

Dielectric Properties of Strontium-substituted Lead Magnesium Tungstate up to Microwave Frequencies

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$Pb_{1-x}Sr_x(Mg_{1/2}W_{1/2})O_3$ ceramics for application in the microwave frequency range were investigated by dielectric constant and X-ray diffraction measurements. The dielectric constant curves showed two concentration dependent characteristics in the $Pb(Mg_{1/2}W_{1/2})O_3$ -rich region. As the Sr content further increases to $x=0.3$ the dielectric curve levels off. In the concentration range between $x=0.4$ and $x=1$ in which dielectric constant dependence on temperature is negligible, it decreases and Qf value increases in the microwave frequency with increasing Sr. The temperature coefficient (τ_ϵ) of the dielectric constant changes from the negative to positive value between $x=0.9$ and $x=1$. The dielectric constant, Qf and τ_ϵ are correlated with the tolerance factor (t). From the X-ray diffraction results for $0.1 \leq x \leq 1$ the cell parameter is found to decrease as x increases and B-site ordering is observed in all the composition ranges.

Key words : $Pb_{1-x}Sr_x(Mg_{1/2}W_{1/2})O_3$, Perovskite, Microwave dielectric, Tolerance factor

I. Introduction

Microwave applications have made remarkable progress together with the recent development of advanced communication systems. The dielectric resonator filter is one of the key components in microwave circuits. The dielectric materials for resonators require the high dielectric constant ($\epsilon > 20$), low loss (Qf > 20000) and the low temperature coefficient of resonant frequency (0~10 ppm/°C). The high dielectric constant makes it possible to reduce the size of the resonator so that size of the electrical circuit can be reduced considerably and the high Qf values enable low insertion loss.

Many ABO_3 and $A(B'B'')O_3$ type perovskite materials have been used for dielectric resonator filters. High ϵ materials such as $(Ca, Pb)Fe_{1/2}Nb_{1/2}O_3$ and $(Ca, Pb)ZrO_3$ have been studied,^{1,2)} on the other hand, high Q-materials such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ ³⁾ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ ⁴⁾ have also been studied. In this study the Sr-substituted $Pb(Mg_{1/2}W_{1/2})O_3$ as a microwave dielectric has been investigated. We report the dielectric properties in the composition range ($0 \leq x \leq 0.3$) of $(1-x)Pb(Mg_{1/2}W_{1/2})O_3 \cdot xSr(Mg_{1/2}W_{1/2})O_3$ system at low frequency and then the same ceramic system in the different composition range ($0.4 \leq x \leq 1$) to show the small dependence of the dielectric constant on temperature is studied at the microwave frequencies. X-ray diffraction analysis has been conducted for $0.1 \leq x \leq 1$. A systematic variation of the dielectric properties of the compounds in terms of tolerance factor is considered.

II. Experimental Procedure

The starting materials were $SrCO_3$, PbO , MgO and

WO_3 . They were mixed with ZrO_2 balls in acetone media for 24 hours, dried in oven and calcined at 870~950°C for 3 hours. The calcined powder was re-milled for 24 hours, and dried again. Disks of 10 mm in diameter and 5~6 mm thick were pressed by cold isostatic pressing at 150 Mpa. To prevent the loss of PbO during sintering, proper PbO atmosphere was maintained by using a mixture of $PbZrO_3$ and ZrO_2 (10 wt%). The sintered ceramics were polished to the precise dimensions to achieve a ratio of thickness to diameter of 0.4~0.5. The dielectric constant ϵ and unloaded Q in the microwave frequency range were measured using the parallel plate method combined with a network analyzer (HP-8720C).

In order to measure the temperature coefficient τ_ϵ of dielectric constant the specimens of 1 mm thick cut from the sintered body for dielectric investigations were electroded with silver paste by firing at 590°C for 5 minutes. The electrical capacitance was measured at a frequency, 100 kHz, using a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer interfaced with a IBM PC/AT, while the test specimen was heated at a constant rate of 2°C/minute.

X-ray diffraction experiments were carried out on a two-circle Rigaku Rotaflex X-ray diffractometer. A curved graphite monochromator was used in order to select $CuK\alpha$ radiation from scattered beam.

