Microwave dielectric properties of $(Zn_{1-x}Mn_x)_2P_2O_7$

JIANJIANG BIAN
Department of Inorganic Materials, Shanghai University, 149YanChang Road, Zhabei District, Shanghai 200072, People's Republic of China

DONGWAN KIM, KUGSUN HONG
School of Material Sciences & Engineering, Seoul National University, Seoul 151-742, Korea

With the rapid development of modern microwave communication system, such as mobile phones, 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 (τ_f). Some kinds of materials have been investigated such as Al_2O_3 and rare-earth aluminates (such as $LaAlO_3$) [1, 2]. Although these compounds exhibit good microwave dielectric properties, their sintering temperature is as high as 1600 °C. So, the search for new materials with much better sintering and microwave dielectric properties continues. Pyrophosphate $A_2P_2O_7$ (A = Ca, Sr, Ba; Mg, Zn, Mn) have been reported to posses good microwave dielectric properties as well as relative low sintering temperature [3]. Among them, thortveitite-type pyrophosphate α-$Zn_2P_2O_7$ exhibits rather low sintering temperature (875 °C), which is a very promising LTCC material. However, its temperature coefficient of resonant frequency is still too large (−204 ppm/ °C) due to the existence of reversible phase transformation near 130 °C [3]. Another thortveitite-type pyrophosphate $Mn_2P_2O_7$, which has been found to exist in allotropic forms, exhibits relatively low-temperature coefficient of resonant frequency (−95.8 ppm/ °C) [3]. The intention of this study is to investigate the microwave dielectric properties of $(Zn_{1-x}Mn_x)_2P_2O_7$.

Synthesis of $(Zn_{1-x}Mn_x)_2P_2O_7$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0) was conducted by using traditional solid-state reaction techniques. High purity ZnO (99.9%), Mn_3O_4 (99.9%), and $(NH_4)_2HPO_4$ (99%) were used as raw materials. Stoichiometric mixtures of starting materials were homogenized by ball milling with ZrO_2 media in ethanol for 24 hrs and calcined at 800 °C/2 hrs. The calcined powders were then milled again, uniaxially pressed into pellets at the pressure of 1000 kg/cm^2 and sintered at the temperature from 875 to 1100 °C for 2 hrs. The sintering temperature increased with the increase of Mn content and optimized until highest bulk density was obtained.

The phase constituting the calcined and sintered samples were identified by X-ray powder diffraction (XRD) (Model M18XHF, Macsciense Instrument, Japan). The bulk density of the sintered specimens was identified by Archimedes' method. Linear shrinkage behavior was measured using a horizontal-loading dilatometer with alumina rams and boats (Model DIL 402C, Netzsch Instrument, Germany). Microwave dielectric properties of the sintered samples were measured at the frequency of about 10 GHz using network analyzer (Hewlett Packard, Model HP8720C, USA). The dielectric constant was measured according to the Hakki–Coleman method [4] using the TE_{011} resonant mode. Silver-coated copper was used for the conducting plate. The quality factor was measured by the transmission cavity method using the TE_{011} resonant mode which has been widely used by researchers [5, 6]. A cylindrical copper cavity having the same aspect ratio as the cylindrical sample and a ratio of the cavity diameter over the sample diameter between 2 and 3 was used here. The sample was placed in the cavity on a low-loss Teflon spacer. The conductor losses can be neglected even for very high Q values of the dielectric material [5]. The temperature coefficient of the resonator frequency (τ_f) was measured using the invar cavity according the method described above in the temperature range from 20 to 80 °C.

The XRD patterns of calcined $(Zn_{1-x}Mn_x)_2P_2O_7$ powders are shown in Fig. 1. It indicates that the sample with $x = 0.1$ exhibits the isotypical structure to α-$Zn_2P_2O_7$, and a continuous solid solution of phase isotypical to $Mn_2P_2O_7$ could be formed when $0.2 \leq x \leq 1.0$, which is in agreement with the results in the literature [7]. The existence of mixed phases between α-$Zn_2P_2O_7$ and $Mn_2P_2O_7$ could not be distinguished by powder diffraction. Substitution of Mn^{2+} for Zn^{2+}(increasing x) results in a small displacement of unit cell parameters, which are indicated by the shift of the peak position in the XRD patterns.

