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Ultra-low temperature sintering and microwave dielectric properties of a novel temperature stable $Na_2Mo_2O_7$-$Na_{0.5}Bi_{0.5}MoO_4$ ceramic

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Abstract

The novel ultra-low temperature sintering (1-x)$Na_2Mo_2O_7$-x$Na_{0.5}Bi_{0.5}MoO_4$ ceramics have been obtained via solid-state reaction method for passive integration use. The $Na_2Mo_2O_7$ and $Na_{0.5}Bi_{0.5}MoO_4$ crystal phases are found to be compatible with each other from the results of XRD and SEM-EDS. With the x value changing from 0.36 to 1.00, the ε_r increases from 16.0 to 32.0 and the τ_f value varies from -58 to 47 ppm/°C. At x = 0.75, the 0.25$Na_2Mo_2O_7$-0.75$Na_{0.5}Bi_{0.5}MoO_4$ ceramic sintered at an ultra-low sintering temperature of 580 °C can be densified (>96%) and possesses good microwave dielectric properties of an ε_r of 24.0, a Q×f value of 13,000 GHz (at 6.2 GHz), and a τ_f value of 3 ppm/°C. The theoretical ε_r and τ_f of the (1-x)$Na_2Mo_2O_7$-x$Na_{0.5}Bi_{0.5}MoO_4$ composites were calculated using the mixing law and in accordance with the measured values.

***Keywords*：** Ceramics; Dielectrics; Microwave dielectric properties; Temperature stable material; Ultra-low temperature sintering.

1. Introduction

In recent years, with the development of wearable wireless communication, it requires that microwave dielectric ceramics have a suitable permittivity, low loss, a near zero temperature coefficient of the resonant frequency (τ_f) and an ultra-low sintering temperature to co-fire with semiconductor, polymer and electrode materials, such as the Al paste (550 °C) or the nano particle silver ink [1-4]. However, most of the ultra-low firing microwave ceramics have the negative temperature coefficient of the resonant frequency. Many kinds of ultra-low temperature co-fired ceramic (ULTCC) materials (about 100) have been reported in the literature [4]. However, among the materials with sintering temperatures below 600 °C, there are only two ceramics with temperature stability, namely $BaTe_4O_9$-40wt%$TiTe_3O_8$ (ε_r = 25.0, Q×f = 19,300 GHz, τ_f = -3 ppm/°C) and 0.47$BaTe_4O_9$-0.53$TiTe_3O_8$ (ε_r = 28, Q×f = 12,000 GHz, τ_f = 4 ppm/°C) [5,6]. However, tellurium oxide is highly toxic. Therefore, the temperature-stable ultra-low firing ceramics especially sintered below 600 °C still need to be studied.

The previous study demonstrates that the ceramics in A_2O-MoO_3 (A = Na, K, Ag) systems have ultra-low sintering temperatures of 460-660 °C and good microwave dielectric properties (ε_r = 4.1-14.0, Q×f = 8,500-62,400 GHz and τ_f = -142~-57 ppm/°C) [7,8]. Among them, the $Na_2Mo_2O_7$ ceramic sintered at 575 °C has the best Q×f value of 62,400 GHz, an ε_r of 12.9 and a τ_f of -72 ppm/°C [8]. Among the microwave dielectric materials with ultra-low sintering temperatures and positive τ_f values, the $Na_{0.5}Bi_{0.5}MoO_4$ ceramic sintered at 690 °C has a high Q×f value of 12,300 GHz, an ε_r of 34.4 and a τ_f of 43 ppm/°C [9]. However, their τ_f values limit the application in ULTCC technology. In this work, $Na_2Mo_2O_7$ was combined with $Na_{0.5}Bi_{0.5}MoO_4$ to tune the τ_f value to zero. The new temperature stable ceramic with a sintering temperature below 600°C was obtained. The phase composition, microstructures, densities and microwave dielectric properties of the (1-x)$Na_2Mo_2O_7$-x$Na_{0.5}Bi_{0.5}MoO_4$ ceramics were all investigated in detail.

