



Structural and Dielectric Properties of CaZrO₃ and SrZrO₃ Zirconate

S.K. YADAV, A.N. THAKUR*, A. KUMAR, S.N. SINGH and PRIYANKA RANI

Department of Physics, T.D. Post Graduate College, Jaunpur-222 002, India

*Corresponding author: E-mail: ant_tdc@yahoo.com

(Received: 9 October 2010;

Accepted: 14 March 2011)

AJC-9745

The polycrystalline samples CaZrO₃ and SrZrO₃ have been prepared by solid state reaction technique and characterised by XRD, DTA, TGA and DTG. The XRD characterisation shows them to be orthorhombic. The dielectric constant (ϵ') and dielectric loss (ϵ'') of above compounds have been studied at 1 kHz in temperature range of 300 to 1150 K. The $\log \epsilon'$ vs. T and $\log \epsilon''$ vs. T graph show rapid increase of dielectric constant above 730 and 720 K, respectively.

Key Words: Dielectric constant, Dielectric loss, XRD, DTA, TGA, DTG, CaZrO₃ and SrZrO₃.

INTRODUCTION

Perovskite materials are important materials for various functional devices. SrZrO₃ based perovskite oxides have been studied because of the interest in their high temperature protonic conductivity^{1,2} and promising use in MHD generators^{3,4}. Besides these, SrZrO₃ still has many characteristics which are suitable for high-voltage and high reliability capacitor applications. Calcium zirconate (CaZrO₃) with a perovskite structure has a high melting temperature, an excellent thermal and chemical stability and a good thermal shock resistance⁵⁻⁷. It is an interesting material for both mechanical and electrical applications, such as fuel cells⁸, filter⁹, resonator¹⁰ for microwave telecommunication and temperature compensating materials of capacitance in multilayer ceramic capacitor. In this study the dielectric constant and dielectric loss of SrZrO₃ and CaZrO₃ were measured as a function of temperature.

EXPERIMENTAL

Sample preparation: CaZrO₃ and SrZrO₃ ceramics were synthesized by a conventional solid state reaction technique, using high purity powders of CaO, SrO and ZrO₂ (99.99 % pure, procured from Alfa Aesar, A Johnson Matthey company, USA) were used as the starting materials. The stoichiometric amount of these oxides were mixed and heated in alumina crucible for 50 h at 1300 K. In this process the mixture was followed by one intermediate grinding and the final product was cool down slowly. The calcined powders are isostatically pressed into pellets at a pressure of $7.19 \times 10^8 \text{ Nm}^{-2}$ followed by sintering at 1500 K for 24 h in air.

For confirmation regarding the complete formation of the compounds, X-ray diffraction pattern of the sample was taken at room temperature using CuK α line ($\lambda = 0.15418 \text{ nm}$). The DT, TG and DTG studies of the compounds were carried out in nitrogen atmosphere using a thermal analyzer (Perkin-Elmer Pyris) at a heating rate of 283 K/min and flow rate of 100 mL/min from 323 to 1123 K.

The dielectric constant and dielectric loss were obtained by measuring the capacitance (c) and quality factor (Q) of the pressed and sintered pellets of the studied sample at a frequency of 1 kHz, using LCR-Q meter model-928, systronic, India.

RESULTS AND DISCUSSION

From XRD pattern the values of d_{hkl} plane have been obtained using the relation¹¹.

$$d_{hkl} = \frac{0.15418}{2\sin\theta} \quad (1)$$

From d_{hkl} values, structure of the studied compounds were resolved. All the peaks have been assigned with proper hkl values. This confirms that the prepared compound has single phase and no unreacted part of the starting material was left. The XRD pattern of the compounds are shown in Figs. 1 and 2. The crystal structure of the compounds with lattice parameters are given in Table-1.

The differential thermal (DT), thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of CaZrO₃ and SrZrO₃ are shown in Figs. 3 and 4. DT curves of each compound show a broad peak ca. 673 K which is indicative of exothermic reaction.