Fig. 2 shows the shrinkage behaviors of the compact samples. The pure α-$Zn_2P_2O_7$ exhibits a rapid shrinkage above 700 °C and reaches the shrinkage of about 16% at 875 °C. For $Mn_2P_2O_7$, rapid shrinkage occurs above the temperature of about 900 °C and reaches the shrinkage of about 14% at 1000 °C. In contrast, the shrinkage of $(Zn_{1-x}Mn_x)_2P_2O_7$ solid solution does not occur as rapidly as that of α-$Zn_2P_2O_7$.

The dielectric constant at the microwave frequency (10 GHz) of the sintered samples is shown in Fig. 3. The dielectric constant of the solid solution increases firstly and then decreases with the increase of $Mn_2P_2O_7$

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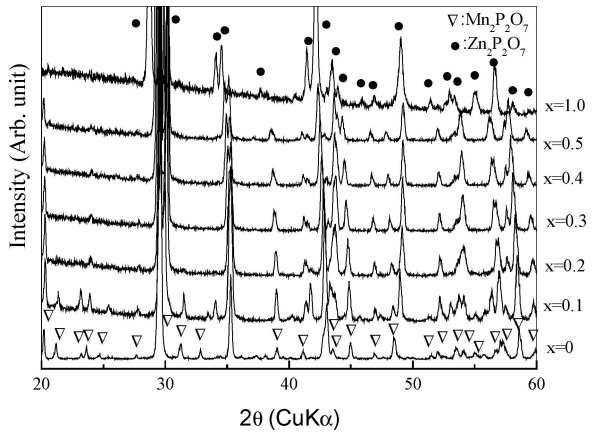

Figure 1 XRD patterns of $(Zn_{1-x}Mn_x)_2P_2O_7$.

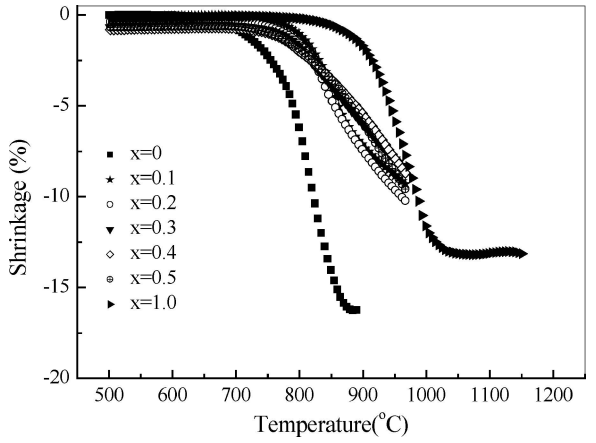

Figure 2 Shrinkage behavior of $(Zn_{1-x}Mn_x)_2P_2O_7$ as a function of temperature.

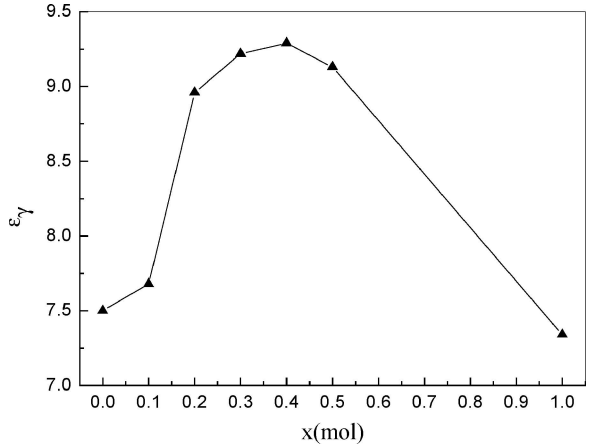

Figure 3 Dielectric constant of $(Zn_{1-x}Mn_x)_2P_2O_7$ as a function of $Mn_2P_2O_7$ content.

