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Synthesis, Characterization, and Microwave Dielectric Properties of $Sr_{2-x}La_2Mg_{1+x}W_2O_{12}$ ($x = 0$, 1) Ceramics

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$SrLa_2Mg_2W_2O_{12}$ and $Sr_2La_2MgW_2O_{12}$ ceramics were prepared by the conventional solid-state ceramic route and their dielectric properties were investigated in the radio and microwave frequency regions. $SrLa_2Mg_2W_2O_{12}$ sintered at 1500°C has $\varepsilon_r = 25.2$, $Q_u \times f = 15\,900$ GHz (at 4.9 GHz), and $\tau_f = 0$ ppm/°C. $Sr_2La_2MgW_2O_{12}$ sintered at 1525°C has $\varepsilon_r = 24.7$, $Q_u \times f = 35\,000$ GHz (at 4.7 GHz), and $\tau_f = -83$ ppm/°C. The dielectric properties of these ceramics are reported for the first time.

I. Introduction

The current revolution in mobile communication technology is largely due to the development of temperature-stable dielectric materials having a high dielectric constant and quality factor. These materials have proved to be cost effective, compact, and easily integrable in microwave circuits. They find applications in microwave subsystems such as oscillators, filters, and antennas. The important characteristics required for substrate applications are low-relative permittivity, high quality factor >2000 (at 10 GHz), and low temperature coefficient of resonant frequency in the range of −10 to +10 ppm/°C. The medium permittivities in the range 20–50 are used for satellite communications and in cell phone base stations.[1] Complex perovskite systems such as BMT and BZT have been extensively studied in the literature.[1] The dielectric properties of many tungstate materials such as AWO_4 (A = Mg, Zn, Ni, and Co) and $RE(Ti_{0.5}W_{0.5})O_4$ (RE = Pr, Nd, Sm, Gd, Tb, and Dy) are reported in the microwave frequency range.[2,3] In this communication, we report the radio frequency (MHz) as well as the microwave dielectric properties of two compositions: $SrLa_2Mg_2W_2O_{12}$ and $Sr_2La_2MgW_2O_{12}$. To the best of our knowledge, the microwave dielectric properties of these compositions have not been reported to date. Although the ceramics appear similar at the first glance, they differ significantly in their crystal structure and electronic properties. However, both the ceramics are suitable candidates for applications in microwave circuitry; particularly as substrates in monolithic microwave integrated circuits.

Torri[4] reported for the first time the preparation, defect structure, and characterization of $Sr_{2-x}La_2Mg_{1+x}W_2O_{12}$ ($x = 0$, 1) ceramics. The powder pattern for $SrLa_2Mg_2W_2O_{12}$, in general features, has been shown to be very similar to that of $La_{2.67}(Mg_2W_2)O_{12}$[5] with an orthorhombic cell with parameters $a = 7.841$ Å, $b = 7.858$ Å, and $c = 7.893$ Å. The ions Mg^{2+} and W^{6+} show NaCl-type ordering in the octahedral sites while the A site vacancies show an ordering on the c plane. These A site vacancies appear to be randomly distributed only to half of the A sites in alternate c-planes. The X-ray diffraction (XRD) pattern of $Sr_2La_2MgW_2O_{12}$ is similar to that of $Ba_4(CoRE_2)O_{12}$[5] except for the relative intensity and systematic shift in 2θ. The reflections correspond to a hexagonal cell with $a = 5.5943$ Å and $c = 26.606$ Å. The Mg^{2+} ions occupy all the corner-sharing octahedra and the W^{6+} ions occupy three-face-shared octahedral, which interpose a vacant octahedron.