III. Results and Discussion

The dielectric properties of the $(1-x)Pb(Mg_{1/2}W_{1/2})O_3 \cdot xSr(Mg_{1/2}W_{1/2})O_3$ system ($0 \leq x \leq 0.3$) were investigated at the frequency of 100 kHz as shown in Fig. 1. Figure 1(a) shows that pure $Pb(Mg_{1/2}W_{1/2})O_3$ has a sharp transition at 39°C as predicted in a previous study.⁵⁾ The dielectric con-

stant curve indicates two phase transitions at $x=0.08$ as shown in Fig. 1(b). As the Sr concentration is further increased to $x=0.12$, only high temperature transition remains whereas the low temperature one disappears. But as the Sr concentration is further increased beyond $x=0.12$, i.e. at $x \geq 0.3$, the dielectric constant vs temperature curve flattens. Thereby even the remaining transition becomes weakened. This clue provides a criterion to study the system as a dielectric resonator because the temperature coefficient of resonance frequency, which is one of the most important factors in dielectric resonator application, is influenced mainly by the ϵ temperature change by the following equation.

$$\tau_f = -\alpha_\epsilon - \tau_e/2 \quad (1)$$

where α_ϵ is the thermal expansion coefficient, usually several ppm in ceramics and almost constant in case of ceramics of similar crystal structure. Therefore, the microwave dielectric properties were mainly investigated in the composition range of $0.4 \leq x \leq 1$ because its ϵ has a small dependence on temperature.

Figure 2 shows the room temperature X-ray powder diffraction patterns of ceramic specimens of compositions in $(1-x)\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3-x\text{Sr}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ for $0.1 \leq x \leq 1$ at room temperature. Single perovskite patterns were obtained in all the samples. The superlattice peaks due to B-site ordering marked by filled square in addition to main reflections were observed in the whole composition range. Pure $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ has two types of different superlattice reflections below its transition temperature (39°C).⁶ One is ascribed to B-site ordering originated from the large valence difference between Mg^{2+} and W^{6+} ions and the other is the extra superlattice reflections attributed to Pb-ion antiparallel displacement. In this composition range no superlattice reflections were observed. The absence of superlattice reflections is associated with

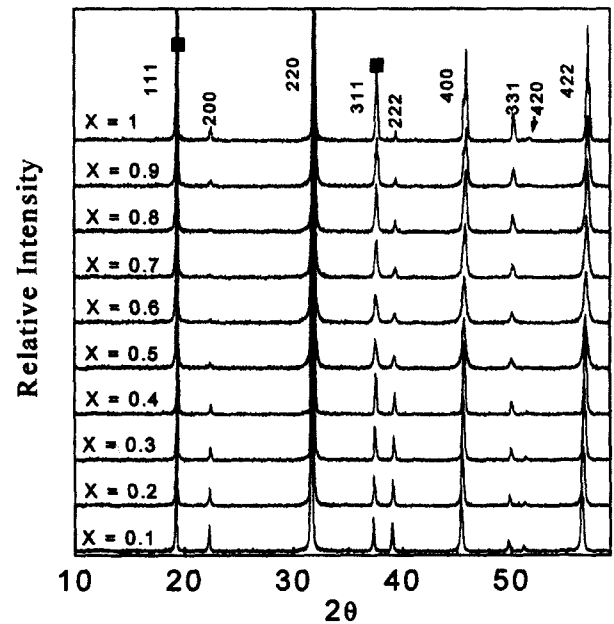


Fig. 2. X-ray diffraction patterns of $(1-x)\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3-x\text{Sr}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ at room temperature.

the lowering of antiferroelectric transition temperature in the dielectric curve. The XRD peaks shift to high angle with increasing Sr content. It means the decrease of lattice parameter corresponding to the substitution of the large Pb-ion by smaller Sr-ion in the solid solution.

