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New Microwave Dielectric Ceramics $BaLn_2(MoO_4)_4$ (Ln = Nd and Sm) with Low Loss

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In the present work, a pure monoclinic phase of $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ was formed at 850°C and 600°C, respectively, via a solid-state reaction method. The ceramic samples were found to be well densified at 960°C. Dense and homogeneous microstructures were revealed from the scanning electron microscopy. The microwave dielectric behaviors were studied as a function of sintering temperature and characterized in the temperature range 25°C–120°C. The best properties were obtained in ceramics sintered at 960°C with a permittivity ~11.7, a $Q \times f$ value of 45 000 GHz and a temperature coefficient of frequency about −41 ppm/°C for $BaNd_2(MoO_4)_4$ ceramic at 9.9 GHz, and a permittivity ~11.8, a $Q \times f$ value of 20 000 GHz, and a temperature coefficient of frequency about −34 ppm/°C for $BaSm_2(MoO_4)_4$ ceramic at 9.7 GHz, respectively.

I. Introduction

Microwave dielectric ceramics have been studied for more than 40 years since they were applied in the microwave devices application, such as dielectric resonator, dielectric filter, dielectric antenna, etc. The search for new microwave dielectric ceramic has never been stopped due to the fast development of wireless communication technology and devices, such as portable phones, car-telephones, Bluetooth technology, global position system (GPS), wireless fidelity (WIFI), etc. Microwave dielectric ceramics with a series of dielectric permittivities ε_r, high $Q \times f$ value, small temperature coefficient of resonant frequency τ_f, nontoxic constituents are needed.[1–5]

Many MoO_3-rich systems have been found to show high performance of microwave dielectric properties and advantage in the low temperature co-fired ceramic technology (LTCC), such as $AMoO_4$ (ε_r = 7–11, $Q \times f$ = 37 000–90 000 GHz, τ_f = −57 to −87 ppm/°C),[6,7] Bi_2O_3–MoO_3 (ε_r = 17–38, $Q \times f$ = 9300–21 800 GHz, τ_f = −215 to +31 ppm/°C),[8,9] Ln_2O_3–MoO_3 (Ln = La and Nd) (ε_r = 8.2–10.1, $Q \times f$ = 60 000–80 000 GHz, τ_f = −60 to −80 ppm/°C).[10] It seems that most MoO_3-rich binary systems show high microwave dielectric properties, especially for the alkali metals molybdates and lanthanon molybdates. However, there is only few report on the microwave dielectric properties of alkali metal, lanthanon and molybdenum ternary system. Recently, James and Ratheesh reported the preparation and microwave dielectric properties of $BaCe_2(MoO_4)_4$ ceramics with a $\varepsilon_r \sim$ 12.3, $Q \times f \sim$ 16 000–24 000 GHz, and $\tau_f \sim -37$ ppm/°C.[11] In 2011, the $BaNd_2(MoO_4)_4$ crystal was grown by Han *et al.* and a potential value as a solid-state laser material has been shown.[12] These results attracted our attention to study the microwave dielectric properties of other $BaLn_2(MoO_4)_4$ ceramics. Considering the slightly smaller but close ionic radii of Nd and Sm ions than Ce ion,[13] the $BaLn_2(MoO_4)_4$ (Ln = Nd and Sm) ceramics were chosen in the present work. The phase evolution, microstructure, and microwave dielectric properties (in temperature range 25°C–120°C) were studied.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of $BaCO_3$ (>99%, Shu-Du Powders Co. Ltd., Chengdu, China), Nd_2O_3, Sm_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 $BaLn_2(MoO_4)_4$ (Ln = Nd and Sm) (Nd_2O_3 and Sm_2O_3 were pre-fired at 850°C for 4 h before use). 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. Some of the mixed oxides were then calcined at 600°C, 700°C, 850°C and 950°C for 4 h for phase evolution analysis. Most mixed oxides were calcined at 700°C for 4 h for the further processing (re-milling, molding, sintering, etc.). After being crushed and re-milled 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 5 wt% PVA binder addition under a uniaxial pressure of 200 MPa. Samples were sintered in the temperature range from 920°C to 1000°C for 2 h in the air atmosphere.

