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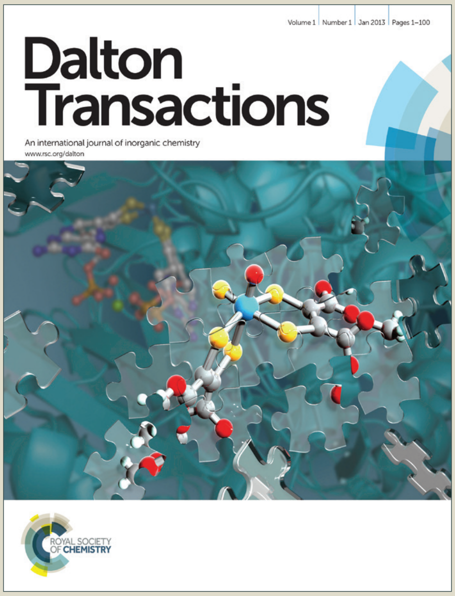

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Hafnium Silicate: A New Microwave Dielectric Ceramic with Low Thermal Expansivity

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The $HfSiO_4$ ceramic are prepared by conventional solid state synthesis method by sintering at 1600 ^oC. The morphology of sintered surface is characterized using scanning electron microscopy and atomic force microscopy and the average surface roughness is about 118 nm. The sintered $HfSiO_4$ ceramics has ε_r = 7.0, Qu*f = 25,000 and τ_f = -44 ppm/^oC at 10 GHz. It exhibits promising thermal properties such as low linear thermal expansivity (CTE) of -1.8 ppm/^oC (dilatometer) in the temperature range of 30-800 ^oC and room temperature thermal conductivity of 11 W/mK.

Introduction

The unprecedented growth of wireless communication has led low loss dielectric materials as one of the most vibrant research areas in recent years. In general, wireless communication covers various applications ranging from wireless fax, cellular phones, global position satellite (GPS), military radar systems, intelligent transport system (ITS), Internet of Things (IoTs) and direct broadcast satellites [1]. Electronic data transmission with low signal attenuation is quite common using low relative permittivity (ε_r > 15) ceramics in digital or analog modes throughout the radio and microwave frequency ranges [2]. The important characteristics required for such applications are low relative permittivity, low dielectric loss, high thermal conductivity and matching coefficient of thermal expansion to that of the materials attached to it, in addition to low temperature coefficient of resonant frequency [3].

The silicates with low relative permittivity and low dielectric loss tangent are attracting attention as a suitable dielectric material for ultrahigh frequencies [4]. Orthosilicates are generally used for refractory purposes because of its high thermal stability, dimensional accuracy, metal penetration resistance, low thermal expansion and high thermal conductivity. Moreover $ASiO_4$ [A = Zr, Hf, Th] ceramics are suitable for fission reactor and storage of nuclear wastes because of their effective radiation resistance [5, 6].This resemblance is due to the similarity in their electronic structures and ionic radii which permits complete miscibility in most Zr-Hf compounds [7]. One of the major advantage of these orthosilicates based materials is low coefficient of thermal expansion and high thermal conductivity among the silicates. The dielectric properties of some of the alkali earth orthosilicates such as A_2SiO_4 (A = Ba, Ca, Sr) have been well characterized and are found to be suitable for packaging as well as millimeter wave communication applications due to their low ε_r and high $Q_u\times f$ values [8]. The values of ε_r were decreased (14.1, 10.4, 10.1) in the order Ba_2SiO_4> Sr_2SiO_4>Ca_2SiO_4. The $Q_u\times f$ values obtained were 17900 GHz, 19100 GHz and 26100 GHz for Ba_2SiO_4, Sr_2SiO_4 and Ca_2SiO_4 respectively [8]. The τ_f of Ba_2SiO_4 was -17 ppm/^oC, whereas Sr_2SiO_4 and Ca_2SiO_4exhibited high values of τ_f, -205 ppm/^oC and -89 ppm/^oC respectively [8]. The coefficient of thermal expansion (CTE) of A_2SiO_4 (A = Ba, Sr) ceramics exhibit positive values CTE of +10.3 ppm/^oC for Ba_2SiO_4, +6.2 ppm/^oC for Sr_2SiO_4 and +7.0 for Ca_2SiO_4 [8]. For practical applications, in addition to the dielectric properties the materials should have high thermal conductivity and low thermal expansion, which are important parameters for heat dissipation and integration of these materials in microwave devices especially for hard ceramic substrate applications [9]. However, no attempt has been made to explore the microwave dielectric properties of $ASiO_4$ [A = Hf, Zr] group of materials. Recently we reported the microwave dielectric properties of $ZrSiO_4$ sintered at 1550 ^oC [10].

