.P., ULTCCs are usually rich in oxides such as TeO_2 (733°C), MoO_3 (795 °C), Bi_2O_3 (817°C), and V_2O_5 (690°C).[7-15] However, most single phase ULTCCs possess a large negative or positive temperature coefficient of resonant frequency (TCF) and solid solutions or composites are needed to tune TCF to zero.[16,17] As reported previously,[18] the $K_{1/2}Bi_{1/2}MoO_4$ ceramic, which adopts an A site ordered monoclinic scheelite-related structure, may be densified at 630°C with a permittivity (ε_r) = 37, a quality factor (Q_f) ~4000 GHz and a large positive TCF = +117 ppm/°C. Although it is chemically compatible with aluminum (M. P. ~660°C), its large TCF requires tuning. Lanthanide ions (R_{Ln} = 0.99-1.16 Å for CN8) partially substitute for Bi^{3+} (R_{Bi} = 1.17 Å for CN8) in many systems.[19-21] In previous work,[22] $(K_{0.5}Nd_{0.5})MoO_4$ was also reported to crystallize in a A-site ordered scheelite structure but with TCF ~ −62 ppm/°C and thus constitutes an ideal end member in a solid solution with $K_{1/2}Bi_{1/2}MoO_4$ to create temperature stable compositions. In the present work, the sintering, crystal structure, microstructure, and microwave dielectric properties of the $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ($0.2 \le x \le 0.7$) ceramics were studied.

2 | EXPERIMENTAL PROCEDURE

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Chengdu, China), K_2CO_3, Nd_2O_3 (>99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and MoO_3 (>99%, Fuchen Chemical Reagents, Tianjin, China) were measured according to the stoichiometric formulation $[K_{0.5}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.3, 0.4, and 0.7). Ceramic samples were prepared via the traditional solid-state reaction method as described in our previous work.[2,15] Samples were calcined at 550°C and sintered in air from 580°C to 720°C. Room temperature X-ray diffraction (XRD) was performed with CuK_α radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Prior to examination, sintered pellets were crushed in a mortar and pestle. Diffraction patterns were obtained between 2θ of 5°-65° at a step size of 0.02°. To examine the grain morphology, as-fired and fractured surfaces were examined by scanning electron microscopy (SEM; FEI, Quanta 250F, Hillsboro, OR, USA). Density was measured using Archimedes' method. Dielectric properties at MW frequencies were measured with the $TE_{01\delta}$ dielectric resonator method with a network analyzer (8720ES, Agilent, Palo Alto, CA, USA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA, USA). The temperature coefficient of resonant frequency TCF (τ_f) was calculated with the following formula:

$$\mathrm{TCF}(\tau_f) = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \tag{1}$$

where the f_T and f_{T_0} were the $TE_{01\delta}$ resonant frequencies at temperature T and T_0, respectively.

3 | RESULTS AND DISCUSSIONS

XRD traces of $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ with $0.2 \le x \le 0.7$ calcined 4 hours at 550°C are shown in Figure 1A. All samples crystallized in an A-site ordered monoclinic scheelite phase[23] with equivalent traces of sintered ceramics. Except for the main reflection peaks as indexed according to PDF card No. 32-0817, many super lattice reflection peaks were also observed, which is similar to the literature's report.[23] The strongest peak at 27.5° moved to lower 2θ with the increase in Bi^{3+} concentration due to its larger ionic radius (1.17 Å) than Nd^{3+} (1.109 Å).[24] As shown in

