Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 11125–11131

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Structural evolution, low-firing characteristic and microwave dielectric properties of magnesium and sodium vanadate ceramic

Jianzhang Gong, Huanfu Zhou*, Fen He, Xiuli Chen, Jie Chen, Liang Fang

State Key Laboratory Breeding Base of Nonferrous metals and specific Materials Processing, Key Laboratory of Nonferrous Materials and New Processing Technology, Ministry of Education, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, PR China

Received 8 April 2015; received in revised form 11 May 2015; accepted 11 May 2015
Available online 21 May 2015

Abstract

A low-firing microwave dielectric ceramic with the composition of $NaMg_4V_3O_{12}$ was prepared by a solid state reaction method. $NaMg_4V_3O_{12}$ ceramic could be indexed as a tetragonal phase and the unit cell parameters were calculated as $a=b=6.894$ Å, $c=19.308$ Å. Room temperature X-ray diffraction data shown that the ceramic displayed an obvious peak variations. After sintered at 830 °C for 4 h, the ceramic could be well densified and exhibited good microwave dielectric properties with a relative dielectric constant (ε_r) of 9.53, quality factor ($Q\times f$) of 32,820 GHz (at ~11 GHz), and temperature coefficient of resonator frequency (τ_f) of −90 ppm/°C. With increasing the sintering temperatures, the curve of the relative dielectric constant exhibits a similar trend to that of the relative density. The $Q\times f$ values were related to the average grain size. Due to the decline of the average grain size, the $Q\times f$ values decrease above 830 °C. The variation of τ_f values was attributed to microstructure variations with increasing the sintering temperatures. Moreover, an X-ray photoelectron spectroscopic analysis illustrated that the mass percentages of vanadium element in the sample (sintered at 830 °C) are 96.34% for vanadium (V) and 3.66% for vanadium (IV).

Keywords: C. Dielectric properties; Low-firing vanadate compounds; Ceramics; Microstructure; X-ray diffraction.

1. Introduction

The rapid growth of wireless communication industry has created a great demand for microwave components. Generally, low relative dielectric constant (ε_r) to reduce the signal propagation delay, high quality factor ($Q\times f$) for frequency selectivity and near-zero temperature coefficient of resonator frequency (τ_f) for temperature stability are required for the application of microwave substrates [1–4]. Many ceramics have been reported as potential candidates for millimeter-wave devices, such as $MgSiO_3$ [5], Al_2O_3 [6,7], $ZnAl_2O_4$ [8], $ZnNb_2O_6$ [9], $(1-x)ZnTa_2O_6$–$xMgNb_2O_6$ [10] etc. However, higher sintering temperature restricted the further application of these ceramics in low temperature co-firing ceramics devices [11]. Therefore, more and more studies are focused on researching new material systems with a low-firing temperature and good microwave dielectric properties (low ε_r, high Q and near-zero τ_f), such as AMP_2O_7 (A=Ca, Sr; M=Zn, Cu) [12], $(Li_{0.5}M_{0.5})WO_4$ (M=Nd, Sm) [13,14], $(K_{0.5}Ln_{0.5})MoO_4$ (Ln=Nd and Sm) [15], $BaLn_2(MoO_4)_4$ (Ln=Nd and Sm) [16], $Li_2M_2^{2+}Mo_3O_{12}$ [17], $Li_3M^{3+}Mo_3O_{12}$ [17].

Some low-firing vanadate compounds possessed good microwave dielectric properties [18,19]. Tyutyunnik et al. [20] reported that $LiMg_4V_3O_{12}$ exhibited a tetragonal structure with unit cell parameters of $a=b=6.86707(2)$ Å and $c=18.9545(1)$ Å. In our previous work [21], $LiMg_4V_3O_{12}$ ceramic showed good microwave dielectric properties with $\varepsilon_r=10.7$, $Q\times f=24{,}000$ GHz (at ~10 GHz), and $\tau_f=-11.7$ ppm/°C. Na^+ exhibits an equal electrovalence and similar ionic radius to that of Li^+, however, the dielectric properties at microwave frequency of $NaMg_4V_3O_{12}$ ceramic have never been studied. In this work, $NaMg_4V_3O_{12}$ ceramic was fabricated by a traditional solid-state reaction method. Furthermore, the phase evolution, sintering characteristic and microwave dielectric properties of ceramic were investigated.

*Corresponding author. Tel.: +86 7735896436.
E-mail address: zhouhuanfu@163.com (H. Zhou).

http://dx.doi.org/10.1016/j.ceramint.2015.05.060
0272-8842/

2. Experimental

$NaMg_4V_3O_{12}$ ceramic was prepared by the solid state reaction method from high-purity raw materials ($\geq 99\%$, Guo-Yao Co. Ltd., Shanghai, China) of Na_2CO_3, MgO and NH_4VO_3. Stoichiometric proportion of the above raw materials was mixed in alcohol medium using zirconia balls for 4 h and then calcined at 680 °C for 4 h. Subsequently, the mixture was milled in the same way as the raw powders. After drying, the powders were mixed with 5 wt % polyvinyl alcohol (PVA) and pressed into the cylinders with 12 mm in diameter and 6–7 mm in height by uniaxial pressing under a pressure of 200 MPa. Finally, the samples were sintered at 770–870 °C for 4 h in air at a heating rate of 5 °C/min and then cooled in a furnace to room temperature.

