Influence of different Milling Process on the properties of CaTiO$_3$-NdAlO$_3$ Dielectric Ceramics and its Microwave Devices

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Abstract. The high performance CaTiO$_3$-NdAlO$_3$ dielectric ceramics were prepared with different milling process. The phase composition, microstructure of the CaTiO$_3$-NdAlO$_3$ dielectric ceramics and dielectric properties of its microwave devices were analyzed. The results indicated that CaTiO$_3$-NdAlO$_3$ dielectric ceramics are single-phase orthogonal perovskite-structure. The temperature drift index of the microwave resonator manufactured by CaTiO$_3$-NdAlO$_3$ dielectric ceramics and the assembled cavity filter are consistent with the technical requirements of microwave resonant components and cavity filters for communication base station.

1. Introduction
Different spherical microwave dielectric ceramics, as electronic ceramic materials mainly used in microwave frequency band circuits to complete one or more functions, have been widely used in mobile communications, satellite communications, global positioning system (GPS), Bluetooth technology, mobile phones, televisions and Wireless local area network (WLAN) and other modern microwave communication fields. Dielectric ceramics are not only an effective way to achieve miniaturization, high stability and microwave circuit integration of microwave devices, but also have become the basis and key materials for achieving microwave control functions and technologies; among them, 0.7CaTiO$_3$-0.3NdAlO$_3$ based ) Dielectric ceramics are the most representative microwave dielectric ceramic materials [1-6]. The traditional mechanical mixing and solid phase reaction sintering CaTiO$_3$-NdAlO$_3$ dielectric ceramic preparation methods have the following defects [7-10]: The particle size distribution of mechanically mixed powder depends on the particle size range of the raw material, and the amount of powder particle size change during processing is small, the powder has poor reactivity during high-temperature calcination, resulting in a high calcination temperature, and the ceramic powder synthesized by the reaction has a large particle size, a wide particle size distribution, and many doping phases, which affects the dielectric of CaTiO$_3$-NdAlO$_3$ ceramics performance. In general, the addition of low melting point oxides or low melting point glasses (such as B$_2$O$_3$, V$_2$O$_5$, Bi$_2$O$_3$) can reduce the sintering temperature of ceramic materials, but the reduction of the firing temperature is limited, and the sintering aids will also vary Damage the dielectric properties of CaTiO$_3$-NdAlO$_3$ ceramics[8, 9]. The chemical synthesis method (metal molten salt method or sol-gel method) can produce uniform and fine ceramic powder, but often requires complex control processes and high-priced raw materials, which will further increase the batch volume of microwave dielectric components Production cost and technical difficulty. High-Energy
Ball Milling (High-Energy Ball Milling) method as a new electronic ceramic powder preparation technology, not only significantly reduces the reaction activation energy, refines the grain, greatly improves the powder activity, and improves the uniformity of particle distribution, thereby improving it is a kind of energy-saving and high-efficiency material preparation technology that includes the degree of densification, dielectric and thermoelectric properties of ceramic materials [11-14]. In this paper, CaTiO$_3$-NdAlO$_3$ dielectric ceramics were prepared by different ball milling processes, and the phase composition and microstructure of CaTiO$_3$-NdAlO$_3$ dielectric ceramics and the passband frequency stability of microwave devices were analyzed.

2. Experiment

2.1. Sample Preparation

Based on traditional planetary ball milling wet grinding and mixing (hereinafter referred to as "traditional planetary ball milling"), dry high-energy ball milling-mechanical alloying (hereinafter referred to as "high-energy ball milling") and wet circulating stirring grinding (hereinafter referred to as "circular stirring") The basic process, this paper uses high energy ball milling and circular stirring composite process combined with solid-phase reaction sintering process to prepare CaTiO$_3$-NdAlO$_3$ dielectric ceramic material process shown in Figure 1, which specific process parameters mainly include:

1) According to the chemical formula 0.7CaTiO$_3$-0.3NdAlO$_3$, CaCO$_3$, Al$_2$O$_3$, Nd$_2$O$_3$, TiO$_2$ powders are circulated and stirred (or planetary ball mill mechanical mixing); ZrO$_2$ grinding balls are used as grinding media, and absolute ethanol or deionized water are used as organic solvents. The ratio of balls, mixed powder and solvent (weight) is 3:1:3, the overall volume of which accounts for 60% to 80% of the spherical tank, and the mixing time of raw materials is 12 hours. Note: The purity of CaCO$_3$, Al$_2$O$_3$, Nd$_2$O$_3$ and TiO$_2$ in the raw materials are all greater than 99.5%.

2) Using ZrO2 milling balls as the grinding medium, the first step of high-energy ball milling (dry method) is performed after drying the powder in step 1). Among them, the high-energy ball milling time is 2 hours, the ball to material ratio is 12:1, and the rotation speed is 800 rpm.

3) Place the mixed raw materials after drying in a closed high-temperature crucible to synthesize the precursor powder with single-phase orthogonal perovskite structure phase after high-temperature reaction. Among them, the calcination temperature is 900°C and the holding time is 10 hours.