2. Experimental procedures

Solid state reaction method was used to synthesize the (1-x)$Na_2Mo_2O_7$-x$Na_{0.5}Bi_{0.5}MoO_4$ (0.00 mol ≤ x ≤ 1.00 mol) composite ceramics. The mixtures of the raw materials of high-purity Na_2CO_3 (99.8%), Bi_2O_3 (99.0%) and MoO_3 (99.5%) were ball-milled for 4 h in alcohol medium. The dried powders were calcined at 480-550 °C for 8 h with a heating rate of 3°C/min. After re-milling for 5 h and drying, the powders with polyvinyl alcohol (PVA) as a binder were pressed into pellets 12 mm in diameter and 5 mm in height under pressure of 300 MPa. The pellets were treated at 550°C for 5 h with a heating rate of 1°C/min to eliminate the PVA binder. Then the samples were sintered at 570-600 °C for 4 h with a heating rate of 3°C/min. The way of natural cooling was used in all the heat-treatment schedules.

The crystalline phases were identified by powder X-ray diffraction (Rigaku D/MAX-2400 X-ray diffractometer, Japan) with Cu-Ka radiation. A scanning electron microscope (FEI QUANTA FEG 250, USA) and energy dispersive spectrometer were used to observe the surface microstructures. Archimedes method was adopted to measure the bulk density of sintered samples. The network analyzer (8720ES, Agilent, CA) and temperature chamber (Delta 9023, CA) were used to measure the microwave dielectric properties by the $TE_{01\delta}$ shielded cavity method. The resonant frequencies (f_T) were measured in the range of 25-85 °C. Then the τ_f was calculated according to $(f_{85}-f_{25})/(f_{25}\times60)$.

3. Results and discussion

The (1-x)$Na_2Mo_2O_7$-x$Na_{0.5}Bi_{0.5}MoO_4$ is called NMNB for short. Fig. 1 shows the X-ray diffraction patterns for the sintered NMNB ceramics. The pure $Na_{0.5}Bi_{0.5}MoO_4$ (PDF card 79-2240, I41/a) and $Na_2Mo_2O_7$ (PDF card 73-1797, Cmca) were obtained at the sintering temperature of 560 °C and 575 °C, respectively. A two-phase system with tetragonal $Na_{0.5}Bi_{0.5}MoO_4$ (marked as "o") and orthorhombic $Na_2Mo_2O_7$ (marked as "*") can be seen in NMNB. With the increasing of x value, the intensities of $Na_2Mo_2O_7$ peaks weaken and the intensities of $Na_{0.5}Bi_{0.5}MoO_4$ peaks get enhanced. Therefore, it can be concluded that $Na_2Mo_2O_7$ coexists well with $Na_{0.5}Bi_{0.5}MoO_4$.

Fig. 2 shows the backscattered electron micrographs, scanning electron micrographs, and EDS analysis of the surfaces of the NMNB ceramics sintered at 580 °C/4 h. It can be seen that two types of grains coexist, which agrees with the XRD result. They have different shapes. The analysis of EDS shows that grains (marked as "2") with a smaller size of 1 μm belong to the $Na_{0.5}Bi_{0.5}MoO_4$ phase and grains (marked as "1") with a larger size of 2-6 μm belong to the $Na_2Mo_2O_7$ phase. As the x value increases, the number of $Na_{0.5}Bi_{0.5}MoO_4$ grain increases and the number of $Na_2Mo_2O_7$ grain decreases. All the NMNB ceramics show a dense microstructure.

Fig. 3 presents the densities and the relative densities of the NMNB ceramics sintered at 580 °C/4 h. The density of the composite ceramics can be calculated as follows:

$$\rho_{theo} = v_1\rho_1 + v_2\rho_2 \tag{1}$$

Where ρ_{theo} is the theoretical density of the composite. The subscripts of "1" and "2" indicate the material 1 and material 2, respectively. ρ_1 and ρ_2 represent the theoretical densities. v_1 and v_2 are the respective volume fractions. Here the theoretical densities of $Na_{0.5}Bi_{0.5}MoO_4$ and $Na_2Mo_2O_7$ are 5.694 g/cm^3 and 3.724 g/cm^3 according to PDF card 79-2240 and 73-1797, respectively. With the x value increasing, the densities of NMNB ceramics rise from 3.59 g/cm^3 to 5.52 g/cm^3 and all the relative densities are above 96%, demonstrating that the NMNB ceramic can be easily densified at 580 °C.