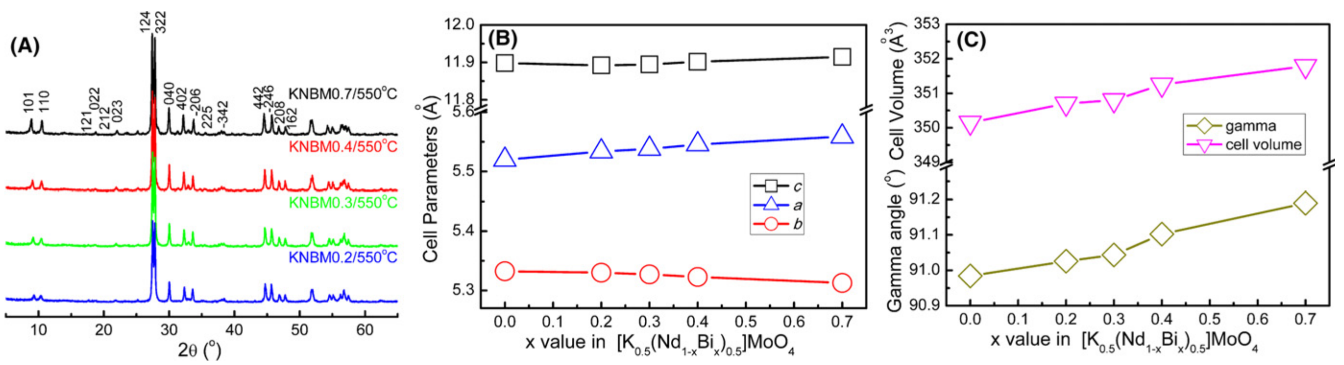

FIGURE 1 XRD patterns of the $[K_{0.5}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ samples (x = 0.2, 0.3, 0.4, and 0.7) calcined at 550°C for 4 h (A) and their cell parameters (B) and (C) [Color figure can be viewed at wileyonlinelibrary.com]

Figure 1B, a increased linearly with x while b decreased. The non-contiguous behavior of a and b reflects further deformation of the monoclinic structure caused by Bi^{3+} substitution of Nd^{3+}, and is commensurate with an increase in gamma, as shown in Figure 1C. Nonetheless, Bi^{3+} substitution for Nd^{3+} resulted in a linear increase in cell volume.

SEM images of the $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ceramics sintered at their optimal temperature are shown in Figure 2. The end members, $(K_{0.5}Nd_{0.5})MoO_4$ and $(K_{0.5}Bi_{0.5})MoO_4$, sintered at 720°C and 630°C, respectively, but for the $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ solid solutions, Bi substitution lowered the sintering temperature from 720°C for $x = 0.2$ to 580°C for $x = 0.7$. A homogeneous microstructure was retained for all compositions with grain size, 1-3 μm, in agreement with previous reports.[18,22] Relative densities of all the ceramic samples are above 95% as measured by Archimedes' method.

ε_r, Q_f, and TCF of the $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ $(0.2 \le x \le 0.7)$ ceramics as a function of sintering temperature and composition are shown in Figure 3. ε_r increased with sintering temperature and saturated above optimal densification while Q_f achieved a maximum in a narrow range of sintering temperature. According to Shannon's additive rule,[25] polarizability of Bi^{3+} and Nd^{3+} in the MW region are 6.12 and 5.01 $Å^3$, respectively. Hence, ε_r increased linearly from 9.8 to 37 from x = 0-1 while TCF tuned linearly from −62 ppm/°C to +117 ppm/°C. Near zero TCF was obtained for $0.3 \le x \le 0.4$. However, Q_f exponentially decayed with x. According to the classic oscillator model, Q_f value is inversely proportional to permittivity value as shown in the following:

$$Q \times f \approx \frac{(ze)^2/mV\varepsilon_0}{2\pi\gamma \times (\varepsilon'(\omega) - \varepsilon(\infty))} \tag{2}$$

