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Mg_2SnO_4 ceramics
II. Electrical characterization

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Abstract

The inverse spinel-structured Mg_2SnO_4 possessing steady capacitance over the temperature range between 27 and 300°C in a frequency domain spanning nearly four decades has been examined by an a.c. technique. The samples investigated in this study were synthesized by using solid state reaction (SSR) and self-heat-sustained (SHS) techniques. The a.c. immittance (impedance or admittance) measurements in the frequency range 5 Hz–13 MHz were carried out on bodies sintered at 1500°C/6 h and 1600°C/2 h. The acquired electrical data exhibited relaxation in the Z^*-plane alone, in the form of a small arc of a large semicircle. The magnitude of the terminal capacitance was found to be in a narrow window of ~8–11 pF, while the average dielectric constant was about 10. Further analysis also revealed that this material system possessed ultra-low temperature coefficient of capacitance (TCC) and dielectric constant (TCK) along with very small magnitude of loss tangent.

Keywords: Magnesium orthostannate; Stable capacitor component; Electroceramics; Temperature coefficient of capacitance; Temperature coefficient of dielectric constant; Loss tangent

1. Introduction

In high speed computing devices, where temperature is prone to increase due to fast electronic transition and inefficient heat dissipation in smaller volume (which is becoming smaller and smaller due to the emphasis on miniaturization of future devices), research endeavors in this direction are warranted. One common-sense solution to this problem is to increase the number of fans in the device, but the problem is not as simple as to be solved by removing the heat in a fast mode. When the temperature rises, it interferes with functioning characteristics of the electronic components, such as resistors, capacitors and inductors, arranged in a simple or complex fashion within the device. However, most of these components are room temperature or near room temperature materials. That is, their characteristics show sensitive variation with temperature. Thus, with rising temperature, the component behavior changes and the total signal/calculations become erroneous. In most cases, it is the capacitor that shows signs of failure first. Therefore, from a material point of view, it is envisaged that development and incorporation of capacitor components, which have very weak temperature dependence, are very much needed to cater to the need of current and futuristic smart electronic materials.

The temperature coefficient of capacitance (TCC) or dielectric constant (TCK) becomes an important parameter in R-C, R-L, R-L-C or hybrid circuit elements as high dielectric loss results in the generation of heat during the operating processes at normal application conditions (such as at applied voltages, currents, frequencies, temperatures, etc.). This heat generation causes increase in temperature of the capacitors, which in turn makes the functioning of the components complicated. In such applications, the required level of variation with temperature should either be zero (ideally) or a small reproducible value (*negative positive zero*, NP0) that compensates for a variation in the rest of the circuit [1]. As the improved computer and communication technologies are emerging, the electronic information is also progressing in large volume. Therefore, the demand for equipment with accurate and quick information dissemination is growing. To meet these demands, electronic devices must use higher frequencies than ever before, as single-layer

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ceramic capacitors, microchip capacitors can have very high frequencies in the latest information and communication equipment. The non-variance of capacitance and dielectric constant with frequency in the MHz to GHz regime makes the components attractive as microchip capacitors in the telecommunication, microwave, and radio applications. Conventional disc-type monolithic ceramic capacitors resonate at lower frequencies due to the complexing of their lead wires and shapes. This makes them unstable for use in GHz range. Moreover, they are stable only at very restricted temperatures (up to $\sim$105°C). Therefore, materials that exhibit a dielectric constant in the MHz to GHz range, as well as non-variance of capacitance with temperature, are required. Microchip capacitors are compact, lightweight and have simple structure. They are more reliable because they use gold electrodes. These characteristics make them useful for very high frequency applications [2].

The perovskite-structured compounds in the MO–SnO_2 (M = Ca, Sr, and Ba) system, represented as $MSnO_3$, have recently been projected as novel electroceramic material due to their potential applications as novel gas sensors [3–6] and capacitor components in a variety of electronic circuits [7–10]. We have recently reported the synthesis, processing and microstructural evolution in the $MSnO_3$ compounds in ample detail [11–14]. In-depth analyses of the as-acquired a.c. electrical data on sintered bodies of calcium and strontium metastannates have demonstrated their great potential as thermally stable capacitive devices up to about $\sim$300°C [15–17]. Based on intuitive perception, magnesium stannate system was also recently investigated with respect to compound synthesis and sintering behavior [18]. This paper presents, perhaps for the first time, the results of electrical characterization of the dielectric properties of magnesium orthostannate, Mg_2SnO_4.

