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A Novel Temperature Stable Microwave Dielectric Ceramic with Garnet Structure: $Sr_2NaMg_2V_3O_{12}$

Huaicheng Xiang,[‡] Liang Fang,[‡,†] Xuewen Jiang,[‡] Ying Tang,[‡] and Chunchun Li[‡,§,†]

[‡]State Key Laboratory Breeding Base of Nonferrous metals and specific Materials Processing, Guangxi universities key laboratory of non-ferrous metal oxide electronic functional materials and devices, College of Material Science and Engineering, Guilin University of Technology, Guilin 541004, China

[§]College of Information Science and Engineering, Guilin University of Technology, Guilin 541004, China

A garnet vanadate ceramic $Sr_2NaMg_2V_3O_{12}$ was prepared by the conventional solid-state route, and the sinterability, microwave dielectric properties, and its chemical compatibility with Ag electrodes were investigated. $Sr_2NaMg_2V_3O_{12}$ sample could be well sintered at 900°C for 4 h with a relative density of 96.1%. X-ray diffraction data showed that $Sr_2NaMg_2V_3O_{12}$ ceramics crystallized into a cubic garnet structure with a space group *Ia-3d* over the sintering temperature range (830°C–930°C). The $Sr_2NaMg_2V_3O_{12}$ ceramic sintered at 900°C obtained the optimum microwave dielectric properties with a relative permittivity of 11.7, a $Q\times f$ of 37 950 GHz (at 11.0 GHz), and a almost zero τ_f value of −2.9 ppm/°C. Chemical compatibility experiments showed no reaction between $Sr_2NaMg_2V_3O_{12}$ ceramics and Ag electrodes.

I. Introduction

Compounds with the nominal composition $A_3B_2C_3O_{12}$ are known as garnets.[1–5] In the garnet structure, three different sites (A, B, and C) are available for a wide variety of cations.[4] As illustrated in Fig. 1, C ions are surrounded by four oxygens to form CO_4 tetrahedron; B ions are located in octahedral. The tetrahedra and octahedral are corner shared, forming dodecahedra where A ions are located. Garnet compounds usually crystallize in the cubic system with a space group of *Ia-3d*. Despite $A_3B_2C_3O_{12}$, garnet-type compounds have been extensively investigated as promising materials in the field of phosphors, lasers, and ferrite materials,[6–8] there are few reports on the microwave dielectric properties of these compounds.

Kim et al.[9] firstly reported the microwave dielectric properties of some $Re_3Ga_5O_{12}$ [(Re=Nd, Sm, Eu, Dy, Yb, and Y) garnets with high quality factors (40 000–192 173 GHz), low relative permittivities (11.5–12.5), and relatively stable temperature coefficients of resonant frequency (−33.7 to −12.4 ppm/°C). However, their sintering temperatures are too high (1350°C–1500°C). In our previous work, some garnet vanadates were reported to have combined low sintering temperatures and good microwave dielectric properties, which make them potential candidates in low-temperature co-fired ceramics (LTCC) technology.[10–12] For example, $LiCa_3MgV_3O_{12}$ ceramic sintered at 900°C has a relative permittivity (ε_r) ~ 10.5, a quality factor ($Q\times f$) ~ 74 700 GHz, and a temperature coefficient of resonant frequency (τ_f) ~ −61 ppm/°C][10] and $NaCa_2Mg_2V_3O_{12}$ ceramic has a ε_r = 10, $Q\times f$ = 50 600 GHz, and τ_f = −47 ppm/°C when sintered at 915°C.[11] Meanwhile, the microwave dielectric properties of some cation-deficient garnets in the $Ca_5A_4(VO_4)_6$ (A=Mg, Zn, and Co)[13,14] system were characterized. Researches have shown that these garnet vanadates possessed a combination of low sintering temperatures, relatively high $Q\times f$ values, and low bulk densities, but their large negative τ_f precluded their possible use in practical applications, the search for temperature stable garnets is still going on.

$Sr_2NaMg_2V_3O_{12}$ belongs to the garnet family. Hu et al.[15] firstly reported the synthesis of $Sr_2NaMg_2V_3O_{12}$ through solid-state reaction method in detail. Recently, $Sr_2NaMg_2V_3O_{12}$ has been widely investigated for applications in high-pressure mercury lamp field-emission display and color TV industry[15–18] due to its luminescent properties. To the best knowledge of us, however, the microwave dielectric properties of $Sr_2NaMg_2V_3O_{12}$ ceramics have not been investigated. In the present work, the sintering behavior and microwave dielectric properties of $Sr_2NaMg_2V_3O_{12}$ ceramic were studied. Moreover, the chemical compatibility of $Sr_2NaMg_2V_3O_{12}$ ceramics with Ag electrode was also investigated.