Synthetic $HfSiO_4$ is isostructural with $ZrSiO_4$ (zirconium orthosilicate) and is named as hafnon by Curtis et al. a terminology later approved by the International Mineralogical Association. Hf and Zr are observed to be alike in their chemical properties [7, 11]. Recently, $HfSiO_4$ was proposed as a high κ gate dielectric material for silicon electronics because of its high dielectric constant, low leakage current, excellent integrability and thermal stability with semiconductor Si [12,13,14,15]. Very recently, Pr^{3+} doped $HfSiO_4$ film was reported as a promising candidate for optoelectronic applications [16]. Interestingly, the recent years saw an influx of theoretical studies on the structural, elastic, electronic and optical properties of tetragonal orthosilicates which indicates the importance of $HfSiO_4$[17, 18, 19]. The main objective of the present paper is to exploit the structural, dielectric and thermal properties of $HfSiO_4$ ceramics whose ultralow CTE can find potential applications in the ever growing microwave substrate market.

Results and discussion

The $HfSiO_4$ dielectric ceramics were prepared by solid-state reaction route. The room temperature powder X-ray diffraction pattern for $HfSiO_4$ fired at 1400, 1500, and 1600 °C is shown in figure 1. All the reflections can be indexed according to a single-phase tetragonal structure corresponding to the I41/amd (141) space group with a = 6.580 Å, b = 5.980 Å and density of 6.941 g/cm^3. The indexing was done based on the standard ICDD file No (77-1759) belonging to hafnon, suggesting a completion of reaction between HfO_2 and SiO_2 which otherwise are present at firing temperatures ≤1500 °C.

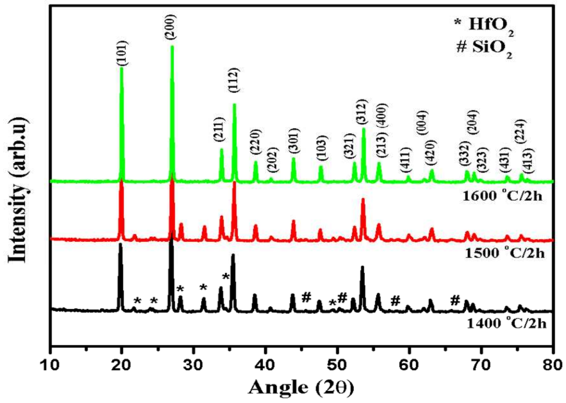

Figure 1 Powder X-ray diffraction pattern of $HfSiO_4$ ceramic sintered at 1600 °C

Figure 2 shows the infrared spectrum of $HfSiO_4$ ceramics sintered at 1600 °C. The strongest absorption peak is observed at ~ 915 cm^{-1}, which is ascribed to the asymmetric stretching vibration of the Si-O-Si bond [20, 21]. The peaks near 800 and 440 cm^{-1} are ascribed to bending modes of O-Si-O and Si-O-Si bonds, respectively [21, 22]. The shoulder observed at 1020 cm^{-1} is assigned to the Si-O-Si asymmetric bond stretching vibration [22]. Comparing with earlier reports, it can be suggested that $HfSiO_4$ ceramic is isostructural with $ZrSiO_4$ ceramic whose band at 615 cm^{-1} in the spectra can be associated with the Hf-O bond in the HfO_8 group, similar to that of Zr-O bond in the ZrO_8 group [22].

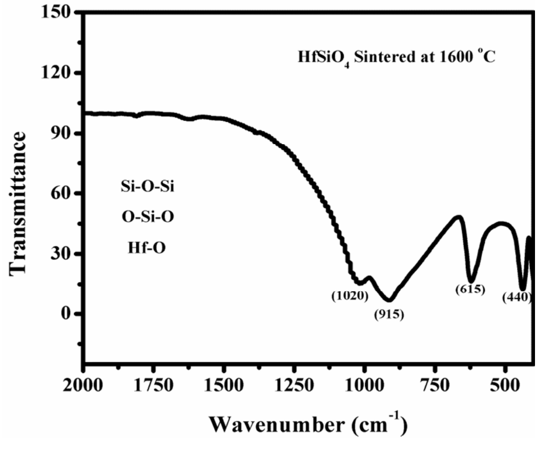

Figure 2 FTIR spectrum of $HfSiO_4$ sintered at 1600 °C

Figure 3 (a, b, c) shows the microstructure of $HfSiO_4$ sintered at 1400, 1500 and 1600 °C/2 hrs and has grains of variable sizes in the range 1-5 μm. The presence of a few bigger grains can be observed in silicates sintered at 1600 °C/2hrs (figure 3a) which may try to reduce the internal energy by reducing the total area of grain boundary, resulting in subsequent grain growth. The figure 3 b and c indicates more porosity as compared to figure 3 a. The XRD and IR studies indicate the formation of $HfSiO_4$ and the ceramic found to be thermally stable at least up to 1600 °C.

