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Microwave assisted sol-gel synthesis of high dielectric constant CCTO and BFN ceramics for MLC applications

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Abstract

$Ba(Fe_{1/2}Nb_{1/2})O_3$ (BFN) and $CaCu_3Ti_4O_{12}$ (CCTO) ceramic powders were synthesized by microwave assisted sol-gel synthesis technique and sintered at 1100 °C and 1000 °C, respectively. Calcination and sintering processes were carried out in a microwave furnace. Dielectric constant (ε_r) ~2450 and dielectric loss ($\tan\delta$) ~0.5 at frequency of 1 kHz and 20 °C were observed for the BFN ceramic samples. Higher value of $\varepsilon_r \sim 3600$ and lower value of $\tan\delta \sim 0.07$ at frequency of 1 kHz and in 20–60 °C temperature range for the CCTO ceramic samples suggested its utility for MLC applications. Sharp decrease of ε_r and sharp increase of $\tan\delta$ at higher frequencies of BFN ceramic samples indicated the presence of Debye like relaxation.

Keywords: *$Ba(Fe_{1/2}Nb_{1/2})O_3$, $CaCu_3Ti_4O_{12}$, microwave assisted sol-gel process, dielectric properties*

I. Introduction

With the increase in miniaturization scaling of electronic devices, requirements of high dielectric constant (ε_r) materials with good temperature and frequency stability are increasing [1]. Generally, high capacitance in a material is related to its ferroelectric nature [2]. Recently, high dielectric response has been observed in non-ferroelectric materials. $Ba(Fe_{1/2}Nb_{1/2})O_3$ (BFN) and $CaCu_3Ti_4O_{12}$ (CCTO) ceramics are the non-ferroelectric systems showing excellent dielectric properties [3–5]. Wang *et. al.* [4] reported dielectric characteristics of BFN ceramics over a broad temperature and frequency range. In BFN system, giant dielectric behaviour with very strong frequency dispersion was observed in 406–650 K temperature range [4]. CCTO ceramics has also attracted much interest due to its extraordinary dielectric properties [5]. This system also exhibits giant dielectric permittivity, which is almost constant in 100–400 K temperature range [6]. In BFN and CCTO ceramics, neither a phase transition nor a crystal structure change is detected [7]. Therefore, high dielectric constant in BFN and CCTO systems is considered to be extrinsic in nature. In spite of seemingly important possible dielectric applications, dielectric loss ($\tan\delta$) of these ceramics is very high [8]. The major drawback of BFN and CCTO ceramics is the difficulty of obtaining high density and single phase formation by conventional solid state synthesis route [9]. The solid state route (SSR) requires high processing temperatures, which is detrimental to multilayer ceramic capacitors (MLCC) because of the electrode oxidation. On the other hand, chemical technique, often referred to as sol-gel processing, has advantage of control over purity and stoichiometry with the reduction of processing temperatures [10]. Materials produced with this technique have lower calcination and sintering temperatures with grains of submicron size, which allow thinner layers and enhanced dielectric breakdown strength with the lower dielectric loss. Although, processing temperatures are decreased in sol-gel processing technique, the processing duration is nearly still the same as that of the solid state reaction route. With a longer processing duration, the chances of creation of non-uniform grains, defects and development of pores are high. These disadvantages of the sol-gel processing technique can be avoided by using microwave processing technique. The microwave processing technique has several advantages like: rapid heating, penetrating radiation, obtaining more uniform microstructure and hence higher density. Moreover, this technique is inherently dry and fumeless process, which means environmentally clean, therefore it is also known

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as clean processing technique [11,12]. In the microwave processing of ceramics, electromagnetic waves interact with the ceramic materials, leading to volumetric heating. The presence of high dielectric loss in BFN and CCTO ceramic samples can be exploited for their synthesis with lower processing temperature and time by using microwave synthesis technique. Microwave heating also has the potential for energy and cost savings when compared with conventional heating processes. Besides that, nearly theoretical density and uniform grains, which in turn improves physical properties of ceramics, can be achieved in microwave processed ceramic samples [11,12]. Therefore, the synthesis of BFN and CCTO ceramic samples by microwave assisted sol-gel processing technique can help obtaining dense and uniform grain size with pore free microstructures, which can improve the material's electrical properties.

