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Microstructure characteristics and microwave dielectric properties of calcium apatite ceramics as microwave substrates

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ABSTRACT

Apatite structure of $CaLa_4Si_3O_{13}$ ceramics was prepared by the conventional solid-state reaction route. The Rietveld refinement of powder X-ray diffraction (XRD) and analysis of scanning electron microscope images demonstrated that $CaLa_4Si_3O_{13}$ belonged to a hexagonal structure with space group of $P6_3/m$ (No. 176) and grew in a shape of hexagonal prism. The effects of crystallinity, porosity, grain morphology, grain size distribution, and oxygen vacancy on the microwave dielectric properties were investigated in detail as a function of sintering temperature. The existence of Oxygen vacancies and the stretching and bending modes of SiO_4 tetrahedral units were discussed by Raman spectra. Excellent microwave dielectric properties were obtained with $\varepsilon_r = 14.5$, $Q \times f = 31{,}100$ GHz (at 9.05 GHz), $\tau_f = -22$ ppm/°C, indicating possible potential applications for microwave substrate applications.

1. Introduction

Recent years, the Information Communications Technology (ICT) has developed rapidly in an explosive way. The progresses in Internet of Things (IoT) technology, microwave telecommunications, Direct-broadcast satellite television (DBS TV), satellite broadcasting, Intelligent Transport Systems (ITS) and Industry 4.0 have brought enormous changes in our lives and affected the scientific research of new materials [1–3]. Microwave dielectric materials applied in dielectric resonators, filters, substrates, etc. play a key role in communication system [4,5]. In order to promote the development of information technology, scientists are searching for novel microwave materials with high-quality factor ($Q \times f$ values) to depress energy loss, low dielectric constant (ε_r) to reduce the delaytime of electronic signal transmission, and near zero temperature coefficient of resonant frequency (τ_f) for frequency stability [6,7]. Many novel microwave ceramic materials have been reported, such as $MgZrNb_2O_8$ [8], $Li_2Mg_3TiO_6$ [9], $ZnTiTa_2O_8$ [10], $Li_2ZnGe_3O_8$ [11], $BaMg_2V_2O_8$ [12], $Li_2ZnTi_5O_{12}$ [13], etc. In addition to these novel dielectrics materials, there are many kinds of low ε_r silicate compounds reported and the microwave dielectric properties of which are summarized in Table 1. Due to the strong effects of covalent bond in silicate basic units of [SiO_4] tetrahedrons, silicates usually have low dielectric constants which indicate potential application as microwave subtracts [14].

Felsche reported the rare earth silicates $(Mg, Ca, Sr, Ba)_2RE_8[SiO_4]_6O_2$ with the apatite structure for the first time in 1972 [24]. Apatite is named for a large family of isomorphous compounds with general formula $A_{10}(MO_4)_6O_2$, where A represents a divalent cation, MO_4 represents a trivalent or tetravalent anion. In apatite structure, A^{2+} cations are located in two different sites: 4f with nine-fold coordination and 6h with seven-fold coordination. The cation in 6h site is coordinated to O(4) oxygen ion presented in the channel, resulting in larger average A-O covalence than that of the 4f site. Over decades, considerable attention was focused on substitutions at the A and M lattice sites [25–28]. Boyer et al. presented the dependence of site occupation on luminescent properties in apatite phosphor [25]. Sebastian et al. addressed the microwave dielectric properties of $SrRE_4Si_3O_{13}$ and $CaRE_4Si_3O_{13}$ ceramics (RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, and Y) [29,30].

In this paper, $CaLa_4Si_3O_{13}$ ceramics were prepared via a conventional solid-state reaction route. The evolutions of crystallinity, porosity, grain morphology, distribution of grain length size, and

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Table 1
The microwave dielectric properties of some silicate ceramics reported in references.

Silicate Ceramics	Q × f (GHz)	ε_r	τ_f (ppm/°C)	Ref
Mg_2SiO_4	240,000	6.8	−70	[15]
Zn_2SiO_4	21,900	6.6	−65	[16]
$LiAlSiO_4$	36,000	4.8	8.6	[17]
Al_2SiO_5	41,800	4.4	−17	[18]
$Sr_2Al_2SiO_7$	33,000	7.2	−37	[19]
$Ba_2ZnSi_2O_7$	26,600	8.1	−51	[20]
$Y_3MgAl_3SiO_{12}$	57,340	10.1	−32	[21]
$Ba_9Y_2Si_6O_{24}$	22,400	14.9	36	[22]
$Mg_2Al_4Si_5O_{18}$	39,000	6.3	−32	[23]

oxygen vacancy were systematically analyzed along with their effects on the microwave dielectric properties. The presence of oxygen vacancies were confirmed and investigated by Raman spectra tests along with the analysis of vibrational modes of SiO_4.