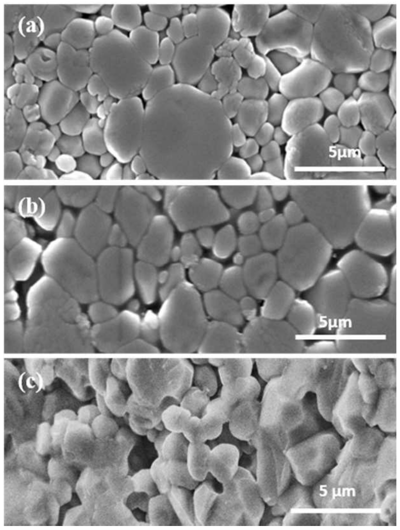

Figure 3 The SEM images of thermally etched $HfSiO_4$ ceramics sintered at 1400, 1500 and 1600 °C

Figure 4 (a, b, c) shows the variation of densification and dielectric properties of $HfSiO_4$ ceramic sintered in the temperature range of 1350-1650 °C. Sintering temperature of $HfSiO_4$ ceramic is optimized with the best of densification and dielectric properties. In the present investigation, $HfSiO_4$ ceramic shows a maximum densification of 95 % when sintered at 1600 °C. It is well known that, the reduction in surface free energy of a sintering compact due to the elimination of internal surface area associated with the pores, provides driving force for sintering [23]. It is clear from figure 4 (a) that further increase in the sintering temperature above 1600 °C cause a slight decrease in densification which is due to partial melting of the ceramic and hence leads to increases in porosity. Similar trends are also observed in the relative permittivity as a function of sintering temperature while the dielectric loss values of $HfSiO_4$ ceramics reach the lowest at a firing temperature of 1600 °C. It has relative permittivity of 9.71 and dielectric loss of 0.0007 at 1 MHz when sintered at 1600 °C. The porosity corrected relative permittivity at this temperature is 10.26, which is calculated using the equation derived by Penn et al. [24]. Figure 4 (b) shows the variation of relative permittivity of $HfSiO_4$ ceramic fired at various temperature ranges 1350-1600 °C as a function of frequency. Figure 4 reveals that the relative permittivity decreases with increase in frequency, which is consistent with the existing theories. It should be noted that the dielectric properties of ceramics are influenced by a number of factors such as processing conditions, phase transitions, purity of the raw materials, inherent crystal defects and porosity [25, 26].At low firing temperature of 1350 °C, relative permittivity variations are from 20 to 5 and is because of low densification (~ 80 %) of $HfSiO_4$ ceramic compact. The sample sintered at higher temperatures the relative permittivity variations gradually decreases and reaches about 10 to 7 (200 Hz to 1 MHz) at 1600 °C and the ceramics have better densification of 95 %. This is because at lower densification influenced by interfacial polarization, which is contributed mainly by polar and volatile molecules present in the pores.

Table 1 shows the microwave dielectric properties of $HfSiO_4$ ceramic sintered at 1600°C. It has relative permittivity (ε_r) of 7.0, quality factor (Qu*f) of 25,000 GHz and temperature coefficient of resonant frequency of -44 ppm/°C at 10 GHz frequency. The porosity corrected relative permittivity of this ceramic at this frequency is 7.4. The split post dielectric measurement performed on a square sheet of dimensions 50 x 50 mm made of $HfSiO_4$ ceramic sintered at 1600 °C also revealed similar microwave dielectric properties (ε_r =7.5 and tanδ = 0.0006 at 5 GHz). It must be noted that he relative permittivity and dielectric loss of this $HfSiO_4$ ceramic is suitable for microwave substrate applications.

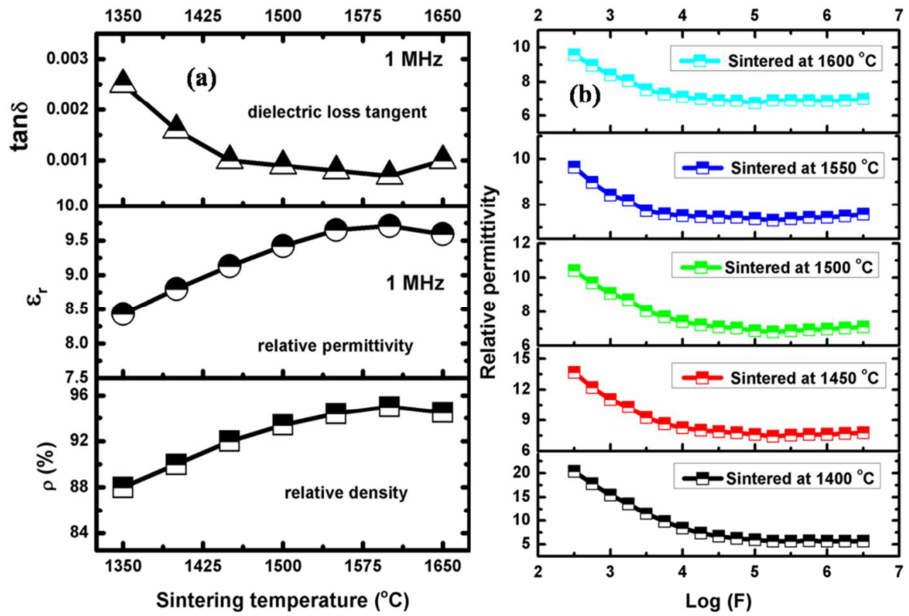

Figure 4(a) Variation of relative density, relative permittivity and dielectric loss with respect to sintering temperature and (b) Variation of relative permittivity with respect to frequency of $HfSiO_4$ ceramics

