J. Am. Ceram. Soc., **97** [7] 2032–2034 (2014)
DOI: 10.1111/jace.12996

Journal
Rapid Communication

Low-Temperature Sintering and Microwave Dielectric Properties of $CaMoO_4$-Based Temperature Stable LTCC Material

Li-Xia Pang,[‡] Di Zhou,[§,†] and Wei-Guo Liu[‡]

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

[§]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

The $CaMoO_4$–xY_2O_3–xLi_2O ceramics were prepared by the solid-state reaction method. The sintering behavior, phase evolution, microstructure, and microwave dielectric properties were investigated. $CaMoO_4$ solid solution was obtained when $x = 0.030$, and two-phase system including tetragonal $CaMoO_4$ phase and cubic Y_2O_3 phase formed when $0.066 \le x \le 1.417$. A temperature stable $CaMoO_4$-based microwave dielectric ceramic with ultralow sintering temperature (775°C) was obtained in the $CaMoO_4$–xY_2O_3–xLi_2O system when $x = 0.306$, which showed good microwave dielectric properties with a low permittivity of 9.5, a high Q_f value of 63 240 GHz, and a near-zero temperature coefficient of resonant frequency of +7.2 ppm/°C.

I. Introduction

With the development of mobile communication, satellite communication, global position system (GPS), and other communication technologies, low-temperature firing microwave dielectric ceramic materials have attracted much attention due to its use in low-temperature cofired ceramic (LTCC) technology, which becomes an important electronics manufacturing method because of its predominance in enabling fabrication of three-dimensional ceramic modules with low dielectric loss and cofired metal electrodes. Hence, search for microwave dielectric ceramic materials with wide range of dielectric permittivity (ε_r), high quality factor (Q_f value), near-zero temperature coefficient of resonant frequency (TCF value), and lower sintering temperature (ST) has been worked on all over the world.[1–3]

As the $BaTe_4O_9$ ceramic with a ST around 550°C, dielectric permittivity ~17.5, and Q_f value about 54 700 GHz was reported by Kwon *et al.*,[4,5] many ultralow sintering microwave dielectric ceramics have been explored.[3,6–10] The prototype of mutilayer capacitors prepared via the tape casting and screen printing methods based on the $Bi_2Mo_2O_9$ and $LiMgPO_4$ glass free ceramics have been studied in the literature.[11,12] Dielectric constant and anisotropy of the single crystal and microwave dielectric properties of the ceramic of $CaMoO_4$ were firstly reported by Brower[13] and Choi,[14] respectively. $CaMoO_4$ ceramic could be well densified at around 1100°C with a permittivity $\varepsilon_r = 10.79$, a $Q_f = 89\,700$ GHz, and a large negative TCF value −57 ppm/°C.[14] Vidya *et al.*[15] reported nanosized $CaMoO_4$ could be well sintered at a very low temperature around 775°C. However, its large negative TCF value still limited its application. Recently, the rutile TiO_2 has been selected to adjust the TCF value of $CaMoO_4$ ceramic and temperature stale LTCC material was obtained.[16] Meanwhile $(Li_{0.5}Bi_{0.5})^{2+}$ substitution for Ca^{2+} could also modify the TCF value to near zero.[17] In the present work, Y_2O_3 combining with Li_2O was used to tailor the TCF value of $CaMoO_4$ ceramic and improve the sintering behavior to satisfy the requirements of LTCC application.

II. Experimental Procedure

Proportionate amount of reagent-grade starting materials of $CaCO_3$ (>99%, Guo-Yao Co. Ltd., Shanghai, China), MoO_3 (>99%; Fuchen Chemical Reagents, Tianjin, China), Y_2O_3 (>99%; Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), and Li_2CO_3 (>99%; Guo-Yao Co. Ltd.) were prepared according to the stoichiometric compound $CaMoO_4$–xY_2O_3–xLi_2O (x = 0.030, 0.066, 0.075, 0.083, 0.167, 0.306, 0.583, 1.417). Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China), and then the mixture was dried and calcined at 650°C for 4 h. The calcined powders were milled again for 5 h and dried. Then, the powders were pressed into cylinders (10 mm in diameter and 4–5 mm in height) in a steel die with 5 wt% polyvinyl alcohol binder addition under a uniaxial pressure of 20 MPa. Samples were sintered in the temperature range from 700°C to 825°C for 2 h.

Room-temperature X-ray diffraction (XRD) was performed using a XRD with CuK_α radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). To examine the grain morphology, the as-fired surfaces and fractured surfaces of the samples were measured by scanning electron microscopy (SEM) (JSM-6460; JEOL, Tokyo, Japan). Dielectric properties at microwave frequency were measured with the $TE_{01\delta}$ dielectric resonator method with a network analyzer (HP 8720 Network Analyzer; Hewlett-Packard, Palo Alto, CA) and a temperature chamber (Delta 9023; Delta Design, Poway, CA). The TCF value was calculated with the following formula:

$$\mathrm{TCF} = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \quad \mathrm{ppm/^\circ C} \tag{1}$$

where f_T and f_{T_0} were the $TE_{01\delta}$ resonant frequencies at temperature T (85°C) and T_0 (25°C), respectively.