2. Experimental procedure

Samples used for electrical measurements were synthesized via solid-state reaction (SSR) and self-heat-sustained (SHS) techniques. Details of the materials synthesis and processing have been reported in the previous paper [18], and hence are not repeated here. Electrical measurements were carried out on sintered specimen of finite geometry. As was found earlier [18], the formulation with the molar ratio 2:1 of magnesium to tin consisted of a pure single-phase magnesium orthostannate (Mg_2SnO_4). Therefore, the electrical data were generated on samples derived from 2:1 molar mixtures that were sintered at 1500 and 1600°C for 6 and 2 h, respectively. The a.c. electrical data on sintered samples were acquired over a wide range of applied frequencies (5 Hz $<$ f $\leqslant$ 13 MHz) using the HP4192A LF Impedance Analyzer (Hewlett-Packard, Yokogawa, Japan) at temperatures between 27 and 300°C. The data acquisition was accomplished using a fully automated experimental control via a desktop personal computer as the instrument controller. The small-signal amplitude was about 1 V and the acquired a.c. data were reproducible with the varying signal voltage amplitude. These data were analyzed using a proprietary software package. This package allowed automated data acquisition in any of the desired forms such as, impedance or admittance or phasor, including analyses in the four complex plane formalisms and Bode plane analysis [19–21]. Necessary electrical parameters were extracted from these representations of the a.c. electrical data that employed complex non-linear least-squared (CNLS) curve-fitting. This extraction procedure does not assume or simulate any equivalent circuit configuration a priori, which is often done using commercial software.

Sintered samples of cylindrical geometry ($\sim$12 mm diameter and 1–2 mm thickness) were coated with silver paint (Electrolube Ltd, UK), cured at 500°C for 2 h, and secured between two highly polished circular stainless steel discs (mounted on Perspex walls) serving as electrodes. The sample was fitted with adjustable screws on both sides of the holder. This arrangement allowed better sample-holding capability in the accessories for the HP4192A at room temperature. The stainless steel screws serving as contact electrodes with the silver paint did not exhibit any contribution to the terminal immittance as it formed an ohmic contact (resistance $\leqslant$ 2 Ω). For the acquisition of the a.c. data at elevated temperatures (above room temperature through 300°C), an indigenously designed and fabricated sample holder was mounted on an alumina brick ($25 \times 25 \times 10$ mm^3). To ensure good adherence, high-temperature alumina cement was used and cured at 225°C for 30 min. Gold wires, 0.25 mm in diameter (D.F. Goldsmith Chemical and Metal Corp., Evanston, IL, USA) welded to freshly cut circular gold foils from the same supplier, were used as electrode leads. The samples were snugly sandwiched between the gold foils. Each sample was introduced into the uniform temperature zone of a custom-designed small, low-thermal mass, precalibrated horizontal furnace. The furnace was heated to the desired temperature, at a constant rate of 10°C/min. Sufficient time was allowed to equilibrate at the measurement temperature within the sample before the acquisition of a.c. electrical data. The temperature fluctuations at the measurement points were not more than ±1°C. The sample thickness and the electrode area in all the measurements were kept identical so that the geometric configuration ensured a fixed effect to the terminal immittance data. Thus, the terminal immittance data did not require a state of normalization for the entire analysis. As an example, it can be mentioned that the terminal capacitance can be converted to the relative dielectric constant using the state of normalization.