II. Experimental Procedure

The $Sr_{2-x}La_2Mg_{1+x}W_2O_{12}$ ($x = 0.1$) ceramics were prepared using the conventional high-temperature solid-state synthesis route using high-purity powders of $SrCO_3$, WO_3, $C_4H_2Mg_5O_{14} \cdot 5H_2O$ (>99%; Sigma Aldrich, St. Louis, MO), and La_2O_3 (99%, IRE). Stoichiometric proportions of the chemicals were weighed and ball milled for 24 h using zirconia balls in distilled water media. The slurry was dried and then calcined twice at 1200°C for 6 h. The calcined powders were finely ground, mixed with 4 wt% poly vinyl alcohol (3 wt%; BDH laboratory, Poole, U.K., molecular weight ≈22 000, degree of hydrolysis >98%), and dried. They were then pressed into disk-shaped pucks of 18 mm diameter and 9 mm height at a pressure of about 200 MPa using a tungsten carbide die. The green compacts were fired at a rate of 5°C/min up to 600°C and soaked at this temperature for half an hour to expel the binder. The pellets were sintered in air at temperatures in the range 1350°–1600°C for 4 h. The cooling rate was 3°C/min up to 800°C. They were polished to remove surface irregularities and subsequently characterized to determine the dielectric properties. The phase purity and crystallinity were determined using an X-ray diffractometer (Philips Corp., Almelo, the Netherlands). The bulk density was measured using the Archimedes principle. The dielectric constant and the dielectric loss were measured in the radio frequency region using an LCR meter (HIOKI 3532-50 LCR Hi Tester, Nagano, Japan). The dielectric properties Q_u, ε_r, and τ_f of the materials were measured in the microwave frequency range (2–6 GHz) using a vector network analyzer (Model 8753 ET, Agilent Tech., Palo Alto, CA) with a copper invar resonant cavity and the $TE_{01\delta}$ mode of resonance. The interior of the cavity is coated with silver and a low-loss quartz spacer is used for supporting the ceramic. To measure the coefficient of thermal variation of resonant frequency, the variation of the resonant frequency of the $TE_{01\delta}$ mode was studied in the range of 20°–80°C. The sintered samples were thermally etched by heating $SrLa_2Mg_2W_2O_{12}$ to 1450°C and $Sr_2La_2MgW_2O_{12}$ to 1475°C at a rate of 10°C/min. The samples were kept at these temperatures for 30 min and then cooled to 1000°C at 10°C/min and then allowed to cool to room temperature by natural cooling. The surface morphology of the etched samples was studied

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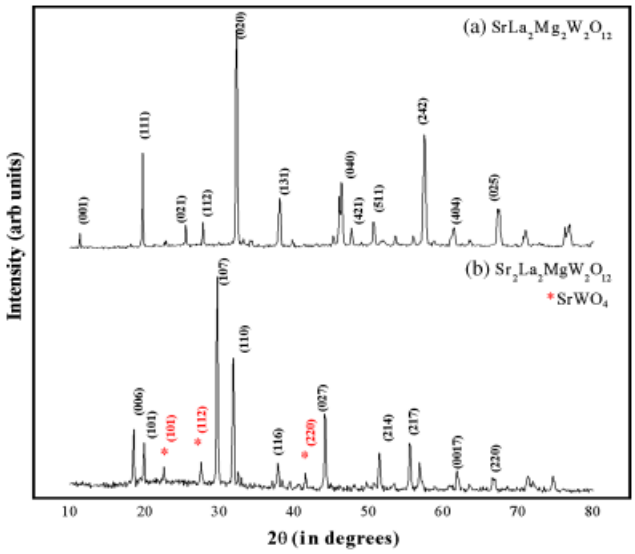

Fig. 1. Powder X-ray diffraction pattern of (a) $SrLa_2Mg_2W_2O_{12}$ and (b) $Sr_2La_2MgW_2O_{12}$.

using a scanning electron microscope (SEM, Model S-2400, Hitachi, Tokyo).

III. Results and Discussion

The room-temperature powder X-ray diffraction patterns of $SrLa_2Mg_2W_2O_{12}$ and $Sr_2La_2MgW_2O_{12}$ are given in Fig. 1. The powder pattern of $SrLa_2Mg_2W_2O_{12}$ is fully indexed as a single-phase orthorhombic crystal (JCPDS file no: 35-0259), while that of $Sr_2La_2MgW_2O_{12}$ is indexed as a hexagonal cell (JCPDS file no: 34-1327). The diffractogram for $Sr_2La_2MgW_2O_{12}$ shows the presence of $SrWO_4$ as a secondary phase. The two phases being $Sr_2La_2MgW_2O_{12}$ and $SrWO_4$, the obtained diffraction pattern is then utilized to determine the volume percentage using the equation,[6]

$$Sr_2La_2MgW_2O_{12}(\text{vol}\%) = \frac{I_{A(107)}}{I_{A(107)} + I_{B(112)}} \times 100 \quad (1)$$

where I_A and I_B are the linear intensities of the main peaks of $Sr_2La_2MgW_2O_{12}$ $(107)_A$ and $SrWO_4$ $(112)_B$, respectively. The intensity calculations indicate the presence of about 4 vol% $SrWO_4$ in the $Sr_2La_2MgW_2O_{12}$ phase. The scanning electron images of the two systems are presented in Fig. 2. Dense grain formation is visible in both the systems with a nearly uniform grain size distribution.