III. Results and Discussion

Figure 1 presents the XRD patterns of sintered $CaMoO_4$–xY_2O_3–xLi_2O (x = 0.030, 0.066, 0.075, 0.083, 0.167, 0.306,

C. Randall—contributing editor

Manuscript No. 34526. Received February 10, 2014; approved April 15, 2014.
[†]Author to whom correspondence should be addressed. e-mail: zhoudi1220@gmail.com

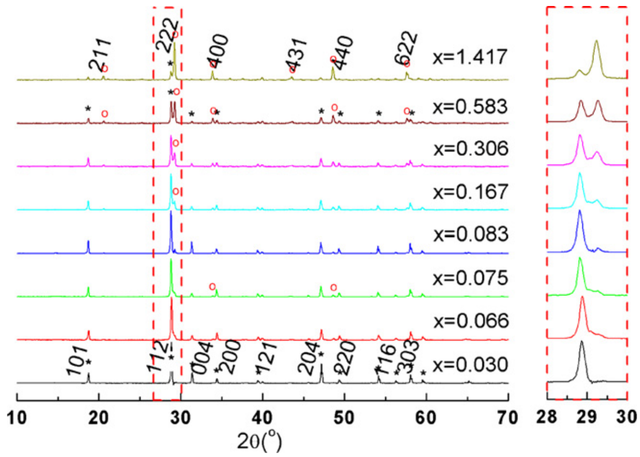

Fig. 1. X-ray diffraction patterns of $CaMoO_4$–xY_2O_3–xLi_2O (x = 0.030, 0.066, 0.075, 0.083, 0.167, 0.306, 0.583, 1.417) ceramics sintered at 750°C for 2 h (*—$CaMoO_4$, o—Y_2O_3).

0.583, 1.417) ceramics, and the diffraction peaks in the range of 2θ = 28°–30° were studied specialized to analyze the phase compositions. It was seen that when x = 0.030, all the diffraction peaks of the $CaMoO_4$–xY_2O_3–xLi_2O compounds could be indexed as tetragonal scheelite phase (space group $I4_1/a$). It means that solid solution formed in the $CaMoO_4$–xY_2O_3–xLi_2O system when x = 0.030. Then, cubic Y_2O_3 phase appeared and its amount increased with x value. In other words, two-phase system including tetragonal $CaMoO_4$ phase and cubic Y_2O_3 phase formed when $0.066 \le x \le 1.417$ in the $CaMoO_4$–xY_2O_3–xLi_2O ceramic system.

To investigate the microstructure of the $CaMoO_4$–xY_2O_3–xLi_2O compounds with two phases, both the as-fired and fractured surfaces were measured and are shown in Fig. 2. It was seen that well-densified ceramic matrix with little pores was obtained after the $CaMoO_4$–xY_2O_3–xLi_2O (x = 0.167) compound was sintered at 775°C for 2 h. As shown in Fig. 2, there were two kinds of grains in the ceramic matrix, bigger gains with size about 2 μm and smaller ones with nanoscale. Combining with the XRD results, it was maintained that the bigger gains and the smaller ones were $CaMoO_4$ solid solution grains and Y_2O_3 grains, respectively. The Y_2O_3 grains lay around the $CaMoO_4$ solid solution grains.

The STs and microwave dielectric properties of $CaMoO_4$–xY_2O_3–xLi_2O ceramics are listed in Table I. The $CaMoO_4$–$0.030Y_2O_3$–$0.030Li_2O$ ceramic possessed low ST around 725°C, low K (permittivity) of 9.8, high Q_f value of 65 500 GHz, and negative TCF value about −58 ppm/°C. Comparing with pure $CaMoO_4$ ceramic,[14] the ST of the solid solution was lowered greatly from 1100°C to 725°C by a small amount of Y_2O_3–Li_2O addition, whereas the Q_f value decreased from 89 700 to 65 500 GHz. In the two-phase system ($0.066 \le x \le 1.417$), all the ceramics could be well densified at low STs (725°C–800°C), and the Q_f value shifted in the range of 61 500~66 600 GHz. The permittivity increased slightly from 10.1 to 10.3 when x value increased from 0.066 to 0.075, which might result from the improvement of the sintering behavior, and then it decreased to 9.1 when x value increased further. The TCF value shifted from −57 to +63 ppm/°C as the x value increased from 0.066 to 1.417. According to mixing rules of permittivity[18] and TCF value,[19] it could be maintained that the Y_2O_3 phase possessed a lower permittivity and positive TCF value, and the TCF value of the compound could be tailored to near zero by adjusting the amount of Y_2O_3 phase and $CaMoO_4$ solid solution phase. In this case, a temperature stable microwave dielectric ceramic material was obtained when x = 0.306 in the $CaMoO_4$–xY_2O_3–xLi_2O system, and it showed good microwave dielectric properties with a low permittivity of 9.5, a high Q_f value of 63 200 GHz, and a near-zero TCF value of +7 ppm/°C. It was a good candidate for LTCC application with ultralow ST.

