Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Low temperature sintering and microwave dielectric properties of $Ca_5Ni_4(VO_4)_6$ ceramics

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ARTICLE INFO

Keywords:
Ceramics
Sintering
Rietveld analysis
Dielectric properties

ABSTRACT

Low-temperature sinterable $Ca_5Ni_4(VO_4)_6$ ceramics were prepared by the conventional solid-state reaction route and its microwave dielectric properties were investigated. The crystalline phase, microstructure, and sintering behavior were studied by XRD and SEM. At the sintering temperatures ranging from 825 °C to 900 °C, pure phase $Ca_5Ni_4(VO_4)_6$ was obtained. The variation trend of ε_r was in accordance with that of relative density. The Q×f value was closely related to the packing fraction and relative density. The $Ca_5Ni_4(VO_4)_6$ ceramics sintered at 875 °C for 5 h possessed good microwave dielectric properties: $\varepsilon_r = 9.5$, Q×f = 54, 100 GHz (at 10.5 GHz) and $\tau_f = -60$ ppm/°C, which also exhibited good chemical compatibility with silver electrode.

1. Introduction

The ever-growing advancements in microwave telecommunication systems demand development of new materials and methods for circuit miniaturization. The low temperature co-fired ceramic (LTCC) technology offers significant benefits over other established packaging technologies for high-stability, low-cost and miniaturization for the microwave devices [1,2]. Recently, great efforts have been made to fabricate advanced substrate materials with a low dielectric constant (ε_r), a high quality factor (Q×f), and a near-zero temperature coefficient of resonant frequency (τ_f) [3]. To meet the requirement of LTCC technology, the advanced substrate materials must have lower sintering temperature than the melting point of Ag electrode. However, at present reducing the sintering temperature without affecting the dielectric performance is still a challenge.

The current trend is to develop genuine low firing ceramics and the most recent investigations have explored the applicability of garnet structure compounds containing vanadium elements, which show some interesting physical properties such as dielectric and luminescence [4–6]. Among them, the cubic structure $Ca_5Mg_4(VO_4)_6$ was first reported by Slobodin et al [7]. In our previous work, the $Ca_5A_4(VO_4)_6$ ceramics sintered at below 900 °C exhibited good microwave dielectric properties: $\varepsilon_r = 9.9–11.2$, Q×f = 71738–120000 GHz and $\tau_f = -48 \sim -30$ ppm/°C [8]. The crystal structure, magnetic and photocatalysis properties of $Ca_5Ni_4(VO_4)_6$ were reported by He and Seo et al [9,10]. However, there is only few report on its microwave dielectric properties of $Ca_5Ni_4(VO_4)_6$ [11]. This motivated us to investigate the microwave dielectric properties of the $Ca_5Ni_4(VO_4)_6$ ceramics. In this study, the sintering behavior, microwave dielectric properties and chemical compatibility with Ag of $Ca_5Ni_4(VO_4)_6$ ceramics were studied for the first time.

2. Experimental procedure

Samples of the $Ca_5Ni_4(VO_4)_6$ ceramics were synthesized by a conventional solid-state method using high-purity oxide powders (> 99%): NiO, $CaCO_3$ and V_2O_5. The pre-dried raw materials were mixed according to the desired stoichiometry of the $Ca_5Ni_4(VO_4)_6$ ceramics. The powders were ground for 8 h in a nylon jar with agate balls and ethanol as media. The $Ca_5Ni_4(VO_4)_6$ powders were calcined at 775 °C for 3 h. The calcined powders were reground for 8 h, dried, mixed with 5 wt% PVA as a binder, and granulated. The granulated powders were uniaxially pressed into pellets with 10 mm in diameter and 4–5 mm in height under the pressure of 200 MPa. These pellets were sintered from 825 °C to 900 °C for 5 h in air with a heating rate of 5 °C/min.

The bulk densities of the sintered ceramics were measured by Archimedes' method. Thermal (TG/DTA, SDTQ600, TA instruments, Schaumburg, IL) analysis was performed from room temperature to 950 °C at 10 °C/min for the as-mixed milled powders to determine the weight loss and phase transformation temperatures. The crystal structures were analyzed using powder X-ray powder diffraction

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http://dx.doi.org/10.1016/j.ceramint.2017.05.314

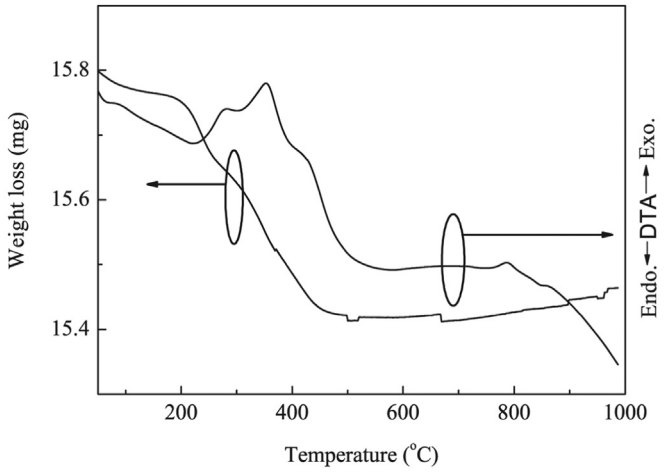

Fig. 1. TG/DTA curves of as-mix-milled powder of $Ca_5Ni_4(VO_4)_6$.