The factors which influence the microwave dielectric properties of perovskite oxides for dielectric resonator applications are understood to be tolerance factor that determines the degree of packing of ions in the unit cell. For $\text{A}(\text{B}'\text{B}'')\text{O}_3$ structures tolerance factor t is defined as⁷

$$t = \frac{R(\text{A}) + R(\text{O})}{\sqrt{2} \left(\frac{R(\text{B}') + R(\text{B}'')}{2} + R(\text{O}) \right)} \quad (2)$$

where $R(\text{A})$, $R(\text{B})$, and $R(\text{O})$ correspond to the radii of the A, B and O ions in a complex perovskite structure respectively. It is assumed that for $t < 1$, A-site ions have too much room for vibrations which results in large anharmonicity, i.e., damping of the A-ion phonons which decrease the Q-factor, and similarly, where $t > 1$, B-site ions have too much room. The lowest anharmonicity and therefore lowest microwave loss is expected near $t=1$.⁸

As the Sr content increases in the solid solution the tolerance factor linearly decreases. The ionic radii used to calculate the tolerance factor are from Muller and Roy.⁹ The variation of dielectric constant and the Qf with t is given in Figs. 3 and 4 respectively. It is seen that the dielectric constant decreases and the Qf value increases with the decrease of the tolerance factor which is contrary to what is observed in complex perovskite materials.^{10,11} The previous studies^{10,11} explained the correlation between the dielectric constant and the tolerance factor as responsible for the high Q in $\text{Ba}(\text{B}'\text{B}'')\text{O}_3$ complex perovskite

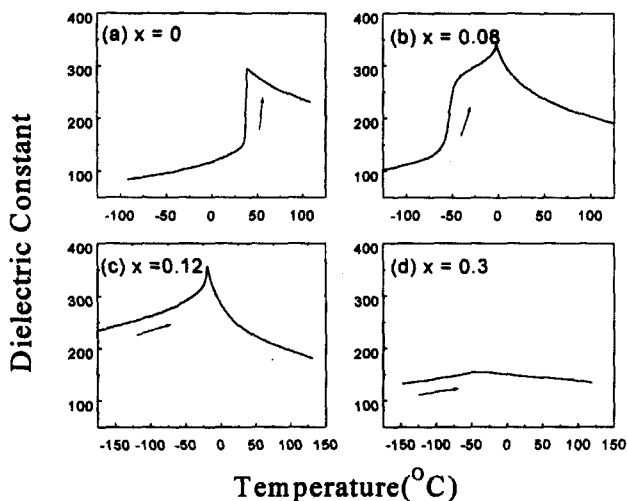


Fig. 1. Temperature dependence of the dielectric constant as a function of Sr concentration (x) at 100 kHz in $(1-x)\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3-x\text{Sr}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$.

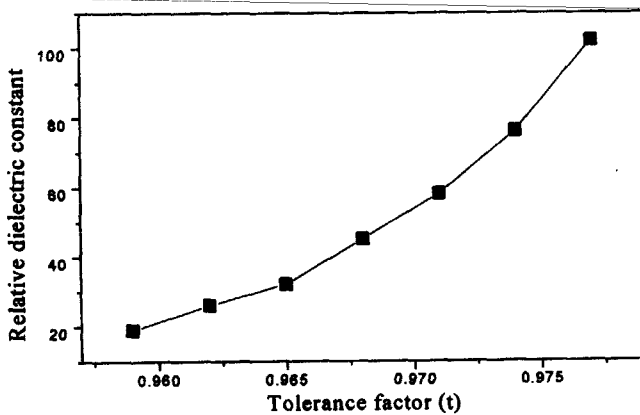


Fig. 3. Variation of relative dielectric constant with t at 4-12 GHz.

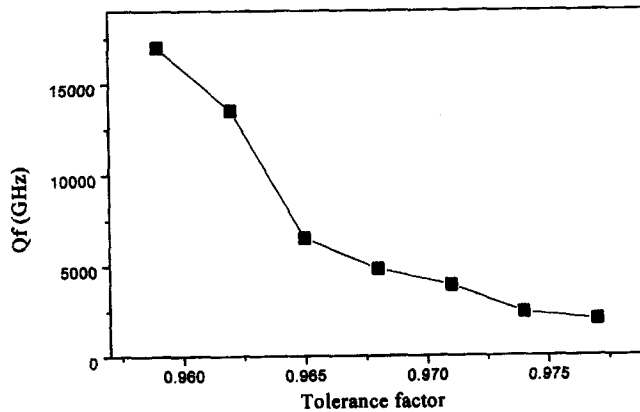


Fig. 4. Variation of Qf with t for $0.4 \leq x \leq 1$ in $(1-x)\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3-x\text{Sr}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$.