3. Results and discussion

The acquired a.c. electrical data were in the form of capacitance (Cp) and conductance (Gp) as a function of applied frequency in the range 5 Hz to 13 MHz at temperatures between 27 and 300°C. The data were found to show meaningful relaxation in the Z^*-plane alone. Attempts to represent the data in other complex planes did not yield any meaningful interpretation. Some representative Z^*-plots for Mg_2SnO_4 derived from SSR and SHS techniques and sintered at 1600°C/2 h are shown in Fig. 1. As can be seen, the acquired data forms an arc of a large single semicircle both at 27 and 300°C. A single semicircular relaxation means a bulk (total) behavior, indicating that the individual contributions of different physical regions of the sample (such as grains, grain boundaries, second phases, etc.), were masked and could not be resolved under the experimental conditions employed (viz., temperature, frequency range, etc.). In the fitting procedure, the left-intercept coincides with the intersection of the real and imaginary component axes (zero), so that the sample resistance is given by the length of the fitted chord (i.e. the distance between the origin and the right-intercept) on the x-axis. Fitting of the data showed that the semicircles were depressed (though the depression angles were small; $\theta \sim 2$–8°) signifying that the material under study was a near Debye-like system. In general, the bulk resistance was found to be of the order of 10^7–10^8 Ω, with the samples derived from SSR technique being about 4 times more resistive than those from the SHS technique. Such high resistance implied low capacitance of the material.

On the other hand, the data presented in the form of sample capacitance (C), derived dielectric constant (K) and loss tangent (tan δ), as a function of frequency and the measurement temperature could be more meaningfully interpreted. These results are illustrated in the form of Bode plots in the following subsections. To maintain clarity of interpretations, the discussion is presented according to the method of material synthesis, viz., the solid-state reaction (SSR) or the self-heat-sustained (SHS) technique.