The $SrLa_2Mg_2W_2O_{12}$ showed a densification of 96.2% when sintered at 1500°C for 4 h. The dielectric properties such as the dielectric constant and the dielectric loss are measured for $SrLa_2Mg_2W_2O_{12}$ at 1 MHz. These properties vary substantially with sintering temperature as shown in Table I. The dielectric constant of $SrLa_2Mg_2W_2O_{12}$ is corrected for porosity using the following equation derived by Penn *et al.*[7]

$$(\varepsilon_r)_0 = \varepsilon_r\left(1 - \frac{3P(\varepsilon_r - 1)}{2\varepsilon_r + 1}\right) \quad (2)$$

where $(\varepsilon_r)_0$ is the measured dielectric constant of the compound, which contains a fractional porosity P and ε_r is the actual dielectric constant of the dielectric. The dielectric constant is maximum at 1500°C with $\varepsilon_r = 25.2$ (microwave frequency). The lowest value of the loss tangent is also shown at this sintering temperature with $\tan\delta = 2.1 \times 10^{-4}$. The relationship between dielectric constant and sintering temperature of $SrLa_2Mg_2W_2O_{12}$ shows a similar trend as between density and sintering temperature. The $SrLa_2Mg_2W_2O_{12}$ shows a maximum $Q_u \times f$ of 15 900 GHz (4.98 GHz) at 1500°C and τ_f of 0 ppm/°C, which makes them very attractive materials for practical applications. With a further increase in temperature, the sign of τ_f changes from positive to negative.

The dielectric properties and the variation of density with sintering temperature of $Sr_2La_2MgW_2O_{12}$ are given in Table II. A maximum densification of 92.4% is obtained when sintered at 1525°C. The density of the composites is calculated using the equation

$$\rho_{mixture} = V_1\rho_1 + V_2\rho_2 \quad (3)$$

where V_1 and V_2 are the volume fraction, $\rho_{mixture}$ is the calculated theoretical density and ρ_1 and ρ_2 are the densities of $Sr_2La_2MgW_2O_{12}$ and $SrWO_4$, respectively. The density increased continuously from 1400° to 1500°C and becomes almost constant above 1500°C. The presence of a small amount of low-density secondary phase $SrWO_4$ (theoretical density: 6.35) in $Sr_2La_2MgW_2O_{12}$ decreases the overall density of the matrix. The volume fraction of $SrWO_4$ in the ceramic matrix has been calculated to be about 4% by the intensity analysis of the XRD. The dielectric constant of $Sr_2La_2MgW_2O_{12}$ is calculated from the mixture rule of ceramic composites using the equation[8]

$$\varepsilon_r = V_1\varepsilon_{r1} + V_2\varepsilon_{r2} + V_3\varepsilon_{r3} \quad (4)$$

where V_3 is the volume fraction of porosity, ε_{r1}, ε_{r2}, and ε_{r3} are the dielectric constant of $Sr_2La_2MgW_2O_{12}$, $SrWO_4$, and air ($\varepsilon_{r3} = 1$), respectively, and ε_r is the dielectric constant of the mixed phase ceramic. The dielectric constant increases with the sintering temperature, reaches a maximum of 25.4 at 1 MHz when sintered at 1525°C, and then starts decreasing. Very low dielectric loss tangent of the order of 10^{-4} is also obtained at this sintering temperature. The dielectric constant depends on the density and phase constituents. Because of porosity and the presence of $SrWO_4$ secondary phase with a very low dielectric constant of 8.1,[9] it is believed that the actual value of the dielectric constant of phase-pure $Sr_2La_2MgW_2O_{12}$ is higher than