in which $\varepsilon'(\omega)$ is the real part of permittivity, $\varepsilon(\infty)$ is the electronic part of the static permittivity, γ is the damping parameter, z is the equivalent electric charge number, e is the electric charge for a electron, m is the equivalent atom weight and V is the unit volume. This relation explains well the trend of Q_f value vs x value. Optimum MW properties were obtained for $K_{0.5}(Nd_{0.3}Bi_{0.2})MoO_4$ ($x = 0.4$) ceramics sintered at 620°C with ε_r ~17.3, Q_f ~13 050 GHz and TCF ~+4 ppm/°C and for $K_{0.5}(Nd_{0.35}Bi_{0.15})MoO_4$ ($x = 0.3$) ceramics sintered at 660°C with ε_r ~15.4, Q_f ~19 650 GHz and TCF ~−15 ppm/°C. A comparison of microwave dielectric ceramics with similar permittivities are listed in Table 1.[26-29] Compared with other LTCC microwave dielectric ceramics, the TCF values of the $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ceramics can be easily adjusted by changing the content of Bi. The low-sintering temperature and chemical compatibility with aluminum powders, suggest that $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ceramics are candidates for ultra-low temperature co-fired ceramics technology.

4 | CONCLUSIONS

$K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ $(0.2 \le x \le 0.7)$ ceramics were prepared via solid-state reaction method. Optimal density

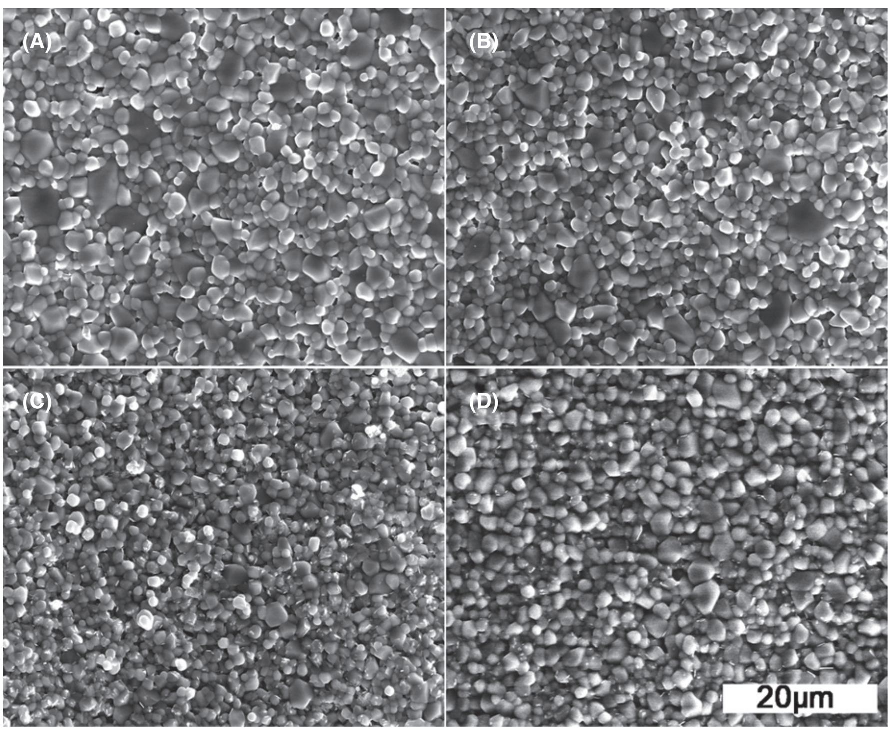

FIGURE 2 SEM images of the $[K_{0.5}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ ceramics sintered at 720°C for $x = 0.2$ (A), at 660°C for $x = 0.3$ (B), at 600°C for $x = 0.4$ (C) and at 580°C for $x = 0.7$ (D)

