

Preparation and properties of pressureless-sintered dense calcite ceramics



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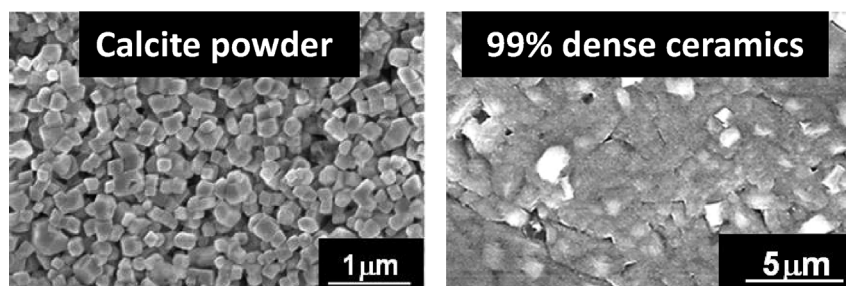
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HIGHLIGHTS

- Calcite powder was sintered to 99% density in air.
- Sintering aid in the LiF - NaF - KF eutectic mixture was used.
- Mechanical, thermal, and electrical properties were evaluated.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper describes a method for pressureless sintering of calcite (CaCO_3) powders and the physical properties of the obtained dense calcite ceramics. Eutectic mixture of the KF - NaF - LiF system was found to be a good sintering aid that promoted the densification and the grain growth of calcite. Calcite sample with high relative density of 99.0% was attained on sintering the calcite fine powder at temperatures as low as 723 K for 3 h in air, without calcite undergoing thermal decomposition. Particle size of the calcite powder was found to be an important factor in achieving densification. The thermal conductivity and dielectric constant were found to be close to those of calcite single crystals; however, Vickers hardness and Young's modulus were lower than those of calcite single crystals. Thermally stimulated depolarization current of calcite ceramics was higher than that of calcite single crystals and hydroxyapatite ceramics.

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1. Introduction

Calcium carbonate, calcite, aragonite, and vaterite, is known to exhibit a high biocompatibility and a good bioresorbability [1–3]. The marine coral, consisting mainly of aragonite, and its phosphorylated derivatives, the framework of which closely resembles

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the human cancellous bones, have been clinically used as bone augmentation materials [4,5]. However, the synthetic calcium carbonate materials intended to be used for biomedical applications are either fine powders or microspheres because it is difficult to fabricate calcium carbonate monoliths in dense or porous forms.

The main reason for the difficulty in consolidating calcium carbonate into bulk monoliths is that calcium carbonate decomposes into calcium oxide and carbon dioxide on heating above 900 K in ambient atmosphere [Eq. (1)], making it difficult to sinter calcium carbonate.



However, numerous potential advantages exhibited by the calcium carbonate monoliths including their biological compatibility have prompted many attempts to consolidate calcium carbonate into bulk monoliths using various methods. Ishikawa et al. [6–8] prepared a porous monolith of CaCO_3 having a porosity of 40% by exposing $\text{Ca}(\text{OH})_2$ green bodies to an atmosphere of CO_2 and H_2O , with a strategy based on the setting phenomenon of lime plaster. Tempieri et al. [9] fabricated porous calcium carbonate monoliths having a microstructure from natural wood via a multistep process starting from pyrolysis of wood followed by the successive conversion of the resultant carbon to CaC_2 , CaO , and subsequently to CaCO_3 without disturbing the microstructure. Attempts for preparing dense CaCO_3 ceramics have been carried out employing an extremely high pressure of 1 GPa [10], pulsed direct current hot-pressing [11], hydrothermal hot-pressing [12–14] or sintering of calcite under high-pressure CO_2 atmosphere (0.2 MPa) [15,16], and the latter method resulted in the production of a material with a high relative density of 93.4% as compared to the theoretical density of calcite (2.711 g/cm^3). Pressureless sintering of calcite in the presence of sintering aids has also been investigated. He et al. [17,18] sintered calcite at 923 K in air using phosphate glass as the sintering aid; however, no description on the sintered density was provided. Other sintering aids such as lithium fluoride [19,20], lithium carbonate [21], sodium carbonate [22,23], and lithium phosphate have been used [24]; however, the properties of the resultant ceramics have not been well described.

In the present work, we prepared dense calcite ceramics by pressureless sintering in air. Eutectic mixture of the KF - NaF - LiF system was selected for the process for achieving the liquid phase formation at a temperature as low as possible. Monodisperse calcite fine powder was used for achieving a high sinterability. The physical, mechanical, thermal, and electrical properties of the resultant ceramics were evaluated.

