Synthesis and Characterization of CaTiO3-LnAlO3 (Ln=La, Nd) Ceramics Manufactured by Reaction Sintering Method

Shicheng Zhou
Guilin University of Technology

Qiang Wu
Guilin University of Technology

Hanrui Xu
Guilin University of Technology

Xiaowen Luan
Guilin University of Technology

Sang Hu
Guilin University of Technology

Xianjie Zhou
Guilin University of Technology

Sen He
Guilin University of Technology

Xi Wang
Guilin University of Technology

Hailin Zhang
Guilin University of Technology

Xiuli Chen
Guilin University of Technology

Huanfu Zhou (zhouhuanfu@163.com)
Guilin University of Technology

Research Article

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Synthesis and characterization of CaTiO$_3$-LnAlO$_3$ (Ln=La, Nd) ceramics manufactured by reaction sintering method

Shicheng Zhou[†], Qiang Wu[†], Hanrui Xu, Xiaowen Luan, Sang Hu, Xianjie Zhou, Sen He, Xi Wang, Hailin Zhang, Xiuli Chen, Huanfu Zhou*.

Collaborative Innovation Centre for Exploration of Hidden Nonferrous Metal Deposits and Development of New Materials in Guangxi, Key Laboratory of Nonferrous Materials and New Processing Technology, Ministry of Education, School of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China.

Abstract

CaTiO$_3$-LnAlO$_3$ (Ln=La, Nd) ceramics were manufactured by reaction-sintering for produce low cost and high efficiency materials. Using reaction-sintering method to manufacture these ceramics, which have excellent comprehensive properties. The subtle variations on densification behavior, phase transformation, phase composition, microstructure evolution and performances of CaTiO$_3$-LnAlO$_3$ (Ln=La, Nd) ceramics were studied systematically. The XRD pattern indicates that the Ca$_{0.61}$La$_{0.39}$Al$_{0.39}$Ti$_{0.61}$O$_3$ phase and Ca$_{0.7}$Nd$_{0.3}$Ti$_{0.7}$Al$_{0.3}$O$_3$ phase were generated under certain environmental conditions respectively. The ceramics exhibited excellent performance parameters: when $\varepsilon_r$ is 42.03 (45 635), the quality factor is 45500GHz (45 635) In addition, even in the environment of large temperature changes the ceramics can still maintain good performance. In conclusion, the reaction sintering method is an economic, convenient, available preparation means of making the CaTiO$_3$-

[†] These authors have equal contribution to this work

* Corresponding author, E-mail: zhouhuanfu@163.com
LnAlO$_3$(Ln=La, Nd) ceramics and has broad prospects of application and development.

**Keywords:** CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics; Reaction sintering method; Microwave dielectric properties
1. Introduction

The wireless communication industries led by microwave communication technology are developing at a rapid pace. A better and serious request about the performance of the functional ceramics was also put forward by this prospect.[1-3]. Because of smallness, lightness, and cheapness microwave dielectric ceramics are excellent candidate materials for communication technologies [4-6].

In actual application, process flow and production cost are factors that must be considered. High production expenses will limit the prospect of numerous microwave ceramics, as (1-x)ZnNb2O6-xBa(Zn1/3Nb2/3)O3[7]. For the sake of practical application, appropriate raw materials and efficient processes are necessary. Suvorov et al. reported that although the CaTiO3 ceramics demonstrate favorable microwave dielectric properties ($\varepsilon_r = 170$), its practical application is hindered by quality factor ($Q \times f = 3500$ GHz) and temperature coefficient ($\tau_f = +800$ ppm/°C). It is easy to acquire useful microwave dielectric ceramics via synthesizing two perovskite structure compounds together[8]. CaTiO3-LnAlO3(Ln=La, Nd) solid solution ceramics exhibited good performances, which preserves excellent comprehensive properties: $\varepsilon_r = 37-44$, $Q \times f = 41,000-47,000$ GHz, $\tau_f = -1.5-6$ ppm/°C. Ravi et al. reported that 0.7CaTiO3-0.3LaAlO3 ceramics doped with 0.25wt% Al2O3 sintered at 1500°C, and the ceramic showed great performance parameters: $\varepsilon_r = 46$, $Q \times f = 38,289$ GHz, and $\tau_f = +12$ ppm/°C[9].

In this work, using reaction sintering method to manufacture CaTiO3-LnAlO3(Ln=La, Nd) ceramics to simplify experimental procedures and optimize the dielectric properties. Also, the solid-state reaction mechanism of the CaTiO3-LnAlO3(Ln=La, Nd) solid solution was also investigated, which determine the origin
of the intermediate phase.