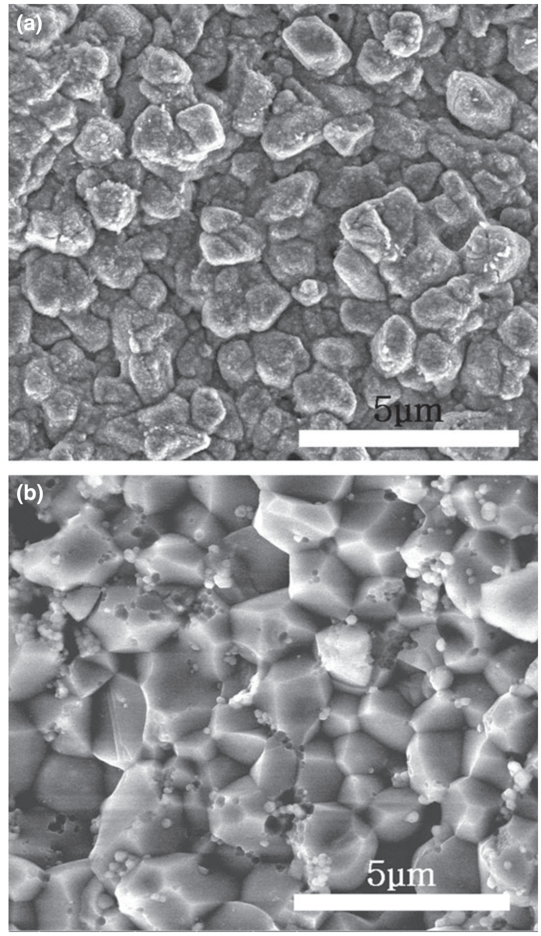

Fig. 2. SEM micrographs of the as-fired (a) and fractured (b) surfaces of $CaMoO_4$–xY_2O_3–xLi_2O (x = 0.167) ceramic sintered at 775°C.

Table I. Sintering Temperatures and Microwave Dielectric Properties of $CaMoO_4$–xY_2O_3–xLi_2O Ceramics

$CaMoO_4$–xY_2O_3–xLi_2O	ST (°C)	Permittivity	Q_f (GHz)	TCF (ppm/°C)
x = 0[12]	1100	10.79	89 700	−57
x = 0.030	725	9.8	65 500 ± 400	−58 ± 0.5
x = 0.066	775	10.1	66 600 ± 300	−57 ± 0.7
x = 0.075	750	10.3	63 200 ± 400	−56 ± 0.8
x = 0.083	775	9.9	66 000 ± 500	−48 ± 0.5
x = 0.167	775	9.9	64 500 ± 400	−27 ± 0.5
x = 0.306	775	9.5	63 200 ± 300	+7 ± 0.4
x = 0.583	800	9.3	62 700 ± 300	+50 ± 0.5
x = 1.417	725	9.1	61 500 ± 300	+63 ± 0.5

ST, sintering temperature.

IV. Conclusions

$CaMoO_4$–xY_2O_3–xLi_2O (x = 0.030, 0.066, 0.075, 0.083, 0.167, 0.306, 0.583, 1.417) ceramics were prepared by solid-state reaction method, and all the ceramics could be well densified at low ST of 725°C–800°C. $CaMoO_4$ solid solution was obtained when x = 0.030, and two-phase system including tetragonal $CaMoO_4$ phase and cubic Y_2O_3 phase formed when $0.066 \leq x \leq 1.417$. A temperature stable LTCC material was obtained by adjusting the amount of Y_2O_3 phase and $CaMoO_4$ solid solution phase. The $CaMoO_4$–xY_2O_3–xLi_2O ($x = 0.306$) ceramic sintered at 775°C for 2 h showed good microwave dielectric properties with a low permittivity of 9.5, a high Q_f value of 63 200 GHz, and a near-zero TCF value of +7 ppm/°C.

Acknowledgments

This work was supported by NSFC project of China (51202182, 51202178), the Fundamental Research Funds for the Central University, the International Cooperation Project of Shaanxi Province (2013KW12-04), the National Science Foundation of Shaanxi Province (2014JQ6200), and the 111 Project of China (B14040). The SEM work was partially 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.