4) Using zirconium dioxide grinding balls as the grinding medium, the calcined powder is subjected to circular stirring grinding (planetary ball mill mechanical mixing) to further uniformly refine the ceramic powder. Among them, please refer to step 1) for circular mixing grinding or planetary ball mill mechanical mixing process parameters, and for high energy ball milling process parameters, please refer to step 2).

5) Add a mass percentage of 8% polyvinyl alcohol (PVA) aqueous solution (concentration is 5%) to the powder obtained in step 4, and use a spray drying tower or granulator to make spherical and fluid particles.

6) Use a press (manual or automatic filler) to make the powder particles into a compact of the desired shape, and use double-sided pressing, the pressing pressure of which is 120MPa.

7) Place the green compact in a sealed high-temperature alumina crucible, use an appropriate amount of mixed powder of calcium carbonate and titanium oxide as a cushion powder, and place the green compact in a sealed casket for continuous sintering. Among them, the maximum sintering temperature is 1550°C, and the holding time is 4 hours.

8) Take out the sintered porcelain body, and after surface treatment such as end grinding, polishing, and metallized sintered silver conductive layer, obtain the size of the required resonant element sample, and then use a network analyzer to measure its dielectric performance index.
Figure 1. Schematic diagram of preparation process of CaTiO$_3$-NdAlO$_3$ dielectric ceramic samples.

2.2. Sample testing

Using the D / Max-2500PC phase and crystal structure of X-ray diffraction were employed to characterize the alloy samples. ULTRA 55 thermal field emission scanning electron microscope (Zeiss, Germany) was used to analyze the surface and cross-sectional morphology of the sample, and X-MAX50 energy spectrometer (Oxford, UK) was used to analyze the local chemical composition of the sample. The standard method in the ISO 1183-1:2012 Plastics -- Methods for determining the density of non-cellular plastics -- Part 1: Immersion method, liquid pyknometer method and titration method is used to measure the relative density of the dielectric ceramic sample.

Figure 2. Schematic diagrams of the dielectric properties-testing system for CaTiO$_3$-NdAlO$_3$ ceramic samples.

When a medium is applied with an electric field, the induced charge will be generated to weaken the electric field. The ratio of the reduction of the electric field in the medium to the original applied electric field (in vacuum) is the relative dielectric constant. Dielectric constant is the product of relative dielectric constant and absolute dielectric constant in vacuum. If there is a high dielectric constant material is placed in an electric field, the electric field strength will have a substantial drop in the dielectric. The size of the resonator is inversely proportional to the square root of the dielectric constant of the dielectric material. Therefore, the greater the dielectric constant of the dielectric material, the smaller the required dielectric ceramic block and the smaller the size of the resonator [3-6]. Another important indicator of the filter is the low insertion loss. The dielectric loss of the ceramic material is a key factor affecting the insertion loss of the dielectric filter. The quality factor value of the microwave dielectric material is inversely proportional to the dielectric loss, that is, the larger the quality factor value, the lower the filter insertion loss. The working environment temperature of the communication device cannot be constant. If the resonance frequency of the dielectric material changes greatly with temperature, the carrier signal of the filter will drift at different temperatures, thereby affecting the performance of the device. This requires that the resonance frequency of the material should not change too much with temperature. Therefore, the actual requirement of the frequency-temperature coefficient of the microwave dielectric ceramic material is generally not greater than 10 ppm/°C at -40 to 100°C, thereby achieving high stability and reliability of the device.
In this paper, the Agilent HP4396B network analyzer is used to measure the dielectric constant of the dielectric ceramic sheet and the quality factor and temperature coefficient of the self-made single cavity microwave resonator and the "temperature drift" index of the cavity filter. Figure 2 shows the schematic diagram of the test system for measuring the dielectric constant, quality factor and temperature coefficient of dielectric ceramic test pieces.

3. Result and discussion

3.1. Phase composition and dielectric properties

Figure 3 shows the XRD patterns of CaTiO$_3$-NdAlO$_3$ dielectric ceramic powders prepared by the same calcination process and different ball milling processes; of which (a) and (b) respectively correspond to the preparation of samples using traditional planetary ball milling and circular mixing and high energy ball milling composite processes. It can be seen from Figure 3 that the phase structures of the samples prepared by the three ball milling processes are all orthogonal perovskite crystal forms, but the traditional planetary ball milling samples have more small-angle diffraction peaks corresponding to the samples (as shown by the black arrows in the figure), However, the small-angle diffraction peaks of the samples prepared by the compound ball milling process were basically submerged. Therefore, the phase structure of the dielectric ceramic sample prepared by the circular stirring and high-energy ball milling composite process is a single-phase orthogonal perovskite crystal form.

