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Formation characteristics of calcium stannate from SnO_2 and $CaCO_3$ synthesized in CO-CO_2 and air atmospheres

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ABSTRACT

Calcium stannate (Ca_2SnO_4) is a common dielectric ceramic that is generally prepared by a high-temperature solid-state method in an air atmosphere with a roasting temperature of more than 1300 °C. In this study, Ca_2SnO_4 was much more easily synthesized in a CO-CO_2 atmosphere at a relatively low temperature of less than 1000 °C for 30 min. We comparatively investigated the formation behavior and microwave dielectric properties of Ca_2SnO_4 synthesized from tin dioxide (SnO_2) and calcium carbonate ($CaCO_3$) by a solid-state method in air and CO-CO_2 atmospheres using X-ray diffraction, scanning electron microscopy, inductively coupled plasma atomic emission spectroscopy, and vector network analysis. The formation behavior of calcium stannate indicated that the reactions between SnO_2 and $CaCO_3$ in CO-CO_2 and air atmospheres were both controlled by three-dimensional diffusion. In a CO-CO_2 atmosphere, the reaction had a higher reaction rate constant (k) and lower apparent activation energy (E). In addition, Ca_2SnO_4 was synthesized by a low-temperature solid-state method in a CO-CO_2 atmosphere. The results indicated that Ca_2SnO_4 ceramics had a higher dielectric constant and lower dielectric tangent loss than those synthesized by the high-temperature solid-state method in air. However, the synthesis temperature and time were reduced by more than 300 °C and 8 h, respectively.

1. Introduction

In the past few decades, alkaline earth stannates with typical perovskite crystal structure have displayed the advantages of high capacity, low potential, high sensitivity, and chemical stability, so they have been widely used as anode materials for lithium ion batteries [1], ceramic dielectrics [2], fluorescent materials [3], optical devices [4], photocatalysts [5], etc. Calcium stannate is one of the most popular stannates and has attracted more and more attention. $MSnO_3$ (M = Ca, Sr, and Ba) ceramics have a low dielectric constant and small dielectric loss tangent [6]. Generally, a dielectric loss tangent as small as possible is required for most applications. The dielectric constant and dielectric loss tangent are determined mainly by the density (porosity) [7,8]. These materials have highly promising potential for application in a low-capacitance component. They can be applied in numerous modern communication systems, such as mobile radio and wireless communications, as resonators, filters, and antennas.

The high-temperature solid-state method is the most popular industrial synthesis technique for calcium stannate (Ca_2SnO_4) ceramics because of its high productivity and short experimental procedure [9]. Two kinds of calcium stannate of high purity, Ca_2SnO_4 and $CaSnO_3$, are formed by roasting of tin dioxide (SnO_2) and calcium carbonate ($CaCO_3$) samples (Sn/Ca molar ratio of 1:2 and 1:1) at a temperature higher than 1300 °C for more than 10 h in air [10]. Moreover, Ca_2SnO_4 is easily produced through a solid-state reaction ($2CaO + SnO_2 = Ca_2SnO_4$) when the temperature is increased up to 1500 °C for about 4 h for the purpose of obtaining materials for microwave devices [11]. However, in an air atmosphere the solid-state synthesis process for calcium stannate is characterized by a higher temperature and a longer time. In addition, much research on the synthesis of calcium stannate has been conducted by different methods, including use of a peroxide precursor [12], a self-heat-sustained reaction method [6], co-precipitation [13], sol-gel combustion [14], a hydrothermal method [15], and a reverse microemulsion method [16]. The main reaction mechanisms and experimental conditions are listed in Table 1. Through these methods, Ca_2SnO_4 with greater homogeneous granularity was synthetized at relatively low temperatures. However, these methods have very low productivity, so most of them are conducted only on a laboratory bench scale. Low sintering temperature material with good microwave dielectric properties can be used for microwave device applications such as dielectric resonator antennas [17].

Roasting of SnO_2 and $CaCO_3$ in a low-temperature solid state in a CO-CO_2 atmosphere has been performed by the authors' group [18]. It

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Table 1
Comparison of the main reaction mechanisms, characteristics and experimental conditions for the formation of calcium stannate by different methods.

Method	Reaction mechanisms	Experimental conditions
Peroxide precursor	$SnCl_4{\cdot}5H_2O + 2Ca(OH)_2 = 2CaCl_2 + SnO_2{\cdot}H_2O(s) + 6H_2O(g)$ $2CaO + SnO_2 = Ca_2SnO_4$	Prepared solid precursors, roasting at 400 °C for 4 h
Sol-gel combustion	$Sn(C_2O_4) + C_6H_8O_7 + H_2O_2 + Ca(NO_3)_2 \rightarrow Ca_2SnO_4 + CO_2 + H_2O + NO_2$	Liquid reaction for 7 h, calcination at 900 °C for 6 h in air
Hydrothermal	$2CaCl_2 + 2Na_2SnO_3 = Ca_2SnO_4 + 4NaCl$	Hydrothermal treatment at 140 °C for 10 h, calcination at 500 °C for 5 h
Self-heat-sustained reaction	$Sn(l) + 2Ca(NO_3)_2 = Ca_2SnO_4(s) + 4NO_2(g)$	Heating at 250 °C for 4 h, then temperature raised gradually to 800 °C for 4 h, calcination at 1100 °C for 12 h
High-temperature solid state	$2CaO + SnO_2 = Ca_2SnO_4$	Roasting at 1300–1500 °C for 4–10 h in air