The crystal structures of the samples were measured by an X-ray diffractometer (XRD) ($CuK_{\alpha 1}$, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland) operated at 40 kV and 40 mA. The microstructural observation of the samples was performed using a scanning electron microscopy (SEM) (Model JSM6380-LV SEM, JEOL, Tokyo, Japan), which took along energy dispersive spectrometer (EDS) for elementary analysis at the same time. Thermo gravimetric analysis (TG) of green compact powder was carried out by a Netzsch STA-449C analyzer. The sample powders were heated at a rate of 10 °C/min in protected nitrogen gas flow using an alumina crucibles from 700 °C to 870 °C. The apparent densities of the sintered samples were measured by the Archimedes method. The relative dielectric constant (ε_r) and quality factor (Q) of specimens at microwave frequency were measured in the range of 10–11 GHz by the $TE_{01\delta}$ mode dielectric resonator technique [22] using a vector network analyzer (Model N5230A, Agilent Co., CA, 10 MHz to 40 GHz) in the S_{21} transmission mode. A semi closed copper cavity with 100 mm in diameter and 120 mm in height was employed in the measurement. The temperature coefficients of resonant frequency (τ_f) were measured by the open cavity method using an invar cavity in a temperature chamber (DELTA9039, Delta Design, USA) at 25–85 °C, and calculated by the formula as follows:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \quad (1)$$

where f_T, f_0 are the resonant frequencies at the measuring temperature T (85 °C) and T_0 (25 °C), respectively.

3. Results and discussion

3.1. Phase evolution and microstructure of $NaMg_4V_3O_{12}$ ceramic

Fig. 1(a) shows the room-temperature X-ray diffraction (XRD) patterns of $NaMg_4V_3O_{12}$ samples. The X-ray diffraction data from 770 °C to 870 °C agree well with the tetragonal $NaMg_4V_3O_{12}$ (PDF code: 01-079-0672). No separate second phases can be observed in the diffraction data. The unit cell parameters of the $NaMg_4V_3O_{12}$ compounds in different sintering temperatures were listed in Table 1. When the sintering temperature is 870 °C, the parameters are $a=b=6.894$ Å, $c=19.308$ Å. Fig. 1(b) is the details with enlarged scale of Fig. 1(a). It can be seen that the main peak (204) shifts to low angle from 770 °C to 790 °C, and then moves to high angle from 790 °C to 810 °C. With further increasing the sintering temperature, the main peak (204) shifts to low angle. This change is mainly related to the evaporation of Na^+. Firstly, when the samples were sintered at a lower temperature, the unit cell parameters of the $NaMg_4V_3O_{12}$ compounds increased due to cell expansion. However, the evaporation of Na^+ gets worse at 810 °C, which restricts the unit cell parameters and causes the shift of the main peak (204) to high angle. When the samples were sintered above 810 °C, the

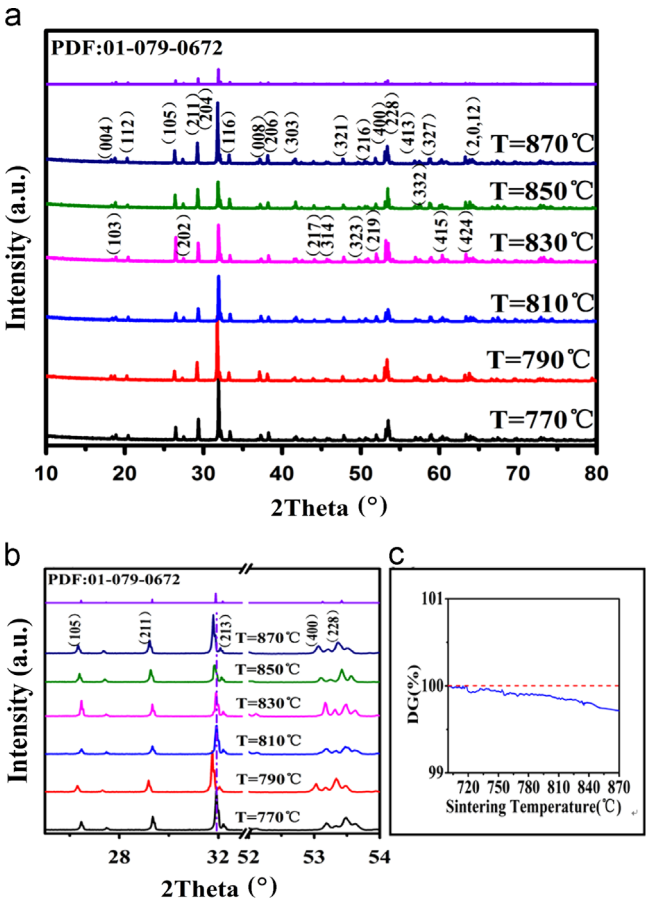

Fig. 1. (a) XRD patterns of $NaMg_4V_3O_{12}$ ceramics sintered at different temperatures (770–870 °C), (b) details with enlarged scale and (c) TG curve of $NaMg_4V_3O_{12}$ powders with 700–870 °C.

Table 1
The unit cell parameters of the $NaMg_4V_3O_{12}$ compounds based on different sintering temperatures.

Sintering temperature (°C)	a(Å)	b(Å)	c(Å)	Volume (ppm/ °C)
PDF code: 01-079-0672	6.89	6.89	19.292	915.83
770	6.882	6.882	19.272	912.70
790	6.898	6.898	19.305	918.73
810	6.883	6.883	19.266	912.87
830	6.884	6.884	19.268	913.14
850	6.889	6.889	19.283	915.18
870	6.894	6.894	19.308	917.71