

# Microwave dielectric properties of $\text{Ca}_2\text{P}_2\text{O}_7$

Jian-jiang Bian, Dong-Wan Kim, Kug Sun Hong\*

*School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul, South Korea*

## Abstract

Microwave dielectric properties of  $\alpha$ - and  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  ceramic materials were investigated, by a network analyzer at the frequency of 10 GHz. It was found that  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  could be sintered at 1150 °C for 2 h with high bulk density (98% TD) and  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  could be sintered at 1290 °C/4h with bulk density of 95.8% TD. The dielectric constant ( $\epsilon_r$ ) of  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  sintered at 1150 °C/2 h is 8.4, the temperature coefficient of resonant frequency ( $\tau_f$ ) is  $-53$  ppm/°C, and the  $Q \times f$  value is 53,500 GHz.  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  sintered at 1290 °C/4 h has  $\epsilon_r$  of 7.8,  $\tau_f$  of  $-97$  ppm/°C and  $Q \times f$  value of 14,115 GHz.

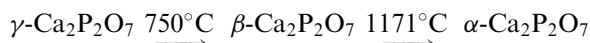
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## 1. Introduction

With the rapid development of modern microwave communication system, such as mobile telephones, high quality microwave dielectric ceramics have attracted much scientific and commercial attention. In the case of microwave substrate application, low dielectric constant less than 10 are ideal values for integrated circuits. In addition, substrate materials should have low dielectric loss ( $\tan\delta$ ) and low temperature coefficient of resonant frequency ( $\tau_f$ ). Materials that have been investigated which could be possible substrate include  $\text{Al}_2\text{O}_3$  and rare-earth aluminates (such as  $\text{LaAlO}_3$ ).<sup>1,2</sup> Although these compounds exhibit good microwave dielectric properties, the search for new materials with much better sintering and microwave dielectric properties continues.

Pyrophosphate  $\text{Ca}_2\text{P}_2\text{O}_7$  is a compound with dichromate structure. Its current applications lie mainly in the fields of luminescence and biomaterials.<sup>3,4</sup> The crystal structure of  $\text{Ca}_2\text{P}_2\text{O}_7$  has been extensively studied.<sup>5,6</sup> X-ray diffraction studies of  $\text{Ca}_2\text{P}_2\text{O}_7$  show that it exists in three different forms depending on the temperature of firing:<sup>7</sup>



Lattice parameters of the two crystal phases are listed in Table 1. The crystal structures of  $\alpha$  and  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  generated using the ATOMS software developed by Eric Dowty,<sup>8</sup> are shown in Fig. 1.  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  is tetragonal and the high temperature form of  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  crystallizes in the monoclinic space group. Each of the two independent pyrophosphate groups is an essentially eclipsed configuration with a P–O–P angle of 131°, 138° for  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and angle of 130° for  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$ .

Apart from the investigation of crystal structure and luminescence characteristics, to the best of our knowledge, no dielectric properties have been reported for  $\text{Ca}_2\text{P}_2\text{O}_7$ . The intention of this study is to investigate the microwave dielectric properties of  $\alpha$ - and  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ . The microwave dielectric properties are discussed from the point view of bond valence and infrared (IR) reflectivity analysis.

## 2. Experimental procedure

Synthesis of  $\text{Ca}_2\text{P}_2\text{O}_7$  was conducted by using traditional solid-state reaction techniques. High purity  $\text{CaCO}_3$  (99.9%) and  $(\text{NH}_4)_2\text{HPO}_4$  (99%) were used as raw materials. Stoichiometric mixtures of starting materials were homogenized by ball milling with  $\text{ZrO}_2$  media in ethanol for 24 h and calcined at 1000 °C and 1250 °C for 2 h in order to obtain  $\beta$  and  $\alpha$  form  $\text{Ca}_2\text{P}_2\text{O}_7$ , respectively. The calcined powders were then milled again, uniaxially pressed into pellets at the pressure

\* Corresponding author. Tel.: +822-880-8316; fax: +822-886-4156.