Table 1 Microwave dielectric properties of $HfSiO_4$ sintered at 1600 °C

Sample	Density (%)	Hakki and Coleman		Resonant Cavity Method	Qu*f
		10 GHz TE01δ Mode			
		ε_r	τ_f ppm/°C	Q_u	
Cylindrical	95	7.0	-44	2500	25000
Rectangular Sheet	95	SPDR Method 5 GHz			
		ε_r		tan δ	
		7.5		0.0006	

Figure 5 depicts the surface topography of $HfSiO_4$ ceramic sintered at 1600 °C. Surface roughness is of great importance for manytechnological applications requiring well-defined surfaces or interfaces [27]. Usually the desired surface engineering is achieved by various methods like machining, surface treatment and coating to produce surface with characteristics required for applications. TheAFM scan area used for the present study was ~ 60 × 60 µm. The surface roughness (Sa) is calculated to be 118 nm, which is defined as arithmetic mean of the absolute values of the surface departures above and below the mean plane within the sampling area.The root mean square values of the surface departure within the sampling area (Sq) are given as 161 nm. A positive value of skewness (Ssk) = 2.2 indicates that the specified surface is more or less flatter with more peaks than valleys. It has a kurtosis value (Sku) of 8.5 indicate that the surface is spiky since a centrally distributed surface has a kurtosis value larger than 3,whereas the kurtosis of a well spread distribution is smaller than 3 indicating bumpy surfaces [28].

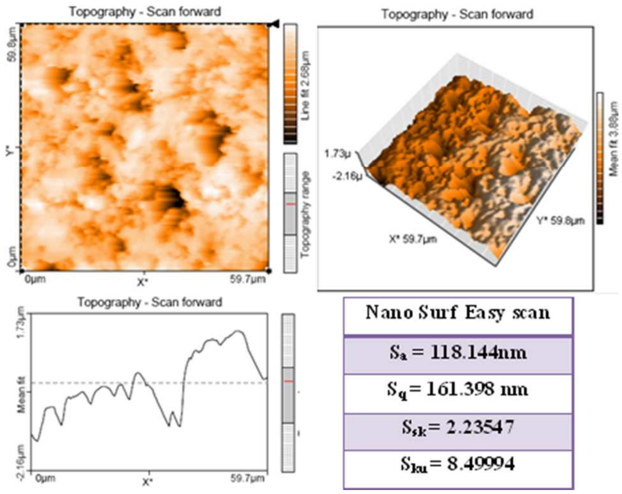

Figure 5 Surface topography of $HfSiO_4$ pellet sintered at 1600°C

Figure 6a shows the variation of the linear dimension of the $HfSiO_4$ ceramic as a function of temperature in the range of 30-800 ^{o}C. In general, brittle ceramic materials possess low thermal expansion as compared to metals and polymers. The thermal expansion of ceramics can be categorized in to distinct groups such as negative thermal expansion ($\alpha < 0$ ppm/^{o}C), very low expansion ($0 < \alpha < 2$ ppm/^{o}C), low expansion ($2 < \alpha < 8$ ppm/^{o}C) and high expansion ($\alpha > 8$ ppm/^{o}C) [29]. The $HfSiO_4$ is found to have a negative coefficient of thermal expansion (CTE) of -1.8 ppm/^{o}C in the measured temperature range with an accuracy of 1 %. The average values of CTE calculated in different temperature ranges are also depicted in the Figure 6a. It can be observed that except at very low temperatures, CTE remains almost the same. In General, most of the electronic ceramics possess low positive coefficient of thermal expansion with a value < 15 ppm/^{o}C. In order to confirm the expansion mechanism, temperature variable powder x-ray diffraction (in the range 25-800 ^{o}C) of $HfSiO_4$ ceramic sintered at 1600 ^{o}C was studied, which is given in Figure 6 b and c. Figure 6 c represents high intensity plane (100) varies with respect to the temperature ranges, a shift to low angle is clear from the results. Similarly figure 6 d depicts the variation of lattice parameter and cell volume of tetragonal $HfSiO_4$ with respect to temperature. Thus the in-situ XRD results indicates that $HfSiO_4$ ceramic sintered at 1600 ^{o}C shows the positive volume thermal expansion of the unit cell, which is contradicting with the linear CTE measurements. In 1993, Yoshinori Kanno reported the thermal expansion coefficient of $HfSiO_4$ as 3.6 ppm/^{o}C which is based on an earlier paper by B. Yoshiki in 1952 [30, 31]. In the present case the linear a and c axis CTE is 3.2 and 6.1 ppm/^{o}C respectively.