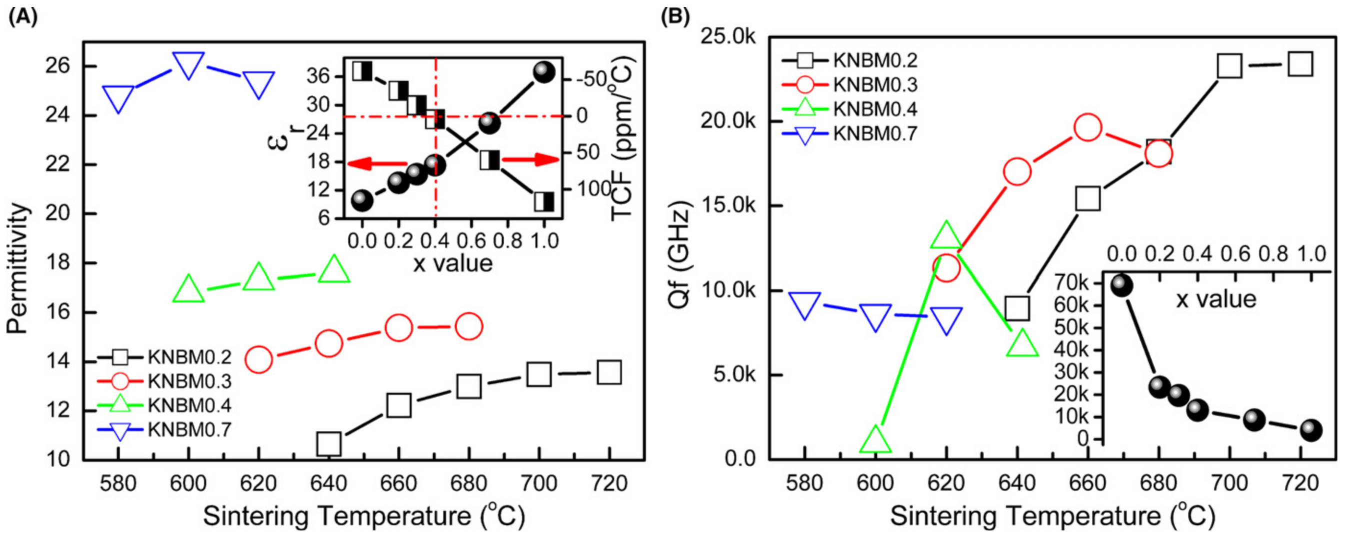

FIGURE 3 Microwave dielectric permittivity (A) and Q_f values (B) of the $[K_{0.5}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ (x = 0.2, 0.3, 0.4, and 0.7) ceramics as a funciton of sintering temperature and composition [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Sintering temperatures and microwave dielectric properties of LTCC materials with permittivity between 15.2 and 17.5

Composition	Sintering temperature	ε_r	Q_f value (GHz)	TCF Value (ppm/°C)	References
$CeTe_2O_6$	680	15.2	45 400	−68	[26]
$K_{0.5}(Nd_{0.35}Bi_{0.15})MoO_4$	660	15.4	19 650	−15	This work
$Cu_3Nb_2O_8$	900	15.6	48 400	−75	[27]
Pb_2WO_5	520	16.4	14 800	−95	[28]
$CoCu_2Nb_2O_8$	985	16.6	36 800	−37	[29]
$ZnCu_2Nb_2O_8$	900	16.7	41 000	−77	[29]
$K_{0.5}(Nd_{0.3}Bi_{0.2})MoO_4$	620	17.3	13 050	+4	This work
$BaTe_4O_9$	500	17.5	54 700	−90	[9]

for $[K_{0.5}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ ($0.2 \le x \le 0.7$) ceramics decreased from 720°C for x = 0.2 to 580°C for x = 0.7 with no change in the grain size (1-3 μm). ε_r of $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ($0.2 \le x \le 0.7$) ceramics increased linearly from 13.6 at x = 0.2-26.2 at x = 0.7 while the Q_f decreased from 23 400 to 8620 GHz. The best MW properties were obtained for x = 0.3 (sintered at 660°C) and 0.4 (sintered at 620°C) with ε_r ~15.4, Q_f ~19 650 GHz and TCF ~ −15 ppm/°C, and ε_r ~17.3, Q_f ~13 050 GHz and TCF ~+ 4 ppm/°C, respectively. This novel solid solution ceramic is a candidate for (U)LTCC technology.

ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (grant no. 2017YFB0406301), the Young Star Project of Science and Technology of Shaanxi Province (2015KJXX-39), Headmaster Foundation of Xi'an Technological University (XAGDXJJ1401), the Fundamental Research Funds for the Central University, and the State Key Laboratory of New Ceramic and Fine Processing Tsinghua University. The SEM work was done at International Center for Dielectric Research (ICDR), Xi'an Jiaotong University, Xi'an, China and the authors thank Ms. Yan-Zhu Dai for her help in using SEM.

ORCID

Di Zhou http://orcid.org/0000-0001-7411-4658
Da-Wei Wang http://orcid.org/0000-0001-6957-2494

REFERENCES

1. Sebastian MT, Jantunen H. Low loss dielectric materials for LTCC applications: a review. *Int Mater Rev*. 2008;53:57-90.
2. Zhou H, Liu X, Chen X, Fang L, Wang Y. $ZnLi_{2/3}Ti_{4/3}O_4$: a new low loss spinel microwave dielectric ceramic. *J Eur Ceram Soc*. 2012;32:261-265.

3. Zhang YD, Zhou D. Pseudo phase diagram and microwave dielectric properties of Li_2O-MgO-TiO_2 ternary system. *J Am Ceram Soc*. 2016;99:3645-3650.
4. Zhou D, Randall CA, Wang H, Pang LX, Yao X. Microwave dielectric ceramics in Li_2O–Bi_2O_3–MoO_3 system with ultra-low sintering temperatures. *J Am Ceram Soc*. 2010;93:1096-1100.
5. Kagata H, Inoue T, Kato J, Kameyama I. Low-fire bismuth-based dielectric ceramics for microwave use. *Jpn J Appl Phys*. 1992;31:3152-3155.
6. Li J, Fang L, Luo H, Tang Y, Li C. Structure and microwave dielectric properties of a novel temperature stable low-firing $Ba_2LaV_3O_{11}$ ceramic. *J Eur Ceram Soc*. 2016;36:2143-2148.
7. Zhou D, Wang H, Pang LX, Randall CA, Yao X. Bi_2O_3–MoO_3 binary system: an alternative ultra low sintering temperature microwave dielectric. *J Am Ceram Soc*. 2009;92:2242-2246.
8. Sebastian MT, Wang H, Jantunen H. Low temperature co-fired ceramics with ultra-low sintering temperature: a review. *Current Opinion Solid State Mater Sci*. 2016;20:151-170.
9. Kwon DK, Lanagan MT, Shrout TR. Microwave dielectric properties and low-temperature co-firing of $BaTe_4O_9$ with aluminum metal electrode. *J Am Ceram Soc*. 2005;88:3419-3422.
10. Zhou D, Pang LX, Guo J, et al. Influence of Ce substitution for Bi in $BiVO_4$ and the impact on the phase evolution and microwave dielectric properties. *Inor Chem*. 2014;53:1048-1055.
11. Pang LX, Zhou D, Qi ZM, Liu WG, Yue ZX, Reaney IM. Structure–property relationships of low sintering temperature scheelite-structured $(1-x)BiVO_4$–$xLaNbO_4$ microwave dielectric ceramics. *J Mater Chem C*. 2017;5:2695-2701.
12. James NK, Ratheesh R. Microwave dielectric properties of low-temperature sinterable $BaCe_2(MoO_4)_4$ ceramics. *J Am Ceram Soc*. 2010;93:931-933.
13. Varghese J, Siponkoski T, Teirikangas M, Sebastian MT, Uusimäki A, Jantunen H. Structural, dielectric, and thermal properties of Pb free molybdate based ultralow temperature glass. *ACS Sustainable Chem Eng*. 2016;4:3897-3904.
14. Joseph N, Varghese J, Siponkoski T, Teirikangas M, Sebastian MT, Jantunen H. Glass-free $CuMoO_4$ ceramic with excellent dielectric and thermal properties for ultralow temperature cofired ceramic applications. *ACS Sustainable Chem Eng*. 2016;4:5632-5639.
