Silica–calcium zirconate nanocomposite, studying its thermal and electrical properties

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Abstract. Silica–calcium zirconate nanocomposite was prepared in a two-step procedure. First, nanocalcium zirconate was synthesized by the modified sol–gel method; then, silica was added to the prepared sol and the resulting product was calcined at 700–1000°C. Dilatometric measurements were performed to determine the coefficient of thermal expansion (k_α). It was concluded that k_α was decreased from 15.96×10^{-6} to $10.26 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ with the increase in calcium zirconate/silica ratio. Moreover, studies on the dielectric properties and calcination temperature showed that the dielectric constant (ϵ_r) was increased from 3.9 to 5.7.

Keywords. Nanocomposite; silica–calcium zirconate; thermal coefficient expansion; dielectric constant.

1. Introduction

Calcium zirconate (CaZrO_3) is the most stable compound in the ZrO_2 – CaO quasi-binary systems and has received great attention due to its unique characteristics.¹ CaZrO_3 has perovskite structure and bears orthorhombic crystalline lattice.^{2–4} Materials with perovskite structure are well known because of their significant electrical properties, including ferroelectricity, piezoelectricity and superconductivity. Thus, CaZrO_3 is a potential candidate for multilayer ceramic capacitors or dielectric resonators, especially at short wavelengths, because of its high dielectric constant and low dielectric loss.^{5–8} Furthermore, high melting point, improved resistance to chemical degradation and slog and low coefficient of thermal expansion of CaZrO_3 , made it suitable for refractory ceramic applications.^{9–12} Bin *et al*¹³ reported that the dielectric properties of BaTiO_3 can be improved with the addition of CaZrO_3 . There are different methods for the preparation of CaZrO_3 , including chemical and ceramic methods. Ceramic methods have a few disadvantages such as large particle size, low surface area, lack of chemical homogeneity and high agglomeration degree.^{14–16} Moreover, chemical approach gains much interest due to its high crystallinity and low temperature.⁴

Different factors can affect the dielectric properties of perovskite ceramics. Among these properties, grain size has attracted great interests. Buessem *et al*¹⁷ reported that the dielectric constant of BaTiO_3 increases with the decrease of grain size in the range of 0.8–50 μm resulting from the

contribution of residual stress in grains. Also, Tang *et al*¹⁸ showed that the dielectric constant of $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ reduces with the decrease of grain size in the range of 2–60 μm which is due to the transition from normal to relax ferroelectric in small particles. Arlt *et al*¹⁹ also proposed that there is an optimum grain size of 0.8 μm to reach the maximum dielectric constant. Generally, grain boundaries have undesirable effects on dielectric properties due to the accumulation of impurities, porosity and changes in ferroelectric domains.²⁰

Materials with low dielectric constant can be applied as electrical insulators and can cause a fast signal transmission. Dielectric properties depend on the following parameters: porosity, the amount of crystalline phase, grain size distribution and density. The dielectric constant decreases with the increase on porosity and therefore study of the sinterability in dielectric properties is of great importance.^{18,21,22}

Silica has valuable characteristics, such as low dielectric constant and dielectric loss, high melting point and chemical stability and low coefficient of thermal expansion which make it suitable for numerous applications. For example, low dielectric constant of silica reduces the thickness of parasitic capacitance, resulting in fast switching and less heat loss.^{23–26} Silica and CaZrO_3 have nearly similar physical properties such as low thermal expansion coefficient and good thermal shock resistance. Therefore, studies on the preparation of composites with improved mentioned properties are considered.

In the current study, silica–calcium zirconate (CZS) nanocomposite was prepared according to the sol–gel method and their characteristics were investigated. Moreover, their thermal and dielectric properties were evaluated as well.

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2. Experimental

The chemicals used in this study to synthesize CZS nanocomposite were all of analytical grade. Stearic acid ($C_{18}H_{36}O_2$), calcium acetate ($Ca(CH_3COO)_2$) were purchased from Merck, zirconium butoxide ($Zr(OCH_2CH_2CH_2CH_3)_4$) was provided from Sigma and nanosilica (SiO_2) was obtained from Razi adv. Mat.

2.1 Synthesis of CZS nanocomposite

CZS nanocomposite was prepared according to the sol-gel method as shown in figure 1. Zirconium butoxide and calcium acetate with the molar ratio of 1:1 were first dissolved in stearic acid. Different weight percentages of silica (80, 85, 90 and 95) were then added to the prepared calcium zirconate (CZ) sol. After heating and stirring at $80^\circ C$, a transparent aqueous precursor solution was obtained. The precursor was then heated until the solution evaporated, leaving a soft, grey and aerated gel. The dried gel was calcined at 700, 900 and $1000^\circ C$ for 4 h in air. Finally, CZS nanocomposite was produced successfully.