E-mail address: kshongss@plaza.snu.ac.kr (K.S. Hong).

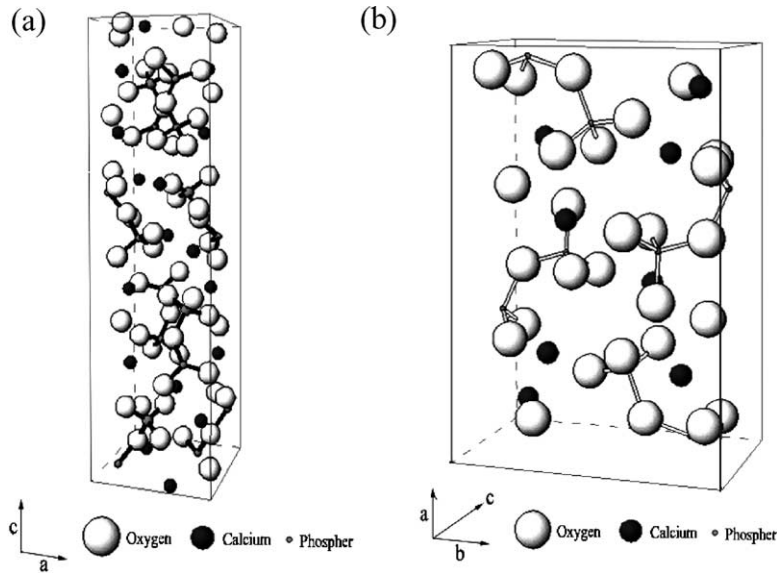


Fig. 1. Unit cell structures of (a)  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and (b)  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$ .

of 1000 kg/cm<sup>2</sup> and sintered at 1150 °C/2 h for  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and 1290 °C/4 h for  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$ .

The phases present in the calcined, sintered and quenched samples were identified by X-ray powder diffraction (XRD) (Model M18XHF, Macscience Instrument, Japan). The bulk density of the sintered specimens was identified by Archimedes' method. The microstructure analysis of the sintered sample was characterized by scanning electron microscopy (SEM) (Model XL20, Philips Instruments, Netherlands). The infrared reflection spectrum was measured using Fourier infrared spectrometer (Model DA8-12, Bomem, ON, Canada) from 400 to 4000 cm<sup>-1</sup>. Microwave dielectric properties of the sintered samples were measured at x-band using network analyzer (Hewlett Packard, Model HP8720C, USA). The quality factor was measured by the transmission cavity method. The relative dielectric constant  $\epsilon_r$  was measured by post resonator method and the temperature coefficient of the resonator frequency ( $\tau_f$ ) was measured using invar cavity in the temperature range from 20 to 80 °C.

### 3. Results and discussion

The XRD patterns of calcined and sintered specimens are shown in Fig. 2. It shows that the powder calcined

at 1000 °C/2 h exhibits a single phase of  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ , and a pure  $\alpha$  form could be obtained when it was fired at 1250 °C/2 h.  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  sintered at 1150 °C/2 h and  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  sintered at 1290 °C/4 h exhibit the same phase as their calcined powders, respectively. A bulk density as high as 98% theoretical density (TD) is obtained when  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  is sintered at 1150 °C/2 h. For  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$ , bulk density of 95.8% TD is obtained when it is sintered at 1290 °C for 4 h (Table 2). SEM photographs of the sintered  $\alpha$ - and  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  are shown in Fig. 3. The  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  exhibits a denser and more homogeneous microstructure than  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$ . It should be noted that there are many micro-cracks penetrating into the grains of  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  [indicated by

