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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] and Ian M. Reaney[*2]

[1]Micro-optoelectronic Systems Laboratories, Xi'an Technological University, Xi'an 710032, Shaanxi, China

[2]Materials Science and Engineering, University of Sheffield, Sheffield, S1 3JD, UK

[3]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China

[4]State Grid Gansu Electric Power Research Institute, 730070, Lanzhou, China

[5]State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

[*]Corresponding author. Tel (Fax): +86-29-82668679; E-mail address: zhoudi1220@gmail.com (Di Zhou) & i.m.reaney@sheffield.ac.uk (Ian M. Reaney)

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 GHz to 8,620 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, Qf ~19,650 GHz, and ε_r ~ 17.3, Qf ~ 13,050 GHz, respectively. Ceramics in this novel solid solution are a candidate for ultra low tempertaure co-fired ceramic (ULTCC) technology.

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 ^{o}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). Since densification temperature is strongly related to M.P., ULTCCs are usually rich in oxides such as TeO_2 (733^{o}C), MoO_3 (795 ^{o}C), Bi_2O_3 (817^{o}C) and V_2O_5 (690^{o}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 ^{o}C with a permittivity (ε_r) = 37, a quality factor (Qf) ~ 4,000 GHz and a large positive TCF = + 117 ppm/^{o}C. Although it is chemically compatible with aluminum (M. P. ~ 660 ^{o}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/^{o}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 $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ($0.2 \leq x \leq 0.7$) ceramics were studied.

2. EXPERIMENTAL

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 ^oC and sintered in air from 580 ~ 720 ^oC. Room temperature X-ray diffraction (XRD) was performed with Cu Kα 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 ^{o} at a step size of 0.02 ^{o}. To examine the grain morphology, as-fired and fractured surfaces were examined by scanning electron microscopy (SEM, FEI, Quanta 250 F). 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 (HP 8720 Network Analyzer, Hewlett-Packard) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency TCF (τ_f) was calculated with the following formula:

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

where the f_T and f_{T0} 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 $0.2 \leq x \leq 0.7$ calcined 4 h at 550 ^oC are shown in Fig. 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 degree moved to lower 2θ with the increase of Bi^{3+} concentration due to its larger ionic radius (1.17 Å) than Nd^{3+} (1.109 Å).[24] As shown in Fig. 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 Fig. 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 Fig. 2. The end members, $(K_{0.5}Nd_{0.5})MoO_4$ and $(K_{0.5}Bi_{0.5})MoO_4$, sintered at 720 ^oC and 630 ^oC, 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 ^oC for x = 0.2 to 580 ^oC for x = 0.7. A homogenous 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, Qf and TCF of the $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ($0.2 \leq x \leq 0.7$) ceramics as a function

of sintering temperature and composition are shown in Fig. 3. ε_r increased with sintering temperature and saturated above optimal densification whilst Qf 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 $Å^3$ 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/^oC to + 117 ppm/^oC. Near zero TCF was obtained for $0.3 \leq x \leq 0.4$. However, Qf exponentially decayed with x. According to the classic oscillator model, Qf value is inversely proportional to permittivity value as shown in the following:

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

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 Qf value versus 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 ^oC with ε_r ~ 17.3, Qf ~ 13,050 GHz and TCF ~ + 4 ppm/^oC and for $K_{0.5}(Nd_{0.35}Bi_{0.15})MoO_4$ (x = 0.3) ceramics sintered at 660 ^oC with ε_r ~ 15.4, Qf ~ 19,650 GHz and TCF ~ − 15 ppm/^oC. A comparison of microwave dielectric ceramics with similar permittivities are listed in Table I.[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

$K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ($0.2 \leq x \leq 0.7$) ceramics were prepared via solid state reaction method. Optimal density for $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ ($0.2 \leq x \leq 0.7$) ceramics decreased from 720 ^oC for x = 0.2 to 580 ^oC for x = 0.7 with no change in the grain size (1 ~ 3 μm). ε_r of $K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO_4$ ($0.2 \leq x \leq 0.7$) ceramics increased linearly from 13.6 at x = 0.2 to 26.2 at x = 0.7 while the Qf decreased from 23,400 GHz to 8,620 GHz. The best MW properties were obtained for x = 0.3 (sintered at 660 ^oC) and 0.4 (sintered at 620 ^oC) with ε_r ~ 15.4, Qf ~ 19,650 GHz and TCF ~ − 15 ppm/^oC, and ε_r ~ 17.3, Qf ~ 13,050 GHz andTCF ~ + 4 ppm/^oC, respectively. This novel solid solution ceramic is a candidate for (U)LTCC technology.