Fig. 4 shows the microwave dielectric properties of the NMNB ceramics sintered at 580 °C/4 h as a function of the x values. The two materials distribute randomly in the NMNB composite ceramics, so the dielectric constants of composite ceramics are predicted by Lichtenecker logarithmic rule [10]. The semi-empirical linear model is used to calculate the theoretical τ_f values of the mixture [10].

$$\ln\varepsilon = v_1\ln\varepsilon_1 + v_2\ln\varepsilon_2 \tag{2}$$

$$\tau_f = v_1\tau_{f1} + v_2\tau_{f2} \tag{3}$$

Where the subscripts of "1" and "2" indicate the material 1 and material 2, respectively. v_1 and v_2 represent the volume fractions. The permittivity gradually becomes bigger with the x value increasing, and the measured dielectric constants (16.0-28.5) are slightly larger than the calculated values (15.9-26.0). The interfacial effect in the composite ceramics may increases the permittivity. With the x value changing from 0.36 to 1.00, the τ_f value varies from -58 ppm/°C to 47 ppm/°C. The measured τ_f values are consistent with the calculated τ_f. It indicates that the logarithmic rule and semi-empirical linear model are useful methods to predict the effective permittivity and τ_f of a composite mixture. The Q×f values are in the range of 13,000-20,000 GHz with the x value of 0.36-1.00. The Q×f values of NMNB ceramics are dominated by the Q×f value of $Na_{0.5}Bi_{0.5}MoO_4$ ceramic (~14,000 GHz). The resonant frequencies of NMNB ceramics decrease with the x value increasing. The temperature stable $0.25Na_2Mo_2O_7$-$0.75Na_{0.5}Bi_{0.5}MoO_4$ ceramic can be densified at 580 °C for 4 h (>96%), meanwhile it has good microwave dielectric properties of an ε_r of 24.0, a τ_f value of 3 ppm/°C and a Q×f value of 13,000 GHz.

A variety of ULTCC materials have been developed. Table 1 show the microwave dielectric properties of some typical ceramics with sintering temperature <600 °C. Some ceramics materials, such as $NaAgMoO_4$, Ag_2MoO_4 and $K_2Mo_2O_7$, have ultra-low sintering temperature <500 °C, but their τ_f values limit their application. At present, there are only two kinds of microwave dielectric ceramics reported with ultra-low sintering temperatures of <600 °C and good temperature stability, namely $BaTe_4O_9$+40wt%$TiTe_3O_8$ and $0.47BaTe_4O_9$-$0.53TiTe_3O_8$, but the tellurium oxide is toxic. Compared with the reported ULTCC materails, the Q×f value of $0.25Na_2Mo_2O_7$-$0.75Na_{0.5}Bi_{0.5}MoO_4$ is not the highest. However, synthetically considering the temperature stability, ultra-low sintering temperature and environmental protection, the $0.25Na_2Mo_2O_7$-$0.75Na_{0.5}Bi_{0.5}MoO_4$ ceramic is very promising for microwave device application, especially ULTCC technology.

4. Conclusions

A novel series of (1-x)$Na_2Mo_2O_7$-x$Na_{0.5}Bi_{0.5}MoO_4$ microwave dielectric ceramics were prepared by solid-state reaction method. The XRD and EDS analysis demonstrated that $Na_2Mo_2O_7$ did not react with $Na_{0.5}Bi_{0.5}MoO_4$. The temperature stable 0.25$Na_2Mo_2O_7$-0.75$Na_{0.5}Bi_{0.5}MoO_4$ ceramic sintered at 580 °C has been obtained with a relative density of 96% and good microwave properties of ε_r = 24.0, Q×f = 13,000 GHz (at 6.2 GHz), τ_f = 3 ppm/°C. Comprehensive considering the ultra-low sintering temperature of 580 °C, temperature stability, low dielectric loss and environmental protection, the 0.25$Na_2Mo_2O_7$-0.75$Na_{0.5}Bi_{0.5}MoO_4$ ceramic is one of the best materials for ULTCC technology at present.

