Investigating structural, dielectric, and ferroelectric properties of CaTiO₃ nano-ceramics

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This article describes an investigation of the chemical and physical characteristics of calcium titanium oxide (CaTiO₃), with a focus on its structural and electrical properties. Nanocrystalline CaTiO₃ was synthesized using the solid-state technique. The samples' crystal structure was characterized using X-ray diffraction (XRD) and Raman spectroscopy. At room temperature, the study identified an orthorhombic crystal structure with a *Pbnm* (62) space group. In addition to structural characterization, the study investigated the ferroelectric and impedance properties of CaTiO₃. These measurements were crucial for understanding charge transport mechanisms, revealing insights into polarization behavior and charge mobility, and highlighting the material's potential in electronic devices.

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1. Introduction

Electroceramics nowadays has a broad range of applications in transducers, actuators, sensors, high dielectric constant capacitors, resistors, etc. Perovskite materials with the ABO₃ formula are the most used materials in these applications [1-9]. These materials with ABO₃ structures are well known as perovskite with its A cation sitting at the corner of the unit cell with an octahedral of BO_6 . This structure is usually distorted by chemical substitution or external stresses. In these applications, leadbased perovskite materials such as lead zirconate titanate, lead titanate and modified lead zirconate titanate are widely used. But to make environment -friendly lead-free perovskite is yet to be established compared to lead-based perovskite materials. Hence, various lead-free perovskites such as; K_{0.5}Na_{0.5}NbO₃, Bi_{0.5}Na_{0.5}TiO₃, BaTiO₃, etc. have been investigated by the researchers. Calcium titanate (CaTiO₃) is one of the perovskite materials investigated for these applications. Its structural change with temperature and chemical pressure tune its physical properties for applications. As the temperature rises, it undergoes a structural shift from orthorhombic to tetragonal, followed by tetragonal to cubic [10]. It also shows promising electrical and optical properties and, is used for capacitors in electronic circuits, microwave resonators, ceramic condensers, radioactive waste detectors, and high-frequency filters [11]. The properties of it can be altered by doping at the Ca, Ti, or both Ca and Ti sites. While the material's electrical and optical properties have been explored, further exploration into its structure, electrical characteristics, and ferroelectric properties is required to improve its ferroelectric and dielectric performance. This will allow for a deeper understanding of how to tailor its structure for a wide range of applications.

2. Experimental

Calcium titanate was prepared using a solid-state reaction method. The precursor materials were taken as calcium oxide (CaO) and titanium oxide (TiO₂) powders, and ground in mortar pastel for 6

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hours with acetone as the medium. After 3 hours of calcination at 730°C, the powder was left in the furnace to cool to room temperature. Calcined samples were extremely hard. These were ground for 3 hours to bring them to the powder form. Polyvinyl alcohol (PVA) was used to bind the calcined powder to prepare the pellets. The crushed powder of the sintered pellet was analyzed for phase identification and structural investigation using a Smart Lab 9 kW X-ray diffractometer (Rigaku, Japan). The Cu-K α radiation source has a wavelength of 1.54052 Å. The 2θ range of 20° to 80°, with a scanning rate of 2°/min of X-ray diffraction data has been taken at room temperature. For electrical measurements, silver electrodes were placed to the pellets' smooth, polished surfaces with silver paste, which was then dried at 150°C. Field Emission Scanning Electron Microscope (FESEM, Sigma 300) of Carl Zeiss was used to examined the surface morphology of the materials. An N4L LCR meter (PSM 1735) was used to evaluate impedance qualities at room temperature between 10² and 10⁶ Hz. The Raman spectra were measured at room temperature using a 514.5 nm laser source from a Micro-Raman spectrometer (Seki Technotron Corp). Radiant Technologies' RT6000S Ferroelectric Test System was utilized to measure the ferroelectric hysteresis loops.

3. Result and discussion

The X-ray diffraction pattern of CaTiO3 is illustrated in Figure 1. CaTiO3's XRD peaks match the JCPDS database (No. 22-0153) [13], indicating a perovskite structure with orthorhombic symmetry. The average crystallite size has been calculated using the Debye-Scherrer formula as follows; [12]

$$D = \frac{k\lambda}{\beta Cos\theta} \tag{1}$$

To account for the expected circular shape of the grains, the shape-dependent constant k is set to 0.89. The parameter β represents the full width at half maximum (FWHM) of the diffraction peak. The average crystallite size is estimated to be about 42nm.



Fig. 1. XRD diffraction pattern of CaTiO₃.