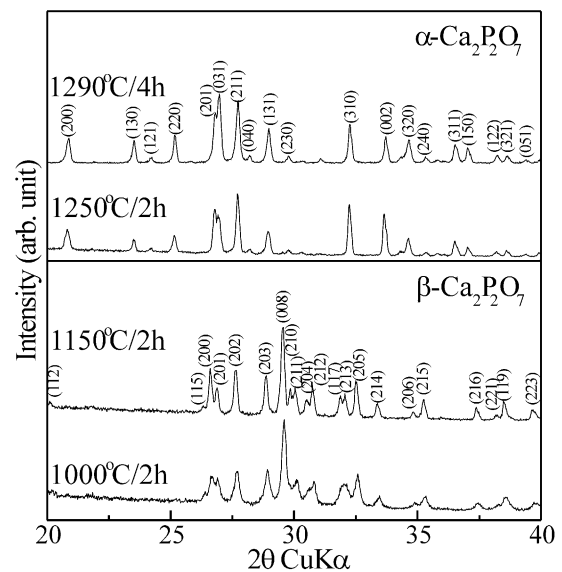


Fig. 2. XRD patterns for  $\alpha$ - and  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  calcined and sintered at different temperatures.

Table 1  
Crystal structure parameters of  $\alpha$ - and  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ <sup>5,6</sup>

$\text{Ca}_2\text{P}_2\text{O}_7$	Unit cell parameters				Space group	Z	$\rho_{\text{calc.}}$ (g/cm <sup>3</sup> )
	a (Å)	b (Å)	c (Å)	$\beta$ (°)			
$\beta$	6.684	6.684	24.144	90	P4 <sub>1</sub>	8	3.129
$\alpha$	12.66	8.542	5.315	90.3	P2 <sub>1</sub> /n	4	2.950

Table 2  
Microwave dielectric properties of the sintered  $\beta$ - and  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>

Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Sintering temperature (°C)	$Q \times f$ (GHz)	$\epsilon_r$ (measured)	$\epsilon_r$ (calc)	$\tau_f$ (ppm/°C)	$\rho_{rel}$ (%)
$\beta$	1150/2 h	53500	8.4	9.426	-53	98.0
$\alpha$	1290/4 h	14115	7.8	8.31	-97	95.8

arrow in Fig. 3(b)]. These micro-cracks are induced by large volume change (6.6 vol.%) caused by the phase transformation between  $\alpha$  and  $\beta$  during the sintering process.<sup>9</sup>

Microwave dielectric properties of  $\alpha$ - and  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> sintered at 1290 °C/4 h and 1150 °C/2 h, respectively, are shown in Table 2. The dielectric constant of  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is 8.4, which is a little higher than that of  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. At microwave frequencies, the total dielectric polarizabilities are the sum of ionic and electronic components. The total ionic polarizabilities can be calculated by the additivity rule with Shannon's ionic polarizability data.<sup>10</sup> The total electronic polarizabilities can be estimated by the equation:  $\epsilon_\infty = (1 + R)^2 / (1 - R)^2$ , where  $R$  is the reflectivity of IR at 4000 cm<sup>-1</sup> (Fig. 4). So, the mean static dielectric constants of  $\alpha$ - and  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> can be estimated by the well-known Clausius-Mosotti equation