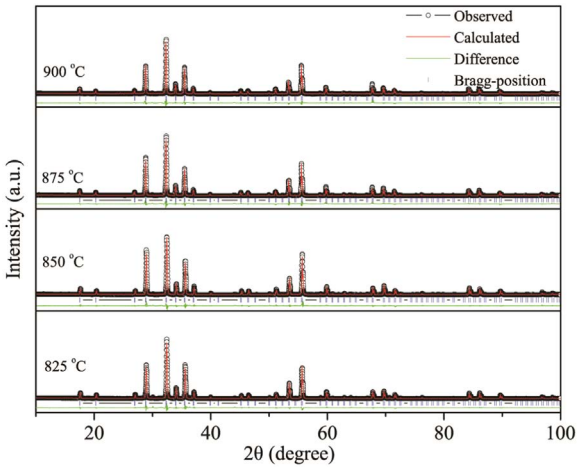

Fig. 3. Rietveld refinement patterns of $Ca_5A_4(VO_4)_6$ ceramics sintered at various temperatures.

(XRPD) with Cu Ka radiation (Rigaku D/MAX2550, Tokyo, Japan). The XRPD data for Rietveld refinement were collected over the range of 2θ=10–100°, with a step size of 0.01° and a count time of 2 s. The Rietveld structure calculations were carried out with the GSAS-EXPGUI program [12]. The microstructure of pellets was investigated using a scanning electron microscope (SEM, Fei Quanta 200, Eindhoven, Holland). The grain sizes in the samples were obtained from SEM micrographs using the Image Tool software for Windows. (version 3.00; Microsoft, Redmond, WA). The microwave dielectric properties of sintered samples were measured using a network analysis (ZVB20, Rohde & schwarz, Munich, Germany) with the TE_{018} shielded cavity method. The temperature coefficient of resonant frequency (τ_f) was calculated with the following equation:

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times (80 - 20)} \quad (1)$$

where f_{80} and f_{20} are the resonant frequency at 80 °C and 20 °C, respectively.

3. Results and discussion

Fig. 1 shows the TG/DTA analysis of $Ca_5Ni_4(VO_4)_6$ powder mixed in the stoichiometric proportions. Weight loss usually occurs when heat treating the reactants due to the decomposition of the oxides of the raw materials used in the solid state ceramic route. The TG curve in Fig. 1 of as prepared $Ca_5Ni_4(VO_4)_6$ indicates that mass loss occurred in two stages. The first stage mainly occurred between room temperature and 200 °C was due to the evaporation of absorbed moisture and the release of molecular water. In the temperature range from 200 °C to 500 °C, the TG curve showed a distinct weight loss. Meanwhile, two exothermic peaks were observed in the DTA curve, which were related to the second weight loss. These exothermic peaks are considered to be caused by the combustion of the organic species [13], during the powder processing step. In the temperature range of 500–1000 °C, there is negligible weight loss but a small exothermic peak at about 775 °C, which could be attributed to the minimum temperature of the solid state reaction that yields $Ca_5Ni_4(VO_4)_6$ phase.

Fig. 2 depicts the XRPD patterns of $Ca_5Ni_4(VO_4)_6$ ceramics sintered at different temperatures. The pure phase $Ca_5Ni_4V_6O_{24}$ was detected in all the temperatures. All of the peaks can be well indexed by the $Ca_5Ni_4(VO_4)_6$ (JCPDS No. 52-0469) standard card with a cubic structure (space group Ia-3d). Of particular note is that the main peak (420) of $Ca_5Ni_4(VO_4)_6$ firstly shifted toward higher angle and then toward lower angles with increasing firing temperatures. Herein, Rietveld refinement was employed to illustrate such anomaly. The refinement results of $Ca_5Ni_4(VO_4)_6$ sintered at various temperatures are presented in Fig. 3. The refined lattice parameters and reliable factors are listed in Table 1. It can be clearly seen from Table 1, with the increment of sintering temperature, the lattice parameters of $Ca_5Ni_4(VO_4)_6$ compound first declined and then increased. According to Zuo et al [14], the reduction in lattice parameters could be related to

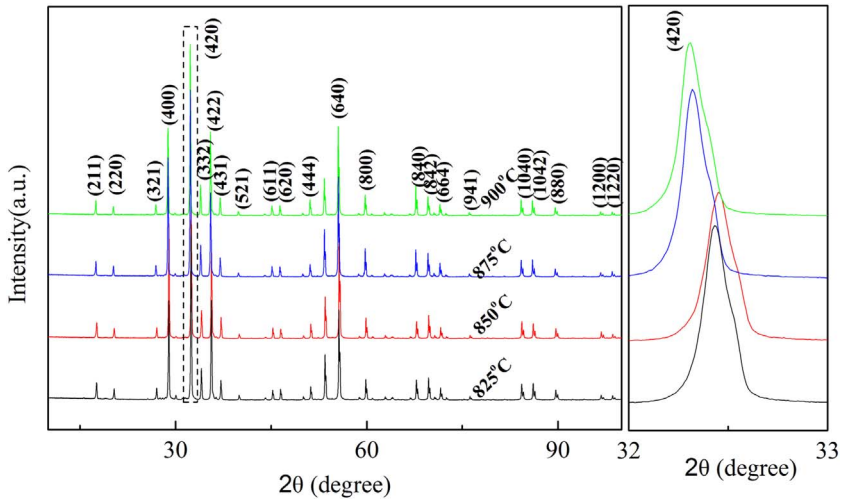

Fig. 2. XRPD patterns of $Ca_5Ni_4(VO_4)_6$ ceramics sintered at different temperatures.