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 surface with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). Dielectric behaviors at microwave frequency were measured with the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of

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resonant frequency τ_f (TCF) 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 $TE_{01\delta}$ resonant frequencies at 85°C and 25°C, respectively.

III. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ compositions calcined and sintered at different temperatures. For $BaNd_2(MoO_4)_4$ composition calcined at 600°C for 4 h, a monoclinic $BaNd_2(MoO_4)_4$ phase, a tetragonal $BaMoO_4$ phase and other unknown phases marked with "x" were observed from the XRD patterns. The "x" phases might be Nd_2O_3–MoO_3 compounds and cannot be identified from the PDF data base. When calcinations temperature reached 850°C, only pure monoclinic $BaNd_2(MoO_4)_4$ phase was observed and all the peaks

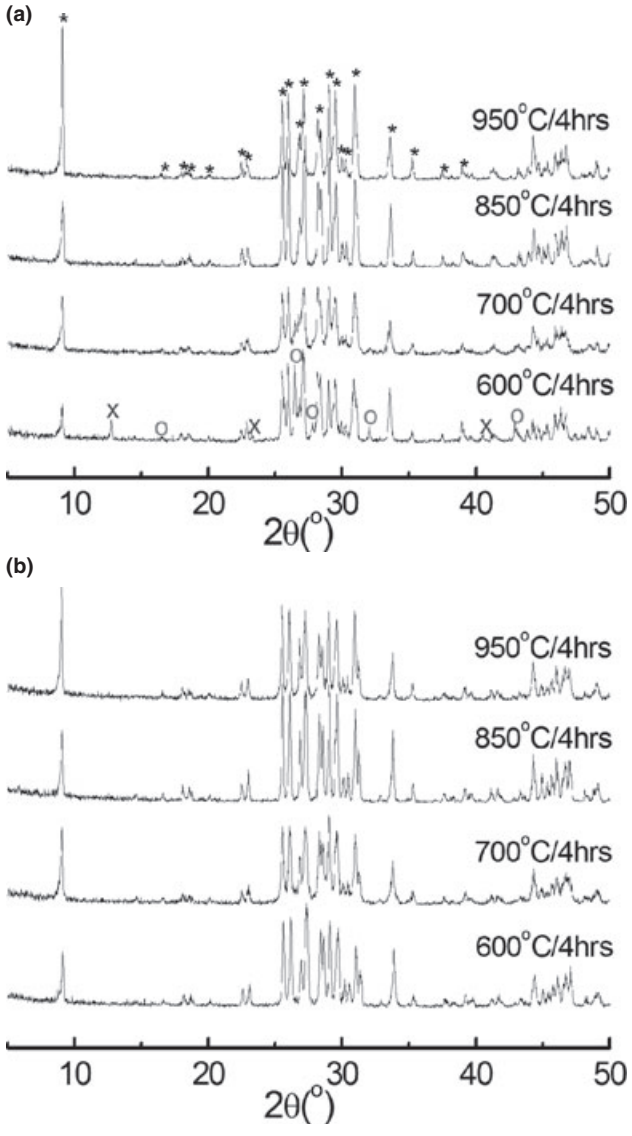

Fig. 1. X-ray diffraction patterns of the $BaNd_2(MoO_4)_4$ (a) and $BaSm_2(MoO_4)_4$ (b) ceramics calcined and sintered at different temperatures (*–$BaNd_2(MoO_4)_4$ phase, PDF: 84-0145; o-$BaMoO_4$ phase; x-unidentified phase)

can be indexed in accordance with the standard JCPDS Card File 84-0145,[14] which is similar to work of Han *et al.*[12] For $BaSm_2(MoO_4)_4$ composition, the pure monoclinic phase can be formed at a low calcination temperature 600°C, which is much lower than 850°C for $BaNd_2(MoO_4)_4$ composition. Although detailed crystal structure analysis of $BaSm_2(MoO_4)_4$ composition has not been reported so far, all the peaks can also be indexed as a monoclinic structure similar to $BaNd_2(MoO_4)_4$.