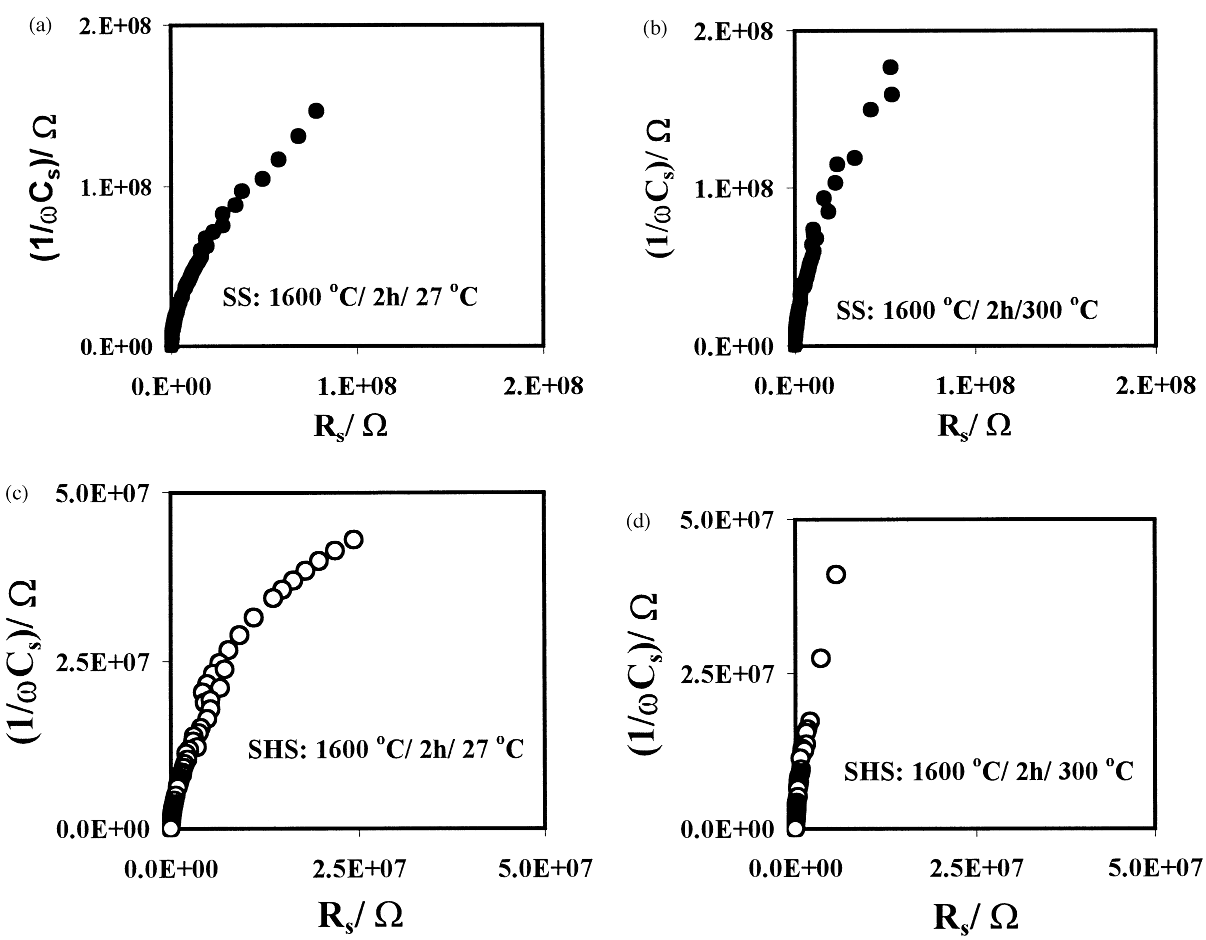

Fig. 1. Some typical impedance plots at different for Mg_2SnO_4. The symbol SS and SHS stands for the solid-state reaction and self-heat-sustained derived samples, respectively; the numbers following these symbols represent the sintering temperature, soak-time and measurement temperature, respectively.

3.1. Electrical behavior of SSR-derived Mg_2SnO_4

The Bode plane representation consisted mainly of the variation of capacitance, computed dielectric constant and loss tangent (dissipation factor) as a function of frequency at the measurement temperature. For a material to be a useful capacitor element, the temperature dependence of its capacitance and the dielectric constant are of prime importance and the commercial quality of the material is adjudged in terms of both these factors [1,2]. Therefore, it is imperative that though the two quantities are intimately related, the dependence of each of them on the operating temperature be evaluated. However, since the terminal capacitance of the sample and the dielectric constant are interrelated to one another through a simple relationship (shown subsequently), for simplicity of representation, frequency and temperature dependence of dielectric constant alone has been illustrated in this paper. It may nevertheless be pointed out at this juncture that the variation of capacitance displayed an identical behavior, both with temperature and applied frequency.

3.1.1. Variation of relative permittivity with temperature

Dielectric constant (relative permittivity, K) is the terminal capacitance which is normalized by using the geometrical factors such as the cross-sectional area and the length/thickness of the material. This quantity was calculated at each of the seven measurement temperatures from the acquired capacitance data using the relationship,

$$K = C(d/A)/\varepsilon_0 \tag{1}$$

where, C = sample capacitance in farad (F); d = sample thickness; A = sample cross-section; ε_0 = permittivity of the vacuum, 8.854×10^{-12} F m^{-1}.

The dielectric constant thus calculated from the as-measured capacitance and sample geometry at various measurement temperatures was plotted as a function of frequency and a typical behavior of Mg_2SnO_4 sintered at 1600°C for 2 h is shown in Fig. 2. An interesting feature of Fig. 2 is that the K-value remained almost parallel to the x-(frequency) axis over a wide range, signifying near zero dependence of K on the applied frequency. This and the fact that no peaks were noticed in the entire frequency domain, brings out that the relaxation observed in this material is not a thermally activated process. From this plot, it is clear that as the sample experienced a gradual rise in temperature from 27 to 300°C, the dielectric constant showed a rather weak dependence on temperature. In addition, at each of these measurement temperatures the capacitance also remained remarkably constant over a wide frequency domain (~3–4 decades). Since the material possesses small capacitance (of the order of a few pF), the dielectric constant value also is small. Therefore, magnesium orthostannate can be classified as a high resistance, low capacitance and low K material. From the linear portions of the K vs $\log f$ plots at different temperatures, average values of dielectric constant were computed. It was found that the average value of K was in the range ~8–10 while the capacitance value was ~8 pF over the range 27° to 300°C. These average values plotted against temperature are shown in Fig. 3 for Mg_2SnO_4 sintered at 1600°C for 2 h. The behavior of samples sintered at 1500°C/6 h was very similar and hence is not repeated. The parametric equations describing the temperature dependence of K obtained from least-squared fitting procedure is also shown on the curve. The near-independence of K on temperature is easily manifested in the very small value of the slope of the straight line. The values of the temperature coefficients of the dielectric constant (TCK) and capacitance (TCC) are listed in Table 1.