In the present work, dielectric properties of BFN and CCTO ceramic samples, synthesized by microwave assisted sol-gel process are reported and discussed in detail.

II. Experimental

$Ba(Fe_{1/2}Nb_{1/2})O_3$ (BFN) and $CaCu_3Ti_4O_{12}$ (CCTO) ceramic samples were synthesized using grade reagents barium acetate, calcium acetate, niobium chloride, ferric nitrate, copper acetate and titanium isopropoxide as starting precursors. For the synthesis of BFN ceramic powders, stoichiometric amount of barium acetate and niobium chloride were separately dissolved in acetic acid and concentrated HCl solvents, respectively, with continuous magnetic stirring. Stoichiometric amount of ferric nitrate was dissolved in distilled water. These solutions were mixed together and stirred slowly with continued heating until a transparent solution was obtained. For the synthesis of CCTO ceramic powders, stoichiometric amounts of calcium acetate and copper acetate were dissolved together in acetic acid with continuous magnetic stirring at 70 °C. Once calcium acetate and copper acetate were dissolved, stoichiometric amount of titanium isopropoxide was added to the solution and stirred slowly with continued heating until a transparent solution was obtained. Transparent solutions of BFN and CCTO systems were heated at ∼110 °C to form precipitates and finally dried powders. To determine the sintering temperatures, the dried powders were subjected to DSC/TGA characterization by using a thermal analyser (Netzsch, Germany STA449C/4/MFC/G). Calcinations of BFN and CCTO dried powders were carried out in a microwave furnace at 900 °C for 40 minutes and at 800 °C for 40 minutes, respectively. Development of phase formation was studied by using X-ray diffraction (XRD) (Rigaku Ultima IV X-ray diffractometer, Tokyo, Japan) technique. Calcined powders were mixed thoroughly with 2 wt.% polyvinyl alcohol (PVA) and pressed into disks of diameter ∼10 mm and a thickness ∼1.5 mm under ∼60 MPa pressure using a hydraulic press. Microwave sintering of BFN and CCTO pellets was carried out at 1100 °C for 1 h and 1000 °C for 1 h, respectively, with a heating rate of 40 °C/min by placing the green pellets at the centre of 4.4 kW, 2.45 GHz multi-mode microwave cavity [12]. Microwave furnace temperature was recorded by using a Raytek non-contact sensor (XRTG5). Experimental density of the sintered samples was calculated by using Archimedes method. Microstructures of the sintered samples were studied using JEOL T-330 scanning electron microscope (SEM). Silver paste was applied on both sides of sintered pellets and fired at 400 °C for 30 min for good adhesion. Dielectric properties (ε_r and $\tan\delta$) were measured as a function of temperature at different frequencies using computer interfaced HIOKI 3532-50 LCR-HITESTER.

III. Results and discussion

Figure 1a shows the DSC and TGA curves of the uncalcined BFN powder. From room temperature (RT) to 1200 °C, the overall weight loss is ∼35%. In the uncalcined BFN powder, reactions between the starting precursors are starting at ∼300 °C and completing at ∼900 °C. Figure 1b shows the DSC and TGA curves of the uncalcined CCTO powder. There is also an overall weight loss of ∼45% from RT to 30 °C, which can be attributed to the loss of solvents and non-structural