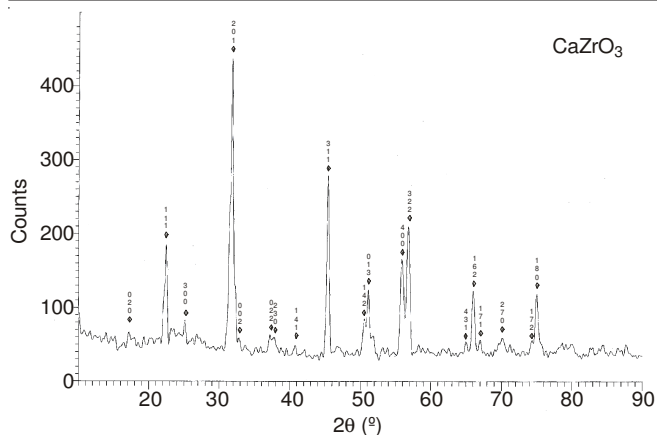
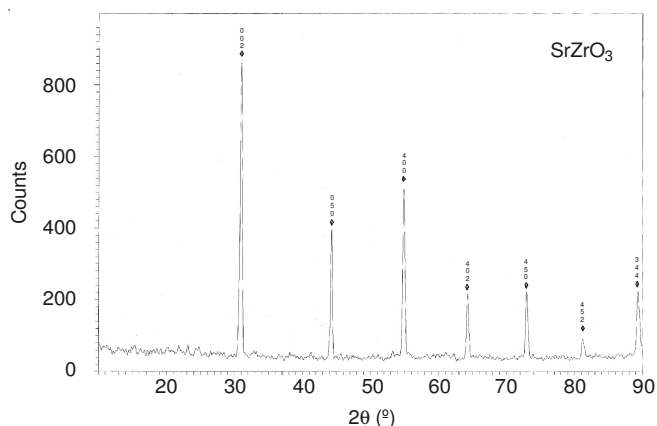
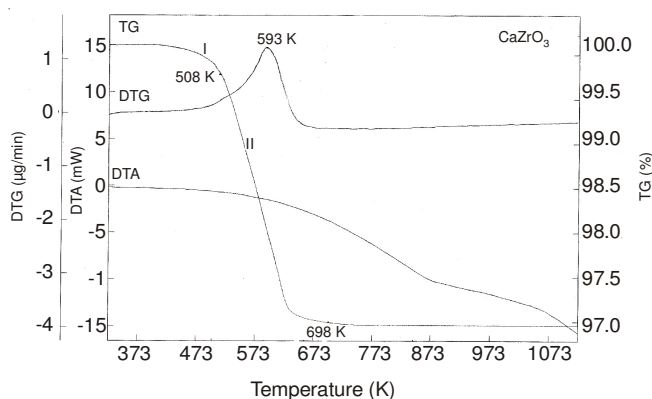
Fig. 1. Room temperature XRD pattern of CaZrO₃Fig. 2. Room temperature XRD pattern of SrZrO₃

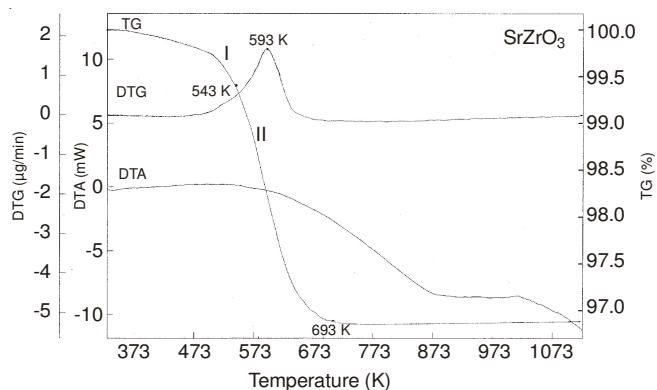
TABLE-1

STRUCTURAL PARAMETERS OF ORTHORHOMBIC UNIT CELL, CALCULATED DENSITY (d_0), DENSITY OF PRESSED PELLETS (d_p) AND VALUES OF PORE FRACTION (f_p)