ceramics. The frequency of A-BO_6 vibrations, corresponding to the restoring force constant F , increased with the tolerance factor approaching one ($t < 1$). By the equation $\Delta\epsilon' \propto 1/F$, the dielectric constant decreases with the increasing tolerance factor ($t < 1$). The dielectric loss which is strong and inversely dependent upon the dielectric constant increases with the tolerance factor approaching unity. In the present system, B' and B'' -site are fixed as Mg^{2+} and W^{6+} respectively and A-site is varied by the different ratio of Pb^{2+} and Sr^{2+} -ions in comparison with $\text{Ba}(\text{B}'\text{B}'')\text{O}_3$ ceramics of fixed A-site (Ba^{2+}). This variation of A-site ions may change some kind of vibration mode and bring out opposite results from previous studies.^{10,11}

A recent work has directly related changes in τ_ϵ of complex perovskites to the onset of structure phase transitions which involve tilting of the octahedra controlled by the tolerance factor (t).¹²

Figure 5 illustrates temperature dependence of dielectric constant for $0.4 \leq x \leq 1$. The temperature coefficient of the dielectric constant is calculated by the equation

$$\tau_\epsilon = \frac{1}{\epsilon} \frac{d\epsilon}{dT} \quad (3)$$

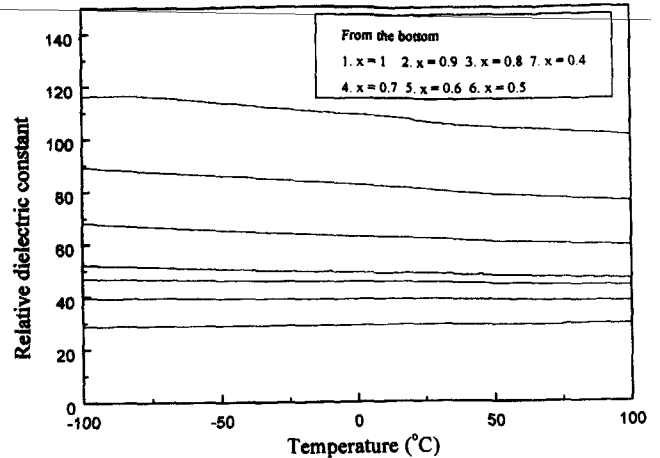


Fig. 5. Variation of relative dielectric constant with temperature at 100 kHz in $(1-x)\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3-x\text{Sr}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$.

Figure 6 shows the tolerance factor t versus τ_ϵ at room temperature. It generally follows the same trend as observed in several complex perovskite materials. All the specimens are included in the tilted region when compared to the diagram reported by Reany *et al.*¹² Pure $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ has no rigid body rotation¹³ while pure $\text{Sr}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ has been found to have two anti-phase tiltings along two different axes and is untilted along the other axis.¹⁴ The substitution of Sr^{2+} for Pb^{2+} may induce some tilting in the system so that the solid solutions for $x \geq 0.4$ are considered to be in the tilted region.

In order to explain the variation of the temperature coefficient of the dielectric constant in terms of structure, a microscope expression is required that relates the dielectric constant and the polarizability of ions in the cell. Bosman and Havinga¹⁵ showed that for cubic ionic compounds the relation between the dielectric constant and the microscopic polarizability can be expressed

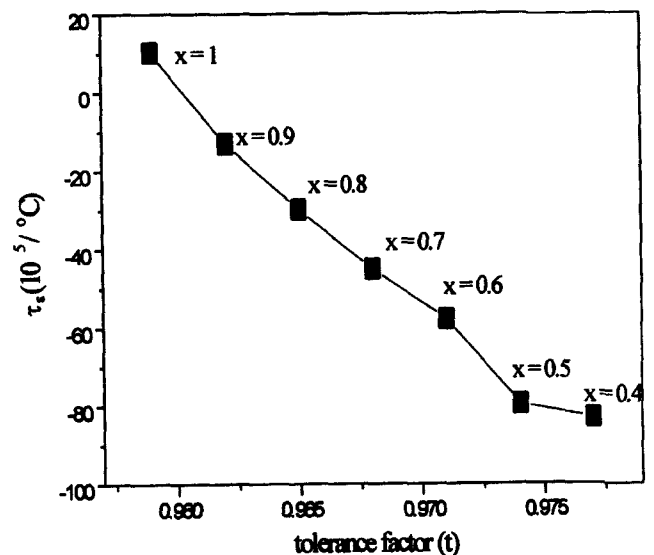


Fig. 6. t versus τ_ϵ in $(1-x)\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3-x\text{Sr}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$.