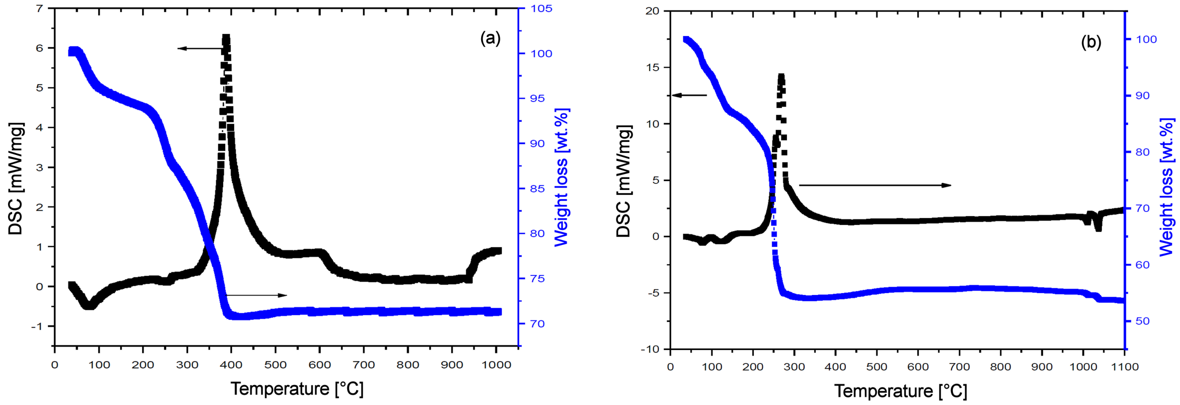

Figure 1. DSC and TGA curves of the uncalcined: a) BFN and b) CCTO powders

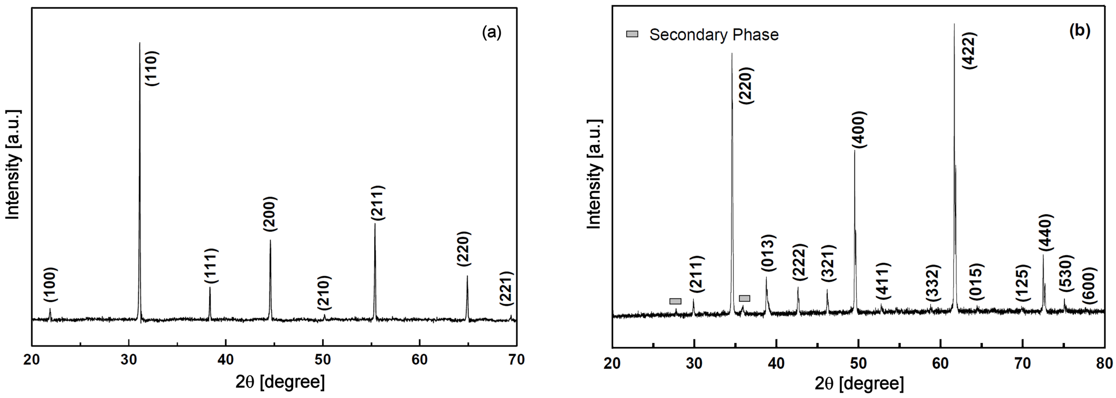

Figure 2. XRD patterns of the sintered: a) BFN and b) CCTO ceramic samples

water desorption and destruction of xerogel network. In the DSC plot, exothermal peaks at ~300 °C can be attributed to the combustion reactions, and formation of intermediate phases. DSC peak at ~1000 °C can be attributed to the decomposition and reactions between the intermediate phases to form the CCTO compound.

Figure 2 shows XRD patterns of the sintered BFN and CCTO samples at 1100 °C and 1000 °C for 1 h each, respectively. The presence of single perovskite phase peaks can be seen from XRD pattern of the sintered BFN sample, while small amount of secondary phase is observed in XRD pattern of the sintered CCTO ceramics. Secondary phase fraction (*SPF*) in the sintered CCTO sample is calculated by using the following equation [13]:

$$SPF = \frac{I_s}{I_p + I_s} \tag{1}$$

where, I_p and I_s are intensities of the most intense peaks corresponding to perovskite and secondary phases, respectively. The secondary phase is found to be CuO, which is below 5% in the sintered CCTO ceramic sample. Compared to other processing techniques [14–16], the microwave assisted sol-gel processing has significantly reduced the processing temperature and time, which highlights its advantage.

Figure 3 shows SEM micrographs of the sintered BFN and CCTO ceramics. Dense distribution of grains can be observed in both ceramic samples. Grains with size ranging from ~2 μm to 10 μm and from 1 μm to 4.5 μm were observed in the sintered BFN and CCTO ceramic samples, respectively. In comparison to the BFN sample, a slight decrease of average grain size is observed in the CCTO ceramics. The average grain size, calculated by using linear intercept method, is found to be ~3 μm and 1 μm for the BFN and CCTO ceramic samples, respectively. Intatha *et al.* [14] and Eitssayeam *et al.* [15] reported grain size of ~9 μm in conventionally prepared BFN ceramics. Zang *et al.* [16,17] synthesized CCTO samples through conventional solid state reaction route and reported grain size of ~10 μm. The present study highlights that through microwave processing technique we can obtain fine and uniform distribution of grains with dense morphology.