Compd.	Lattice parameters (nm)			Density ($\text{kg m}^{-3} \times 10^{-3}$)		Pore fraction
	a_0	b_0	c_0	d_0	d_p	
CaZrO ₃	0.6576	1.0340	0.5461	3.21	3.16	0.016
SrZrO ₃	0.6689	1.0225	0.5772	3.81	3.50	0.081

Fig. 3. DT, TG and DTG curves of CaZrO₃

In TG curves the sample losses mass in two successive steps. The weight loss and temperature region for CaZrO₃ and SrZrO₃ are shown in Table-2.

Fig. 4. DT, TG and DTG Curves of SrZrO₃TABLE-2
WEIGHT LOSS (%) CALCULATED FROM TG CURVES

Compounds	Weight loss (%) in the			
	1st step		2nd step	
	Temp. region (K)	Weight loss (%)	Temp. region (K)	Weight loss (%)
CaZrO ₃	323-508	0.40	508-698	2.60
SrZrO ₃	323-543	0.60	543-693	2.50

Such a small loss in mass is due to moisture. No further mass loss appear over higher temperature in each compounds which indicates that the compounds are stable and do not show decomposition upto 1123 K.

DTG curves of CaZrO₃ and SrZrO₃ show peaks at which the rate of mass change is maximum are 593 and 593 K, respectively.

The dielectric constant (ϵ') and dielectric loss (ϵ'') of the compounds have been determined using the following relation^{12,13}.

$$\epsilon' = \frac{tC}{A\epsilon_0} \quad (2)$$

$$\epsilon'' = \frac{\epsilon'}{Q} \quad (3)$$

where A and t are the face area and thickness of pellet respectively. ϵ_0 is permittivity of the vacuum. These measurements have been done in both heating and cooling cycles, but no significance difference have been observed. The variation of $\log \epsilon'$ and $\log \epsilon''$ with temperature at 1 kHz are shown in Figs. 5 and 6. It is seen from the plots that CaZrO₃ and SrZrO₃ have dielectric constant 28 and 45, respectively at 400 K. Since dielectric constant (ϵ') seems to have temperature independence, these values may be taken as the room temperature value of the materials. The reported value of ϵ' has been calculated using the capacitance value for pressed pellets. The density of these pellets remains less than theoretical density reported for these materials. This means pellet contains air pores. Therefore, a correction for pore fraction is essential to obtain the bulk value of dielectric constant (ϵ'_b) as given by Thakar *et al.*¹⁴.

$$f_p = \frac{d_0 - d_p}{d_0} \quad (4)$$

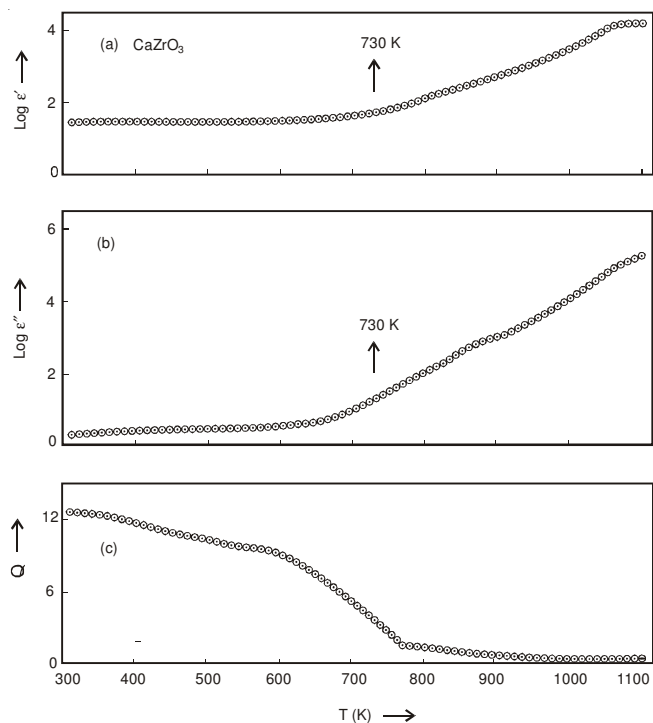


Fig. 5. Plot of dielectric constant (log ε'), dielectric loss(log ε'') and quality factor (Q) against absolute temperature (T) for CaZrO₃