2. Materials and methods

CaTiO$_3$-LnAlO$_3$ (Ln=La, Nd) ceramic samples were made from high purity materials (≥99%) including CaCO$_3$, TiO$_2$, Al$_2$O$_3$, La$_2$O$_3$, and Nd$_2$O$_3$, therefore preprocessing of high purity raw materials is the foremost section in fabrication of high quality dielectric ceramics, especially La$_2$O$_3$, and Nd$_2$O$_3$. Put La$_2$O$_3$, and Nd$_2$O$_3$ into muffle furnace at 900°C for two hours respectively, and the mole ratios of CaTiO$_3$-LaAlO$_3$ and CaTiO$_3$-NdAlO$_3$ were determined to be 0.675:0.325 and 0.695:0.305, respectively. The powder was blended with zirconia pellets in alcoholic medium for 4 h. After drying in an oven, samples in cylindrical molds with a diameter of 10mm and a height of 5mm were fabricated at 20 MPa. Finally, they have been sintered from 1475°C to 1575°C with a gradient of 25°C for 6 h respectively.

Using the X-ray diffraction (Model X’Pert PRO, PANalytical, Almelo, Holland) with Cu K$_\alpha$ radiation at 40 kV and 40 mA (5° ≤ 2θ ≤ 80°) to analyze the microstructure and crystalline of the ceramics. The surface topography and crystal size were observed with SEM (Model JSM6380-LV SEM, JEOL, Tokyo, Japan). Performance parameters of specimens were acquired by using the network analyzer (Model E5071 CENA, Agilent Co, California, USA, 300KHz-20GHz). The $\tau_f$ values of the samples were measured from the resonant frequencies at 25 °C to 85 °C and was defined as:

$$\tau_f = (f_2 - f_1)/f_1(T - T_0)$$  \hspace{1cm} (1),

where $f_2$ and $f_1$ are the resonance frequencies at 85 °C and 25 °C, respectively.

3. Results and discussion
Figure 1 presents the XRD spectrum of CTLA and CTNA samples sintered from 1100 to 1575°C for 6h, respectively. As shown in Fig1(a), the XRD spectrum of the CTLA samples revealed that there are two types of phase CaTiO$_3$(PDF #96-900-2802) and LaAlO$_3$(PDF #01-082-0478) at 1100°C. As the temperature is 1475°C, two phases are completely form a solid solution. All diffraction peaks are homogeneous Ca$_{0.61}$La$_{0.39}$Al$_{0.39}$Ti$_{0.61}$O$_3$ main phase, corresponding to the tetragonal perovskite structure (PDF: 00-052-1773), belonging to the P4$_2$2$_1$2 space group[10]. The tendency of Fig1(b) is similar as Fig1(a). The ceramic specimen was composed of both CaTiO$_3$ and NdAlO$_3$ phases, and the secondary phase gradually disappeared at 1200°C[11]. Upon further increase of the temperature to 1450 °C, the main peak of the CTNA ceramics appeared at 2θ = 33.2°, which matches well with the 2θ value of the Ca$_{0.7}$Nd$_{0.3}$Ti$_{0.7}$Al$_{0.3}$O$_3$ phase (PDF : 96-153-3888), belonging to the Pnma space group[12-14]. Using the GASA software could further enhance the fitting accuracy and ascertain the cation position of the samples accurately, the refinement results are shown in Fig. 2. Both samples exhibited a single CaTiO$_3$ phase with a orthorhombic structure in the Pbmn model, and the lattice parameters of this ceramic are as follows: a = 5.358(6)Å, b = 7.593(10) Å, c = 5.394(5) Å, and α = β = γ = 90°. The small R-values (CTLA: $R_p = 4.09\%$, $R_{wp} = 7.43\%$; CTNA: $R_p = 4.17\%$, $R_{wp} = 7.57\%$) manifest that the XRD result matched faultlessly consistent with CaTiO$_3$ (PDF: 75-0437) with orthorhombic structure, which indicates that CTLA and CTNA ceramics are fused to form a complete solid solution. Ca$^{2+}$, La$^{3+}$, Nd$^{3+}$ take up the A-site of the oxygen octahedron, and Ti$^{4+}$, Al$^{3+}$ take up the B-site of the oxygen octahedron[15, 16].
Figure 3 shows the SEM micrographs of CaTiO$_3$-LnAlO$_3$ (Ln=La, Nd) samples sintered at various temperatures. The micromorphology is variable with the changing of temperature. When the sintering temperatures were less than 1450°C, the particles are composed of small crystal and the structure is not dense enough, which manifest that low temperature cannot provide enough energy for grain growth [17-19]. Raising the temperature again the samples surface becomes more compact and homogeneous and few grain boundaries appears. When the sintering temperature exceeds 1525°C, there were only a few pores in the sample [20, 21]. The above results shown that CaTiO$_3$-LnAlO$_3$ (Ln=La, Nd) ceramics could keep excellent performance in a wide temperature range. Using EDS to verify the molar ratios of elements in CaTiO$_3$-LnAlO$_3$ (Ln=La, Nd) ceramics, which verifies the analysis and conclusion of XDR. Table 1 includes the results of EDS in detail. All samples contain only Ca, Ti, Al, La/Nd and O elements. The calculated result of Ca/Al atomic number ratio is same with the main crystal phase. For example, the atomic number ratio of Ca/Ti to Nd/Al is close to 7:3 in CTNA ceramics, which is very consistent with the stoichiometric ratio of Ca$_{0.7}$Nd$_{0.3}$Ti$_{0.7}$Al$_{0.3}$O$_3$ phase.