The characteristics of the prepared nanocomposite were studied by means of X-ray diffraction (XRD) (Philips D500), Fourier transform infrared (FT-IR) (Bruker-Vector 22), XRF (Oxford ED 2000) and SEM (Philips XL30) analyses. By adding 2 wt% of polyvinyl alcohol (PVA) and applying pressure (150 MPa), pellets with diameter of 1 cm and thickness of 2 mm were prepared. Pellets were then sintered at $1300^\circ C$ and covered with gold after that their capacitance were measured by LCR Meter instrument (AC voltage; 10 mV, frequency; 1–100Hz). The coefficient of thermal expansion was determined using a dilatometer (Model Netzsch DIL 402E) with the heating rate of $30^\circ C\ min^{-1}$ and temperature range of 25– $1200^\circ C$.

Figure 1. Schematic representation of silica-calcium zirconate nanocomposite synthesis with the sol-gel method.

3. Results and discussion

Table 1 shows the elemental analysis of natural nanosilica measured with XRF. It can be seen that the main component of silica is silicon dioxide and other elements including alumina, alkaline and alkaline earth oxides with low percentages. XRD analyses are shown in figures 2 and 3 and show that the SiO_2 and CZ patterns were in agreement with the data in the JCPDS files (standard cards no. 01-085-0457 (SiO_2) and 01-076-2401 (CZ)). It also demonstrated that CZ has orthorhombic structure. Moreover, the absence of phase impurity confirmed purity of these materials. SEM images of silica and $CaZrO_3$ are illustrated in figures 4 and 5, respectively. Silica nanopowders were in spherical shape and their mean particle size was about 95 nm, indicating the silica as a suitable matrix. SEM image of $CaZrO_3$ nanopowder showed uniform particles with the average size of 75 nm. Size distribution of silica and $CaZrO_3$ are shown using Clemex Image Analysis version 3.5, which proved the uniformity of $CaZrO_3$ nanopowder.

The XRD patterns of silica, CZ and CZS, respectively, as matrix, second phase and nanocomposite are compared in figure 6. The pattern of CZS nanocomposite shifted to the left direction in $30.13 (2\theta)$. XRD pattern of silica-5 wt% calcium zirconate (CZS 5%) indicated that CZS 5% nanocomposite did not obtain and only silica peaks are

Table 1. XRF analysis of silica nanopowder.

Element	SiO_2	Al_2O_3	MgO	Fe_2O_3	SO_3	P_2O_5	Na_2O	K_2O	CaO
wt%	93.53	1.92	0.98	0.83	0.83	0.58	0.45	0.43	0.33

Figure 2. XRD pattern of CZ.

Figure 3. XRD pattern of silica.

Figure 4. SEM image and size distribution of silica.

Figure 5. SEM image and size distribution of CZ.

observed at the temperature of 700°C (figure 7a). CaZrO₃ peaks are appeared with increasing temperature to 900°C (figure 7b), implying the production of nanocomposite. Additionally, no change has been observed with enhancing temperature up to 1000°C and the sharpened peaks are only an indicative of grain growth (figure 7c).

Figure 8 illustrates the XRD patterns of CaZrO₃ calcined at 900°C. It can be seen that peak intensity was increased with enhancing CaZrO₃ phase and an insignificant peak in 5 wt% sample was converted to distinct peak in 34.73 (2θ) in 20 wt% CZS with increasing CaZrO₃.

Figure 9 shows the FT-IR patterns of silica, CaZrO₃ and nanocomposite calcined at 900°C. The spectrum of CZS (figure 9c) is shifted to the lower frequency compared to the spectra of silica (figure 9a) and CZ (figure 9b), due to the presence of Si–O covalent bonds in CaZrO₃–SiO₂.^{27,28}

Figure 6. XRD patterns of (a) silica, (b) CZ and (c) CZS 20% after calcination at 900°C.

Thermal behaviour of nanocomposite was evaluated through the calculation of thermal expansion coefficient. Figure 10 demonstrates the thermal behaviour of silica, CZS 10% and CZS 20% nanocomposites, over a temperature range of 25–1000°C. The average value of thermal expansion coefficient for silica, CZS 10% and CZS 20% nanocomposite were 15.96×10^{-6} , 13.44×10^{-6} and $10.2 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, respectively. It should be noted that, the coefficient of thermal expansion was decreased with enhancing CaZrO₃/silica ratio. Thus, the relationship between the nanocomposite components and coefficient of thermal expansion is calculated as follows:^{26,29}

$$\alpha = \alpha_1 + \frac{(\alpha_2 - \alpha_1) V_2 E_2 (1 - 2\nu_1)}{V_1 E_1 (1 - 2\nu_2) + V_1 E_1 (1 - 2\nu_1)}, \quad (1)$$

where α is the coefficient of thermal expansion, E the elasticity modulus, V the volumetric content, ν the Poisson ratio, 1 and 2 are the matrix and secondary phase, respectively.