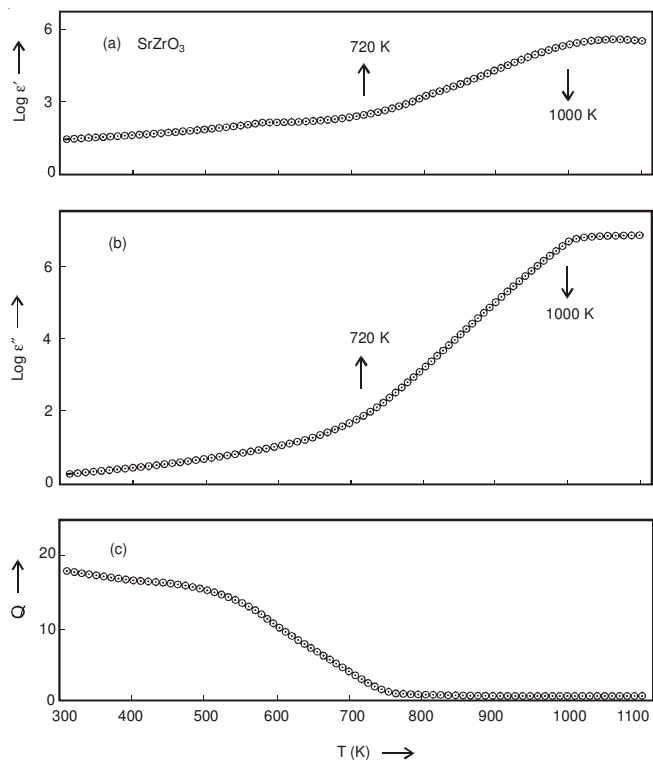


Fig. 6. Plots of dielectric constant (log ε'), dielectric loss(log ε'') and quality factor (Q) against absolute temperature (T) for SrZrO₃

For low conducting solids ε'_b, ε' and f_p are related by the relation¹⁵.

$$\epsilon'_b = \frac{(\epsilon'^{1/3} - f_p)^3}{1 - f_p} \tag{5}$$

The evaluated values of dielectric constant (ε'_b) values for CaZrO₃ and SrZrO₃ were found to be 28 and 42, respectively at 400 K.

The values of ε' of these compounds become large as temperature increased and validity of eqn. 5 becomes doubtful. Further this formula change only the magnitude of ε'_b but not the nature of variation of ε' with temperature. Therefore we have not used this correction at higher temperature.

The values of dielectric constant (ε') and dielectric loss (ε'') of the studied compounds at temperature 400, 600, 800 and 1000 K at frequency 1 kHz are given in Tables 3 and 4, respectively.

Compounds	Dielectric constant at			
	400 K	600 K	800 K	1000 K
CaZrO ₃	28	32	1.45 × 10 ²	2.82 × 10 ³
SrZrO ₃	45	126	1.41 × 10 ³	2.51 × 10 ⁵

Compounds	Dielectric loss at			
	400 K	600 K	800 K	1000 K
CaZrO ₃	3	3	1.26 × 10 ²	1.26 × 10 ⁴
SrZrO ₃	3	10	1.42 × 10 ³	4.46 × 10 ⁶

It is seen from Tables 3 and 4 that the systematic trend of ε' and ε'' variation reveals that polarization mechanism in CaZrO₃ and SrZrO₃ is same. A relatively larger value of ε' in case of SrZrO₃ appears due to the presence of chemical impurities which forms some donor centers and has larger polarizability. The dielectric constant has very slow increase at lower temperature. This shows that there is no chance for the existence of thermally generated charge carriers at lower side of temperature. Well made electrode rules out the chance of interfacial polarization. Therefore this slow increase seems to be the combined effect of lattice and electronic polarizabilities of individual ions. The increase of these polarizabilities seems to compensate the slight decrease of polarizabilities due to decrease in the number of ions per unit volume following the lattice expansion with temperature.