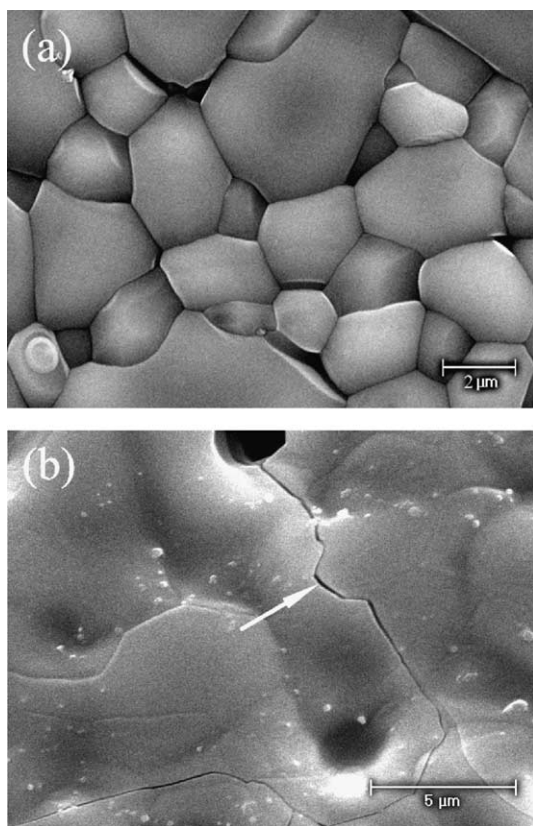


Fig. 3. SEM photographs of (a)  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> sintered at 1150 °C/2 h and (b)  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> sintered at 1290 °C/4 h.

Table 3  
Bond valence sum and average bond strength of P<sup>5+</sup> and Ca<sup>2+</sup> in  $\beta$ - and  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>

Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	$V_{P-O}$	$\langle S_{P-O} \rangle$	$V_{Ca(1)-O}$	$V_{Ca(2)-O}$	$V_{Ca(3)-O}$	$V_{Ca(4)-O}$	$\langle S_{Ca-O} \rangle$
$\beta$	4.7584(4)	1.1896	2.0214(7)	1.9199(9)	2.2087(7)	1.9399(8)	0.2650
$\alpha$	4.8566(4)	1.2142	1.8409(8)	2.0295(8)			0.2419

The coordination numbers of P<sup>5+</sup> and Ca<sup>2+</sup> are shown in parentheses.

(Table 2). It can be seen that the measured relative dielectric constants at a frequency of 10 GHz are almost in agreement with the calculated ones. The slightly lower dielectric constant of  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> than that of  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is mainly due to its higher porosity and lower molecular concentration.

The  $Q \times f$  value of  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is 53,500 GHz, which is about three times larger than that of  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. It is well known that losses in microwave dielectrics consist of intrinsic and extrinsic losses. The former is related to the crystal structure and bonding character of the materials. The bond valence sum ( $V_{P-O}$ ,  $V_{Ca-O}$ ) and average bond strength ( $\langle S_{P-O} \rangle$ ,  $\langle S_{Ca-O} \rangle$ ) of P<sup>5+</sup> and Ca<sup>2+</sup> in  $\beta$ - and  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> were calculated according to the method of Brown<sup>11</sup> (Table 3). Although the observed average bond valence sum for the cations in  $\beta$ - and  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> are all more than 95% of their nominal charges, the individual bond strengths significantly deviate from the ideal value due to the large polyhedral distortion.<sup>8</sup> The average bond strength can be calculated from the average bond valence sum divided by the average cation coordination numbers (Table 3). The average bond strength of P<sup>5+</sup> in  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is 1.1896, which is lower than that in  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (1.2142). In contrast the average bond strength of Ca<sup>2+</sup> in  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is larger than that in  $\alpha$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. Force constants and bond energies increase with the average bond strength for the same type of bond although a quantitative correlation is difficult to determine.<sup>11</sup> According to

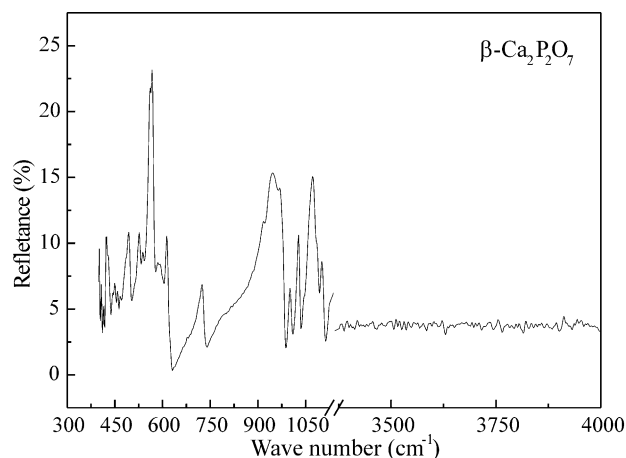


Fig. 4. IR reflectivity spectrum of  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