addition. The maximum dielectric constant of 9.29 could be obtained when $x = 0.4$. Fig. 4 shows the $Q \times f$ values of the $(Zn_{1-x}Mn_x)_2P_2O_7$ sintered samples as a function of x. It indicates that the $Q \times f$ value decreases with the increase of $Mn_2P_2O_7$addition when $x \leq 0.2$, and remains almost constant with the further increase of $Mn_2P_2O_7$ addition ($0.2 \leq x \leq 1.0$). Fig. 5 shows the temperature coefficient of resonant frequency τ_f as a function of $Mn_2P_2O_7$ addition. It indicates that all samples exhibit negative value of τ_f.

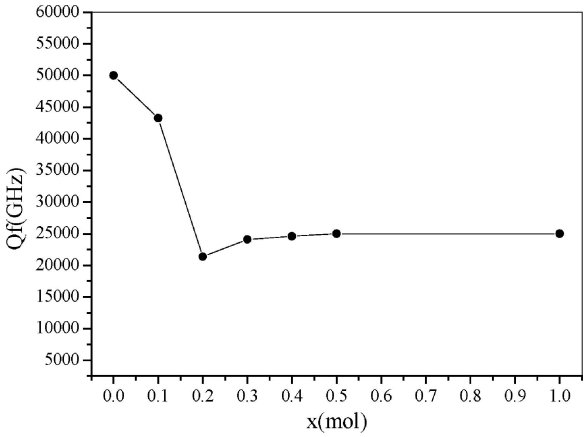

Figure 4 $Q \times f$ value of $(Zn_{1-x}Mn_x)_2P_2O_7$ as a function of $Mn_2P_2O_7$ content.

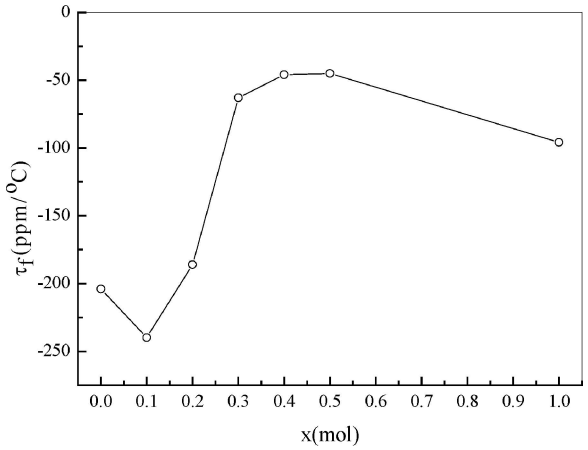

Figure 5 Temperature coefficient of resonant frequency of $(Zn_{1-x}Mn_x)_2P_2O_7$ as a function of $Mn_2P_2O_7$ content.

The absolute value of τ_f increases with addition of $Mn_2P_2O_7$ when $x \leq 0.1$, and decreases greatly with the further increase of $Mn_2P_2O_7$ content ($0.1 \leq x \leq 0.5$) except for pure $Mn_2P_2O_7$. Minimum absolute τ_f value of 45 ppm/°C could be obtained when $x = 0.4$.

TABLE I

	ST (°C)	ρ (g/cm^3)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
$x = 0$	875		7.5	50 000	−204
$x = 0.1$	900	3.65	7.40	16 326	
	950	3.76	7.75	43 243	−240
	1000	3.78	7.68	30 735	
$X = 0.2$	900	3.46	8.23	6 386	
	950	3.65	8.63	21 360	−186
	1000	3.66	8.96	14 697	
$X = 0.3$	900	3.41	8.26	5 943	
	950	3.58	8.80	24 073	−63
	1000	3.74	9.22	16 635	
$X = 0.4$	900	3.52	8.07	19 285	
	950	3.68	8.82	24 587	−46
	1000	3.79	9.29	15 374	
$X = 0.5$	900	3.56	8.09	22 302	
	950	3.70	8.50	24 891	−45
	1000	3.78	9.13	14 845	
$X = 1.0$	1100		7.34	23 847	−95.8

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