The Williamson-Hall (W-H) plot method was also utilized to measure microstructural parameters such as crystallite size and microstrain by broadening XRD peaks. The Williamson-Hall equation is expressed as follows.: [13]

$$\beta Cos \theta = \frac{k\lambda}{D} + 4\varepsilon Sin\theta \tag{2}$$

 θ , β , and ϵ represent the diffraction angle, full width at half maximum (FWHM), and lattice strain. Figure 2 shows the Williamson-Hall plot for CaTiO₃. This process yields an average crystallite size of 38 nm.



Fig. 2. W-H plot of CaTiO₃.



Fig. 3. Raman spectra of CaTiO₃.

Figure 3 shows Raman spectra of CaTiO₃ samples at room temperature. Calcium titanate, with its orthorhombic structure belonging to the *Pbnm* space group, theoretically exhibits 24 Raman-active modes. However, due to low polarizability, only a few of these modes are observed experimentally [14-15]. The absorption band about ~152 cm⁻¹ represents the vibrations of Ca bonds with the Ti₂O₃ group [16]. The bending mode of O–Ti–O bonds has been observed at 175, 218, 241, and 280 cm⁻¹ are attributed to or the tilting of adjacent [TiO₆]-[TiO₆] clusters [17]. Bands between 218-380 cm⁻¹ indicate the rotation of oxygen chains. The band at 196 cm⁻¹ corresponds to the migration of Ca-site ions [18].The Ti-O₃ torsional mode, caused by internal vibrations or bending of the oxygen cage, appears at 463 cm⁻¹. The band at 681 cm⁻¹ is due to the symmetric stretching vibration of Ti-O bonds, which indicates distortions in the titanium octahedra [19-21]. Additionally, stronger interactions between Ti–O bonds at a lower percentage suggest enhanced vibrations of the [TiO₆]-[TiO₆] clusters, particularly around 241 cm⁻¹ in the perovskite structure.



Fig. 4. FESEM micrographs of CaTiO₃.

Figure 4 shows FESEM micrographs of CaTiO₃. The photos show that the grains are almost spherical in form and closely packed together. The grain size is critical in determining the dielectric and ferroelectric characteristics of the samples.



Fig. 5. Variation of dielectric constant with frequency of CaTiO₃ samples.



Fig. 6. Variation of dielectric loss with frequency of CaTiO₃ samples.

Figure 5 shows how the dielectric constant varies with frequency in CaTiO₃ samples, displaying normal dielectric behavior. At low frequencies, polarizations such as ionic, electronic, dipole, and space charge contribute significantly, resulting in a high dielectric constant. Dislocations, voids, and defects inside the crystal structure in nanoferrites also increase the dielectric constant at low temperatures. As the frequency increases, dipoles in weakly bonded interfacial and boundary regions become depolarized, leading to a decrease in the dielectric constant. At higher frequencies, orientation polarization is constrained, hence limiting the dielectric constant. At these frequencies, the dielectric constant is predominantly derived from the grains, whose low resistivity and reduced frequency dependence result in lesser dielectric constant values. The observed Changes in the dielectric constant with frequency is explained by space charge polarization in the homogeneous dielectric structure [22].

Figure 6 shows the frequency-dependent dielectric loss (tan δ) for CaTiO₃ samples. The dielectric loss decreases with an increase in the frequency of the applied field. This behavior is attributed to the inability of charge carriers to hop and follow the changes in the externally applied electric field beyond a certain frequency threshold [22].



Fig. 7. Cole cole plot of CaTiO₃ samples.

Impedance spectroscopy is an effective method for investigating the electrical microstructure of materials [23]. Figure 7 shows the room-temperature Cole-Cole plots of CaTiO₃ samples. The semicircular arcs seen in the figures intersect the real axis at high, non-zero frequencies. A single semicircle at high frequency represents the grain resistance (Rg) [24]. The observed relaxation behavior is polydispersive and non-Debye, as demonstrated by the semicircles' centers falling below the real axis [25]. The experimental data points were fitted using an equivalent parallel resistance and capacitance circuit model, with ZSimpWin software used to calculate the circuit characteristics. The data points are represented as symbols, while the fitted curves are shown as lines. To accommodate the data, several circuit configurations were used, including R_gC_g , $R_e(C_gR_g)$, and $R_e(R_gC_g)(R_{gb}C_{gb})$. Re indicates electrode resistance, Rg indicates grain resistance, and Rgb denotes grain boundary resistance. Similarly, Cg and Cgb are the capacitance of grains and grain borders, respectively. The $R_e(R_gC_g)$ circuit had the best match, with the lowest chi-square value. The fitted parameters for R_e , R_g , and C_g are 1.00×10^{-7} , 1.43×10^{-10} , and 1.00×10^{-21} , respectively.