2. Experimental

2.1. Sample synthesis

Two kinds of calcite powders were used as the raw materials. Powder A, monodisperse calcite powder with an average diameter of approximately 150 nm and a chemical purity of 99.8%, was supplied from Shiraishi Kogyo Kaisha Ltd., Hyogo, Japan. Powder B, a calcite powder of commercial chemical reagent having an average diameter of 12–15 μm and a chemical purity of 99.5%, was obtained from Kanto Chemical Co., Inc., Tokyo, Japan. The sintering aid was prepared by mixing KF, NaF, and LiF in the molar ratio of 40: 11: 49, which corresponds to the eutectic composition of the ternary system with the eutectic temperature of 736 K [25]. The sintering aid was mixed with powder A or B in the ratios of 0.3, 0.6, 1.2, 2.5, and 5.0 mass%. The mixed powders were dry-milled overnight to ensure homogeneous mixing. The powder samples were then slightly wet with a small amount of ethanol (typically 3 drops of

ethanol from an injection needle for 0.5 g powder mixture), and then uniaxially pressed into disc-shaped green compacts with a diameter of 15 mm under a pressure of 2.0 MPa. The role of ethanol was to reduce the friction among the CaCO_3 particles for uniform compression. No other additives such as dispersants or binders were used. The green compacts were sintered in air at temperatures between 693 and 813 K for 3 h. A heating rate of 10 K/min was used. Fig. 1 shows the micrographs of both the powders obtained after mixing with the sintering aid.

2.2. Characterization

In order to roughly estimate the liquid formation temperature, differential thermal analysis (DTA) measurements were carried out with the pristine sintering aid and 50: 50 mixture (mass ratio) of powder A and the sintering aid. The DTA measurements were conducted at a heating rate of 10 K/min with a thermal analyzer (Evo II, Rigaku, Tokyo, Japan).

The sintered specimens were characterized using a scanning electron microscope (SEM, e-SEM, Shimadzu Rika Corp., Tokyo, Japan and JSM-6330F, JEOL, Ltd., Tokyo, Japan) for examining their microstructure, an X-ray diffractometer (XRD, Mini Flex, Rigaku, Tokyo, Japan) for determining the crystalline phases, and by the Archimedeian method using ethanol as the substituting liquid for measuring the relative density. The density of calcite, 2711 kg/m^3 , was used as the theoretical density because of the following two reasons: the real density of the reaction products in the KF - NaF -

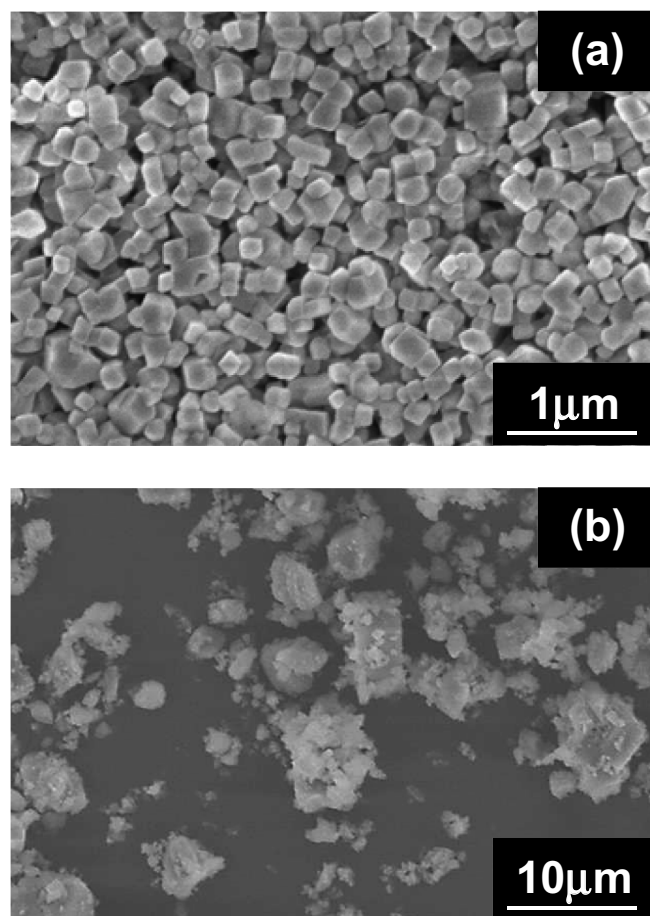


Fig. 1. SEM images of the CaCO_3 powders mixed with the sintering aid; (a) powder A and (b) powder B.

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