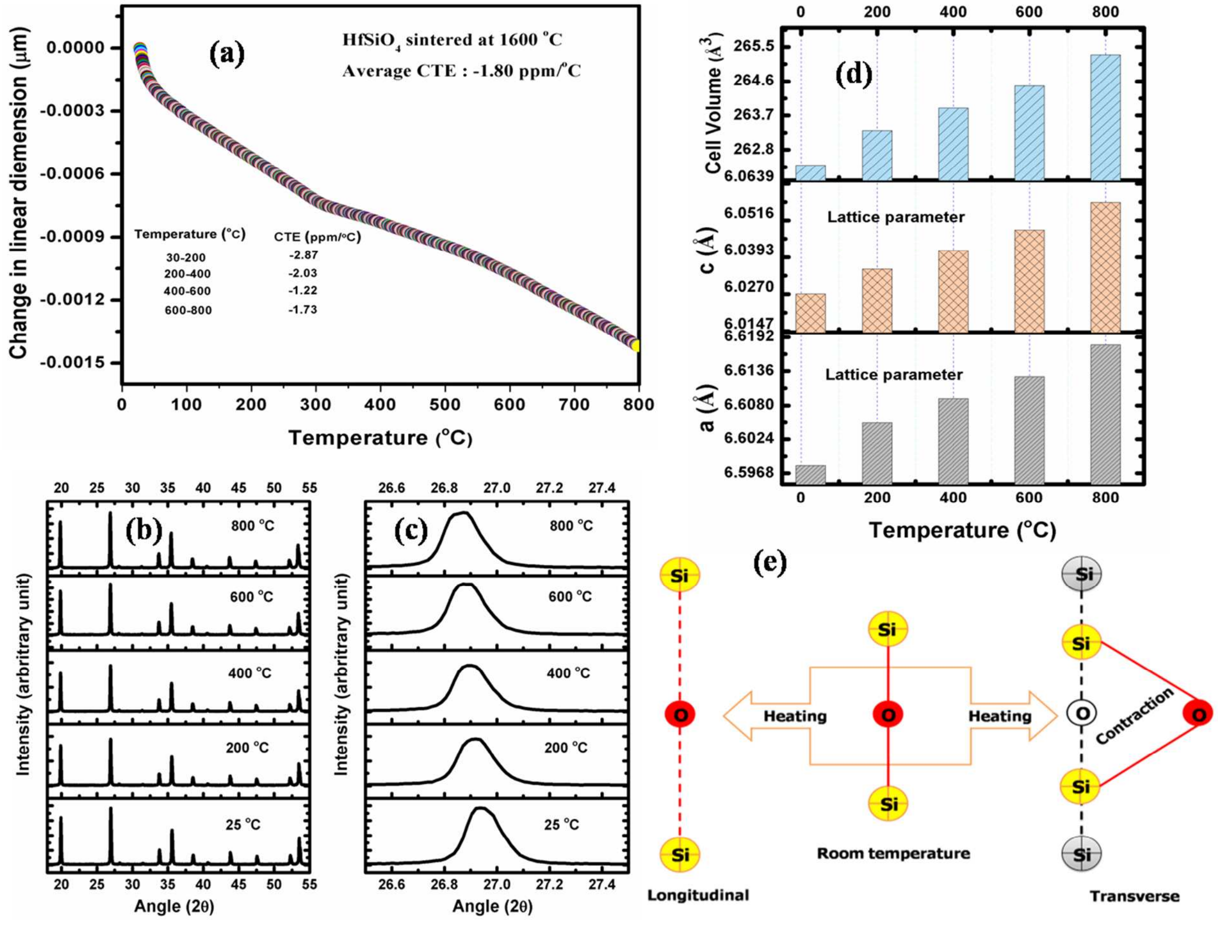

Figure 6 (a) Coefficient of thermal expansion (b) Temperature variable XRD (c) Schematic representation of bond vibrations (d) Calculated lattice parameters and cell volume of $HfSiO_4$ ceramic with respect to temperature and (e) a schematic of the behaviour of longitudinal and transverse vibrational modes on heating.

However, there are other factors such as mechanical stress and porosity of the sample which may also influence the CTE measurements [32]. Hence, based on the above observations, we believe that the apparent negative thermal expansivity of $HfSiO_4$ is not contributed by a visible lattice expansion on heating, but due to some other mechanisms which may intimately be related to their flexible network characteristics. Interestingly, most of the negative CTE ceramics have a common framework structures like rigid tetrahedra (MO_4) and/or octahedra (MO_6) which are connected by corner sharing oxygen atoms [33]. These linkages are typical in metal oxides such as ZrW_2O_8-type solids and zeolites and are fundamental to their negative CTE behaviour [33]. Usually, the negative thermal expansivity materials are characterized by strong atomic bonds, which often have large Pauling bond strengths, Z/p where Z is the cation charge and p is the cation coordination number such as W–O and Si–O. The two important phonon modes for metal oxides are longitudinal and transverse vibrations of Si-O-Si which were clearly visible in the FTIR spectra $HfSiO_4$ given in figure 2. **As** represented in Figure 6e, it can be assumed that in silicates such as $HfSiO_4$, the longitudinal vibrational modes tend to increase the bond length on heating. In contrast, the transverse vibration modes can have an opposing effect on the Si-O-Si bond length. The dominance of transverse modes over the longitudinal modes may be one of the reason for the negative CTE of the $HfSiO_4$ ceramics in the CTE measurements. As a consequence, the dynamical deformation consumes open spaces in a crystal lattice under the condition that the thermal expansion of the core unit such as SiO_4 is suppressed [34]. However further studies are required for explaining the mismatch between the CTE obtained by XRD and dilatometer methods. The coefficient of thermal expansion value of commercially available substrates like silicon, silicon nitride, boron nitride, silicon carbide, aluminum nitride, alumina, berillia are 3.7, 3.8, 4.3, 6.8 and 7.8 ppm/°C respectively [9]. Compared to the commercial substrates, $HfSiO_4$ falls into the category of ultralow CTE materials with high temperature stability.