Figure 8 illustrates how the real component of impedance (Z') changes with frequency at room temperature for CaTiO₃ samples. At low frequencies, Z' is high and decreasing with increasing frequency, most likely due to space charge release and reduced barrier height. These findings are consistent with those of previous studies [26–27]. Figure 9 shows how the imaginary component of impedance (Z'') varies with frequency in CaTiO₃ samples at ambient temperature. An uneven peak appears, showing the presence of several relaxation times and verifying non-Debye relaxation behavior [28-29].



Fig. 8. Variation of the real part of the impedance with frequency of CaTiO₃ samples.



Fig. 9. Variation of the Imaginary part of the impedance with frequency of CaTiO₃ samples.



Fig. 10. Room temperature electric polarization versus electric field of CaTiO₃ sample.

The energy storage density (W) of the P-E loop can be calculated using the equation below:

$$W = \int_{p_r}^{p_{max}} E dP \tag{2}$$

where W represents the material's stored electrical energy density, E represents the external electric field, Pmax represents maximal polarization, and Pr represents remnant polarization. The total energy density equals the sum of stored energy density and energy loss. CaTiO₃ has energy loss density, stored energy density, and total energy density of 2.83, 4.12, and 6.95 J/cm³, respectively.

4. Conclusions

 $CaTi_{1-x}Fe_xO_3$ crystallizes in an orthorhombic structure belonging to the *Pbnm* (62) space group at Fe concentrations of 0, 2, 4, 6, 8, and 10 mol%. Impedance analysis demonstrates polydispersive relaxation behavior that is not of the Debye type. The ferromagnetic nature has been observed in the Fe doped CaTiO₃ and magnetization (~1.5 emu/g at 30 kOe) was found to be the maximum for 10 mol% of Fe cations. The ferroelectric polarization with maximum energy storage density (~300 J/cm³) has been obtained for the 10 mol% of Fe cations doped CaTiO₃. The present observations suggest that CaTi₁. _xFe_xO₃ with x = 10 mol% can be considered as a multiferroic material that needs to be explored in the future for technological applications.

References

[1] W.B. Wang, J. Zhao, W.B. Wang, Z. Gai, N. Balke, M.F. Chi, H.N. Lee, W. Tian, L.Y. Zhu, X.M. Cheng, D.J. Keavney, J.Y. Yi, T.Z. Ward, P.C. Snijders, H.M. Christen, W.D. Wu, J. Shen, X.S. Xu, Phys. Rev. Lett. 110 (2013) 237601; https://doi.org/10.1103/PhysRevLett.110.237601

[2] Jiechun Liang, Tingting Wu, Ziwei Wang, Yunduo Yu, Linfeng Hu, Huamei Li, Xiaohong Zhang, Xi Zhu, Yu Zhao, Energy Mater 2(2022)200016; <u>https://doi.org/10.20517/energymater.2022.14</u>

[3] P. Goel,S. Sundriyal, V.Shrivastav, S.Mishra, D.P.Dubal, K.H. Kim, A.Deep, Nano Energy 80 (2021)105552; <u>https://doi.org/10.1016/j.nanoen.2020.105552</u>

[4] T.Zhu, Y.Yang, X.Gong, ACS applied materials & interfaces, 12(24)(2020)26776-26811; https://doi.org/10.1021/acsami.0c02575

[5] P.P.Lopes, D.Y. Chung, X.Rui, H.Zheng, H. He, Dias Farinazzo Bergamo, P. Martins, D.Strmcnik, V.R.Stamenkovic, P. Zapol, J.F. Mitchell, R.F.Klie, Journal of the American Chemical Society, 143(7)(2021)2741-2750; https://doi.org/10.1021/jacs.0c08959

[6] K. Koumoto, R. Funahashi, E. Guilmeau, Y. Miyazaki, A. Weidenkaff, Y.F. Wang, C.L. Wan, J. Am. Ceram. Soc. 96 (2013) 1e23; https://doi.org/10.1111/jace.12076

[7] C.R. Bowen, H.A. Kim, P.M. Weaver, S. Dunn, Energy Environ. Sci. 7 (2014) 25e44; https://doi.org/10.1039/C3EE42454E

[8]. C.W. Ahn, J.J. Choi, J. Ryu, W.H. Yoon, B.D. Hahn, J.W. Kim, J.H. Choi, D.S. Park, Mater. Lett. 141 (2015) 323e326; <u>https://doi.org/10.1016/j.matlet.2014.11.097</u>

