

Preparation of Calcium Zirconate- Silica nanocomposite and consideration of thermal, electrical and photocatalytic properties

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ABSTRACT

In this research calcium zirconate- silica nanocomposite was synthesized and its thermal, electrical and the photocatalytic properties were evaluated. For preparation of $\text{CaZrO}_3/\text{SiO}_2$, nano powder was synthesized by sol- gel method and was calcined at 700-1000°C. Next nanocomposite was synthesized by adding processing nano silica. The resulting nanocomposite and nano powder were characterized by XRD, FT-IR, SEM techniques. The results showed that by increasing the calcium zirconate phase to the silica matrix, thermal expansion decreases from 15.96×10^{-6} to 10.26×10^{-6} $1/^\circ\text{C}$. Also the dielectric constant increased from 3.9 for pure silica to 5.6 for nanocomposite CZS20. Photocatalytic activity of nanocomposite CZS20 by dye degradation of methylene blue under UV light was improved from 80% to 95% at room temperature.

Keywords: calcium zirconate- silica, nanocomposite.

1 INTRODUCTION

Calcium zirconate is the most stable form in the ZrO-CaO quasi-binary systems. In the case of crystalline structure, calcium zirconate is a perovskite and has an orthorhombic crystalline lattice. Since CaZrO_3 has a high dielectric constant and low heat loss, it can be a potential candidate for capacitors, resonators with short wavelengths, catalysts and solid electrolytes [1].

Low dielectric materials can meet the requirements for electrical insulation applications. Dielectric characteristics depend on porosity, crystalline phase, density and grain size distribution [2-4]. Silica is a chemical compound which can be used in radomes and antennas for its properties of low dielectric loss and dielectric constant, high melting point, high chemical stability, and low thermal expansion [5].

In the current study, calcium zirconate- silica nanocomposite was synthesized by means of sol-gel method, and its properties was investigated.

2 EXPERIMENTAL

Calcium zirconate- Silica nanocomposite was synthesized through sol-gel method. Stearic acid (Merck, 569398), zirconium butoxide (Sigma, 333948), calcium acetate (Merck, 109325) and Silica (Razi Adv. Mat., Iran) were used as chemical reagents.

For this purpose zirconium butoxide and calcium acetate precursors dissolved in stearic acid with (1:1) molar ratio. Then 80, 85, 90, and 95wt% of silica was added to the

calcium zirconate to obtain sol. The sol was aged at room temperature to convert to gel. The prepared gel was then calcined at the temperatures of 700, 900, and 1000 °C for 4h and calcium zirconate- Silica powder was synthesized successfully.

Finally the structural developments were measured by X-ray diffraction (XRD) using a Philips D500 diffractometer. FT-IR spectroscopy was also measured using a Bruker-Vector 22. Surface morphology and particle size of the nanocomposites were determined using a Philips XL30 scanning electronic microscopy (SEM). Both faces of the pellets were covered with gold and the dielectric constant (ϵ_r) of nanocomposites was then calculated (100 kHz, at room temperature) using a LCR Meter instrument Instek 8110G. Thermal coefficient expansion was tested (in the temperature range of 25-1200 °C) by a dilatometer Netzsch 402E. A UnicoSpectroQuest 4802 UV/Vis spectrometer was used to characterize the reflectance spectra of the catalysts over a range of 200-700 nm.

3 RESULT AND DISCUSSION

3.1 Characterization of Silica

The elemental composition of silica was determined using an Oxford ED 2000 instrument. As expected, silicon is the main oxide in silica (93.53%), which also contains small amounts of alumina, alkaline oxides, and alkaline earth oxides can also found in silica. Additionally, XRD analysis revealed that silica consists of single phase quartz (JCPDS Card No. 01-085-0457) (Fig. 1). The SEM micrograph is shown in Fig. 2 indicating that silica has homogeneous and spherical morphology and the average particle size is around 95 nm.

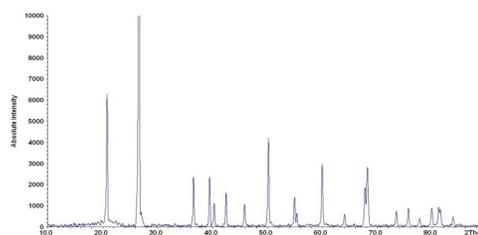


Figure 1: XRD patterns of silica.

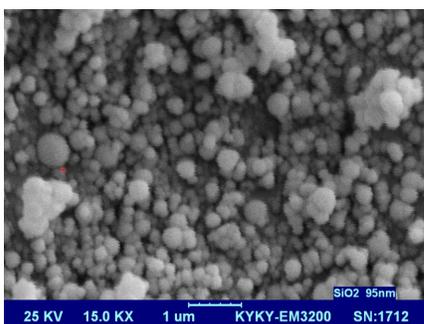


Figure 2: SEM micrograph of silica.