3.1.2. Variation of dissipation factor (tan δ)

The as-measured capacitance (C) and conductance (G) values at different temperatures were used to evaluate the

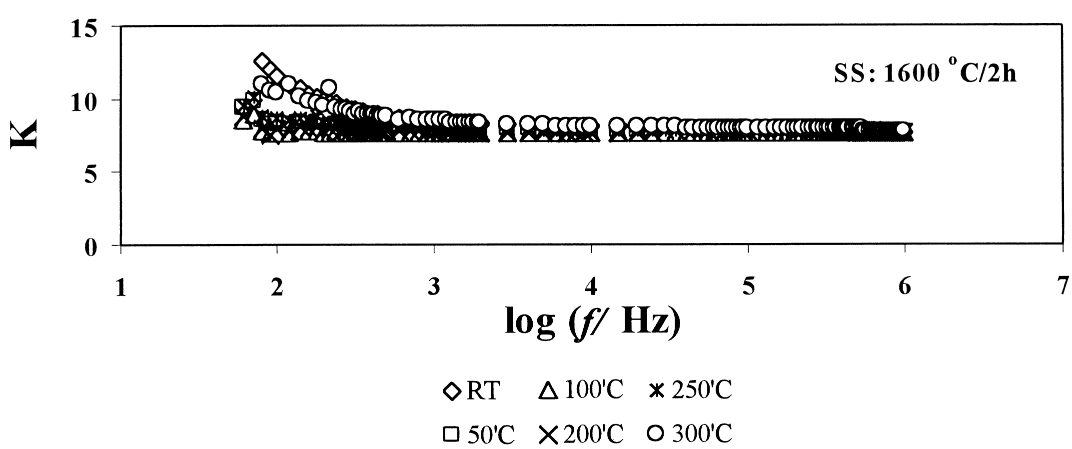

Fig. 2. Temperature-insensitive behavior of dielectric constant of SSR-derived samples sintered at 1600°C/2 h, over a wide frequency range.

loss tangent ($=G_p/\omega C_p$; ω=angular frequency, $2\pi f$) characteristics of the sintered samples. The frequency dependence of dissipation factor at some representative temperatures is shown in Fig. 4. A slight upward trend in loss tangent (as well as in capacitance and dielectric constant) curves in low frequency regions is attributed to the possible electrode polarization effect. Typical values of tan δ(@1 MHz) in SSR derived Mg_2SnO_4 samples sintered at 1600°C/2 h were found to be 9.31×10^{-3} and 3.73×10^{-3} at 27 and 300°C, respectively, that is regarded as very small. In general, the loss factor variations are between zero and 0.1 over about 3 decades of frequency, being infinitesimally small in the 10 kHz–1 MHz regime. At this juncture, it would be interesting to recall that the sintered samples of Mg_2SnO_4 did possess small but a finite amount of porosity in their microstructure [18]. However, near zero values of loss factor obtained here signify that the remnant porosity in fact did not contribute significantly to the loss behavior of the material. This could be attributed to the 'isolated' nature of the pores which do not constitute a connected porous channel which otherwise might have acted as a charge sink and would have led to much larger values of tan δ.

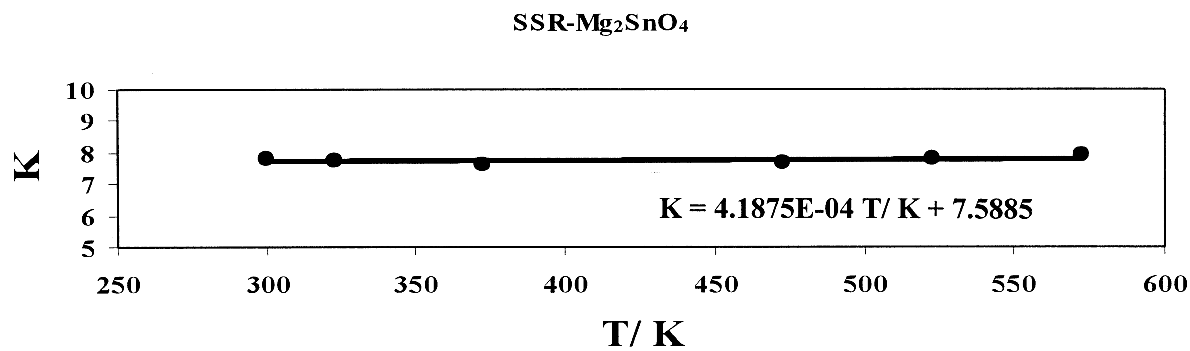

Fig. 3. Temperature dependence of dielectric constant in samples obtained via SSR method and sintered at 1600°C/2 h.

