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Investigation of the relations between structure and microwave dielectric properties of divalent metal tungstate compounds

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Abstract

The microwave dielectric characteristics of AWO_4 (A = Mg, Zn, Mn, Ca, Sr, Ba) compounds and their relations with structure have been investigated as a function of A cations. Crystal structure was investigated by XRD; the structure changed from wolframite to scheelite with increasing size of A cation. Dielectric properties such as permittivity, temperature coefficient of resonant frequency (τ_f), and quality factors ($Q \times f$) were found to be correlated with the size of A cations and the structure of compounds. Permittivity decreased with the size of A cations, and temperature coefficient of resonant frequency was correlated with unit cell volume. AWO_4 compounds are suitable for the applications of low-*k* dielectric materials; permittivity = 8–15, $\tau_f = -50$ to -70, and $Q \times f = 60{,}000$–$70{,}000$.

Keywords: Microwave processing; Sintering; Dielectric properties; Substrates; Tungstate

1. Introduction

According to the rapid progress in mobile telecommunication technologies, such as mobile phones, high quality microwave dielectric ceramics are strongly required. Ceramics using as a microwave substrate application, should be have low permittivity, high quality factor, and low temperature coefficient of resonant frequency. Al_2O_3, rare-earth aluminates and phosphates have been investigated for using this purpose. Although these compounds have good dielectric properties, they have some demerits such as high sintering temperature. Therefore there are attempts to search for new materials with better microwave dielectric properties.[1–3]

The major natural tungsten ores are formed by the minerals scheelite, (Ca, Sr, Ba)WO_4 and wolframite (Mg, Zn, Mn, Fe)WO_4. Depending on the size of the cation, tungstates can crystallize in either the scheelite or the wolframite structure. Scheelite structures with the tungsten in tetrahedral coordination are formed with large bivalent cations like Ca, Ba, Pb and Sr. Alternatively, with smaller bivalent cations (Fe, Mn, Co, Ni, Mg, Zn) the wolframite structure will be formed with the tungsten in octahedral coordination.[4] AWO_4 compounds have attracted much interest in just their use as scintillating medium and in electro-optic application. For application of microwave dielectric materials, little research has been done.[5,6] So, for investigation of possibility of microwave application, and relations between AWO_4 structure and dielectric properties, we researched the divalent metal tungstate compounds.

2. Experimental procedure

The starting materials used were WO_3 (high purity), ACO_3 (A = Ca, Sr, Ba), Mn_3O_4 and AO (A = Mg, Zn). The powders were mixed for 24 h in a ball mill with ZrO_2 media using ethanol. The mixed slurry was dried and then calcined at 800 °C for 2 h in air. The calcined powders were ground for 24 h in a ball mill. After drying milled powders, the dried powders were pressed into a pellet and pellets were sintered in the temperature range of 1000–1150 °C for 2 h at heating rates of 5 °C/min. The bulk density of the sintered samples was measured by the Archimedes' method. Structure of calcined powders and sintered samples was examined by X-ray diffraction (M18XHF, Macscience Instruments, Japan). Polished surfaces of sintered samples were thermally etched in order to examine their microstructures using a scanning electron microscopy (SEM, JEOL-6330F, JEOL, Japan). The quality factor, the dielectric constant, and the temperature coefficient of resonant frequency

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of the sintered specimens were measured with a HP 8720 network analyzer (Model HP8720C, Hewlett Packard, USA).

3. Results

Figs. 1 and 2 shows the X-ray diffraction of calcined AWO_4 compounds. The single-phase structure of all compounds was confirmed by X-ray powder diffraction. Diffraction peaks shifted to lower angle in the same structure as the radius of cation increased. Structure of AWO_4 changed from wolframite structure (A = Mg, Mn, Zn) to scheelite structure (A = Ca, Sr, Ba). Wolframite structure is monoclinic and scheelite is tetragonal.