classic dielectric dispersion theory, intrinsic dielectric losses are mainly related to the anharmonicity of optical lattice vibration modes, which usually can be modeled as an additive system of damped harmonic oscillators. A larger force constant implies a lower damping (weaker anharmonic) constant and hence lower dielectric loss. It implies a reverse influence of  $\langle S_{\text{P-O}} \rangle$  and  $\langle S_{\text{Ca-O}} \rangle$  on the dielectric loss in  $\alpha$ - and  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ . However, it is known that the lowest frequency vibration mode contribution to the microwave dielectric loss is much higher than that of the other modes. The infrared reflectivity spectrum for  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  is shown in Fig. 4. It can be divided into three wave number regions.<sup>12</sup> The modes appearing between 400 and 630  $\text{cm}^{-1}$  are thought to be due to the bending vibration of  $\text{PO}_3$  and rocking vibration of  $\text{O-PO}_3$ . The two modes between 630 and 980  $\text{cm}^{-1}$  can be ascribed to the POP bridge stretching vibrations, and the modes between 980 and 1270  $\text{cm}^{-1}$  should be the stretching vibration of  $\text{PO}_3$ . There are no other vibration modes over 1270  $\text{cm}^{-1}$ . Thus the vibration modes involving  $\text{Ca}^{2+}$  should be lie in far infrared range, outside of the range of experimental measurement. We infer that the intrinsic microwave dielectric losses are due mainly to the vibration modes involving  $\text{Ca}^{2+}$ . On the other hand, the bond strength of  $\text{P}^{5+}$  is much larger than that of  $\text{Ca}^{2+}$  (Table 3). Since the strong bonds will tend to be more covalent, and the weak bonds will tend to be more ionic.<sup>11</sup> Bond valence, therefore, not only measures the number of electrons associated with a bond, but also, in practice, the degree of covalence. The covalence of the P–O and Ca–O bond was calculated by the method of Brown and Shannon.<sup>13</sup> The strong P–O bond gives about 60% covalent character, and the weak Ca–O bond gives about 78% ionic character. The polarization mechanism in microwave dielectrics is mainly due to the cation and anion sublattice displacement induced by an electric field; this is possible only in ionic crystal. So, it is this covalent character of the P–O bond that is responsible for the low dielectric constant of  $\text{Ca}_2\text{P}_2\text{O}_7$ . Hence one may conclude that the intrinsic microwave dielectric losses are mainly from the contribution of the ionic Ca–O bond. Since the average bond strength of  $\text{Ca}^{2+}$  in  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  is larger than that in  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$ , a higher Q value should be expected for  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ , which is in agreement with the experimental data. Furthermore, the inhomogeneous microstructure and micro-cracks in the grains of  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  are the main sources of its extrinsic losses, which is the main reason why the Q value of  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  is much lower than that of  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$ . The  $\tau_f$  of  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  is  $-53$  and  $-97$  ppm/ $^\circ\text{C}$ .

#### 4. Conclusions

$\text{Ca}_2\text{P}_2\text{O}_7$  has low dielectric constant less than 10 because of the covalent character of the P–O bond. Its intrinsic losses are mainly from the contribution of ionic Ca–O bond. The Q value of  $\alpha$ - $\text{Ca}_2\text{P}_2\text{O}_7$  is much lower than that of  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  owing to its weaker Ca–O bond and inhomogeneous microstructure such as micro-cracks introduced by the phase transformation. The  $\beta$ - $\text{Ca}_2\text{P}_2\text{O}_7$  sintered at 1150  $^\circ\text{C}/2$  h has excellent microwave dielectric properties:  $\epsilon_r = 8.4$ ,  $Q \times f = 53,500$  GHz and  $\tau_f = -53$  ppm/ $^\circ\text{C}$ .

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