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Effects of packing fraction and bond valence on microwave dielectric properties of $A^{2+}B^{6+}O_4$ (A^{2+}: Ca, Pb, Ba; B^{6+}: Mo, W) ceramics

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Abstract

Microwave dielectric properties of $A^{2+}B^{6+}O_4$ (A^{2+}: Ca, Pb, Ba; B^{6+}: Mo, W) ceramics were investigated as a function of packing fraction and bond valence. For $A^{2+}B^{6+}O_4$ specimens sintered at 800–1100 °C for 3 h, a single phase with a tetragonal scheelite structure was detected, and the theoretical density was higher than 93% throughout the composition. Although the ionic polarizability of Ba^{2+} ion was larger than that of Ca^{2+} ion, the dielectric constant (K) of $BaB^{6+}O_4$ showed a smaller value than that of $CaB^{6+}O_4$. These results could be attributed to changes of the packing fraction due to the effective ionic size. The $Q{\cdot}f$ value was largely dependent on the packing fraction, as well as the percentages of theoretical density. The temperature coefficients of the resonant frequencies (TCFs) of the specimens were affected by the bond valence of oxygen. The specimens of $CaMoO_4$ sintered at 1000 °C for 3 h showed the K of 10.8, $Q{\cdot}f$ of 76,990 GHz and TCF of −22.8 ppm/°C, respectively.

Keywords: Scheelite structure; Dielectric properties; Packing fraction; Bond valence; Sintering

1. Introduction

During the past couple of decades, IC (Integrated Circuit) technologies have been very successfully developed to meet demand by integrating an increasingly higher number of transistors on the chip, and most electronic systems have been compacted while offering high performance and numerous functions. These integration activities will be accelerated and the working frequencies will be higher in the future (3G Mobile (2.5 GHz), Bluetooth (2.5 GHz), GPS (Global Positioning System) (12.6 GHz), LMDS (Local Multipoint Distribution Services) (24–40 GHz), Automotive (77 GHz)).

With tremendous demand for immediate entertainment, instant access to information, and communications anywhere at any time, dielectric materials for technologies related to the integration of passives have been researched for the fabrication of microelectronic components for use in electronic systems and devices. Applicable material systems for integration technologies, MMIC (Monolithic Microwave Integrated Circuits) technology of thin film, MCIC (Multilayer Ceramic Integrated Circuits) technology based on LTCC (low-temperature co-fired ceramics),[1] and Embedded Passives technology of ceramic–polymer composites based on a multilayer PCB (Printed Circuit Board)[2] are strictly restricted, and several approaches[3] and modifications[4] such as circuit technology and process improvements have been undertaken to overcome these limitations. Most investigations on material systems for GHz application are mainly based on empirical approaches, such as the addition of materials[5] and/or formation of solid solutions[6] with suitable dielectric properties to the target, and the changes of dielectric properties have been explained by the dielectric mixing rule[7] and structural change.[8]

Due to the nature of materials, their dielectric properties are strongly dependent on the chemical nature of constituent ions, the distance between cations and anions and the structural characteristics originating from the bonding type as well as the composition of materials. The fundamental relationships between the structural characteristics and the dielectric properties should also be identified in order to effectively seek out new dielectric materials for GHz applications. Several types of material system such as AO_2, ABO_3 and $A(B, B')O_3$ have been investigated to search the relationships between

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microwave dielectric properties and the characteristics of crystal structure.[9–11] Therefore, the present study focuses on the dependence of the microwave dielectric properties of scheelite compound, $A^{2+}B^{6+}O_4$ (A^{2+}: Ca, Pb, Ba; B^{6+}: Mo, W) ceramics on its structural characteristics.

2. Experimental procedure

$A^{2+}B^{6+}O_4$ (A^{2+}: Ca, Pb, Ba; B^{6+}: Mo, W) was prepared by the conventional mixed oxide method. $CaCO_3$, PbO, $BaCO_3$, MoO_3, and WO_3 powders with high-purity (99.9%) were used as starting materials. They were milled using ZrO_2 balls for 24 h in ethanol and then dried. The dried powders were calcined from 400 to 700 °C for 3 h, and then milled again for 24 h. The milled powders were pressed into 10 mm diameter disks under pressure of 1500 kg/cm^2 isostatically. These disks were sintered from 800 to 1100 °C for 3 h in air.

Crystalline phases of the specimens were identified with powder X-ray diffraction patterns (D/Max-3C, Rigaku, Japan). Microstructure was observed using a scanning electron microscope (JSM6500F, JEOL, Japan). Bond lengths of the specimens were obtained from geometric calculations based on Rietveld refinements of XRD patterns. The dielectric constant (K) and Q value at frequencies of 10–11 GHz were measured by the post-resonant method developed by Hakki and Coleman.[12] TCF was measured by the cavity method[13] at frequencies of 10–11 GHz and a temperature range of 25–80 °C.