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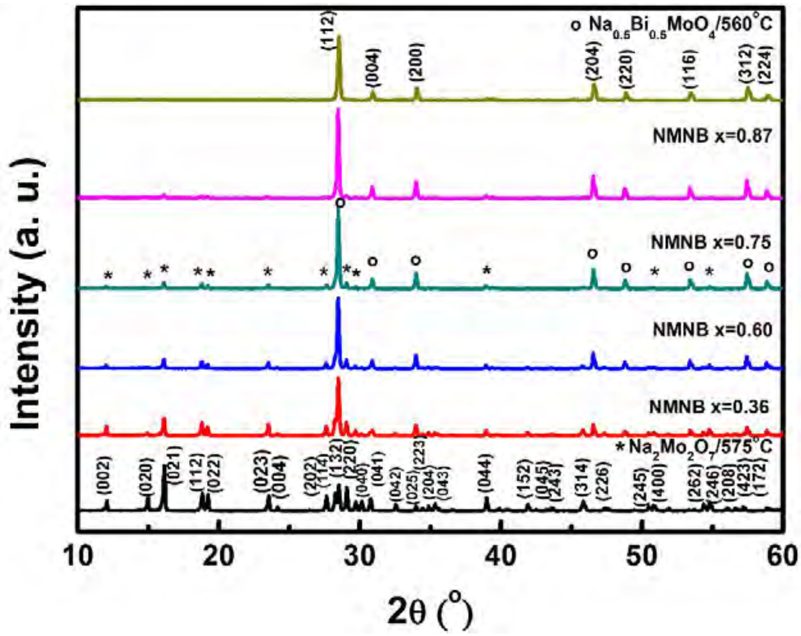

Fig. 1. XRD patterns of the sintered (1-x)$Na_2Mo_2O_7$-x$Na_{0.5}Bi_{0.5}MoO_4$ ceramics.

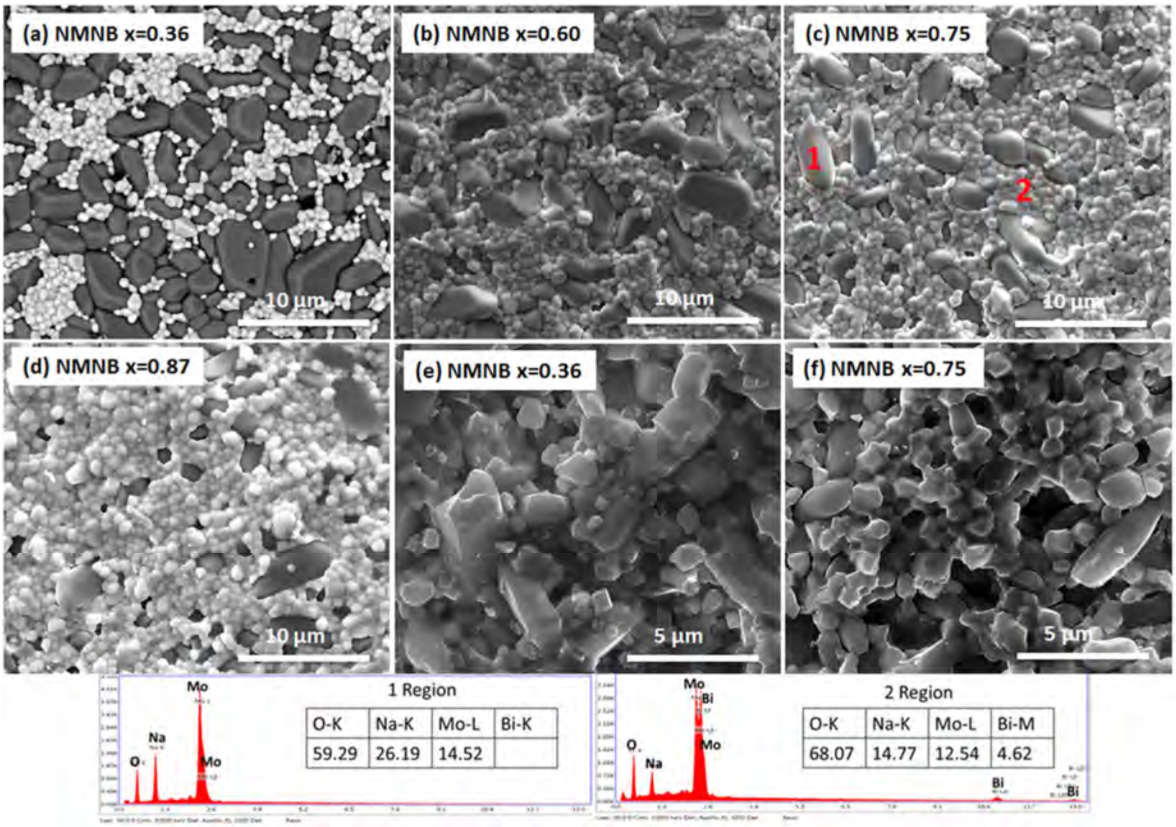

Fig. 2. (a) Backscattered electron micrographs, (b-f) scanning electron micrographs and EDS analysis of the (a-d) as-sintered surfaces and (e-f) polished surfaces of NMNB ceramics sintered at 580 °C/4 h.