3.2 Characterization of Calcium Zirconate

XRD pattern in fig. 3 shows calcium zirconate single phase (JCPDS Card No. 01-076-2401). The SEM micrograph in Fig. 4 indicates that average particle size is around 75 nm.

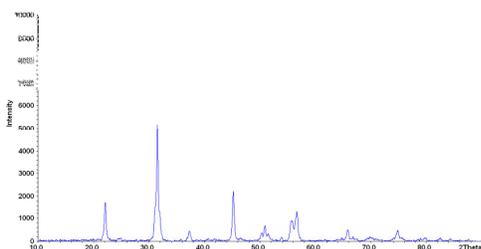


Figure 3: XRD patterns of calcium zirconate.

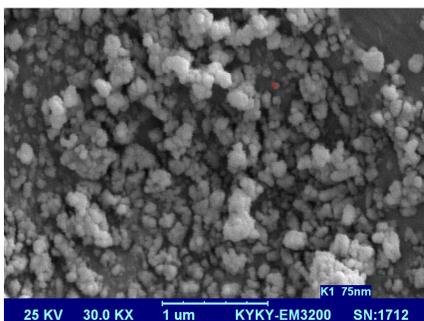


Figure 4: SEM micrograph of calcium zirconate.

3.3 Characterization of Nanocomposite

3.3.1 X-ray Diffraction (XRD)

Fig. 5 depicts the XRD patterns of silica- 5 wt% calcium zirconate nanocomposites. It can be seen that temperature of 700°C is inadequate for the synthesis of nanocomposite and only silica peaks are observed in the patterns. When calcination temperature is increased from 700 to 900°C, calcium zirconate peaks appeared in the patterns indicating that the nanocomposites is synthesized. No change is observed in the pattern when temperature is

increased to 1000°C and sharp peaks can be indicative of grain growth (Fig. 5).

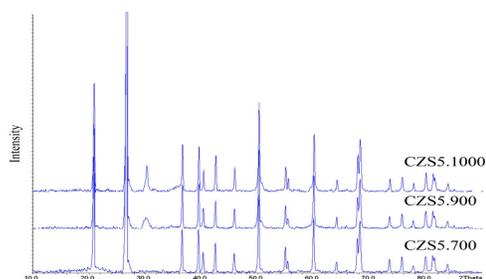


Figure 5: XRD patterns of silica- 5wt% calcium zirconate nanocomposites at 700, 900 and 1000°C.

XRD pattern of calcium zirconate silica nanocomposite at 900°C is shown in Fig. 6. As it can be seen from the patterns, peak intensity increases with the increase of calcium zirconate concentration. Samples containing 5% of calcium zirconate exhibit multiplet peaks and with the increase of second phase concentration, these peaks appeared as singlets.

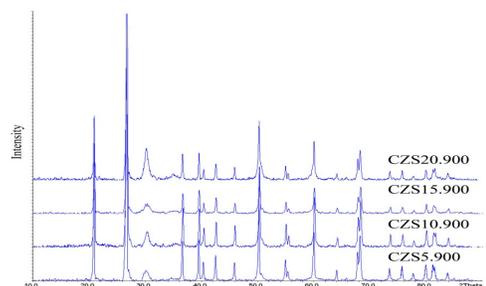


Figure 6: XRD patterns of nanocomposites with different calcium zirconate percentages at 900°C.

3.3.2 FT-IR Spectroscopy

FT-IR spectra of silica, calcium zirconate and nanocomposite are shown in Fig. 7. IR spectra of the prepared nanocomposite was different from spectra of silica and calcium zirconate which is due to the fundamental changes in the crystal lattice, leading to the changes of lattice and crystal energy and finally to the changes in stretching and vibrational frequencies of each bond in the structure [1].

3.3.3 Scanning Electron Microscopy (SEM)

Fig. 8 shows the SEM micrographs of the sintered nanocomposites at 1350°C. As it can be seen from the images, final particle size of the nanocomposites increases from 0.383 to 0.886μm with the increase of calcination temperature from 700 to 1000°C.

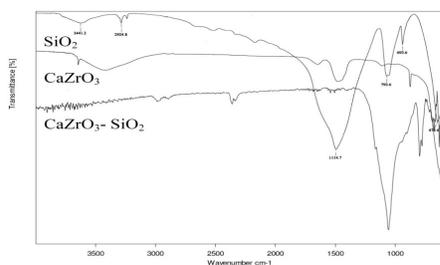


Figure 7: Comparison of the silica, calcium zirconate and 20 wt% nanocomposite spectra at 1000 °C.