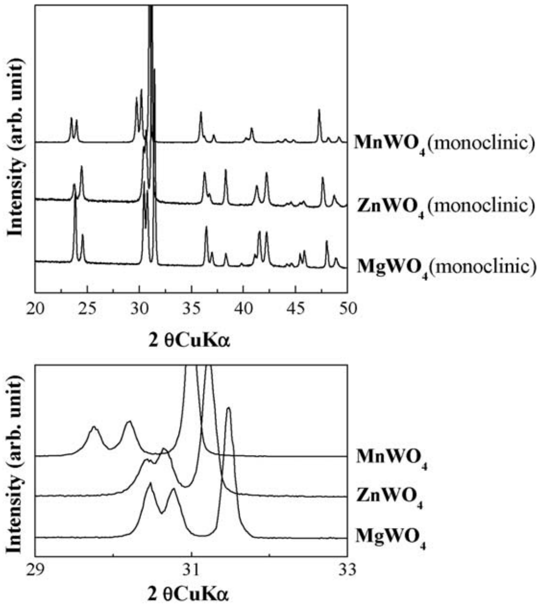

Fig. 1. X-ray diffraction patterns of calcined AWO_4 powders (A = Mg, Zn, Mn).

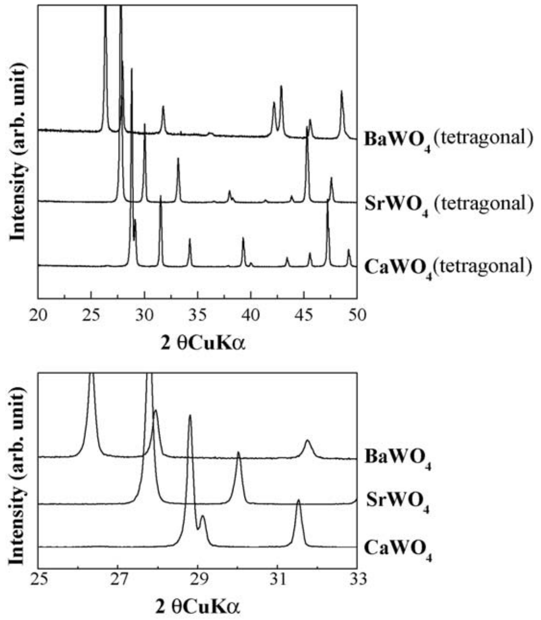

Fig. 2. X-ray diffraction patterns of calcined AWO_4 powders (A = Ca, Sr, Ba).

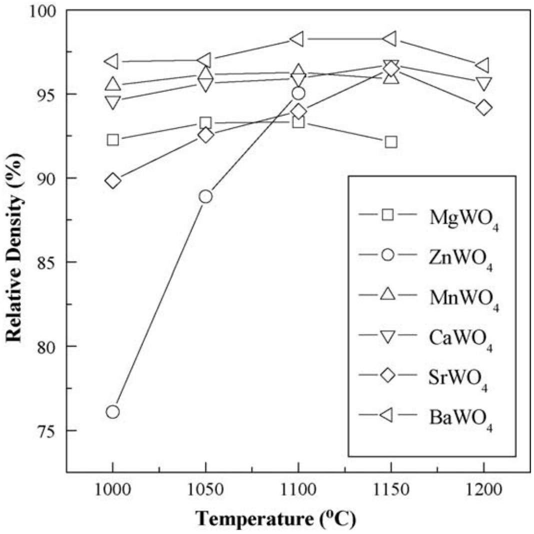

Fig. 3. Bulk density of AWO_4 as a function of sintering temperature.

Table 1
Dielectric properties of AWO_4 compounds

Material	Sintering temperature (°C)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	Porosity
$MgWO_4$	1050	13.5	69,000	−58	0.067
$ZnWO_4$	1100	17.6	65,000	−60	0.050
$MnWO_4$	1100	14.8	32,000	−64	0.037
$CaWO_4$	1150	10.4	63,000	−53	0.033
$SrWO_4$	1150	8.1	56,000	−55	0.035
BaWO4	1150	8.1	57,500	−78	0.017

Fig. 3 shows the bulk relative density of AWO_4 samples. The compounds of AWO_4 could be sintered into dense bodies at the temperature about 1150 °C. Most of the compounds have sintered densities more than 95% of their theoretical densities. The samples of $MgWO_4$, $ZnWO_4$, $MnWO_4$ were melted at 1200 °C, 1150 °C, 1200 °C, respectively.

The SEM micrographs of the surfaces of AWO_4 samples are shown in Fig. 4. Grain size was 3–5 μm and the dense microstructure was confirmed by a SEM.

The dielectric properties of AWO_4 compounds were summarized in Table 1. The samples of scheelite structure had good microwave dielectric properties. In the case of $CaWO_4$, $Q \times f$ was about 60,000 and ε_r about 10, and τ_f about −55 ppm/°C. The compounds of wolframite had higher permittivity than that of scheelite structure.