Table 1
Derived values of TCC and TCK for sintered magnesium orthostannate samples

Sample	History	TCC[a] (ppm/K)	TCK[b] (ppm/K)	Range (K)
SSR-Mg_2SnO_4	1500°C/6 h	184.1	185.3	300–573
SSR-Mg_2SnO_4	1600°C/2 h	54.1	53.9	300–573
SHS-Mg_2SnO_4	1500°C/6 h	93.3	92.2	300–573
SHS-Mg_2SnO_4	1600°C/2 h	124.2	124.4	300–573
$MgSiO_3$	Commercial [1]	–	100–160	218–358
Mg_2SiO_4	Commercial [1]	–	130	218–358
$MgTiO_3$	Commercial [1]	–	100±40	218–358
Mg_2TiO_4	Commercial [1]	130	–	218–358

[a] TCC = $1/C\ (\partial C/\partial T)$.
[b] TCK = $(1/K)\ (\partial K/\partial T)$.

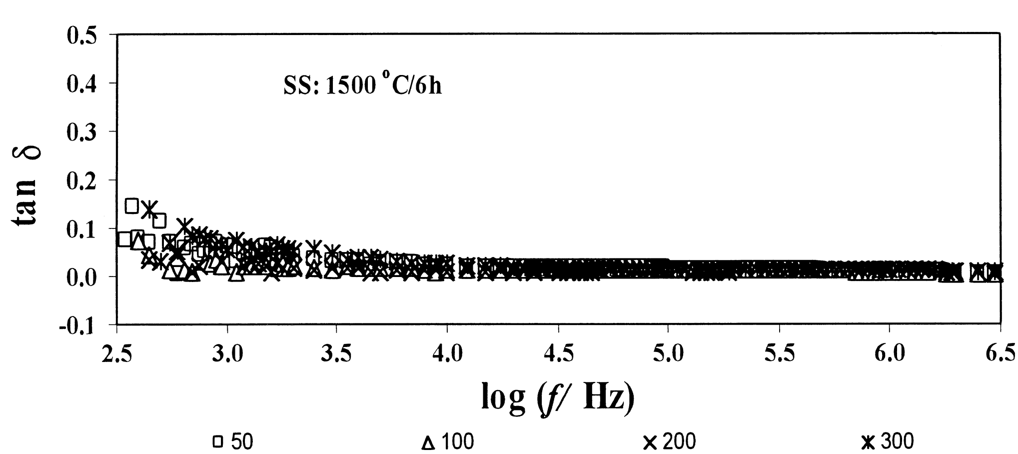

Fig. 4. Variation of tan δ with frequency between 50 and 300°C for SSR-derived Mg_2SnO_4 sintered at 1500°C/6 h.