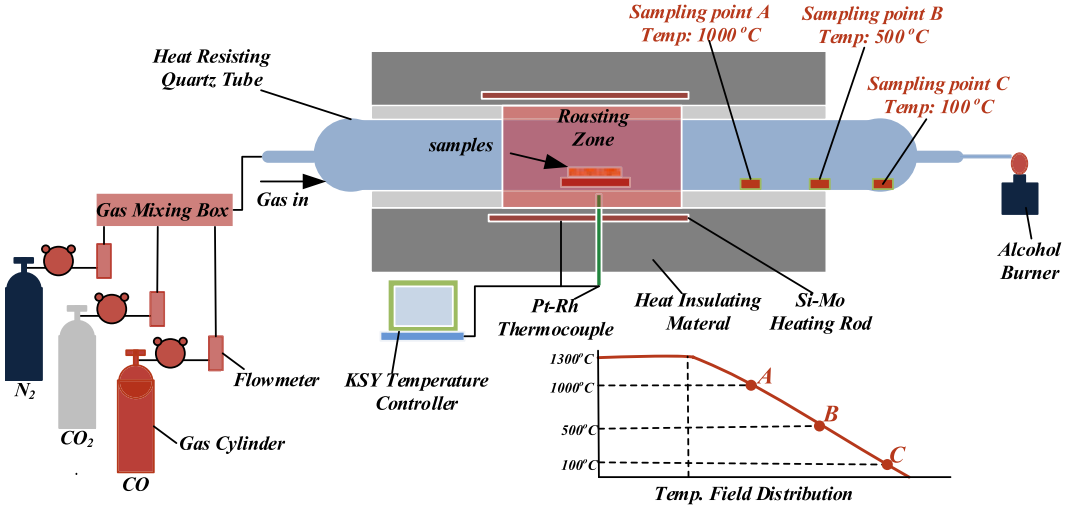

Fig. 1. The equipment for roasting.

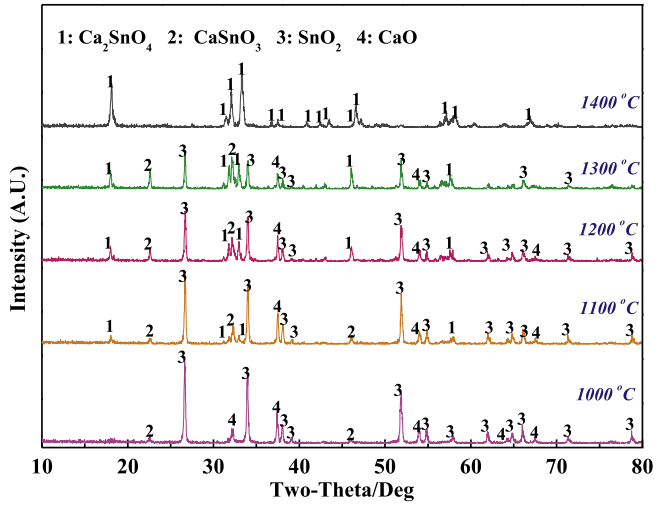

Fig. 2. X-ray diffraction patterns of the products roasted at different temperatures in an air atmosphere (30 min).

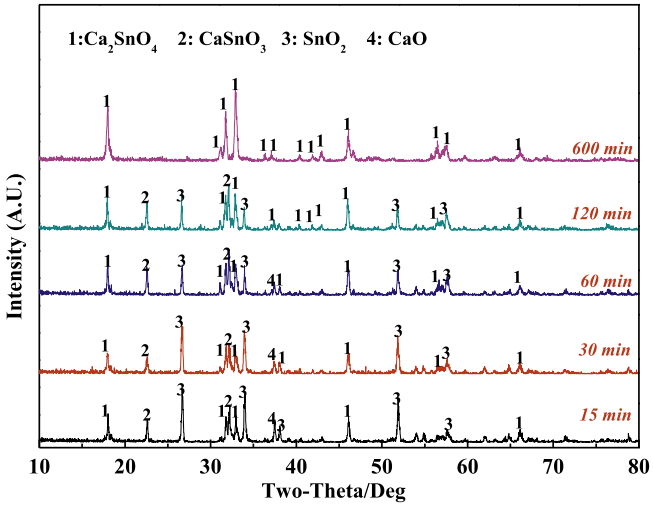

Fig. 3. X-ray diffraction patterns of the products roasted at 1300 °C for different roasting times in air.

was found that Ca_2SnO_4 can be synthesized from SnO_2 and $CaCO_3$ mixtures, which were roasted in a 5–20 vol% $CO/(CO + CO_2)$ atmosphere at 800–1000 °C [19,20]. However, the formation behavior and formation kinetics of calcium stannate synthesized in a CO-CO_2 atmosphere were not revealed, and the dielectric properties of the synthetic products were uncertain.

In the present study, the phase conversion of SnO_2 and $CaCO_3$ samples roasted in air and CO-CO_2 atmospheres was firstly determined. Then we compared the formation kinetics and microwave dielectric properties of calcium stannate products synthesized in different atmospheres.

2. Materials and methods

2.1. Materials

$CaCO_3$ powders were purchased from Changde Fine Chemical Co. Ltd. SnO_2 powders were bought from Tianjin Kernel Chemical Reagent Co. Ltd. The purity of the raw materials ($CaCO_3$ and SnO_2) was more than 99.95 wt%. The two samples were preground by their being passed through a 0.037 mm sieve, and their average particle size was measured as 0.73 μm by a Mastersizer 2000 laser particle size analyzer (Malvern Instruments, United Kingdom). The gases used in this study included