Experimental density of the sintered BFN and CCTO samples (d_{exp}) is calculated by using Archimedes' principle [18]:

$$d_{exp} = d_k \frac{w_{dry}}{w_{soa} - w_{sus}} \tag{2}$$

where w_{dry}, w_{soa}, and w_{sus} are the dry weight, soaked weight and suspended weight of the pellet, respectively,

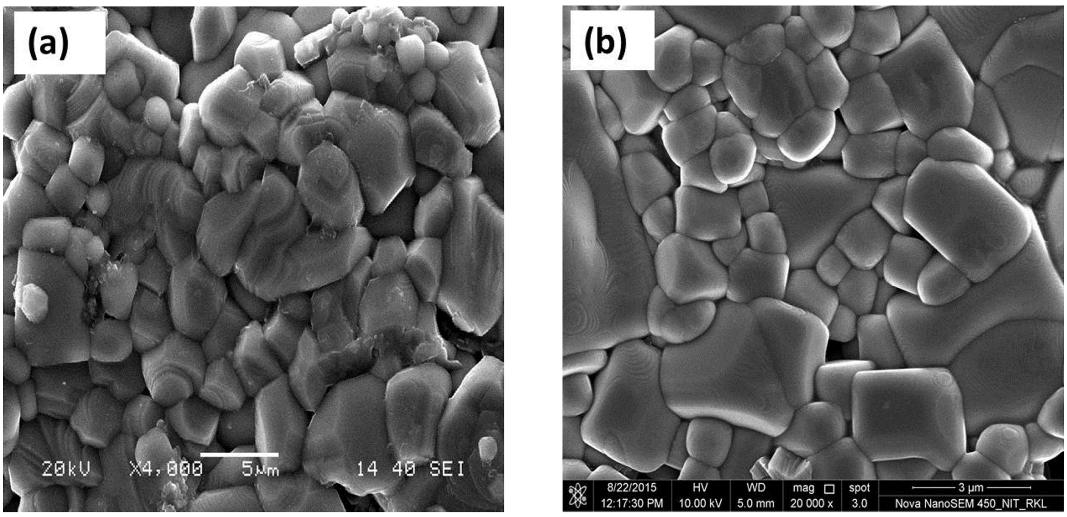

Figure 3. SEM micrographs of the sintered: a) BFN and b) CCTO ceramic samples

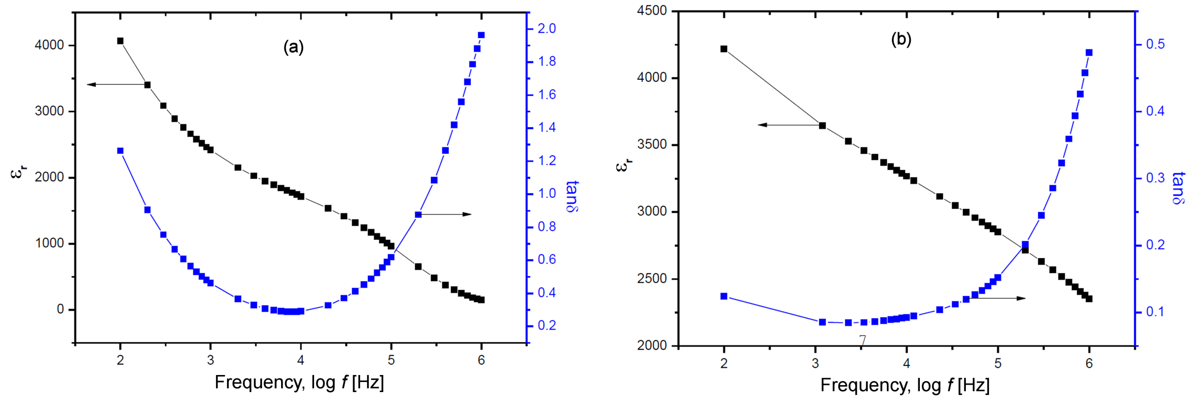

Figure 4. Frequency dependence of ε_r and tan δ of: a) BFN and b) CCTO ceramic samples

and d_k is the density of the kerosene oil. The ratio of the experimental density to the theoretical density (TD) is known as the relative density [19]. Experimental densities of the BFN and CCTO ceramic samples are ~6.28 and 4.73 g/cm^3, which corresponds to ~96 %TD and 95 %TD, respectively. Experimental density of the microwave processed BFN and CCTO ceramic samples is nearly equal to the same samples processed conventionally [14–16].