Figure 7. XRD patterns of CZS 5% calcined at (a) 700°C, (b) 900°C and (c) 1000°C.

Figure 8. XRD pattern of (a) CZS 5%, (b) CZS 10%, (c) CZS 15% and (d) CZS 20% after calcinations at 900°C.

The thermal expansion coefficient of silica–20 wt% CaZrO₃ nanocomposite was calculated using equation (1). According to this equation, the thermal expansion coefficient of CZS ($10.26 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) with 0.03 approximations ($10.29 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) followed the equation (1).

Figure 11 shows the dielectric constants and losses of nanocomposite in the range of 1–100 kHz. As figure 11 clearly shows, the dielectric constant of nanocomposite was decreased from 7.24 in 1 kHz to 5.85 in 100 kHz with the increase of frequency. Dielectric constant of the calcined samples at the frequency of 100 kHz, and at temperatures of 700, 900 and 1000°C, were 4.71, 5.29 and 5.85, respectively. Also, dielectric losses of samples were 0.0351, 0.0422 and 0.05, respectively. All the above-mentioned changes are attributed to the decreasing of space-charge polarization.³⁰

The effect of the addition of CaZrO₃ on the dielectric constant of the synthesized nanocomposite at 1000°C is shown in figure 12. It can be concluded that the dielectric constant of silica (dielectric constant of 4) was increased with the addition of CaZrO₃ (dielectric constant of 27). This increase follows the equation (2) which is presented by Sheen *et al*²¹

$$\varepsilon_{\text{mix}} - \varepsilon_m = \frac{(\varepsilon_d - \varepsilon_m)(\varepsilon_m + 2\varepsilon_d)}{3\varepsilon_d} V_d, \quad (2)$$

where ε_{mix} , ε_m , and ε_d are the dielectric constant of composite, matrix and secondary phase, respectively, and V_d is the secondary volumetric content. Comparison of the mathematical calculations with the obtained results in table 2, imply that the obtained results follow the presented trend with 4% error.

As shown in figure 13 the dielectric constant was increased with the increase of calcination temperature and the calcined samples at 1000°C showed the highest dielectric constant, which can be attributed to the particle size of the nanocomposite (figure 14). Clearly, grain boundaries which are the main drawbacks of a system, can be decreased with enhancing grain size and thus have less undesirable results on the

Figure 9. IR spectra of (a) silica, (b) CZ and (c) CZS 20% after calcination at 900°C.

Figure 10. dL/L_0 alteration of (a) CZS 20%, (b) CZS 10% and (c) silica from 0 to 1200°C (dilatometer test).

Figure 11. The plot of dielectric constant of silica-20 wt% calcium zirconate nanocomposite calcined at 700, 900 and 1000°C from 1 to 100 kHz.

dielectric properties. SEM images of the sintered nanocomposites at 1300°C are shown in figure 14. It is clear that with increasing calcination temperature from 700 to 1000°C, particle size is increased from 0.383 to 0.886 μm .

4. Conclusion

In the present study, various weight percentages of CZS (5–20 wt%) were prepared successfully by the modified sol–gel method. Produced gel was calcined at temperatures of 700, 900 and 1000°C. The XRD patterns revealed that increase of CaZrO₃ and temperature are highly effective on the nanocomposite formation. Also, the presence of CaZrO₃ nanopowder in nanosilica matrix was confirmed. In FT-IR spectra, the effects of Si–O covalent bonds on Ca–O–Zr bonds resulted in a shift of the frequency to the lower values (cm^{-1}). Conspicuously, the spectra of nanocomposite was different from the structures of CaZrO₃ and silica, due to the fundamental changes of crystalline lattice, resulting in changes of the lattice formation energy, crystal energy,

Figure 12. Effect of CZ content on dielectric constant of CZS calcined at 1000°C (100 kHz).

Table 2. Comparison of the theoretical and the experimental results for dielectric constant of CZS.