SEM micrographs of as-fired surfaces of $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ ceramics sintered at 960°C for 2 h are shown in Fig. 2. For $BaNd_2(MoO_4)_4$ ceramic sintered at 920°C for 2 h, a porous microstructure was revealed and the average grain size is below 3 μm as shown in Fig. 2(a), which indicates that the $BaNd_2(MoO_4)_4$ ceramic was not well densified at 920°C. When sintering temperature increased to 960°C, dense and homogeneous microstructures with almost no pores was revealed in $BaNd_2(MoO_4)_4$ ceramic sintered at 960°C for 2 h, which means that $BaNd_2(MoO_4)_4$ ceramic can be well densified at 960°C. The flake-like grains, which look like bar shape from the side, are observed from the SEM photos and grain sizes lie between 2 and 8 μm. With the further increase of sintering temperature to 980°C, the grain size of $BaNd_2(MoO_4)_4$ ceramic increased to above 10 μm along with a secondary growth of grains as shown in Fig. 2(c). Similar to the result for $BaNd_2(MoO_4)_4$ ceramic, dense and homogeneous microstructures of $BaSm_2(MoO_4)_4$ sample can also be obtained in ceramic sintered at 960°C for 2 h as shown in Fig. 2(d).

Microwave dielectric relative permittivity and $Q \times f$ values of $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ ceramics as a function of sintering temperature are shown in Fig. 3. The pore's permittivity at microwave region is about 1 and it affects the microwave dielectric permittivity seriously.[15,16] As the sintering temperature increases along with the elimination of pores, which is consistent with the SEM results above, the microwave dielectric permittivity increases first and then reaches a saturated value about 11.7 for both $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ ceramics sintered at 960°C for 2 h. Usually, the microwave dielectric permittivity decreases slightly with the further increase of sintering temperature after the saturated value was obtained, due to the secondary growth of grains or the volatilization of some elements. According to Shannon's study on the ion polarization,[17] the Nd^{3+} and Sm^{3+} have similar polarization about 5.01 $Å^3$ and 4.74 $Å^3$, respectively, which are both smaller than that of Ce^{3+} with a value 6.15 $Å^3$. This can account for the close microwave dielectric permittivities of $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ ceramics and the difference from that of $BaCe_2(MoO_4)_4$ ceramic. Microwave dielectric loss is influenced by complex factors, such as grain size, grain shape, grain size distribution, grain boundaries, etc. Usually, it is believed that the pores in ceramic sintered at low temperature and the secondary grain growth in ceramic sintered at high temperature deteriorate the $Q \times f$ seriously.[15,16] Nevertheless, the relative high $Q \times f$ values for both $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ ceramics could be maintained in a relative wide sintering temperature range in this work.

The microwave dielectric permittivity and $Q \times f$ value of $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ ceramics sintered at 960°C for 2 h in the temperature range from 25°C to 120°C are shown in Fig. 4 to further understand the wide temperature range dependence of the microwave dielectric behaviors. It is seen that as temperature increases from 25°C to 120°C, the microwave dielectric permittivity of $BaNd_2(MoO_4)_4$ ceramic linearly increases from 11.7 to 11.8 and the $Q \times f$ value fluctuates in the range 35 900–46 000 GHz (at about 9.8 GHz). The temperature coefficient of resonant frequency is about −41 ppm/°C. There is no abnormal phenomenon in the dielectric permittivity spectra, but the $Q \times f$ value has a peak value at about 28°C. For $BaSm_2(MoO_4)_4$ ceramic, its