Figure 4 shows the frequency dependence of ε_r and tan δ of the sintered BFN and CCTO ceramics. Frequency dependence dielectric spectra of both samples reveal that ε_r decreases and tan δ increases with the increase of frequency. The net polarization of a material is the sum of ionic, dipolar, electronic and interfacial polarizations. At low frequencies, all the polarization mechanisms contribute to ε_r whereas different polarization mechanisms filter out with increasing frequency. Therefore, ε_r contributions of both samples decrease with the increase of frequency, which results in decrease of dielectric constant [12,20]. In order to clearly distinguish between the effects of different polarizations on dielectric properties broadband dielectric study must be performed. All the polarizations are active in the low frequency region of applied external AC electric field, and with the increase of frequency the relaxation processes sets in the materials, which results in the high dielectric loss. At lower frequencies, all the dipoles easily respond to the applied frequency whereas with increasing frequency, the dipoles cannot orient instantaneously to the frequency leading to the lag in the polarization and dielectric loss. Therefore, tan δ of both samples increases with the increase of frequency [21]. High dielectric loss at low frequencies for the BFN ceramic sample suggests the presence of relaxation frequency in the lower frequency range. In MHz frequency region, sharp decrease in ε_r and increase in tan δ is observed in the BFN ceramic sample, which indicates Debye like relaxation [22].

Figures 5a,c show the temperature dependence of the dielectric constant (at different frequencies) for the sintered BFN and CCTO ceramics. Dielectric values for both ceramic samples at selected temperatures and frequencies are given in Table 1. Temperature coefficient of capacitance (T_{cc}) is a very important parameter for deciding about the utility of a particular dielectric material for MLC applications. T_{cc}, within a temperature range of T_I to T_{II}, is defined with the following equation:

$$T_{cc} = \frac{\varepsilon_r(T_{II}) - \varepsilon_r(T_I)}{\varepsilon_r(T_I)} \tag{3}$$

where $\varepsilon_r(T)$ is dielectric constant at temperature T. In the 20–60 °C temperature range, value of T_{cc} is negligible for both BFN and CCTO ceramic samples. Figures 5b,d show the temperature variation of tan δ at different frequencies for the sintered BFN and CCTO ceramics. It can be seen that the BFN ceramics has higher tan δ than the CCTO ceramics. Dielectric loss at 1 MHz frequency rises suddenly in both ceramic samples. At lower frequency, different polarizations, present in the materials can follow the field variations. However, with the increase of frequency, polarizations start lagging behind and account the rise in dielectric loss. Higher value of ε_r ~ 3600 and lower value of tan δ ~ 0.07 at frequency of 1 kHz for the CCTO ceramic sample in 20–60 °C temperature range hint about its utility for MLC applications.

Dielectric properties of the obtained BFN ceramics are comparable with the earlier reports [14,23–25]. In the present study, ε_r is lower than in the earlier reports [14,23–25], but low T_{cc}, low tan δ in 20–60 °C temperature range of the BFN ceramics, processed at lower processing temperature and duration, signifies the im-

Table 1. Dielectric properties of BFN and CCTO ceramic samples at 1 kHz

Sample	Calcination temperature [°C]	Sintering temperature [°C]	Grain size [µm]	ε_r at 20 °C	ε_r at 60 °C	tan δ at 20 °C	tan δ at 60 °C
BFN	900	1100	4	2450	2500	0.5	0.5
CCTO	800	1000	1.5	3600	3600	0.075	0.070