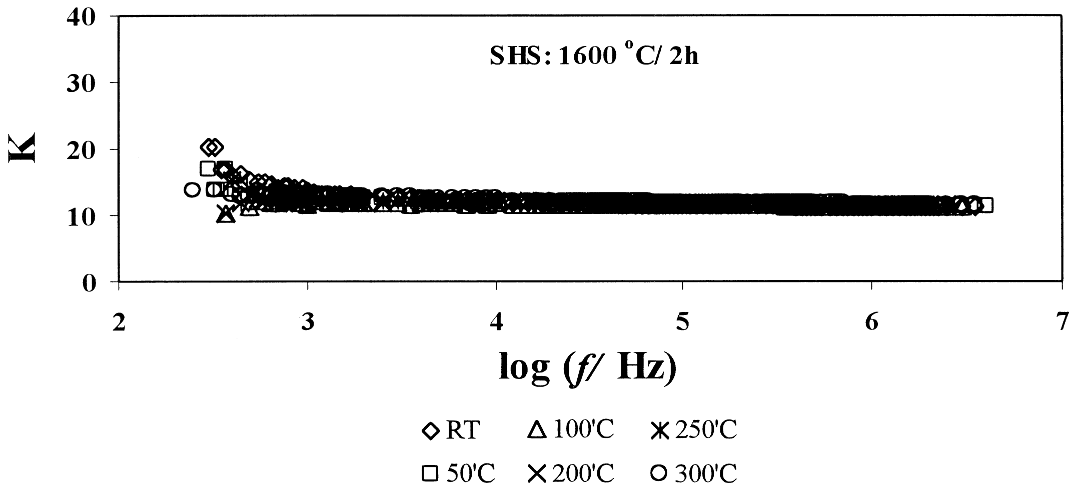

Fig. 5. Temperature-insensitive behavior of dielectric constant of SHS-derived Mg_2SnO_4 sintered at 1600°C/2 h, over a wide range of frequency.

3.2. Electrical behavior of SHS-derived Mg_2SnO_4

3.2.1. Variation of relative permittivity with temperature

The dielectric constant of the SHS samples was calculated using Eq. (1) from the acquired capacitance values. Its variation with the applied frequency at different temperatures is illustrated in Fig. 5 for a typical samples sintered at 1600°C for 2 h. It can easily be seen that the behavior is akin to that of capacitance and also similar to that exhibited by SSR-derived Mg_2SnO_4. It can be seen that the sample showed very weak temperature dependence, as the response at one temperature was quite indistinguishable from the other. This could be attributed to the presence of lesser amount of porosity in samples sintered at 1600°C. It is important to recall that for a given sintering (*T*-*t*) profile, the SHS samples were more porous than the SSR ones [11–14, 18]. However, the temperature dependence of capacitance was still comparable to that of the commercial ceramic capacitors (Table 1). Furthermore, it was earlier noted that the SSR-derived Mg_2SnO_4 was about four times more resistive than the SHS counterpart. It therefore follows that the capacitance of the SHS analogues be higher. It was in fact found that the capacitance of SHS samples was ~1.5 times larger than that of SSR samples.

As was done in the case of SSR samples, the average values of dielectric constant were computed from the linear segments of Fig. 5, at each measurement temperature between 27 and 300°C. These average values are plotted against the measurement temperature and are shown in Fig. 6. In this range, the SHS-derived Mg_2SnO_4 was found to have an average capacitance of ~11 pF and the *K*-value in the range 10–12 over abut four decades of frequency. Once again, highly linear nature of these plots and near independence of *K* on temperature is easily manifested in the small value of the slope of the straight line. The TCC and TCK values are listed in Table 1.

3.2.2. Variation of dissipation factor (tan δ)

The loss tangent was computed from the a.c. data acquired at various temperatures and a typical plot is shown in Fig. 7 for samples soaked for 2 h at 1600°C. Higher values of loss factor in the low frequency region are again due to the possible polarization of the electrodes.

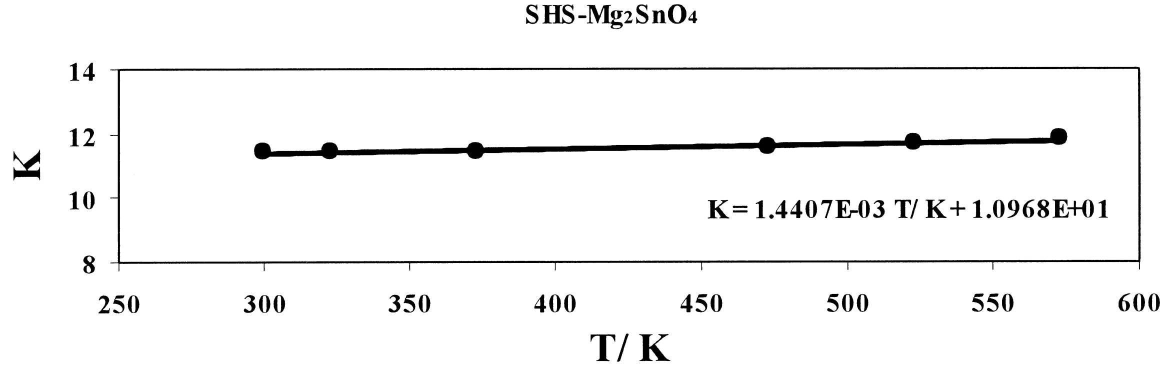

Fig. 6. Temperature dependence of dielectric constant in Mg_2SnO_4 samples obtained via SHS method and sintered at 1600°C/2 h.

