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Low-temperature sintering and microwave dielectric properties of $Ca_5Co_4(VO_4)_6$ ceramics

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Abstract

A novel low temperature firing high Q microwave dielectric ceramic $Ca_5Co_4(VO_4)_6$ was prepared by the conventional solid-state reaction method. The phase purity, microstructure, and microwave dielectric properties were investigated. The $Ca_5Co_4(VO_4)_6$ ceramic sintered at 875 °C exhibited excellent microwave dielectric properties: Qxf = 95,200 GHz (at 10.6 GHz), $\tau_f = -63$ ppm/°C, $\varepsilon_r = 10.1$, and its ε_r corrected for porosity was calculated as 11.1.

Keywords: Dielectric properties; Sintering; X-ray methods; Garnet structure

1. Introduction

With the rapid development of wireless communication technology and the revolution in mobile phone system, even higher requirements are put forward for materials, design, and integration technology when further improvements have been made in the miniaturization, lightening, multifunction and highly reliable of the systems.[1,2] 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.[3,4] In the case of microwave substrate application, the dielectric materials need to have a low dielectric constant (ε_r), a high quality factor (Qxf), and a near-zero temperature coefficient of resonant frequency (τ_f). Therefore, the LTCC substrate materials must have high performance (low ε_r, high Q, near-zero τ_f) and low sintering temperature, which is lower than the melting point of Ag (960 °C).

Recently, compound ceramic systems with intrinsically low sintering temperature have been investigated for LTCC application, such as TeO_2-rich compounds, Li_2O-rich compounds, Bi_2O_3-rich compounds, B_2O_3-rich compounds, MoO_3-rich compounds, and V_2O_5-rich compounds.[5–11] Among them, many V_2O_5-rich low firing ceramics show good microwave dielectric properties and some of them are suitable for the advanced substrate materials.[12–15]

In the CaO–CoO–V_2O_5 ternary system, the phase structure of $Ca_5Co_4(VO_4)_6$ (JCPDS #052-1884) was first reported by Polyakov.[16] However, to the best of our knowledge, the microwave dielectric properties of this composition have not been reported to date. In present study, the microwave dielectric properties, phase structure and microstructure of $Ca_5Co_4(VO_4)_6$ ceramics were investigated.

2. Experimental procedure

Samples of the $Ca_5Co_4(VO_4)_6$ ceramics was synthesized by a conventional solid-state methods using high-purity oxide powders (>99%): Co_2O_3, $CaCO_3$ and V_2O_5. The pre-dried raw materials were mixed according to the desired stoichiometry of the $Ca_5Co_4(VO_4)_6$ ceramics. The powders were ground for 7 h in a nylon jar with agate balls and ethanol as media. All mixtures were dried and calcined at 775 °C for 3 h. The calcined

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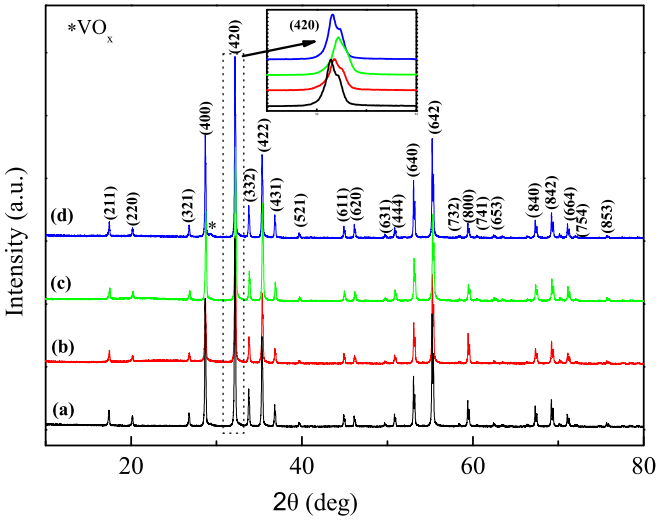

Fig. 1. XRD patterns of $Ca_5Co_4(VO_4)_6$ ceramics sintered at different temperatures: (a) 825 °C, (b) 850 °C, (c) 875 °C, and (d) 900 °C.