II. Experimental Procedure

$Sr_2NaMg_2V_3O_{12}$ ceramics were synthesized by a conventional solid-state method using high-purity oxide powders of Sr_2CO_3 (99%, Guo-Yao Co. Ltd., Shanghai, China), Na_2CO_3 (99%, Guo-Yao Co. Ltd., Shanghai, China), MgO (99%, Guo-Yao Co. Ltd., Shanghai, China), and NH_4VO_3 (>99%, West Long Chemical Co., Ltd., Guangdong, China). MgO was heated at 900°C for 2 h to remove moisture retains. The stoichiometric mixtures of powders were weighed and ball-milled in alcohol medium for 6 h using zirconia balls, followed by the calcination at 800°C for 4 h. The calcined powders were re-milled for 4 h and after drying, the polyvinyl alcohol (PVA, 10 vol%) was added as binders. Then, the powders were pressed into cylinders with 12 mm in diameter and 7 mm in height under a pressure of 200 MPa. The samples were heated to 550°C for 2 h to remove the organic binder and sintered from 830°C to 930°C for 4 h with a heating rate of 5°C/min.

Phase purity of the specimens were studied using an X-ray diffraction measurement (Cu$K\alpha1$, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland) with Cu$K\alpha$ radiation and a monochromator in the 2θ range of 10°–80°. The apparent densities were measured using the Archimedes method. Microstructures of the samples were observed by scanning electron microscope (FE-SEM, Model S4800; Hitachi, Japan).

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[†]Authors to whom correspondence should be addressed. e-mails: fangliang-gl001@aliyun.com and lichunchun2003@126.com

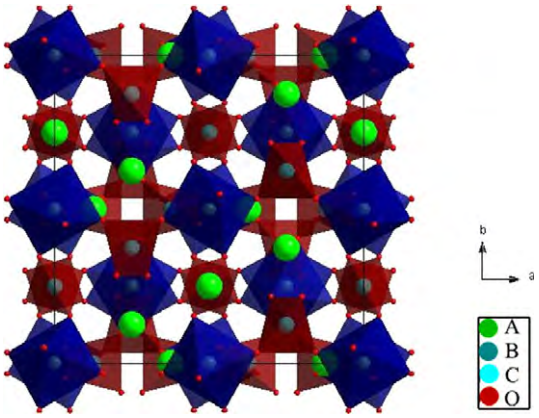

Fig. 1. Crystal structure of $A_3B_2C_3O_{12}$ garnet compound.

The microwave dielectric properties were analyzed using a network analyzer (Model N5230A, Agilent Co., Palo Alto, California) and a temperature chamber (Delta 9039, Delta Design, San Diego, California). The temperature coefficient of resonant frequency (τ_f) was obtained by noting the temperature variations of the TE_{011} resonance scope from 25°C to 85°C. The τ_f value was calculated as the following relationship:

$$\tau_f = \frac{f_{85} - f_{25}}{(85-25) \times f_{25}} \quad (1)$$

where, f_{85} and f_{25} were the resonant frequencies of the dielectric resonator at temperature 85°C and 25°C, respectively.

III. Results and Discussions

Figure 2 shows the X-ray diffraction patterns of $Sr_2NaMg_2V_3O_{12}$ ceramics sintered from 830°C to 930°C. All the sintered $Sr_2NaMg_2V_3O_{12}$ ceramics showed cubic garnet structure with space group of *Ia-3d* (230) according to the standard JCPDS card No. 024-1131.

The bulk densities of $Sr_2NaMg_2V_3O_{12}$ ceramics as a function of the sintering temperature are presented in Fig. 3. With increasing sintering temperature from 830°C to 930°C, the bulk density gradually increased, reached a maximum value of 3.73 g/cm^3 (96.1% of the theoretical density ~ 3.88 g/cm^3) at 900°C, and then decreased slightly. SEM image of the 900°C-sintered sample is shown in the insert of Fig. 3. A uniform and dense microstructure with closely packed grains was observed with average grain size about 3–8 μm.