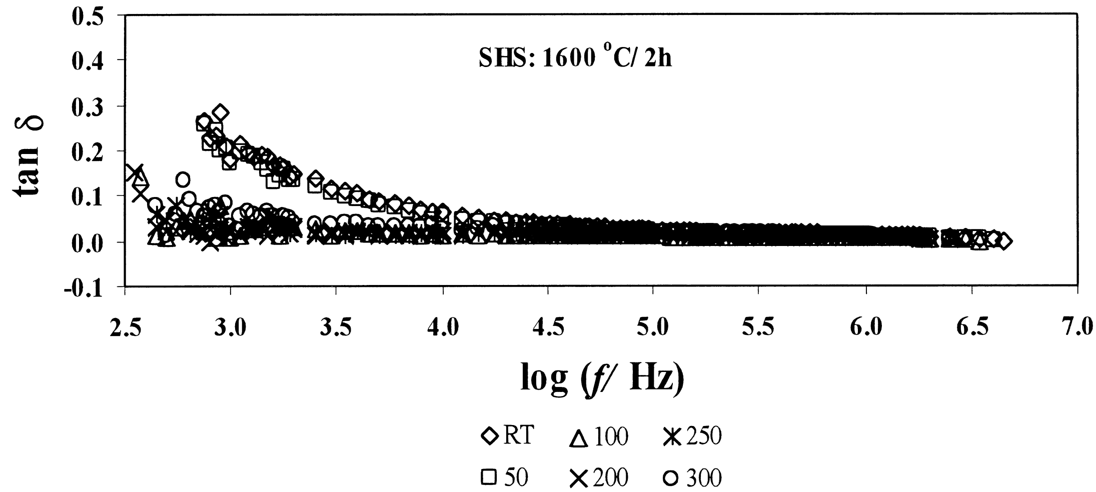

Fig. 7. Variation of dissipation factor with frequency between 27 and 300°C for Mg_2SnO_4 sintered at 1600°C/2 h.

Over more than three decades of frequency, the variation in tan δ is very small, thereby highlighting the fact that despite not-too-insignificant a level of porosity in the SHS samples, the material exhibits excellent 'loss-less' characteristics, especially at the higher frequency regime. Values of the dissipation factor (@ 1 MHz) in SHS derived samples were found to be 1.28×10^{-2}, 7.72×10^{-3} and 3.51×10^{-3}, respectively at 27, 100 and 300°C.

4. Conclusions

The a.c. electrical measurements have been carried out isothermally on sintered bodies of magnesium orthostannate (Mg_2SnO_4) at 27, 50, 100, 150, 200, 250 and 300°C. The analysis of the as-measured data exhibited a small arc of a large semicircle in the Z^*-plane at all measurement temperatures, signifying a highly resistive system under study. As a result of this investigation, two novel electrical characteristics of the sintered ceramic bodies were unraveled. First, the capacitance (C), dielectric constant (K) and the loss factor (tan δ) remained nearly independent of applied frequency in the temperature range 27–300°C. Second, these parameters showed extraordinarily weak dependence of temperature. The two methods (SSR and SHS) used to synthesize the Mg_2SnO_4 ceramic slightly affects these parameters but not their dependence on frequency and/or temperature. Thus the acquired and computed electrical characteristics remained nearly independent on frequency and have weak dependence on temperature. This suggests that Mg_2SnO_4 is a high resistance, low capacitance, low dielectric constant and low loss material with very small TCC and TCK in the range 27–300°C. No other capacitor material (ceramic or otherwise) has perhaps been so far tested for its temperature characteristics up to as high a temperature as employed in this study.

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