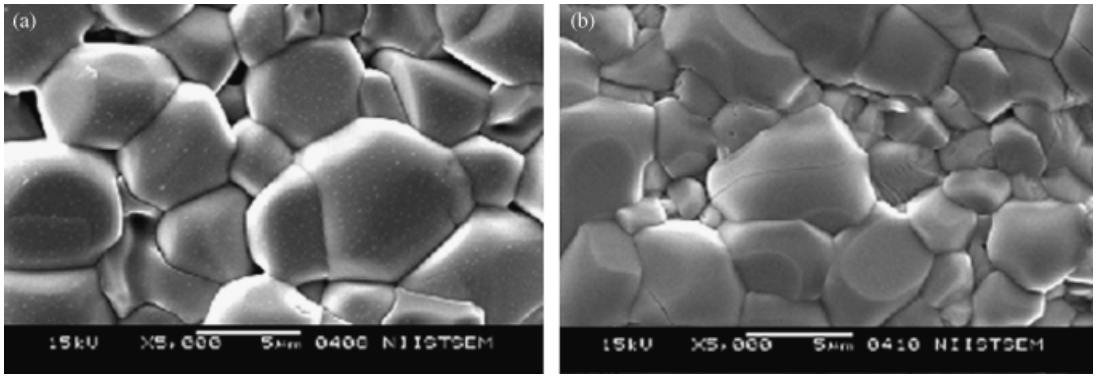

Fig. 2. Scanning electron micrographs of (a) $SrLa_2Mg_2W_2O_{12}$ and (b) $Sr_2La_2MgW_2O_{12}$.

Table I. The Dielectric Properties of $SrLa_2Mg_2W_2O_{12}$ at Radio and Microwave Frequencies

		1 MHz			Microwave frequency region			
Sintering temperature (°C)	Densification (%)	$(\varepsilon_r)_0$	ε_r	tanδ	$(\varepsilon_r)_0$	ε_r	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
1425	93.2	22.6	25.0	4.4×10^{-2}	19.8	21.9	11 800	2.4
1450	94.5	22.8	24.7	9.4×10^{-4}	21.6	23.4	13 300	0.6
1475	94.6	22.9	23.8	6.4×10^{-4}	22.1	23.9	14 300	0.1
1500	96.2	24.0	24.5	2.1×10^{-4}	23.7	25.2	15 900	0.0
1525	95.5	23.6	23.9	9.7×10^{-4}	23.3	24.9	14 250	−1.0

Table II. The Dielectric Properties of $Sr_2La_2MgW_2O_{12}$ at Radio and Microwave Frequencies

		1 MHz			Microwave frequency region			
Sintering temperature (°C)	Densification (%)	$(\varepsilon_r)_0$	ε_r	tanδ	$(\varepsilon_r)_0$	ε_r	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
1450	74.0	15.9	18.8	2.1×10^{-2}	15.0	17.9	14 760	−60.7
1475	87.6	20.8	22.5	1.7×10^{-3}	17.3	18.9	20 260	−66.9
1500	91.4	21.1	22.6	1.3×10^{-3}	19.3	20.7	25 230	−70.9
1525	92.4	23.9	25.4	8.1×10^{-4}	20.5	24.7	35 000	−83.2
1550	92.7	20.1	21.3	8.3×10^{-4}	18.1	19.2	33 200	−84.0

the observed value of 24.7 at microwave frequency. $Sr_2La_2MgW_2O_{12}$ sintered at 1525°C shows a ε_r of 24.7, $Q_u \times f$ of 35 000 GHz, and a τ_f of −83.2 ppm/°C. The $Q_u \times f$ increases with sintering temperature until 1525°C, beyond which it decreases while the τ_f showed a continuous negative increase in magnitude. The high negative τ_f can be partially accounted for by the presence of $SrWO_4$, which itself has a τ_f of −55 ppm/°C.[9]

IV. Conclusion

The dielectric properties of $SrLa_2Mg_2W_2O_{12}$ and $Sr_2La_2MgW_2O_{12}$ ceramics have been studied both at low frequency as well as in the microwave frequency regions. The best dielectric properties of these materials were obtained at 1500° and 1525°C, respectively. $SrLa_2Mg_2W_2O_{12}$ has $\varepsilon_r = 25.2$, $Q_u \times f = 15\,900$ GHz, and $\tau_f = 0$ ppm/°C. $Sr_2La_2MgW_2O_{12}$ has $\varepsilon_r = 24.7$, $Q_u \times f = 35\,000$ GHz, and $\tau_f = -83.2$ ppm/°C. Both the systems have excellent microwave properties, which make them suitable candidates for application as microwave substrates.

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