Acknowledgements

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Table I. Sintering temperatures and microwave dielectric properties of LTCC materials with permittivity between 15.2 ~ 17.5

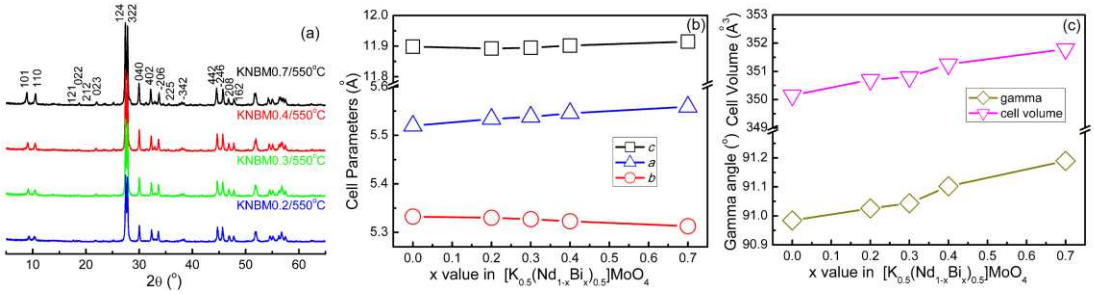
Composition	Sintering Temperature	ε_r	Qf value (GHz)	TCF Value (ppm/^{o}C)	Ref.
$CeTe_2O_6$	680	15.2	45,400	−68	26
$K_{0.5}(Nd_{0.35}Bi_{0.15})MoO_4$	660	15.4	19,650	−15	This work
$Cu_3Nb_2O_8$	900	15.6	48,400	−75	27
Pb_2WO_5	520	16.4	14,800	−95	28
$CoCu_2Nb_2O_8$	985	16.6	36,800	−37	29
$ZnCu_2Nb_2O_8$	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

Figure Captions:

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 ^oC for 4 h (a) and their cell parameters (b) and (c)

FIGURE 2 SEM images of the $[K_{0.5}(Nd_{1-x}Bi_x)_{0.5}]MoO_4$ ceramics sintered at 720 ^oC for x = 0.2 (a), at 660 ^oC for x = 0.3 (b), at 600 ^oC for x = 0.4 (c) and at 580 ^oC for x = 0.7 (d)

FIGURE 3 Microwave dielectric permittivity (a) and Qf 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



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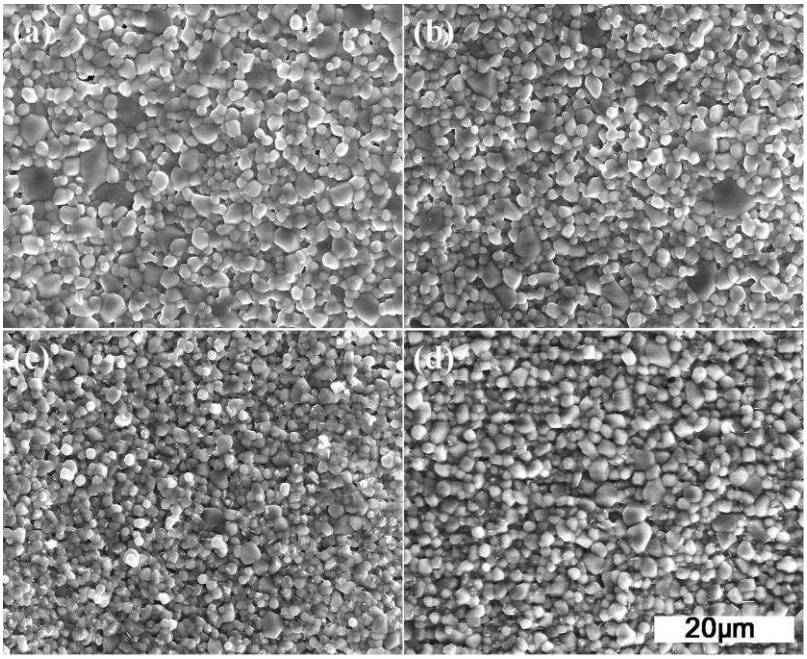

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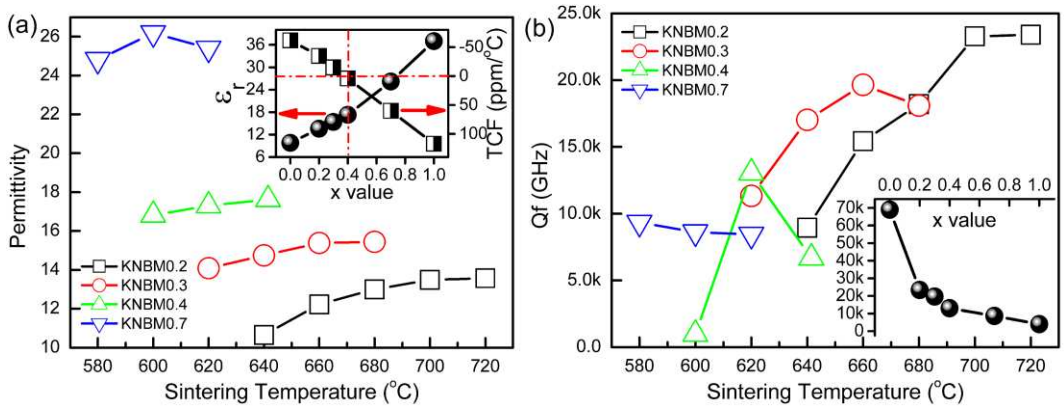

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