2. Experimental

The dense samples were prepared by a conventional solid-state sintering method using high-purity oxide powders $CaCO_3$(Sinopharm Chemical Reagent Co., Ltd, China, 99.9%), La_2O_3(Sinopharm Chemical Reagent Co., Ltd, 99.9%), SiO_2(Aladdin Industrial Corporation, 99.99%) as raw materials. Stoichiometric proportions of the above powders according to the chemical formula of $CaLa_4Si_3O_{13}$ were mixed in ethanol for 24 h with zirconia balls as milling media. The resulting slurries were dried in an oven at 90 °C. After sieving, the powders were calcined at 1250 °C for 4 h at heating rate of 4 °C/min. After ball re-milled, the calcined powders were then mixed with 5 wt % solution of polyvinyl alcohol solution and pressed into pellets at the pressure of 100 MPa using a stainless die. The diameter of pellets is 12 mm and the height is about 6 mm for microwave dielectric property tests. The pellets were sintered at 1300°C-1450 °C in air for 4 h to yield the dense ceramics. After sintering, the samples were cooled to 1000 °C at a rate of 1 °C/min, and then shut down the power, further cooled inside the furnace.

The bulk densities of as sintered pellets were measured by the Archimedes method using distilled water as medium. The room-temperature crystalline phase constituents were identified by powder X-ray diffraction (XRD) (RIGAKU D/max 2550/PC, Rigaku Co., Tokyo, Japan) analysis with CuKα (λ = 1.54,056 Å) radiation at the voltage of 40 kV and current of 30 mA.The scanning rate was 10° min^{-1} in the 2θ range from 10 to 90°. The data for the Rietveld analysis were collected in a step-scanning mode with a step size of 0.02° and 5 s counting time per step over a 2θ range from 5° to 120° [31]. The Rietveld refinement was performed with the general structure analysis system (GSAS) software. The Raman spectra were collected at room temperature using a Raman spectrometer (Renishaw in Via Raman in the Key Laboratory of Submarine Geosciences, State Oceanic Administration) with a CCD detector. The 514 nm line of an Ar^+ ion laser was used as excitation source. Microstructures of the polished and thermal etched surface of the sintered samples were observed using Field Emission Scanning Electron Microscopy (Ultra55, Germany). The thermal etching was carried out at a temperature 50 °C lower than the sintering temperature for 30 min. The grain diameters and lengths were scaled in the SEM patterns using the software of Image J. The dielectric constant ε_r and the temperature coefficient of resonant frequency τ_f were measured by the paralleling plate method [32] using a vector network analyzer (E8363B, Agilent Technologies Inc., Santa Clara, CA). τ_f was measured in the temperature range of 20°C–80 °C. The quality factor Q was evaluated by the resonant-cavity method [33] using a silver-coated cavity connected to the network analyzer. To ensure the accuracy of the data, at least two samples were measured for each composition. As the Q-factor generally varied inversely with frequency (f) in the microwave range, the product Q × f, rather than Q alone, was used to evaluate the dielectric loss.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of $CaLa_4Si_3O_{13}$ powders sintering at different temperature for 4 h. The X-ray diffraction patterns of all samples sintered at different temperatures show the same profile and can be indexed as $CaLa_4Si_3O_{13}$ (JCPDS No.71–1368), with no secondary crystal phase being detected. The XRD analysis indicates the $CaLa_4Si_3O_{13}$ belongs to a hexagonal crystal system with space group of $P6_3/m$ (176). As shown (b) of Fig. 1, the crystallinity of $CaLa_4Si_3O_{13}$ ceramic samples increases with the augment of sintered temperature from 1300 °C to 1375 °C, and decreases with

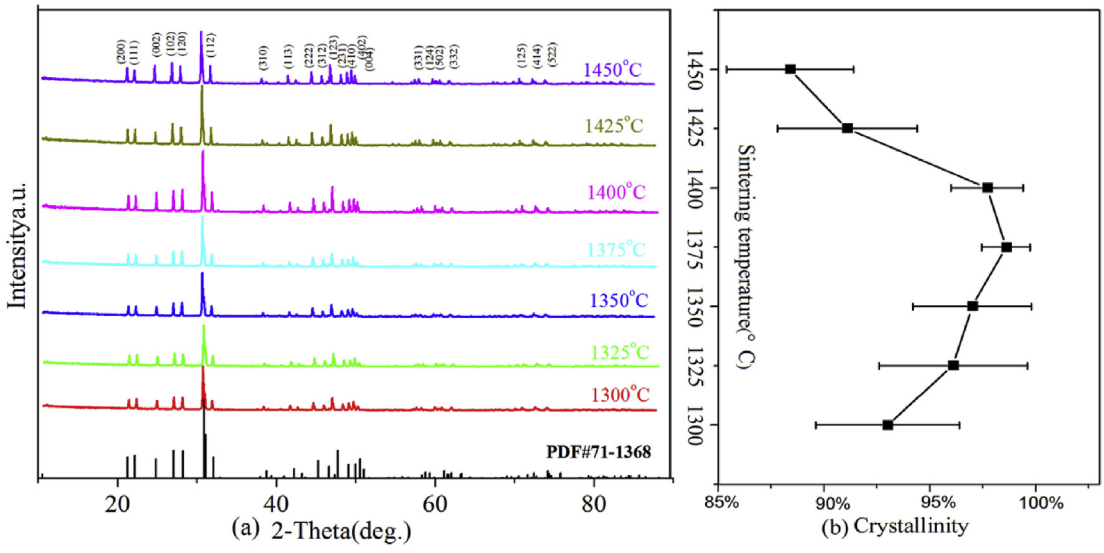

Fig. 1. (a) XRD pattern of $CaLa_4Si_3O_{13}$ ceramic samples sintered at different temperature in air for 4 h. (b) The crystallinity of $CaLa_4Si_3O_{13}$ ceramic samples sintered at different temperature.