through the macroscopic Clausius-Mossotti (CM) formula

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3} \frac{\alpha_m}{V} \quad (4)$$

where ϵ is the relative dielectric constant, α_m is the polarizability of a macroscopic small sphere with volume V . Using the CM formula Bosman and Havinga derived an expression for τ_ϵ at constant pressure.

$$\tau_\epsilon = \frac{1}{\epsilon} \frac{d\epsilon}{dT} = \frac{(\epsilon-1)(\epsilon+2)}{\epsilon} \left(\frac{1}{\alpha_m} \frac{d\alpha_m}{dT} - \alpha_L \right) \quad (5)$$

where α_L is the linear thermal expansion coefficient. The last term of the above equation can be expressed into the following terms.

$$\frac{1}{\alpha_m} \left(\frac{\partial \alpha_m}{\partial T} \right)_V + \frac{1}{\alpha_m} \left(\frac{\partial \alpha_m}{\partial T} \right)_P - \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) = A + B + C \quad (6)$$

The first term (A) represents the dielectric dependence of polarizability on temperature. In general this term is negative, i.e., the dielectric constant decreases as temperature increases. The second term (B) represents the increase in the polarizability of ions with increase in the available volume as the temperature increases. The third term (C) represents the decrease in the number of polarizable ions in the unit cell with increase in the temperature as the volume increases. This term is negative. The last two terms B and C are similar in magnitude and opposite in sign. The sum of B and C are negligibly small positive because the positive B term is usually a little larger than the negative C term. According to the data reported by Colla *et al.*¹⁵⁾ the average contribution of terms B+C to τ_ϵ for the complex perovskite material is of the order of 5 ppm/°C.

Since the system studied in the present work comes under similar complex perovskite family it can be assumed the term B+C is almost the same as 5 ppm/°C. Therefore the only term that changes the sign of τ_ϵ is the negative A term representing the temperature coefficient of polarization.

From $x=0.9$ to $x=1$ the τ_ϵ changes from negative into positive value. This variation of τ_ϵ is mainly attributed to the change of magnitude in negative A term. If $|A| < 5$, τ_ϵ is positive for $x=1$; if $|A| > 5$, τ_ϵ is negative for $x=0.9$. The smaller value in magnitude of the A term for $x=1$ than for $x=0.9$ would be explained by the amount of tilting if the tilting is also present for $x=0.9$ as for $x=1$. In the tilted structure the increasing thermal energy with increasing temperature is used up mostly in changing the tilting amplitude; consequently, the energy contributing to the restoring force on the ionic polarization is small, which could provoke a decrease of the A-term value.¹⁶⁾ The value of the A term becomes small. Probably the compound for $x=1$ will be more tilted structure than that for $x=0.9$, so that the A value of the first is less than that of the latter.

IV. Conclusion

The dielectric constant of $(1-x)\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3 \cdot x\text{Sr}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ system at 100 kHz were studied in the composition range of $0 \leq x \leq 1$. The dielectric constant curve in the $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ -rich region showed two anomalies at 100 kHz and has one flattened anomaly with increasing Sr content for $x=0.3$. The composition over $x=0.4$ that is expected to have good microwave properties was investigated. The system showed the dielectric constant between 19 and 100 and the Qf value of 2000–17000 (4–12 GHz) with the addition of Sr content. The Qf value increases and ϵ decreases with decreasing the tolerance factor which is contrary to what is observed in common complex perovskite in which the Qf value decreases and ϵ increases with the decreasing tolerance factor. The change of sign of τ_ϵ from $x=0.9$ to $x=1$ was considered in terms of the variation of magnitude in the temperature coefficient of polarization.

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