Fig. 4 including the curves of $\rho$, $\varepsilon_r$, $Q\times f$ and $\tau_f$ of CaTiO$_3$-LnAlO$_3$ (Ln=La, Nd) ceramics with the changing of the sintering temperature. The bulk densities of CTLA and CTNA ceramics were 4.47–4.68 g/cm$^3$ and 4.48–4.80 g/cm$^3$. With the rise of temperature, the bulk densities $\rho$ of CTNA ceramics and CTLA ceramics firstly rose due to the growth of grains, reaching the maximum values at a selected temperature, and then its density declines gradually due to the inner defects caused by extra-high
temperature. When the temperature gradually increases to the ideal temperature, the ceramic grains grow and discharge the pores inside the ceramic, making microstructure of the ceramic more compact, and reaching the maximum. When the temperature exceeds the optimal temperature, the phenomenon of overburning occurs. The grain growth rate is too fast to discharge the pores inside the ceramic in time, contributing to the decline in the density[22-24].

As the sintering temperature increases, the dielectric constant of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics reaches a maximum value at the optimum temperature and then decreases. The trend is similar to the relative density. The high density of ceramics is accompanied by high polarizability and thus to an increase in polarization intensity[2, 25]. The relationship between the dielectric constant and the dielectric polarizability and molar volume fraction of the materials can be explained clearly by the Clausius-Mossotti formula used in the literature as follows:

$$\varepsilon_{th} = \frac{3Vm + 8\pi\alpha D}{3Vm - 4\pi\alpha D}$$

(2),

where $Vm$ is the cell volume of the Ca$_{0.61}$La$_{0.39}$Al$_{0.39}$Ti$_{0.61}$O$_3$ and Ca$_{0.7}$Nd$_{0.3}$Ti$_{0.7}$Al$_{0.3}$O$_3$ molecule, and $\alpha$ is their polarization rates. The total ion polarization rate of Ca$_{0.61}$La$_{0.39}$Al$_{0.39}$Ti$_{0.61}$O$_3$ and Ca$_{0.7}$Nd$_{0.3}$Ti$_{0.7}$Al$_{0.3}$O$_3$ can be calculated as follows:

$$\alpha(Ca_{0.61}La_{0.39}Al_{0.39}Ti_{0.61}O_3) = 0.61\alpha(Ca^{2+}) + 0.61\alpha(Ti^{4+}) + 0.39\alpha(La^{3+})$$

$$+ 0.39\alpha(Al^{3+}) + 3\alpha(O^{2-}) = 12.4203(3)$$

$$\alpha(Ca_{0.7}Nd_{0.3}Ti_{0.7}Al_{0.3}O_3) = 0.7\alpha(Ca^{2+}) + 0.3\alpha(Ti^{4+}) + 0.3\alpha(Nd^{3+}) + 0.3\alpha(Al^{3+})$$

$$+ 3\alpha(O^{2-}) = 12.033(4)$$

Where $\alpha(Ca^{2+}) = 3.16\AA^3$, $\alpha(Ti^{4+}) = 2.93\AA^3$, $\alpha(La^{3+}) = 6.07\AA^3$, $\alpha(Nd^{3+}) = 5.01\AA^3$, $\alpha(Al^{3+}) = 0.79\AA^3$ and $\alpha(O^{2-}) = 2.01\AA^3$. The theoretical permittivity of CTLA and CTNA were
40.86 and 31.9, respectively. Due to the high dielectric constant of calcium titanate and the grain priority growth, there is a large difference between the measured and calculated values of $\varepsilon[26]$.