3. Results and discussion

3.1. Crystal structure and physical properties

$A^{2+}B^{6+}O_4$ (A^{2+}: Ca, Pb, Ba; B^{6+}: Mo, W) scheelite compound crystallize in tetragonal symmetry with four molecules per unit cell (space group: $I4_1/a$), as shown in Fig. 1. A-site and B-site ions are positioned at the corner and face-center of the primitive unit cell, respectively, while the oxygen ion is located at the corner of a tetrahedron that also include two A-site ions and one B-site ion. Each B-site ion is surrounded by four oxygen ions, while eight oxygen ions are near to the A-site ion due to the ionic size differences between the A-site and B-site ions. The coordination number of oxygen ion, i.e., 3, agrees well with the neutrality condition of Pauling's law. A- and B-site bond strengths, defined by the ionic valence over the coordination number, are 2/8 and 6/4, respectively. The total charge of cations to oxygen ions is the summation of the bond strength multiplied by the coordination number on each cation site: $(2/8 \times 2) + (6/4 \times 1) = 2$, which corresponds to the charge of oxygen ion. Therefore, the coordination numbers of A- and B-sites and oxygen ions are 8, 4, and 3, respectively. Each ionic position in a unit cell could be described as follows[14]: A-site cation ((0, 0, 1/2), (1/2, 0, 1/4), (1/2, 1/2, 0), (0, 1/2, 3/4)), B-site cation ((0, 0, 0), (0, 1/2, 1/4), (1/2, 1/2, 1/2), (1/2, 0, 3/4)), Oxygen ion ((x, y, z), $(-x, -y, z)$, $(x, 1/2+y, 1/4-z)$, $(-x, 1/2-y, 1/4-z)$, $(-y, x, -z)$, $(y, -x, -z)$, $(-y, 1/2+x, 1/4+z)$, $(y, 1/2-x, 1/4+z)$, ($x = 0.241$, $y = 0.151$, $z = 0.081$)).[14]

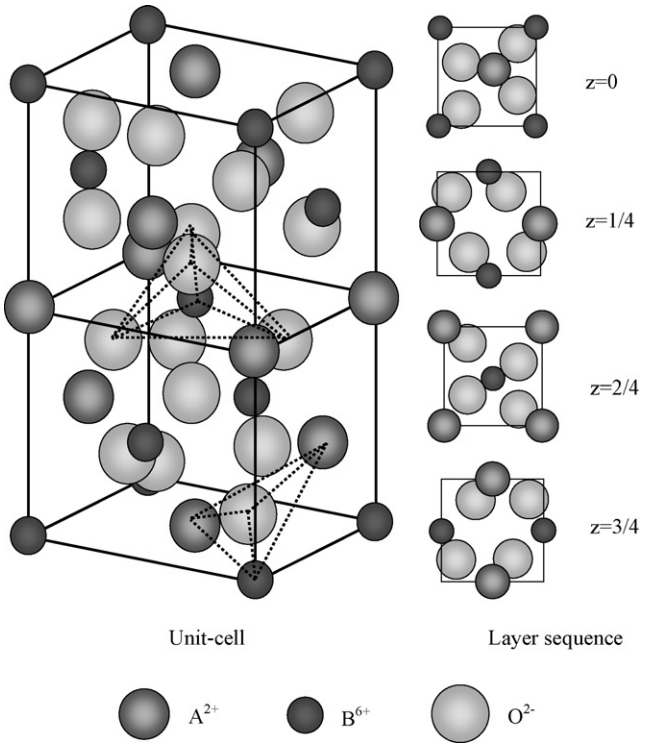

Fig. 1. Crystal structure of $A^{2+}B^{6+}O_4$ scheelite compund.

Assuming a hard sphere of ions, the bond lengths from the A- and B-site cations to oxygen ions could also be obtained from each ionic position and lattice parameters based on geometry, as shown in Eqs. (1)–(4): there are eight bond lengths for the A-site cation to oxygen ion ($d_{A–O}$), where four of the bond lengths are identical, and two sets of different bond lengths, while four bond lengths for the B-site cation to oxygen ion ($d_{B–O}$) are identical.

Four of bond lengths $d_{A–O}$

$$= \sqrt{\left\{\left(\frac{1}{2} - x\right) \times a\right\}^2 + \left\{\left(\frac{1}{2} - y\right) \times a\right\}^2 + (z \times c)^2} \quad (1)$$

Two of bond lengths $d_{A–O}$

$$= \sqrt{\left\{\left(\frac{1}{2} - x\right) \times a\right\}^2 + (y \times a)^2 \left\{\left(\frac{1}{4} - z\right) \times c\right\}^2} \quad (2)$$

Two of bond lengths $d_{A–O}$

$$= \sqrt{\left\{\left(\frac{1}{2} - \mathbf{y}\right) \times a\right\}^2 + (x \times a)^2 \left\{\left(\frac{1}{4} - z\right) \times c\right\}^2} \quad (3)$$

Four of bond lengths $d_{B\text{-}O}$

$$= \sqrt{(x \times a)^2 + (y \times a)^2 + (z \times c)^2} \quad (4)$$

where a and c are lattice parameters, and $x = 0.241$, $y = 0.151$, and $z = 0.081$ are parameters for the position of the oxygen ion, respectively.