References

[1]M. T. Sebastian and H. Jantunen, "Low Loss Dielectric Materials for LTCC Applications: A Review," *Int. Mater. Rev.*, **53**, 57–90 (2008).

[2]A. K. Axelsson and N. M. Alford, "Bismuth Titanates Candidates for High Permittivity LTCC," *J. Eur. Ceram. Soc.*, **26**, 1933–6 (2006).

[3]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.*, **92**, 2242–6 (2009).

[4]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).

[5]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).

[6]G. Subodh and M. T. Sebastian, "Glass-Free $Zn_2Te_3O_8$ Microwave Ceramic for LTCC Applications," *J. Am. Ceram. Soc.*, **90**, 2266–8 (2007).

[7]A. Feteira and D. C. Sinclair, "Microwave Dielectric Properties of Low Firing Temperature $Bi_2W_2O_9$ Ceramics," *J. Am. Ceram. Soc.*, **91**, 1338–41 (2008).

[8]D. Zhou, H. Wang, X. Yao, and L. X. Pang, "Microwave Dielectric Properties of Low Temperature Firing $Bi_2Mo_2O_9$ Ceramic," *J. Am. Ceram. Soc.*, **91**, 3419–22 (2008).

[9]D. Zhou, C. A. Randall, L. X. Pang, H. Wang, X. G. Wu, J. Guo, G. Q. Zhang, L. Shui, and X. Yao, "Microwave Dielectric Properties of $Li_2(M^{2+})_2$-Mo_3O_{12} and $Li_3(M^{3+})Mo_3O_{12}$ (M=Zn, Ca, Al, and In) Lyonsite-Related-Type Ceramics With Ultra-Low Sintering Temperatures," *J. Am. Ceram. Soc.*, **94**, 802–5 (2011).

[10]D. Zhou, C. A. Randall, L. X. Pang, H. Wang, J. Guo, G. Q. Zhang, X. G. Wu, L. Shui, and X. Yao, "Microwave Dielectric Properties of Li_2WO_4 Ceramic with Ultra-Low Sintering Temperature," *J. Am. Ceram. Soc.*, **94**, 348–50 (2011).

[11]D. Zhou, C. A. Randall, A. Baker, H. Wang, L. X. Pang, and X. Yao, "Dielectric Properties of an Ultra-Low-Temperature Cofiring $Bi_2Mo_2O_9$ Multilayer," *J. Am. Ceram. Soc.*, **93**, 1443–6 (2010).

[12]D. Thomas, P. Abhilash, and M. T. Sebastian, "Casting and Characterization of $LiMgPO_4$ Glass Free LTCC Tape for Microwave Applications," *J. Eur. Ceram. Soc.*, **33**, 87–93 (2013).

[13]W. S. Brower and P. H. Fang, "Dielectric Constants of $PbMoO_4$ and $CaMoO_4$," *Phys. Rev.*, **149**, 646–6 (1966).

[14]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. Euro. Ceram. Soc.*, **27**, 3063–7 (2007).

[15]S. Vidya, S. Solomon, and J. K. Thomas, "Synthesis, Sintering and Optical Properties of $CaMoO_4$: A Promising Scheelite LTCC and Photoluminescent Material," *Phy. Status Solidi A*, **209**, 1067–74 (2012).

[16]J. Guo, D. Zhou, L. Wang, H. Wang, T. Shao, Z. M. Qi, and X. Yao, "Infrared Spectra, Raman Spectra, Microwave Dielectric Properties and Simulation for Effective Permittivity of Temperature Stable Ceramics $AMoO_4$–TiO_2 (A=Ca, Sr)," *Dalton Trans.*, **42**, 1483–91 (2013).

[17]D. Zhou, H. Wang, Q. P. Wang, X. G. Wu, J. Guo, G. Q. Zhang, L. Shui, X. Yao, C. A. Randall, L. X. Pang, and H. C. Liu, "Microwave Dielectric Properties and Raman Spectroscopy of Scheelite solid Solution $[(Li_{0.5}Bi_{0.5})_{1-x}Ca_x]MoO_4$ Ceramics with Ultra-Low Sintering Temperatures," *Funct. Mater. Lett.*, **3**, 253–7 (2010).

[18]Y. G. Wu, X. H. Zhao, F. Li, and Z. G. Fan, "Evaluation of Mixing Rules for Dielectric Constants of Composite Dielectrics by MC-FEM Calculation on 3D Cubic Lattice," *J. Electroceram.*, **11**, 227–39 (2003).

[19]L. X. Pang, H. Wang, D. Zhou, and X. Yao, "A New Temperature Stale Microwave Dielectric With Low-Firing Temperature in Bi_2MoO_6–TiO_2 System," *J. Alloy. Compd.*, **493**, 626–9 (2010). □