Figure 7 shows the variation in the thermal conductivity (λ) of $HfSiO_4$ ceramics sintered at 1600 °C as a function of temperature in the range of 25 to 300 °C. Most of the silicates have relatively low thermal conductivities since they include both rigid and soft parts in the structure. $HfSiO_4$ ceramic shows decrease in thermal conductivity value with increase in temperature. Majority of non-metallic compounds also exhibit a similar behaviour with increasing temperature **[35, 36, 37]**. $HfSiO_4$ ceramic has thermal conductivity in the range of 6-11 W/m K in the measured temperature range. Li_4SiO_4 and Y_2SiO_5 ceramic which belong to orthosilicates family have thermal conductivities 4.1 and 4.6 W/mK respectively at room temperature **[38, 39]**. In comparison with reported thermal conductivity of Li_4SiO_4 ceramic, $HfSiO_4$ ceramic shows a higher value of thermal conductivity (11 W/mK) at room temperature for a sample with 95 % of densification.

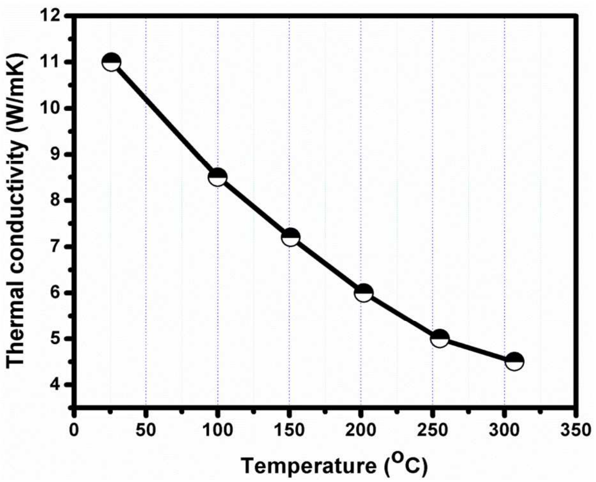

Figure 7 Variation of thermal conductivity of $HfSiO_4$ ceramic sintered at 1600 °C as a function of temperature

In most of the ceramic samples, heat transport is contributed by phonon scattering mechanism which is obviously inefficient in an environment with porosity. Hence we estimated the porosity corrected thermal conductivity of $HfSiO_4$ ceramic at room temperature which is 11.95 W/mK, calculated using the equation $TC = TC_{corrected} + (1-\delta)$, where δ is porosity of the sample and TC-experimental thermal conductivity **[40]**.

Experimental

$HfSiO_4$ ceramic was prepared by the conventional solid state reaction route. Equimolar amounts of HfO_2 (98% Sigma Aldrich, St. Louis, MO-63103 USA) and SiO_2 (99.9% Sigma Aldrich, St. Louis, MO-63103 USA) were ball milled for 24 hrs in a polyethylene bottle using yttria stabilized ZrO_2 balls and distilled water. The mixed powder was dried and calcined successively at 1400 °C for 2 hrs. The calcined powder was ground and mixed with the 4 wt% polyvinyl alcohol (BDH Lab Suppliers, England) and shaped into disks of 11 mm diameter and ~ 2 mm height under an applied pressure of 100 MPa using a tungsten carbide (WC) die. The green compacts were heated in air at a rate of 6 °C/min up to 600 °C and held at this temperature for 30 min for binder burnout. The pellets were then sintered in air at temperatures in the range of 1350 °C to 1650 °C for 2 hrs. The cooling rate was 2.5 ºC/min until it reached 800 °C and was then allowed furnace cooling. The sintering temperature was optimized for the highest density and best of dielectric properties. The bulk densities of the developed ceramic samples were measured using Archimedes method.

The crystal structure and phase purity of the powdered samples were studied by X-ray diffraction technique using Ni-filtered Cu-Kα radiation (Philips X'pert PRO MPD XRD; Philips, Eindhoven, Netherlands) operated at 40 kV and 30 mA. The microstructures of the thermally etched sintered samples were analyzed using scanning electron microscope (JEOL-JSM 5600 LV, Tokyo, Japan). The surface roughness of the sintered $HfSiO_4$ ceramic was measured using Nano Surf Easy Scan Atomic Force Microscopy (AFM) operating in tapping mode and the AFM sampling area used for the measurements was ~ 60 × 60 µm. The AFM cantilever, whose tip is made of 15 µm long monolithic silicon, has a width of 49 µm, thickness 2.2 µm and spring constant 0.21N/m. For IR transmission measurements (Shimadzu Nicolet Impact 400X FTIR Spectrometer), the samples were prepared by mixing $HfSiO_4$ ceramic powder with potassium bromide (KBr) and pressed into pellet under a pressure of ~300 bar. FTIR spectrum was recorded on a Nicolet 400X spectrometer with resolution of 2 cm^{-1}, accumulating 200 scans. The dielectric properties at 1 MHz were measured using a LCR meter (Hioki 3532-50 LCR HiTESTER, Nagano, Japan). The error associated with the LCR measurement is less than ±2 % for relative permittivity as well as dielectric loss.The microwave measurements of relative permittivity, unloaded quality factor and temperature coefficient of resonant frequency were performed by using a Vector Network Analyzer (E5071C, Agilent Technologies, Santa Clara, CA). The microwave relative permittivity and dielectric loss of 50 x 50 mm square sheet of sintered $HfSiO_4$ ceramic were measured using Split Post Dielectric Resonator (SPDR) method at operated 5 GHz using Vector Network Analyzer. Generally, the error associated with SPDR method in computing relative permittivity is less than 1% while it is ± 5 % for dielectric loss measurement with a loss tangent resolution of 2×10^{-5}**[41, 42]**.