15. Varghese J, Vahera T, Ohsato H, Iwata M, Jantunen H. Novel low-temperature sintering ceramic substrate based on indialite/cordierite glass ceramics. *Jpn J Appl Phys* 2017;56:10PE01.
16. Zhou D, Li WB, Guo J, et al. Structure, phase evolution, and microwave dielectric properties of $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic with ultra low sintering temperature. *Inor Chem* 2014;53:5712-5716.
17. Fang L, Chu D, Zhou H, et al. Microwave dielectric properties of temperature stable $Li_2Zn_xCo_{1-x}Ti_3O_8$ ceramics. *J Alloys Comp*. 2011;509:8840-8844.
18. Zhou D, Randall CA, Pang LX, et al. Microwave dielectric properties of $(ABi)_{1/2}MoO_4$ (A= Li, Na, K, Rb, Ag) type ceramics with ultra-low firing temperatures. *Mater Chem Phys*. 2010;129:688-692.
19. Zhou D, Randall CA, Wang H, Pang LX, Yao X. Microwave dielectric properties trends in a solid solution $(Bi_{1-x}Ln_x)_2Mo_2O_9$ (Ln = La, Nd, $0.0 \le x \le 0.2$) system. *J Am Ceram Soc*. 2009;92:2931-2936.
20. Kumar HP, George S, Thomas JK, Solomon S. Synthesis, structural analysis and microwave dielectric properties of $Bi_{(x)}Ln_{(1-x)}$-$TiTaO_6$ (Ln = Ce, Pr and Nd) ceramics. *J Mater Sci Mater Electron*. 2010;21:27-32.
21. Liu X, Yuan CL, Liu XY, et al. Microstructures and microwave dielectric properties of $xLi_{(1/2)}Ln_{(1/2)}TiO_{(3)}$-$(1-x)$ $Na_{1/2}Bi_{1/2}TiO_3$ (Ln = Sm and Nd) ceramic systems. *J Alloys Comp*. 2017;698:329-335.
22. Zhou D, Pang LX, Guo J, et al. Low temperature firing microwave dielectric ceramics $(K_{0.5}Ln_{0.5})MoO_4$ (Ln = Nd and Sm) with low dielectric loss. *J Eur Ceram Soc*. 2011;31:2749-2752.
23. Morozov VA, Arakcheeva AV, Chapuis G, Guiblin N, Rossell MD, Tendeloo GV. $KNd(MoO_4)_2$: a new incommensurate modulated structure in the scheelite family. *Chem Mater*. 2006;18:4075-4082.
24. Shannon RD. Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystal Sec A*. 1976;32:751-767.
25. Shannon RD. Dielectric polarizabilities of ions in oxides and fluorides. *J Appl Phys*. 1993;73:348-366.
26. Li YZ, Bian JJ, Yuan LL. A new glass-free low-temperature fired microwave ceramic. *J Mater Sci*. 2009;44:328-330.
27. Kim DW, Kim IT, Park B, Hong KS, Kim JH. Microwave dielectric properties of $(1-x)Cu_3Nb_2O_8-xZn_3Nb_2O_8$ ceramics. *J Mater Res*. 2001;16:1465-1470.
28. Xie HD, Xi HH, Chen C, Zhou D. Microwave dielectric properties of two low temperature sintering ceramics in the PbO-WO_3 binary system. *Ceram Int*. 2015;41:10287-10292.
29. Pullar RC, Lai C, Azough F, Freer R, Alford NM. Novel microwave dielectric LTCCs based uponV_2O_5 doped $M^{2+}Cu_2Nb_2O_8$ compounds (M^{2+} = Zn Co, Ni, Mg and Ca). *J Eur Ceram Soc*. 2006;26:1943-1946.

How to cite this article: Pang L-X, Zhou D, Wang D-W, et al. Temperature stable $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ microwave dielectrics ceramics with ultra-low sintering temperature. *J Am Ceram Soc*. 2018;101:1806–1810. https://doi.org/10.1111/jace.15388