There are two types of materials losses at microwave frequency: on the one hand the intrinsic loss mainly determined by the lattice vibration mode could influence the properties of materials, on the other hand the external loss determined by the second phase, oxygen vacancies, grain size and densities could also affect the properties of materials[27, 28]. In the same system, the excellent performance of materials depends on the grain size and the number of pores. Therefore, with increasing temperature, the variation of $Q\times f$ value is close to the dielectric constant, which the maximum $Q\times f$ values of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics are 46,269 GHz and 45,635 GHz, respectively. According to the Fig 4, the quality factor of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics is greater than 41,000 under different ranges of temperature. The $\tau_f$ values of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics remain stable at -1.5 to 6 ppm/°C no matter how the temperature changes. The fluctuations in their $\tau_f$ values are mainly caused by grain size, porosity, oxygen vacancies, etc[29, 30]. These indicate that the CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics has achieved excellent performance in a wide temperature range.

4. Conclusion

The densification behavior, phase transformation, phase composition, microstructure evolution and performances of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) have been reported by the reaction-sintering method. Solid-solutions with tetragonal and
orthorhombic perovskite structures were formed. The CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics exhibited the excellent performances as the temperature is between 1475 and 1575°C. The ceramics sintered at 1500 and 1525°C indicated that it has considerable performance parameters CTNA: $Q\times f = 45,635$ GHz, $\varepsilon_r = 39.1$, and $\tau_f = -1.48$ ppm/°C; CTLA: $Q\times f = 46,269$ GHz, $\varepsilon_r = 44.03$, and $\tau_f = 2.63$ ppm/°C). The preparation of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics by reaction-sintering method has the advantages of simple preparation process, low preparation cost, and wide sintering temperature range, which showing good prospects for industrial applications.

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Figure Captions

Figure 1. XRD patterns of CTLA and CTNA ceramics sintered at 1100 to 1575°C for 6h.

Figure 2. Rietveld refinement of the room temperature XRD patterns of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramic (CTLA: $R_p = 4.09\%$, $R_{wp} = 7.43\%$, $\chi^2 = 15.55$; CTNA: $R_{wp} = 7.57\%$, $R_p = 4.17\%$, $\chi^2 = 11.08$).

Figure 3. SEM micrographs of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics sintered at 1475 to 1550°C for 6h.

Figure 4. The curves of $\rho$, $\varepsilon_r$, $Q\times f$ and $\tau_f$ of CaTiO$_3$-LnAlO$_3$(Ln=La, Nd) ceramics as a function of the sintering temperature.

| Element Atomic (%) | Ca | Ti | La/Nd | Al | O |
|---------------------|----|----|-------|----|---|
| CTLA                | 18.76 | 20.09 | 10.19 | 10.09 | 40.87 |
| CTNA                | 19.85 | 20.77 | 9.94  | 7.76  | 41.68 |
Figure 1

[Graph showing X-ray diffraction patterns for Ca$_{0.64}$La$_{0.36}$Al$_{0.39}$Ti$_{0.61}$O$_3$ (PDF: 52-1773) and Ca$_{0.77}$Nd$_{0.33}$Al$_{0.33}$Ti$_{0.77}$O$_3$ (PDF: 96-153-3888) at various temperatures.]
Figure 2

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Intensity (a.u.) vs. 2 Theta (degree)

- $Y_{\text{obs}}$
- $Y_{\text{cal}}$
- $Y_{\text{obs}} - Y_{\text{cal}}$
- Peak Position

- $R_{wp} = 7.43\%$
- $R_p = 4.09\%$
- $\chi^2 = 15.55$

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Intensity (a.u.) vs. 2 Theta (degree)

- $Y_{\text{obs}}$
- $Y_{\text{cal}}$
- $Y_{\text{obs}} - Y_{\text{cal}}$
- Peak Position

- $R_{wp} = 7.57\%$
- $R_p = 4.17\%$
- $\chi^2 = 11.08$
Figure 3
Figure 4
Figures

Figure 1

XRD patterns of CTLA and CTNA ceramics sintered at 1100 to 1575°C for 6h.

Figure 2

Rietveld refinement of the room temperature XRD patterns of CaTiO3-LnAlO3 (Ln=La, Nd) ceramic (CTLA: Rp = 4.09%, Rwp = 7.43%, $\chi^2 = 15.55$; CTNA: Rwp = 7.57%, Rp = 4.17%, $\chi^2 = 11.08$).
**Figure 3**

SEM micrographs of CaTiO3-LnAlO3 (Ln=La, Nd) ceramics sintered at 1475 to 1550°C for 6h.

**Figure 4**

The curves of $\rho$, $\varepsilon_r$, Q×f and $\tau_f$ of CaTiO3-LnAlO3 (Ln=La, Nd) ceramics as a function of the sintering temperature.