4. Discussion

Shannon[7] suggested that molecular polarizabilities of complex substances can be broken up into the polarizabilities of constituent ions. In the case of AWO_4, molecular polarizability can estimate from following equation.

$$\alpha(AWO_4) = \alpha(A^{2+}) + \alpha(W^{6+}) + 4\alpha(O^{2-}) \quad (1)$$

where α is polarizability. The dielectric constants of AWO_4 compounds could be calculated with the polarizability from

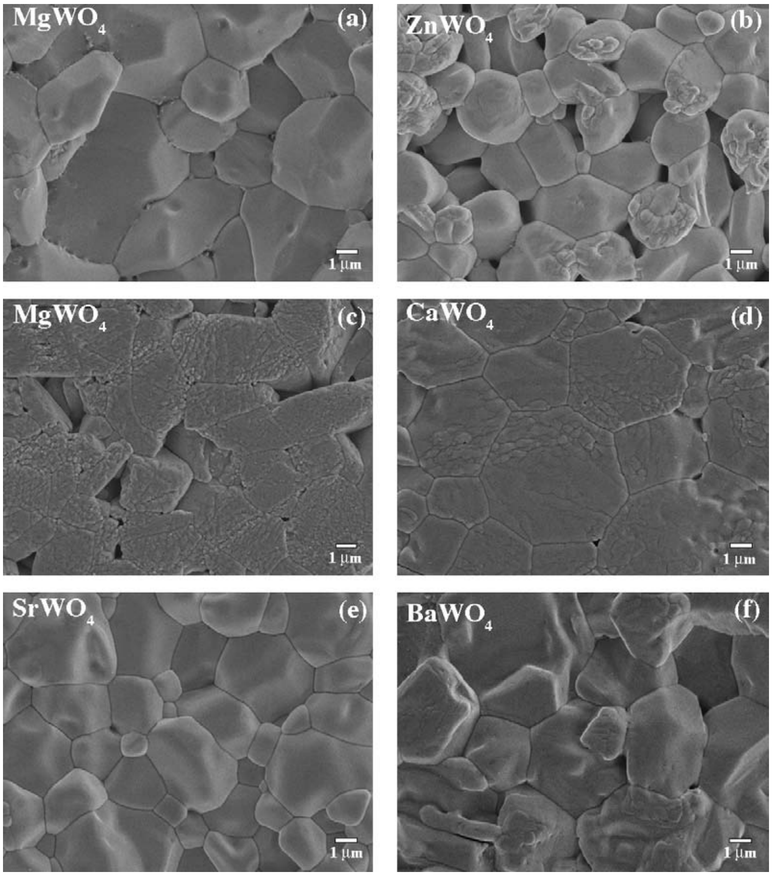

Fig. 4. SEM micrographs of sintered sample of AWO_4: (a) $MgWO_4$ sintered at 1050 °C for 2 h, (b) $ZnWO_4$ sintered at 1100 °C for 2 h, (c) $MnWO_4$ sintered at 1100 °C for 2 h, (d) $CaWO_4$ sintered at 1150 °C for 2 h, (e) $SrWO_4$ sintered at 1150 °C and (f) $BaWO_4$ sintered at 1150 °C for 2 h.

Shannon's suggestion and Clausius–Mosotti relation,[7]

$$\varepsilon_s = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} \tag{2}$$

where V_m is molar volume. Molar volume of AWO_4 can be calculated with the unit cell parameters determined from the diffraction pattern, and the values of molar volume are shown in Table 2. And we calculated the dielectric constants of AWO_4 with 3.2 for the mean value of polarizability of W^{6+} on Shannon's suggestion.[7] The permittivities of AWO_4 compounds are shown in Table 2. The permittivities in the Table 2 were corrected by following equation.

$$\varepsilon_r = \varepsilon^{obs}(1 + 1.5P), \qquad P = 1 - \frac{\rho}{\rho_{th}} \tag{3}$$

Table 2
Polarizability, molar volume, calculated and observed permittivity of AWO_4 compounds