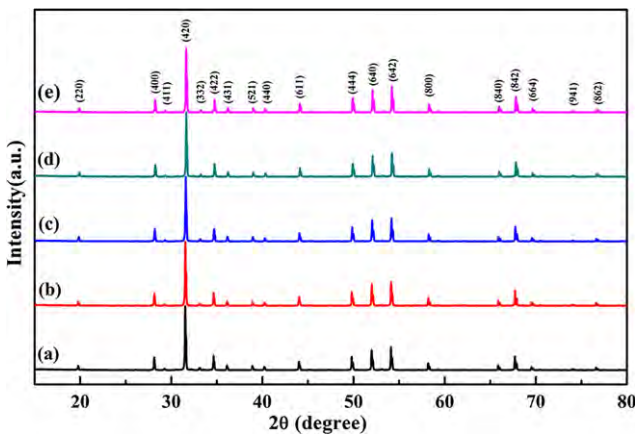

Fig. 2. X-ray diffraction (XRD) patterns of $Sr_2NaMg_2V_3O_{12}$ ceramics sintered at different temperatures: (a) 830°C, (b) 850°C, (c) 880°C, (d) 900°C, and (e) 930°C.

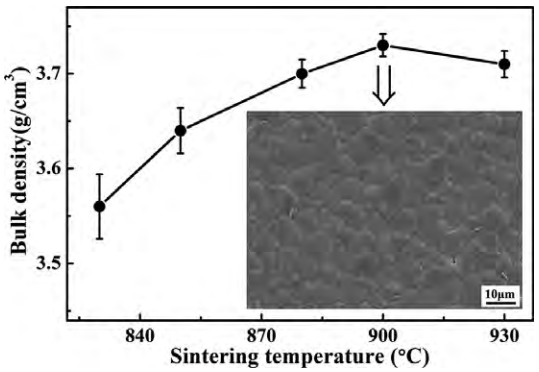

Fig. 3. The bulk densities of the $Sr_2NaMg_2V_3O_{12}$ ceramics as a function of the sintering temperature and the scanning electron microscopy (SEM) image of the fractured surface of ceramic sintered at 900°C.

Figure 4 shows the variation in the relative permittivity (ε_r), quality factor ($Q \times f$), and the temperature coefficient of resonant frequency (τ_f) of $Sr_2NaMg_2V_3O_{12}$ ceramics with sintering temperature. ε_r increased from 11.03 to 11.74 as the sintering temperature increased from 830°C to 900°C, and then slightly decreased thereafter. By comparison, it is observed that the variation in the relative permittivity with sintering temperature is similar to that of the density. The largest ε_r value was obtained at which temperature the highest density was achieved. The influence of the porosity on the microwave permittivity could be eliminated by applying Bosman and Havinga's correction[19] as shown in Eq. (2)

$$\varepsilon_{corrected} = \varepsilon_m(1 + 1.5p) \quad (2)$$

where, $\varepsilon_{corrected}$ and ε_m are the corrected and measured values of permittivity, respectively. p is the fractional porosity. The $\varepsilon_{corrected}$ value is about 12.42 for $Sr_2NaMg_2V_3O_{12}$ ceramic. Furthermore, ε_r can be interpreted by the sum of ionic polarizability of individual ions (α_D^T) and molar volume (V_m) according to Clausius–Mossotti equation[20,21]:

$$\varepsilon_r = \frac{\frac{1+2b\alpha_D^T}{V_m}}{\frac{1-b\alpha_D^T}{V_m}} \quad (3)$$

where, $b = 4\pi/3$. The calculated theoretical permittivity of $Sr_2NaMg_2V_3O_{12}$ is 10.5. The relative error of

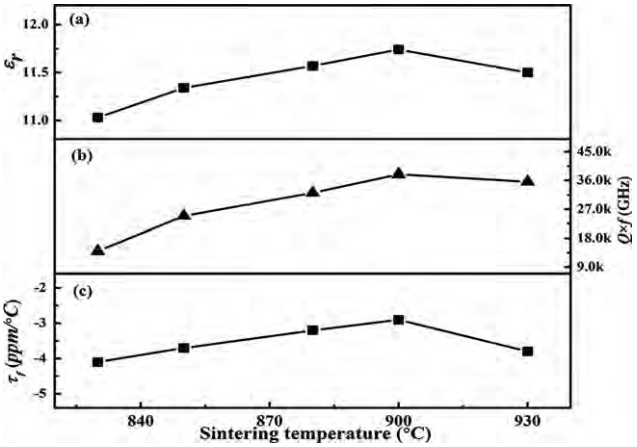

Fig. 4. Variation in the permittivity (ε_r), quality factor ($Q \times f$), and the temperature coefficient of resonant frequency (τ_f) of $Sr_2NaMg_2V_3O_{12}$ ceramics sintered at different temperatures.