[9]. L. Li, M. Zhang, P. Tian, W. Gu, X. Wang, Ceram. Int. 40 (2014) 13813e13817; https://doi.org/10.1016/j.ceramint.2014.05.097

[10] R.F.Gonçalves, N.L.Carreno, V. M.T Escote, K.P.Lopes, A.Valentini, E.R.Leite, E.Longo,
M.A.Machado, Quím. Nova. 27 (2004) 862-865; <u>https://doi.org/10.1590/S0100-40422004000600004</u>

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[11] G.Mi,Y.Murakami, D.Shindo, F.Saito, Powder technology. 104(1)(1999)75-79; https://doi.org/10.1016/S0032-5910(99)00045-5

[12] B.D.Cullity, S.R.Stock, Elements of X-Ray Diffraction (Englewood Cliffs: Prentice-Hall Inc, 2001,pp. 167-171

[13] G.K. Williamson, W.H.Hall, Acta Metall. 1(1953)22; <u>https://doi.org/10.1016/0001-6160(53)90006-6</u>

[14] Y.Li, S.Qin, F.Seifert, J. Solid State Chem. 180(2007) 824-833; https://doi.org/10.1016/j.jssc.2006.12.012

[15] T. M. Mazzo, M. L. Moreira, I. M. Pinatti, F. C. Picon, E. R. Leite, I. L. V. Rosa, J. A.Varela, L.A. Perazolli, E.Longo, Optical Materials.32(9)(2010) 990-997; https://doi.org/10.1016/j.optmat.2010.01.039

[16] T.Hirata, K.Ishioka, M.Kitajima, J. Solid State Chem. 124 (1996) 353-359; https://doi.org/10.1006/jssc.1996.0249

[17] S. Qin, X. Wu, F. Seifert, A.I. Becerro, Dalton Trans.19(2002)3751-3755; https://doi.org/10.1039/B207228A

[18] U.T. Balachandranand, N.G.Eror, Solid State Communications. 44(6)(1982)815-818; https://doi.org/10.1016/0038-1098(82)90280-0

[19] H. Zheng, I.M. Reaney, G.D.C.C. de Gy€orgyfalva, R. Ubic, J. Yarwood, M.P. Seabra, V.M. Ferreira, J. Mater. Res. 19 (2004) 488-495; <u>https://doi.org/10.1557/jmr.2004.19.2.488</u>

[20] A.E. J.Benmokhtar, J.P. Chaminade, P. Gravereau, A. Wattiaux, L. Fournes, J.C. Grenier, D. Waal, Journal of Solid State Chemistry. 179(2006)3709-3717; https://doi.org/10.1016/j.jssc.2006.08.004

[21]. M.L.Moreira, E.C.Paris, G.S.doNascimento, V.MLongo, J.R.Sambrano, V.R.Mastelaro, M.I. Bernardi, J.Andrés, J.A Varela, E. Longo, Acta Materialia. 57(17) (2009) 5174-5185; https://doi.org/10.1016/j.actamat.2009.07.019

[22]. Koops, C.G.: Phys., Rev. 83, 1920 (1951); https://doi.org/10.1103/PhysRev.83.121

[23] A.R West, D.C.Sinclair, N.Hirose, Journal of electroceramics.1(1)(1997) 65-71; https://doi.org/10.1023/A:1009950415758

[24] C.P Smyth, Dielectric Behaviour and Structure, McGraw-Hill, New York ,1965.

[25] J.R. Macdonald, Impedance Spectroscopy: Emphasizing Solid Materials and Systems, Willey & Sons, New York, 1987.

[26] J.R. Macdonald, Impedance Spectroscopy, John Wiley & Sons, New York, 2005; https://doi.org/10.1002/0471716243

[27] B.Wodecka-Dus, M.Adamczyk, J. Dzik, K.Osinska, The European Physical Journal B. 89 (2016)52-59; <u>https://doi.org/10.1140/epjb/e2016-60529-5</u>

[28] A.M.M. Farea, Shalendra Kumar, Khalid Mujasam Batoo, Ali Yousef, Alimuddin, Physica B. 403(2008)684-701; <u>https://doi.org/10.1016/j.physb.2007.09.080</u>

[29] Y.Srinivasa, N.V. Krishna Prasada, U Nareshb, Digest Journal of Nanomaterials and Biostructures 19(2024)1517-1531; <u>https://doi.org/10.15251/DJNB.2024.194.1517</u>

[30] R.C. Pohanka, R.W. Rice, B.E. Walker Jr, Journal of the American Ceramic Society. 59(1-2)(1976)71-74; <u>https://doi.org/10.1111/j.1151-2916.1976.tb09394.x</u>