The coefficient of thermal expansion was measured using a push rod dilatometer (NETZSCH, Model DIL 402 PC, Germany) with an accuracy less than 1 %. The thermal expansion tests were performed according to the specifications of ASTM E228 test method with sintered cylindrical samples of diameter 8 mm and height 10 mm in the temperature range of 30–800 °C. The thermal conductivity is computed from the thermal diffusivity (mm^2/s), specific heat (J/g K) and density (g/cm^3) **[43]** which were measured using a thermal diffusivity system (Anter Corporation, Flashline 2000, Pittsburgh, PA). The flash method with high speed xenon discharge pulse source directed to the top face of the specimen to increase the temperature of the specimen by ΔT as a function of time. The specimens used for thermal diffusivity testing were in the form of a disc, with a diameter of 12.6 mm and a thickness of 2 mm. Specimen preparation involves ensuring the required smoothness and flatness of surfaces, by polishing with a 400 grit SiC grinding paper, followed by coating both sides of the sample with graphite for thermal contacts in order to avoid reflection of the xenon discharge light beam. In a typical measurement, three specimens were tested, at different temperature range up to 300 ^{o}C. The error associated with thermal property measurement is ± 1 %.

Conclusions

The dielectric and thermal properties of $HfSiO_4$ceramic prepared by conventional solid state ceramic route are investigated. The $HfSiO_4$ ceramic sintered at 1600 ^{o}C has a tetragonal structure with a 95 % densification. It has $\varepsilon_r = 7.0$, Qu*f = 25,000 and $\tau_f = -44$ ppm/^{o}C at frequency of 10 GHz. It exhibits a unique negative CTE of -1.8 ppm/^{o}C in the 30-800 ^{o}C temperature range. These ceramics also show a promising room temperature thermal conductivity of 11 W/mK. Thus low dielectric loss and low CTE $HfSiO_4$ ceramic which satisfies the dielectric and thermal requirements of microwave substrates have been developed for wide range of substrate applications.