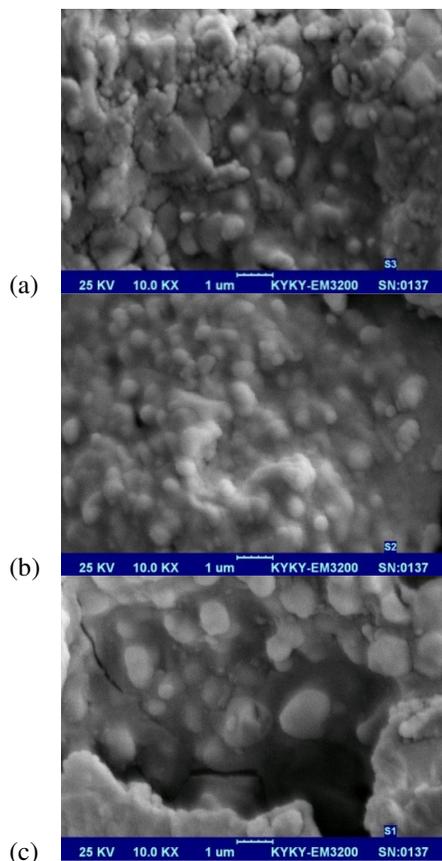


Figure 8. SEM images of 20wt% nanocomposites at 700 (a), 900 (b), and 1000°C (c).

3.4 Thermal Expansion

Thermal behavior of the prepared nanocomposite was studied by evaluating the coefficient of thermal expansion. Fig. 9 depicts the thermal expansion of silica and nanocomposites containing 10 and 20 wt% of calcium zirconate in the temperature range of 25-1000°C. The average thermal coefficient expansion coefficient was $15.96 \times 10^{-6} 1/^\circ\text{C}$, $13.44 \times 10^{-6} 1/^\circ\text{C}$, and $10.26 \times 10^{-6} 1/^\circ\text{C}$, for silica and nanocomposites containing 10 and 20 wt% of calcium zirconate, respectively. As it can be seen, the

coefficient of thermal expansion decreases with increasing of calcium zirconate/silica weight percent ratio.

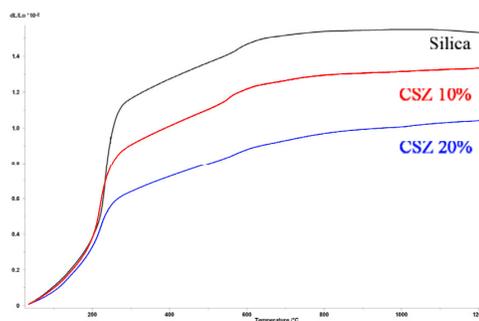


Figure 9. Comparison of thermal coefficient expansion (k_α) of Silica, 10 and 20 %wt nanocomposites in air in the temperature range 25-1200 °C.

3.5 UV-Vis spectroscopy

The degradation rate of methylene blue solution was calculated with 20wt% nanocomposite using UV/Vis spectroscopy at the temperatures of 700, 900, and 1000°C in the range of 200- 800 nm (Fig. 10). Methylene blue degradation decreased from 95% to 80% with the increase of calcination temperature within 60 min. This may correspond to the increase of specific surface area and particle size distribution.

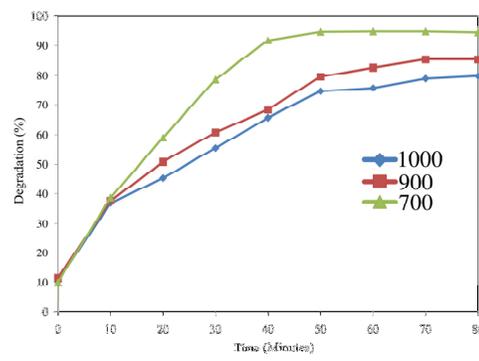


Figure 10: Comparison of Silica- 20 %wt CaZrO₃ nanocomposite calcined at 700-1000°C for methylene blue degradation.

3.6 Consideration of Dielectric Properties

3.6.1 Effect of Frequency

Dielectric constant of nanocomposite in a frequency range from 1 to 100 Hz is shown in Fig. 11. It can be inferred from the figure that the dielectric constant of nanocomposite decreases with the increase of frequency.

3.6.2 Effect of Second Phase

The effect of calcium zirconate phase addition on the nanocomposite dielectric constant at 1000°C is illustrated in Fig. 12. It can be observed that with the addition of calcium zirconate phase (dielectric constant ~ 27) to silica (dielectric constant ~ 4), dielectric constant is increased.