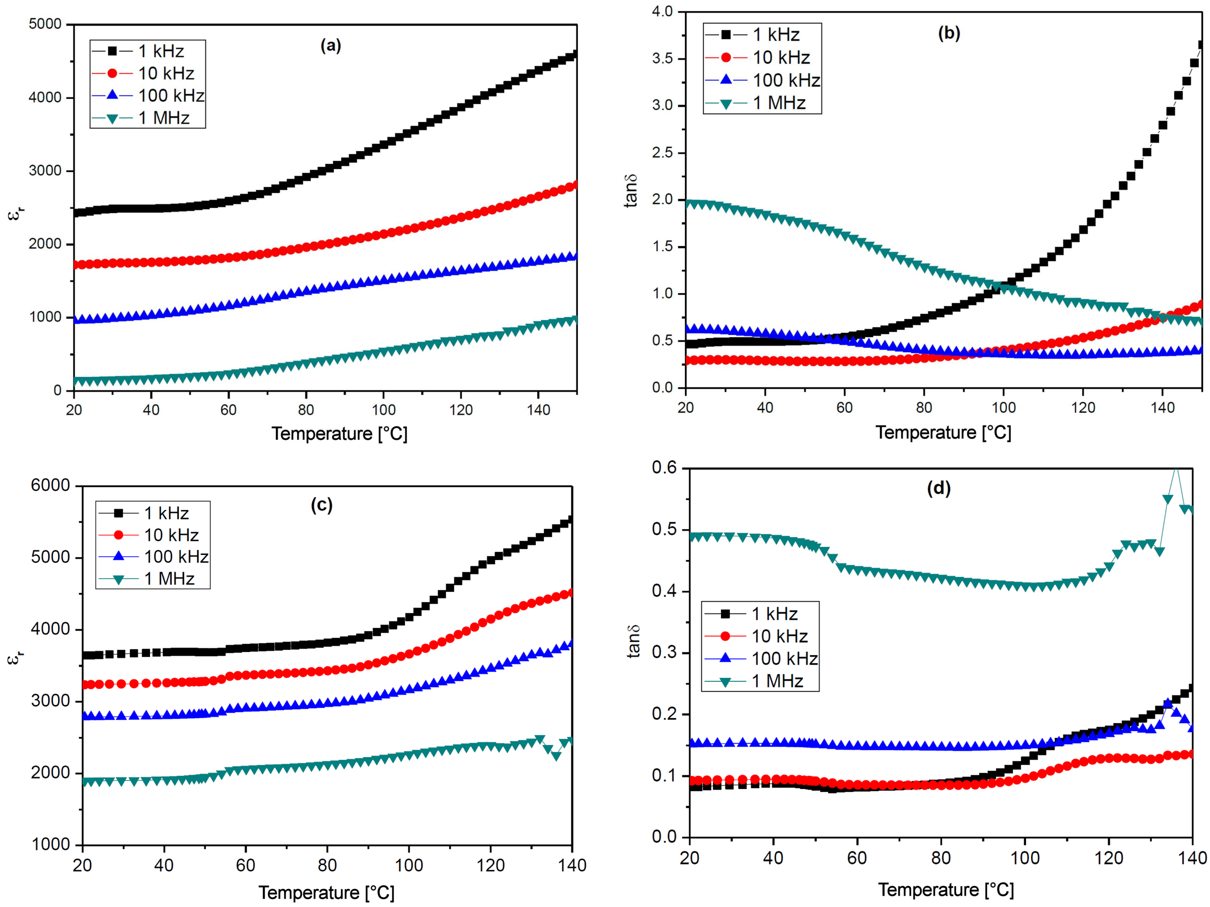

Figure 5. Temperature dependence of: a) ε_r, b) tan δ for BFN, and c) ε_r, d) tan δ for CCTO ceramic samples

portance of present synthesis route. Dielectric loss of the microwave assisted sol-gel synthesized and sintered CCTO ceramics is much lower than that of earlier reports [26]. This suggests that the microwave assisted sol-gel synthesis technique is helpful to inhibit the grain growth and lowers the dielectric loss of CCTO ceramic samples [27].

IV. Conclusions

$Ba(Fe_{1/2}Nb_{1/2})O_3$ (BFN) and $CaCu_3Ti_4O_{12}$ (CCTO) ceramic powders were synthesized by microwave assisted sol-gel technique and sintered at relatively low processing temperatures and durations. Dielectric properties of the sintered CCTO ceramic samples are better than for BFN ceramic samples. Higher value of dielectric constant, lower value of dielectric loss with negligible temperature coefficient of capacitance of the prepared CCTO ceramics suggested its usefulness for MLC applications. Lower processing temperature and processing durations highlighted the advantage of microwave assisted sol-gel synthesis technique.

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