![Figure 3. The XRD spectrums of CaTiO$_3$-NdAlO$_3$ dielectric ceramic samples prepared by different ball milling processes.](image)

Figure 4 shows the SEM photos of CaTiO$_3$-NdAlO$_3$ dielectric ceramic samples prepared by the same sintering process and different ball milling processes; where (a), (b) and (c) respectively correspond to the traditional planetary ball milling, double high energy ball milling and circulating stirring Samples prepared with high energy ball milling composite process. First, the relative density of the above three ceramic samples measured by ISO 1183-1: 2012 (GB/T 1033.1-2008) standard method was 92.7% and 96.5%, respectively.
Secondly, it can be seen from Fig. 4(a) that there are obvious cracks and voids between the ceramic grains fired by the conventional planetary ball milling powder. It can be seen from Figure 4(b) that the grain size of the ceramic sample prepared by the circular stirring-high energy ball milling composite process is significantly increased and there are small white grains filled between the grains, making its structure compact and almost no obvious voids and cracks. Therefore, its densification is superior to the other two processes.

Figure 4. The SEM photographs of CaTiO$_3$-NdAlO$_3$ dielectric ceramic samples prepared by different ball milling processes.

Figure 5. The EDS spectrum of white ceramic grain in the insert picture as shown in Figure 4. Figure 5 shows the EDS spectrum of the white grains shown in the inset in Figure 4(c). It can be seen that its chemical composition complies with the molecular formula of 0.3NdAlO$_3$-0.7CaTiO$_3$, which shows that no aluminum-rich type is found inside the grains and at the grain boundaries. The secondary phase[7]. Therefore, the crystal structure of the sample prepared by the circulating stirring-high energy ball milling method is a single-phase orthogonal perovskite crystal form, which is
completely consistent with the XRD pattern shown in FIG. Using the test method shown in Figure 2, the dielectric constants ($\varepsilon$) of the corresponding dielectric ceramic test pieces of Figures 4(a) and 4(b) were measured to be 42.5 and 45.1; the temperature coefficient ($\tau_f$) was $26.7\times10^{-6}$/K and $1.39\times10^{-6}$/K. It can be seen that the dielectric properties of the ceramic powder fired dielectric ceramics produced by the composite process of high-energy ball milling and cyclic stirring meet the technical requirements of resonant components for microwave devices with both high dielectric constant and extremely low temperature coefficient.

3.2. Microwave device performance analysis

Figure 6 shows the single-cavity test system and quality factor of the TE mode dielectric ceramic resonator produced by CaTiO$_3$-NdAlO$_3$ dielectric ceramic batch trial production based on the high-energy ball milling and circulating stirring composite process (test center frequency is 2250 MHz). The results show that the quality factor of TE-01 mode dielectric ceramic resonators based on CaTiO$_3$-NdAlO$_3$ dielectric ceramics based on high-energy ball milling and circulating stirring composite technology can reach more than 22,000.

![Figure 6. TE mode dielectric ceramic microwave resonator samples and test results for quality factor.](image)

Fig. 7 shows the design structure and the physical and its "temperature drift" performance simulation and actual test curves of the TE-01 cavity filter integratedly assembled using the above TE mode ceramic resonator. Among them, (a) is the full-cavity design structure diagram of the TE01 cavity filter; (b) the S-parameter response curve of the simulated design dielectric filter; (c) is the microwave dielectric of the cavity filter shown in (a) Performance measurement curve. As can be seen from Figure 7(b) and (c), the waveform of the S-parameter response curve reflects the correctness of its cross-coupling in both simulation and measured data; and the passband frequency of the cavity filter is relatively different at different temperatures. The drift of the center frequency is only 0.22~0.35MHz (insertion loss <90dB), which fully meets the technical requirements of the TE cavity filter for communication base stations (the center frequency is 2.3GHz, the "temperature drift" index is 0.20~0.40MHz) (Insertion loss <90dB)).
Figure 7. TE-01 mode cavity filter integrated by dielectric ceramic resonators and its "temperature drift" test curve.

4. Conclusion
High-performance CaTiO$_3$-NdAlO$_3$ dielectric ceramic materials were prepared by different preparation processes. The phase composition, microstructure and microwave dielectric properties of CaTiO$_3$-NdAlO$_3$ dielectric ceramics were analyzed, and the preparation of CaTiO$_3$-NdAlO$_3$ dielectric ceramics by circulating stirring-high energy ball milling was discussed. The passband frequency stability of the resonant element integrated assembly TM and TE mode cavity filter is as follows:

Compared with the traditional planetary ball milling process, the phase structure of CaTiO$_3$-NdAlO$_3$ dielectric ceramic powders prepared by circulating stirring-high energy ball milling is a single-phase orthogonal perovskite crystal form.

The CaTiO$_3$-NdAlO$_3$ dielectric ceramics obtained by the circular stirring-high energy ball milling composite process have a compact structure, almost no obvious voids and cracks, and its degree of densification is higher than that of the traditional planetary ball milling process and has excellent dielectric properties.

The "temperature drift" index of the cavity filter assembled by the CaTiO$_3$-NdAlO$_3$ dielectric ceramic microwave resonant element prepared by the circulating stirring-high energy ball milling composite process meets the technical requirements of the microwave resonant element and cavity filter used in the communication base station.

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