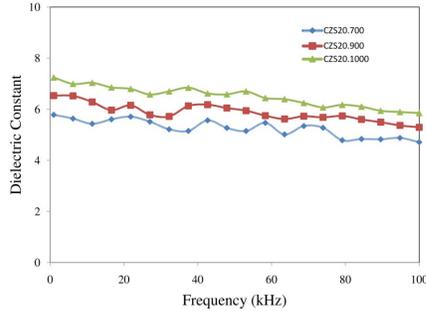


Figure 11: Dielectric constant of silica-calcium zirconate nanocomposites at different frequencies.

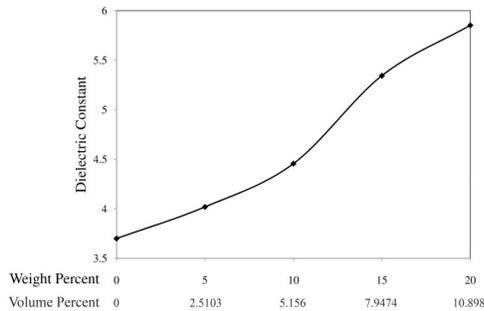


Figure 12: Dielectric constant of nanocomposite according to the required calcium zirconate phase for the synthesis of samples at 1000°C.

The increase of dielectric constant can be calculated from the following model (eq. 1), presented by Sheen et al. [3].

$$\epsilon_{mix} - \epsilon_m = \frac{(\epsilon_d - \epsilon_m)(\epsilon_m + 2\epsilon_d)}{3\epsilon_d} V_d \quad (1)$$

Where ϵ_{mix} , ϵ_m and ϵ_d are the composite dielectric constant, matrix and second phase, respectively. Also, V_d is the volume percent of the second phase. A comparison of the obtained results and mathematical calculations is presented in Table 1. The obtained results follow the equation with percentage error of 4%.

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

Table 1. Comparison of the experimental and theoretical results for the dielectric constant of calcium zirconate-silica nanocomposite.

3.6.3 Effect of Calcination Temperature

The effect of calcination temperature on the dielectric constant of calcium zirconate-silica nanocomposite is shown in Fig. 13. Dielectric constant increases with the increase of calcination temperature and thus samples have the highest dielectric constant at the temperature of 1000°C. This can be due to the increase of nanocomposite particle size (Fig. 8). Such an effect was also studied for barium zirconate titanate system by Tang et al. [4] and same results were obtained.

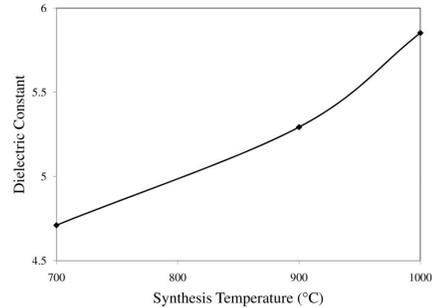


Figure 13: Effect of temperature on the dielectric constant of silica-calcium zirconate nanocomposite.

4 CONCLUSION

Calcium zirconate-silica nanocomposite was synthesized by sol-gel method. The gel was calcined at 700- 1000°C. The presence of CaZrO_3 in nano silica matrix was confirmed by XRD. The formation of CaZrO_3 was further supported by the FT-IR spectra. Thermal behavior of the prepared nanocomposites indicated that an increase of calcium zirconate concentration value lead to the decrease of thermal expansion coefficient from $15.96 \times 10^{-6} \text{ 1}^\circ\text{C}$ to $10.26 \times 10^{-6} \text{ 1}^\circ\text{C}$. The obtained results of dielectric constant of the synthesized nanocomposites revealed that dielectric constant decreases with the increase of frequency. Moreover, the increase of calcium zirconate concentration and synthesis temperature can also leads to the increase of dielectric constant. Photocatalytic characteristics were investigated using methylene blue degradation, indicating that the degradation rate decreases with the increase of calcination temperature.

REFERENCES

- [1] C.S. Prasanth, H. P. Kumar, R. Pazhani, S. Solomon and J.K. Thomas, *J. Alloys Comp.*, 464, 306, 2008.
- [2] J.T. Oh, P. Hing and H.S. Fong, *J. Mater. Process. Technol.*, 89-90, 497, 1999.
- [3] J. Sheen, Z.W. Hong, W. Liu, W.L. Mao and C.A. Chen, *Eur. Polym. J.*, 45, 1316, 2009.
- [4] X.G. Tang, J. Wang, X.X. Wang and H.L.W. Chan, *Solid State Commun.*, 131, 163, 2004.
- [5] S. Ding, Y.P. Zeng and D. Jiang, *Mater. Lett.*, 61, 2277, 2007.