Table I. Comparison of Microwave Dielectric Properties of Some Garnet Vanadates Ceramics

Composition	S.T. (°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)	Reference
$LiCa_3MgV_3O_{12}$	900	10.5	74 700	−61	[10]
$NaCa_2Mg_2V_3O_{12}$	915	10	50 600	−47	[11]
$LiMg_4V_3O_{12}$	740	10.7	24 000	−11.7	[12]
$Ca_5Mg_4(VO_4)_6$	800	9.2	53 300	−50	[13]
$Ca_5Zn_4(VO_4)_6$	725	11.7	49 400	−83	[13]
$Ca_5Co_4(VO_4)_6$	875	10.6	95 200	−63	[14]
$Sr_2NaMg_2V_3O_{12}$	900	11.74	37 950	−2.9	This work

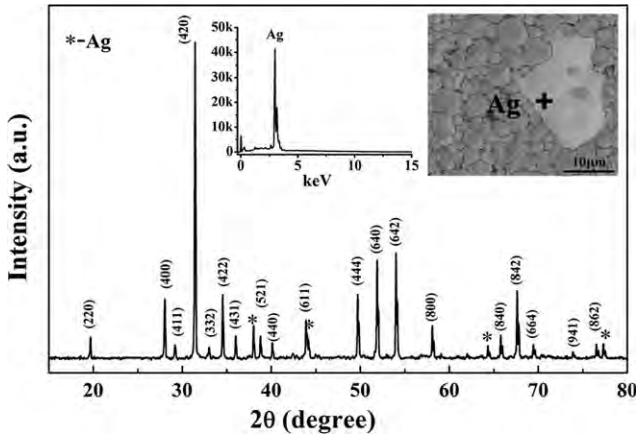

Fig. 5. X-ray diffraction patterns, Backscattered electron image micrograph, and EDS analysis of the $Sr_2NaMg_2V_3O_{12}$ ceramic with 20 wt% silver powder.

$Sr_2NaMg_2V_3O_{12}$ is about 11.8% for the measured value and 18.2% for the porosity corrected value, which implies that there is another polarization mechanism in the $Sr_2NaMg_2V_3O_{12}$ ceramic at microwave region beside ionic and electronic displacement polarization.[22] Similarly, $Q\times f$ value increased firstly with increasing sintering temperature [as shown in Fig. 4(b)]. At 830°C, a relatively low quality factor ~ 14 000 GHz was obtained. After reaching its maximum (~37 950 GHz) at 900°C, the $Q\times f$ slightly declined to 35 640 GHz at 930°C. Figure 4(c) shows the change in τ_f with increasing sintering temperature. As seen, the τ_f values varied in the range from −4.1 to −2.9 ppm/°C over the sintering region from 830°C to 900°C. A near-zero τ_f value of −2.9 ppm/°C was obtained for sample sintered at 900°C.

Compared with the microwave dielectric properties of some garnet vanadates ceramics (as shown in Table I), it is seen that the sintering temperature and the relative permittivity of $Sr_2NaMg_2V_3O_{12}$ ceramic are comparable with other garnet vanadates. The most advantage is the thermal stability of $Sr_2NaMg_2V_3O_{12}$ ceramic with a near-zero τ_f value of −2.9 ppm/°C. The mentioned merits make $Sr_2NaMg_2V_3O_{12}$ a possible candidate in LTCC applications.

To investigate the chemical compatibility of the $Sr_2NaMg_2V_3O_{12}$ ceramic with silver electrodes, 20 wt% Ag was mixed with $Sr_2NaMg_2V_3O_{12}$ ceramic and sintered at 900°C for 4 h. XRD pattern, backscattered electron image, and the EDS analysis of the co-fired $Sr_2NaMg_2V_3O_{12}$ ceramic added with 20 wt% Ag are shown in Fig. 5. From XRD patterns, only the peaks belonging to $Sr_2NaMg_2V_3O_{12}$ and Ag could be observed without secondary phase detected, indicating no reaction between $Sr_2NaMg_2V_3O_{12}$ and Ag. This was further confirmed from the EDS analysis, as shown in the inset of Fig. 5. Two distinct grains could be seen. The larger grains marked as "+" were detected to be Ag.

IV. Conclusions

A novel low-temperature stable microwave dielectric ceramic $Sr_2NaMg_2V_3O_{12}$ with garnet structure was prepared by the conventional solid-state reaction method. The phase purity, packing fraction, and microwave dielectric properties were investigated. Excellent microwave dielectric properties were obtained in $Sr_2NaMg_2V_3O_{12}$ ceramic sintered at 900°C for 4 h, with a permittivity of 11.74, $Q\times f$ value of 37 950 GHz (at 11.0 GHz), and an almost zero τ_f value of −2.9 ppm/°C. Furthermore, the $Sr_2NaMg_2V_3O_{12}$ ceramic showed good chemical compatibility with Ag electrode, which makes it a promising candidate for LTCC technology.

Acknowledgments

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