Sample	Experimental value	Calculated value	Error %
5% CZS	4.0191	4.2170	4.924
10% CZS	4.4559	4.6565	4.501
15% CZS	5.3436	5.1202	4.181
20% CZS	5.8525	5.6104	4.138

Figure 13. The effect of calcination temperature on dielectric constant of CZS (100 kHz).

and stretching frequency of each bond. Moreover, the particle sizes of CaZrO₃ and silica were calculated using SEM images, which were about 75 and 95 nm, respectively. These findings indicated the fact that coefficient of thermal expansion was decreased with the addition of the CZ to the silica from $15.96 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ for pure silica to 10.26×10^{-6}

Figure 14. SEM images of CZS 20% calcined at (a) 700°C, (b) 900°C and (c) 1000°C.

1°C^{-1} for CZS 20%. Results showed that dielectric constant of the produced nanoparticles decreased with the increase of frequency. Additionally, dielectric constant of the nanocomposite was increased with enhancing CaZrO_3 phase and temperature. Dielectric constant of 5.8 and thermal expansion coefficient of $10.26 \times 10^{-6} 1^{\circ}\text{C}^{-1}$ for 20% nanocomposite are an indicative of an optimized conditions in comparison with other composite percentages.

References

1. Rog G, Dudek M, Kozłowska-Rog A and Bucko M 2002 *Electrochim. Acta* **47** 4523
2. Dudek M and Drozd-Ciesla E 2009 *J. Alloys Compd.* **475** 846
3. Ross N L and Chaplin T D J 2003 *J. Solid State Chem.* **172** 123
4. Prasanth C S, Kumar H P, Pazhani R, Solomon S and Thomas J K 2008 *J. Alloys Compd.* **464** 306
5. Yu T, Zhu W G, Chen C H, Chen X F and Krishnan R G 2004 *Physica B: Condens. Matter* **348** 440
6. Dudek M and Bucko M M 2003 *Solid State Ion* **157** 183
7. Dravid V P, Notis M R and Lyman C E 1987 *J. Mater. Sci.* **22** 4546
8. Levin I, Amos T G, Bell S M, Farber L, Vanderah T A, Roth R S and Toby B T 2003 *J. Solid State Chem.* **175** 170
9. Serena S, Sainz M A and Caballero A 2004 *J. Eur. Ceram. Soc.* **24** 2399
10. Jonas S, Nadachowski F and Szwagierczak D J 1998 *Ceram. Int.* **24** 211
11. Stoch P, Szczerba J, Lis J and Madej D Pedzich Z 2012 *J. Eur. Ceram. Soc.* **32** 665
12. Nadler M R and Fitzsimmons E S 1955 *J. Am. Ceram. Soc.* **38** 214
13. Bin T, Ren Z S, Ying Y, Hua Z X and Shuai L Y 2008 *Sci. China Technol. Sci.* **51** 1451
14. Ianos R and Barvinschi P 2010 *J. Solid State Chem.* **183** 491
15. Hwang S C and Choi G M 2008 *Solid State Ion* **179** 1042
16. Wang C C, Chen W H, Akbar S A and Alim M A 1997 *J. Mater. Sci.* **32** 2305
17. Buessem W R, Cross L E and Goswami A K 1966 *J. Am. Ceram. Soc.* **49** 33
18. Tang X G, Wang J, Wang X X and Chan H L W 2004 *Solid State Commun.* **131** 163
19. Arlt G, Hennings D and With G D 1985 *J. Appl. Phys.* **58** 1619
20. Moulson A J and Herbert J M 2003 *Electroceramics: materials, properties, applications* (Wiley and Sons) 2nd ed
21. Sheen J, Hong Z W, Liu W, Mao W L and Chen C A 2009 *Eur. Polym. J.* **45** 1316
22. Oh J T, Hing P and Fong H S 1999 *J. Mater. Process. Technol.* **89–90** 497
23. Mollá J and Ibarra A 2004 *Nucl. Instrum. Phys. Res. Sec. B, Beam Interact. Mater. Atoms* **218** 189
24. Jaln V, Varshneya A K and Bihuniak P P 1990 *J. Am. Ceram. Soc.* **73** 409
25. Ding S, Zeng Y P and Jiang D 2007 *Mater. Lett.* **61** 2277
26. Chen S, Zhang S, Zhou X and Wen Z 2011 *J. Alloys Compd.* **509** 4848
27. Selvam N C S, Manikandan A, Kennedy L J and Vijaya J J 2013 *J. Colloid Interface Sci.* **389** 91
28. Hu Q, Suzuki H, Gao H, Araki H, Yang W and Noda T 2003 *Chem. Phys. Lett.* **378** 299
29. Eberstein M, Glitzky C, Gemeinert M, Rabe T, Schiller W A and Modes C 2009 *Int. J. Appl. Ceram. Technol.* **6** 1
30. Song X, Fu R and He H 2009 *Microelectron. Eng.* **86** 2217