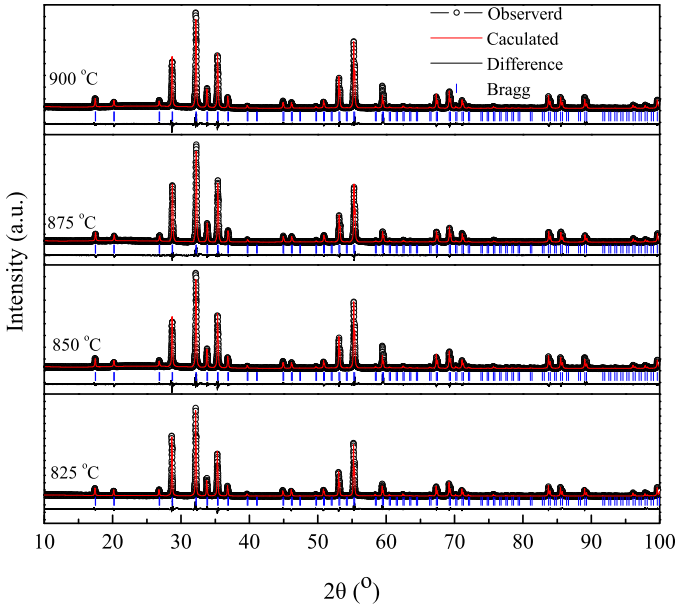

Fig. 2. Structural refinement pattern of $Ca_5Co_4(VO_4)_6$ ceramics sintered at various temperatures.

powders were reground for 7 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. Before being sintered at various temperatures ranging from 825 °C to 900 °C for 5 h in air with a heating rate of 5 °C/min, these pellets were heated in air at 500 °C to remove the binder away.

The bulk densities of the sintered ceramics were measured by Archimedes' method. The crystal structures were analyzed using X-ray powder diffraction (XRPD) with Cu Ka radiation (Rigaku D/MAX2550, Tokyo, Japan). The XRPD data for Rietveld refinement were collected over the range of $2\theta = 10°–100°$, with a step size of 0.016° and a count time of 2 s. The Rietveld structure calculations were carried out with the GSAS program.[17] The microstructure of pellets was investigated using a scanning electron microscope (SEM, Fei Quanta 200, Eindhoven, Holland) coupled with energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) measurements were performed with a spectrometer (AXIS ULTRA, UK) with Al Ka ($E = 1486.6$ eV) radiation. The microwave dielectric properties of sintered samples were measured using a network analysis (ZVB20, Rohde & Schwarz, Munich, Germany) with the $TE_{01\delta}$ 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 XRPD patterns of $Ca_5Co_4(VO_4)_6$ ceramics sintered at different temperatures. In the sintering temperature range 825–875 °C, pure phase $Ca_5Co_4(VO_4)_6$ was obtained within the detectable level of XRPD. The $Ca_5Co_4(VO_4)_6$ ceramics at these temperatures performed cubic garnet structure with space group of Ia–3d (2 3 0), which corresponds well with the data of JCPDS 52-1884 card. At 900 °C, trace amount of secondary phase VO_x (marked as *) was detected, which arises from the partial decomposition of $Ca_5Co_4(VO_4)_6$, our later SEM/EDS results also confirmed this. In addition, as shown in the insert of Fig. 1, with increasing sintering temperature, the main peak (4 2 0) firstly shifted toward higher angle and then shifted toward lower angle again. To understand the unusual change with more details, the lattice parameters were calculated based on Rietveld refinement. The $Ca_5Mg_3Zn(VO_4)_6$ (ICSD #72305) reported by Mueller-Buschbaum and Postel[18] was adopted as the starting model. The Rietveld refinement results are shown in Fig. 2. The lattice parameters, reliability factors and thermal parameters from the refinement results are listed in Table 1. As shown in Table 1, the lattice parameters gradually decreased with increasing sintering temperature up to 875 °C. However, further increasing temperature to 900 °C, the lattice parameter increased. The change on the lattice parameters is consistent with the change of diffraction peaks (Fig. 1). The decrease in lattice

Table 1
Lattice parameters, reliability factors and thermal parameters of $Ca_5Co_4(VO_4)_6$ ceramics with different sintering temperatures.

Sintering temperature (°C)	Lattice parameters (Å)	R_{wp}	R_p	χ^2	Uiso
	a = b = c				
825	12.430044 (30)	8.83	6.80	2.710	0.00419 (32)
850	12.428998 (25)	9.54	7.29	3.153	0.00507 (33)
875	12.428752 (26)	9.49	7.29	3.114	0.00242 (33)
900	12.430721 (32)	9.25	6.92	2.940	0.01477 (35)

R_{wp}: the reliability factor of weighted patterns; R_p: the reliability factor of patterns; χ^2: goodness of fit indicator = $(Rwp/Rexp)^2$.