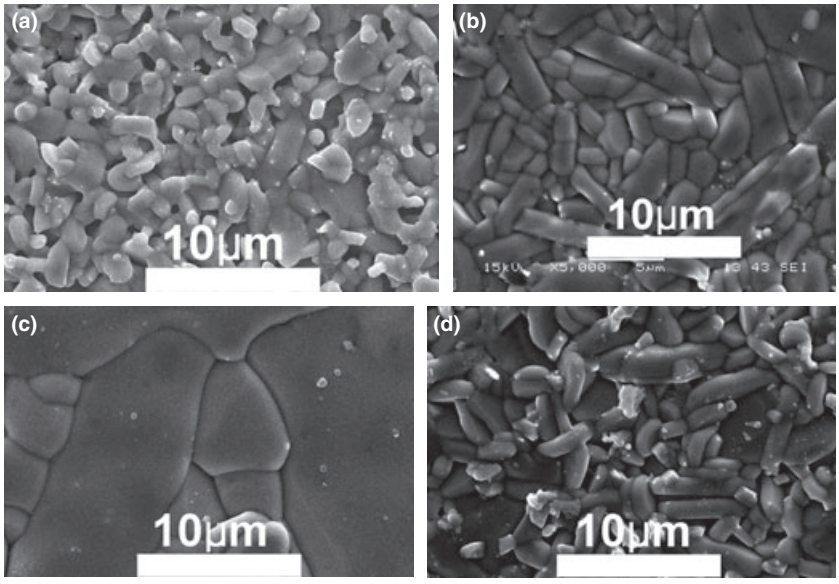

Fig. 2. SEM photos of $BaNd_2(MoO_4)_4$ ceramics sintered at 920°C/2 h (a), 960°C/2 h (b), 980°C/2 h (c), and $BaSm_2(MoO_4)_4$ (d) ceramic sintered at 960°C/2 h

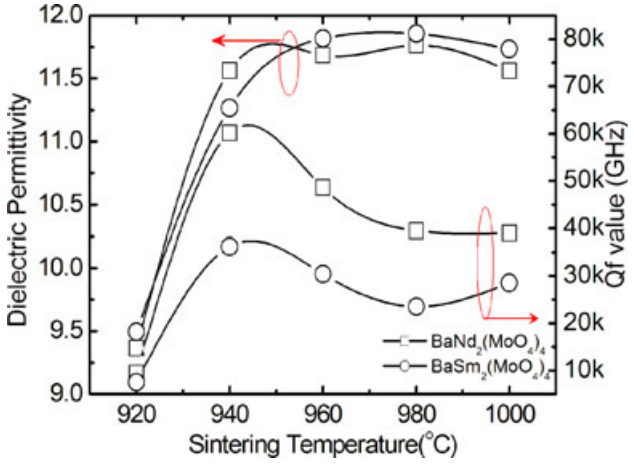

Fig. 3. Microwave dielectric permittivity and $Q \times f$ values of $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ ceramic as a function of sintering temperature

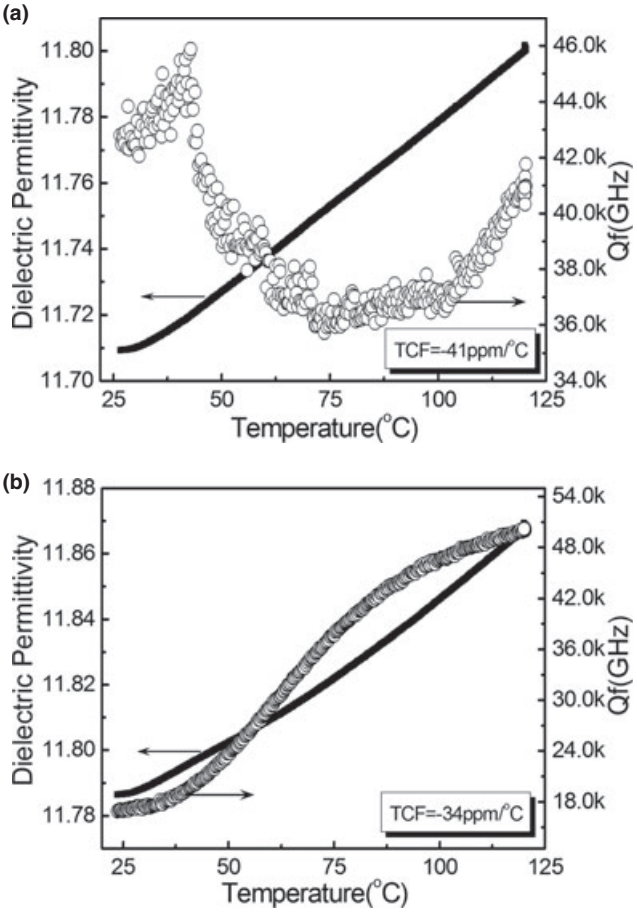

Fig. 4. Microwave dielectric permittivity and $Q \times f$ values of $BaNd_2(MoO_4)_4$ (a) and $BaSm_2(MoO_4)_4$ (b) ceramic as a function of temperature

microwave dielectric permittivity linearly increases from 11.79 to 11.87, which is similar to that of $BaNd_2(MoO_4)_4$ ceramic. Its $Q \times f$ value also increases with the temperature from about 20 000 GHz at room temperature to about 50 000 GHz at 120°C. Its temperature coefficient of resonant frequency is about −34 ppm/°C, which is slightly smaller than that of $BaNd_2(MoO_4)_4$ ceramic.