The dielectric constant (ε') and dielectric loss (ε'') of both compounds have much faster increase above certain critical temperature (T_k). The critical temperature (T_k) observed in ε' and ε'' for CaZrO₃ and SrZrO₃ were found to be 730 and 720 K, respectively. The faster increase in dielectric constant (ε') above T_k is due to space charge polarization^{16,17}. The pressed sample develops a considerable amount of space charge polarization arising out from the defects or impurities present in the bulk or at the surface of the material.

Conclusion

The XRD studies confirm that the studied compounds have single phase orthorhombic structure at room temperature. DT, TG and DTG studies show that the compounds are stable above certain temperature. The dielectric constant and loss have very slow increase upto breaking temperature. Above breaking temperature this increase becomes much faster. The value of breaking temperature (T_k) for CaZrO₃ and SrZrO₃ is 730 and 720 K, respectively. The reason for faster increase of

ϵ' and ϵ'' is due to space charge effect of thermally generated charge carriers.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. K. Das and Mr. N.K. Das, Central Research Facility, IIT Kharagpur for providing DT, TG, DTG facilities and Mr. U.S. Singh, IIT Kanpur for providing XRD facility.

REFERENCES

1. H. Iwahara, T. Esaka, H. Uchida and N. Maeda, *Solid State Ionics*, **314**, 359 (1981).
2. H. Iwahara, in ed.: P. Colomban, *Proton Conductors*, Cambridge University Press, Cambridge, U.K., p. 511 (1992).
3. A.M. Anthony and M. Foex, in: *Proceedings of the Symposium on Magnetic Hydrodynamic Electrical Power*, National Agency for International Publication Inc., New York, Vol. 3, p. 265 (1966).
4. T. Noguchi, T. Okubo and O. Yonemochi, *J. Am. Ceram. Soc.*, **52**, 4178 (1969).
5. W.A. Fisher and D. Janke, *Arch. Eisenhüttenwes.*, **47**, 525 (1976).
6. D. Pretis, F. Ricciardiello and O. Sbaizero, *Powder Metall. Prog.*, **18**, 427 (1986).
7. T. Murakami, H. Fukuyama, T. Kishida, M. Susa and K. Nagata, *Metall. Mater. Trans. B, Proc. Metall. Mater. Proc. Sci.*, **31**, 25 (2000).
8. K. Kiyoshi, Y. Shu and I. Yoshiki, *Solid State Ionics*, **108**, 355 (1998).
9. Y. Sukuki, P.E.D. Morgan and T. Ohji, *J. Am. Ceram. Soc.*, **83**, 2091 (2000).
10. S.K. Lim, H.Y. Lee, J.C. Kim and C. An, *IEEE Microw. Guided wave Lett.*, **9**, 143 (1999).
11. C. Kittel, *Introduction to Solid State Physics*, John Wiley & Sons Inc., edn. 7 (1996).
12. M. Cusak, *The Electrical and Magnetic Properties of Solids*, London: Longmans (1967).
13. J.P. Suchet, *Electrical Conduction in Solid Materials*, London: Pergamon (1975).
14. A.N. Thakar, K. Gaur and H.B. Lal, *Indian J. Phys.*, **70A**, 225 (1996).
15. V.P. Srivastava, Ph.D. Thesis, University of Gorakhpur, India (1998).
16. M.L.G. Nanda, R.N.P. Chaudhary and P.K. Mahapatra, *Indian J. Phys.*, **73A**, 445 (1999).
17. N.K. Singh, S. Sharma and R.N.P. Chaudhary, *Indian J. Phys.*, **74**, 63 (2000).