Material	α_D	V_m	ε_s^{cal}	ε_r
$MgWO_4$	12.56	65.55	13.2	13.5
$ZnWO_4$	13.28	65.50	16.3	17.6
$MnWO_4$	13.88	69.50	16.3	14.8
$CaWO_4$	14.4	78.13	11.1	10.4
$SrWO_4$	15.48	87.83	9.5	8.1
$BaWO_4$	17.64	100.25	9.4	8.1

where P is porosity.[9] The calculated and observed permittivities showed good agreement. The wolframite structure has hexagonally close-packed oxygens with certain octahedral sites filled by A and W cations in an ordered way, on the other hands, the scheelite structure has cubic close-packed array of A^{2+} and $[WO_4]^{2-}$ units with the coordination numbers of 8 and 4 oxygen atoms for the A and W cations, respectively. The atmos Ba, Ca and Sr had larger polarizabilities than the atoms of Mg, Zn, and Mn. However, the dielectric constants of wolframite structure were larger than those of scheelite structure. This can be explained by Clausius–Mosotti equation. As Clausius–Mosotti equation, polarizability and molar volume determine the dielectric constant. And as moral volume increase, dielectric constant decrease rapidly.[7] Therefore, compounds of scheelite structure have smaller dielectric constants in spite of larger polarizabilities by their larger molar volumes.

Fig. 5 shows relation between the temperature coefficient of permittivity, τ_ε and unit-cell volume of AWO_4. Generally temperature coefficient of resonant frequency, τ_f is represented by the thermal expansion coefficient, α_l and the temperature coefficient of permittivity, τ_ε as follows:

$$\tau_f = -\alpha_l - \tfrac{1}{2}\tau_\varepsilon \tag{4}$$

The thermal expansion coefficient of ceramic is generally in the range of 10 ppm/°C, therefore the sign and magnitude of

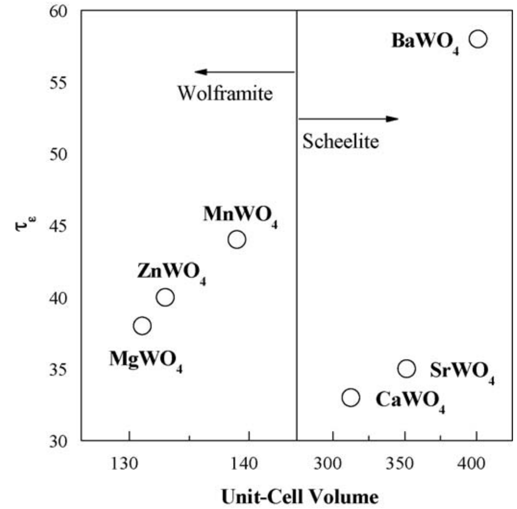

Fig. 5. Temperature coefficient of permittivity of AWO_4 compounds as a function of unit-cell volume.

τ_f depends on τ_ε. From Clausius–Mosotti equation, τ_ε can be derived a following expression.

$$\tau_\varepsilon = \frac{1}{\varepsilon}\left(\frac{\partial\varepsilon}{\partial T}\right) = \frac{(\varepsilon-1)(\varepsilon+2)}{\varepsilon}(A+B+C),$$

$$\left(A = -\frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P, \quad B = \frac{1}{3\alpha_m}\left(\frac{\partial\alpha_m}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P, \right.$$

$$\left. C = \frac{1}{3\alpha_m}\left(\frac{\partial\alpha_m}{\partial T}\right)_V\right) \tag{5}$$

Bosman and Havinga suggested that the terms A and B, which correlate to volume expansion, have very similar in magnitude but opposite in sign, therefore the resulting effect at τ_ε of terms A and B is generally ignored.[8–10] Lee[9] suggested that the term C represents the restoring force acting on the ions and restoring force depends on the shape of potential well, therefore this term correlated with structure and lattice parameter. Since the unit-cell volume has strong correlation with lattice energy, τ_ε is proportional to the relative magnitude of unit-cell volume. As can be seen in Fig. 5 the magnitude of τ_ε increased as the unit-cell volume increased in the same structure of AWO_4.

5. Conclusions

The dielectric properties of AWO_4 have been investigated. AWO_4 are feasible as microwave dielectric materials due to their good dielectric properties, permittivity is 8–17, quality factor is 32,000–69,000, and τ_f is −53 to −78 The changes in permittivities of AWO_4 compounds were described in terms of the difference in ionic polarizability of A cations and molar volume. The temperature coefficients of resonant frequency were shown to be correlated to the unit-cell volume of AWO_4 for both wolframite and scheelite structures.

Acknowledgments

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