IV. Conclusion

The single phase of $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ can be formed at about 850°C and 600°C via the solid-state reaction method, respectively. Both the ceramic samples can be well densified at 960°C for 2 h with grain size distribution between 2 and 8 μm. The best microwave dielectric properties with a permittivity of 11.7 and 11.8, a $Q \times f$ value of 45 000 GHz and 20 000 GHz, a temperature coefficient of frequency about −41 ppm/°C and −34 ppm/°C were obtained in $BaNd_2(MoO_4)_4$ and $BaSm_2(MoO_4)_4$ ceramics sintered 960°C for 2 h, respectively. They might be candidates for microwave devices application.

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]I. M. Reaney and D. Iddles, "Microwave Dielectric Ceramics for Resonators and Filters in Mobile Phone Networks," *J. Am. Ceram. Soc.*, **89** [7] 2063–72 (2006).

[3]R. I. Scott, M. Thomas, and C. Hampson, "Development of Low Cost, High Performance $Ba(Zn_{1/3}Nb_{2/3})O_3$ Based Materials for Microwave Resonator Applications," *J. Eur. Ceram. Soc.*, **23** [14] 2467–71 (2003).

[4]B. Jancar, D. Suvorov, M. Valant, and amd G. Drazic, "Characterization of $CaTiO_3$-$NdAlO_3$ Dielectric Ceramics," *J. Eur. Ceram. Soc.*, **23** [9] 1391–400 (2003).

[5]N. M. Alford and S. J. Penn, "Sintered Alumina with Low Dielectric Loss," *J. App. Phys.*, **80** [10] 5895–8 (1996).

[6]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** [8] 3063–67 (2007).

[7]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**, 2011–15 (2006).

[8]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** [10] 2242–46 (2009).

[9]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** [10] 3419–22 (2008).

[10]L. X. Pang, G. B. Sun, and D. Zhou, "$Ln_2Mo_3O_{12}$ (Ln=La, Nd): A Novel Group of Low Loss Microwave Dielectric Ceramics with Low Sintering Temperature," *Mater. Lett.*, **65** [2] 164–6 (2011).

[11]N. K. James and R. Ratheesh, "Microwave Dielectric Properties of Low-Temperature Sinterable $BaCe_2(MoO_4)_4$ Ceramics," *J. Am. Ceram. Soc.*, **93** [4] 931–3 (2010).

[12]S. J. Han, J. Y. Wang, J. Li, Y. J. Guo, Y. Z. Wang, and L. L. Zhao, "Growth, Thermal and Spectroscopic Characterizations of $BaNd_2(MoO_4)_4$ Crystal," *J. Lumi.*, **13** [2] 244–6 (2011).

[13]R. D. Shannon, "Revised Effective Ionic-radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Crystallogr. B*, **32**, 751–67 (1976).

[14]I. I. Kiseleva, M. I. Sirota, R. P. Ozerov, T. P. Balakireva, and A. A. Mayer, "Double Molybdates of Barium-Lanthanides $BaLn_2(MoO_4)_4$. 2. Crystal-Structure of $BaNd_2(MoO_4)_4$," *Kristallografiya*, **24** [6] 1277–1279 (1979).

[15]S. J. Penn, N. M. Alford, A. Templeton, X. R. Wang, M. S. 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).

[16]D. Zhou D, L. X. Pang, X. Yao X, and H. Wang, "Influence of Sintering Process on the Microwave Dielectric Properties of $Bi(V_{0.008}Nb_{0.992})O_4$ Ceramics," *Mater. Chem. Phys.*, **115** [1] 126–31 (2009).

[17]R. D. Shannon, "Dielectric Polarizabilites of Ions in Oxides and Fluorides," *J. Appl. Phys.*, **73** [1] 348–66 (1993). □