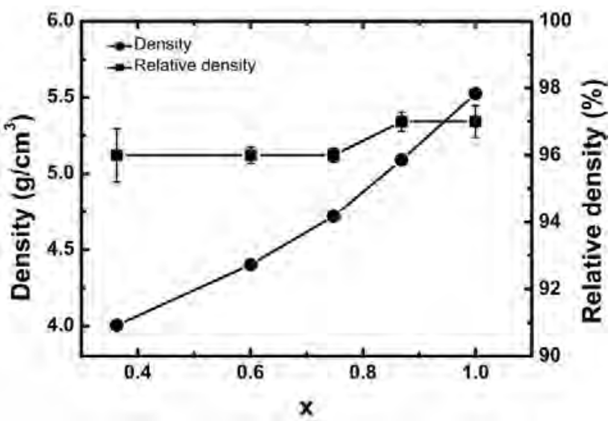

Fig. 3. Densities and relative densities of the NMNB ceramics sintered at 580 °C/4 h.

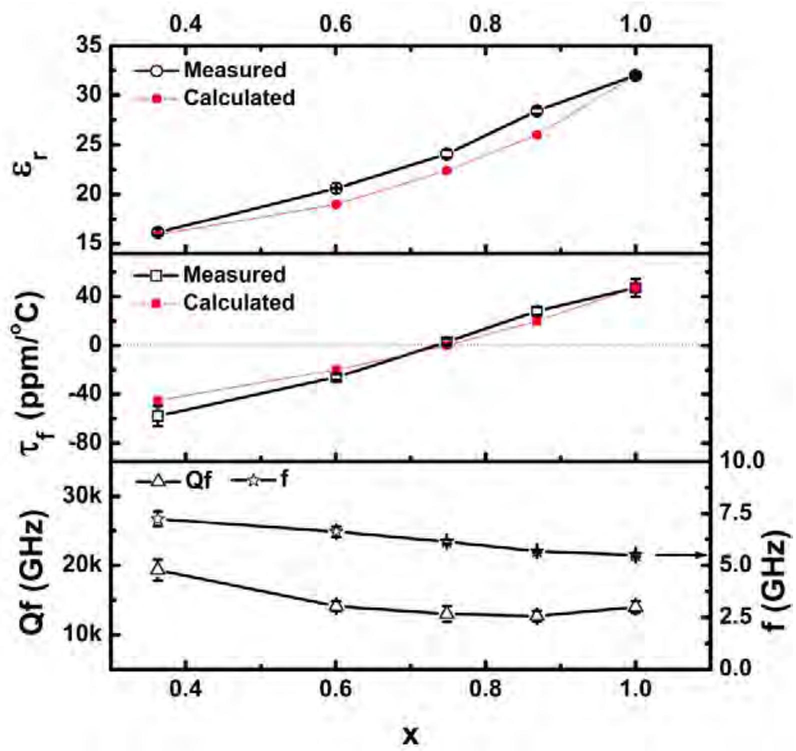

Fig. 4. Microwave dielectric properties of (1-x)$Na_2Mo_2O_7$-x$Na_{0.5}Bi_{0.5}MoO_4$ ceramics sintered at 580 °C/4 h as a function of the x values.

Table 1

Microwave dielectric properties of some typical ceramics with sintering temperature (S.T.) below 600 °C.

Composition	S.T. (°C)	f_r (GHz)	ε_r	Q×f (GHz)	τ_f (ppm/°C)	Ref.
$NaAgMoO_4$	400	—	7.9	33000	-120	[11]
Ag_2MoO_4	450	—	8.1	17000	-133	[12]
$K_2Mo_2O_7$	460	10.0	7.5	22300	-63	[7]
$BaTe_4O_9$+40wt%$TiTe_3O_8$	575	—	25.0	19300	-3	[5]
0.47$BaTe_4O_9$-0.53$TiTe_3O_8$	560	—	28.0	12000	4	[6]
0.25$Na_2Mo_2O_7$-0.75$Na_{0.5}Bi_{0.5}MoO_4$	580	6.2±0.1	24.0±0.4	13000±1000	3±2	This work