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Notes and references

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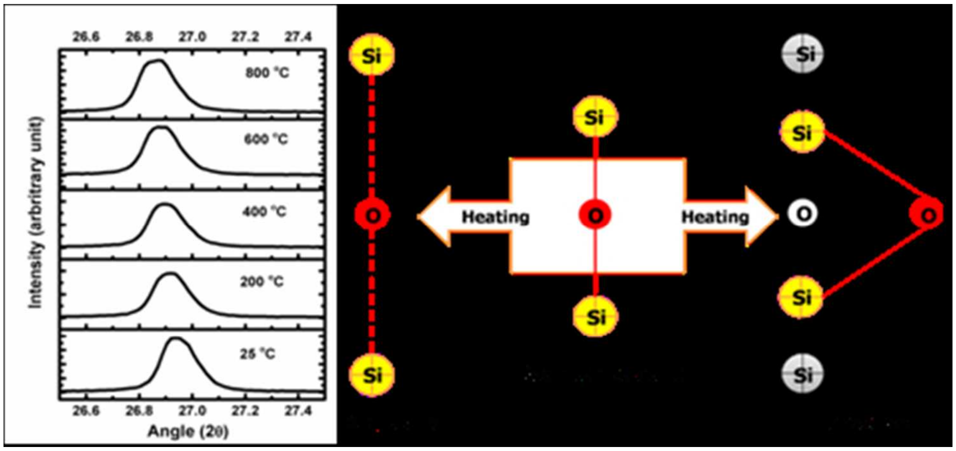
1 S. BindraNarang and S. Bahe, *Journal of Ceramic Processing Research,*2010,**11**, 316.
2 M. T. Sebastian, Dielectric Materials for Wireless Communication, Elsevier Science Publishers, Oxford (2008)
3 D. D. L. Chung, Materials for Electronic packaging, Butterworth-Heinemann, Burlington, MA, (1995)
4 H. Ohsato, T. Tsunooka, T. Sugiyama, K. Kakimoto and H. Ogawa, *Electroceramics in JapanVii*, 2004, **269**, 195.
5 J. A. Speer, Zircon In, P. H. Ribbe, Ed., *Mineralogical Society of America Reviews Mineralogy*, l980a, **5,** 67.
6 R. C. Ewing, W. Lutze and W. J. Weber, *Journal of Materials Research,* **10**, 243, 1995.
7 J. A. Speer B. J. Cooper, *American Mineralogist*, 1982, **67**, 804.
8 J. Tony and M. T. Sebastian, *Material Letters*, 2010, **65**, 891.
9 M. L., Minges, Electronic Materials Handbook: Packaging, Volume-**1**, ASM International, 334-335 (1989)
10 V. Jobin, J. Tony, and M. T. Sebastian, *Material Letters*, 2011, **65**, 1092.
11 C. E. Curtis, L. M. Doney and J. R. Johnson, *Journal of the American Ceramic Society*, 1954, **37**, 458.
12 S. Lee, D. Yun, S. Rhee and K. Yong, *Journal of Materials Chemistry*, 2009, **19**, 6857.
13 J. H. Choi, Y. Mao and J. P. Chang, *Material Science Engineering R*, 2011, **72**, 97.
14 G. He, L. Q. Zhu, Z. Q. Sun, Q. Wan, L. D. Zhang, *Progress in Material Science,* 2011, **56**, 475.
15 G. D. Wilk, R. M. Wallace, J. M. Anthony, *Journal of Applied Physics,* 2000, **87**, 484.
16 A. YongTao, L. Christophe, K. Larysa, M. Magali, P. Xavier and G. Fabrice, *Nanoscale Research Letters*, 2013, **8**, 43.
17 Q. Liu, Z. Liu, L. Feng, H. Tian and W. Zeng, *Brazilian Journal of Physics*,2012,**42**, 20.
18 D. Muñoz Ramo, P. V. Sushko, A. L. Shluger, *Physical Review B,*2012, **85**, 2.
19 A. Meldrum, S. J. Zinkle, L. A. Boatner and R. C. Ewing, *Nature*, 1998, **395,** 56.
20 A. K. Varshneya, N. J Suh. *Journal of American Ceramic Society*, 1987, **70**, C21.
21 C. J. Brinker, D. M. Haaland, *Journal of American Ceramic Society*, 1983, **66**, 758.
22 M. Nogami, *Journal. Non-Crystalline. Solids,* 1985, **69**, 415.
23 S. Soumiya, F. Aldinger, R. Spriggs, K. Uchino, K. Koumoto, M. Kaneno, Handbook of Advanced ceramics, Materials, Applications, Processing and Properties, Chapter-4, Elsevier Science Publisher, Oxford, (2003)
24 S. J. Penn, N. M. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, K. Schrapel, *Journal of American Ceramic Society*, 1997, **80**, 1885.
25 I. M. Reaney, E. L. Colla, N. Setter, *Journal of Applied Physics,* 1993, **74,** 3414.
26 A. Templeton, X. R. Wang, S. J. Penn, S. J. Webb, L. F. Cohen, N. M. Alford, *Journal of American Ceramic Society,* 2000,**83**, 95.
27 Bhushan, Hand book of micro/nanotribology, CRC press, New York, (1995)
28 R. A. A. Saif, N. Ramli, P. Poopalan, *Jordan Journal of Physics,* 2010, **3**, 61.
29 G. Bayer, *Journal of Less Common Metals*, 1972, **26**, 255.
30 Y. Kanno, *Journal of Materials Science Letters*, 1993, 12, 1807.
31 B. Yoshiki, *Kobutsu kogaku*, Gihodo, 1959, p308.
32 J. Lehman, R. Lakes, *Journal of Intelligent Material Systems and Structures,* 2012, **23**, 1263.
33 C. Martinek and F. A. Hummel,*Journal of American Ceramic Society,* 1968, **51**, 227.
34 T. A. Mary, J. S. O. Evans, T. Vogt and A. W. Sleight, *Science*, 1996, **272,** 90.
35 K. Takenaka, *Science and Technology of Advanced Materials*, 2012, **13,** 013001.
36 K. L. Wray, T. J. Connolly, *Journal of Applied Physics,* **30,** 1959, 1702.
37 W. D. Kingery, *Journal of American Ceramic Society*, 1955, **38**, 251.
38 M. J. Maloney, Thermal barrier coatings systems and materials. *U S Patent* 6117560 (2000)
39 A. Abou-Sena, A. Ying and M. Abdou, *Fusion Science and Technology*, 2005, **47**, 1094.
40 J. Marion and R. Beach, Thermophysical Properties of Y_2SiO_5 (YOS), *LRD* 90-038, (1990)
41 W. D. Kingery, Introduction to ceramics, Volume 18, Willey, (1960)
42 J. Krupka, A. P. Gregory, O. C. Rochard, R. N. Clarke, B. Riddle, J. J. Baker, *Journal of the European Ceramic Society*, 2001, **10**, 2673.
43 A. P. F. Albers, T. A. G. Restivo, L. Pagano, J. B. Baldo, *Thermochimica Acta*, 2001, **370**, 111.



Hafnium Silicate: A Low Thermal Expansion Microwave Ceramics
80x37mm (150 x 150 DPI)