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Rietveld refinement and impedance spectroscopy of calcium titanate

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ABSTRACT

Single phase perovskite $CaTiO_3$ has been synthesized by conventional solid state reaction technique. The ceramic was characterized by XRD at room temperature and its Rietveld refinement inferred orthorhombic crystal structure with the space group Pbnm. The field dependence of dielectric relaxation and conductivity was measured over a wide frequency range from room temperature to 673 K. Analysis of Nyquist plots of $CaTiO_3$ revealed the contribution of many electrically active regions corresponding to bulk mechanism, distribution of grain boundaries and electrode processes. The dc conductivity depicted a semiconductor to metal type transition. Frequency dependence of dielectric constant (ε') and tangent loss ($\tan\delta$) show a dispersive behavior at low frequencies and is explained on basis of Maxwell-Wagner model and Koop's theory. Both conductivity and electric modulus formalisms have been employed to study the relaxation dynamics of charge carriers. The variation of ac conductivity with frequency at different temperatures obeys the universal Jonscher's power law ($\sigma_{ac} \alpha \omega^s$). The values of exponent 's' lie in the range $0.13 \leq s \leq 0.33$, which in light of CBH model suggest a large polaron hopping type of conduction mechanism.

1. Introduction

Perovskites with general formula, ABX_3 due to their excellent electric and magnetic properties are extensively used for detectors, computer memories, multilayer ceramic capacitors (MLCC), pyroelectric detectors, field devices, and sensors [1–5]. These have very flexible structure and a variety of foreign cations can be accommodated in its lattice in different degrees letting a great scope of co-substitution to tailor properties of many ferroelectric and piezoelectric materials for various applications. Lemanov et al. stated that $CaTiO_3$ at low temperatures behaves as an incipient ferroelectric or quantum paraelectric [6]. Thus, this material can act as a noble candidate for next generation communication devices [7]. Perovskite structure, ABO_3 is usually illustrated as an idealized cubic structure with A and B cations occupying the cube vertices and body centers respectively while O anions occupying the face centers, but because of tilting of octahedra or Jahn–Teller distortions it is mostly tetragonal or orthorhombic. In case of $CaTiO_3$ the distortions occur by tilting of the TiO_6 octahedra. Depending upon phase transition temperatures, $CaTiO_3$ exists in four space groups: orthorhombic (Pbnm), orthorhombic (Cmcm), tetragonal (I4/mcm) and cubic ($Pm\bar{3}m$). Among them the high temperature form (above 1580 K) is the cubic phase and the stable phase at room temperature is the orthorhombic phase (Pbnm) [8,9]. Kennedy et al. [9] proposed Cmcm space group as an intermediate phase but in the work of Ali et al non existence of the Cmcm group is illustrated [10]. So, the existence of the four phases is controversial. Further, the dielectric properties, viz., dielectric relaxation, modulus formalisms, ac conductivity of $CaTiO_3$ have not been widely studied like other alkaline titanates. Therefore, the purpose of the present work is to (i) analyze the phase of the $CaTiO_3$ at room temperature by Rietveld refinement, (ii) determine the equivalent electrical circuit which can model the experimental data and (iii) characterize the electrical microstructure via impedance spectroscopy in wide range of frequencies and temperatures.

2. Experimental details

Polycrystalline calcium titanate ($CaTiO_3$) ceramic was synthesized by high temperature solid state reaction technique. Analytical reagent grade $CaCO_3$ and TiO_2 chemicals (purity $\geq$ 99.0%) were used as raw materials. The powders were mixed in an appropriate stoichiometric ratio and then ground in an agate mortar to obtain fine particles. The fine mixture was calcined at 873 K for 6 h in air at ramp of 5 K/min, ground to get a homogeneous mixture and finally sintered at 1573 K for 4 h at a ramp of 3 K/min up to 973 K and then at 5 K/min up to 1573 K in a platinum crucible. The sintered ceramic was structurally characterized by using a Rigaku Miniflex-II X-ray

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diffractometer. XRD patterns were obtained at RT in the 2θ range (10–80°) at a scanning rate of 2°/min. The structure refinement and the lattice parameters were obtained using the software GSAS-EXPGUI [11,12]. In order to measure electrical properties of the sample compact discs of 13 mm diameter and 1 mm thickness were formed using pellet press. The discs were then sintered at 1573 K. Silver electrodes were deposited on the opposite faces of the disc and impedance measurement was done using impedance gain/phase analyzer (Newton's 4th Ltd.). The dielectric properties were systematically investigated by impedance spectroscopy over the frequency range 10 Hz–7 MHz and temperature range 300–673 K. The obtained experimental data was analyzed in the Nyquist plot representation by using semiempirical cole–cole equation and the augmented Jonsher relation.

3. Results and discussion

3.1. X-ray diffraction and Rietveld refinement analysis

The phase composition of the sintered ceramic was studied with XRD analysis. The formation of orthorhombic phase of $CaTiO_3$ appears as early as heating at 873 K for 6 h. However, well defined peaks developed in well crystallized powder at 1573 K for 4 h. Fig. 1(a) shows the XRD pattern at RT of the sintered ceramic and Fig. 1(b) displays its Rietveld refinement plot. The formation of $CaTiO_3$ is confirmed as the XRD patterns are matched with the JCPDS no. 06-2149 [13]. The average crystallite size (D) was calculated for the most intense peak in the XRD spectra using the Debye Scherrer relation,

$$D = \frac{K\lambda}{B\cos\theta} \tag{1}$$

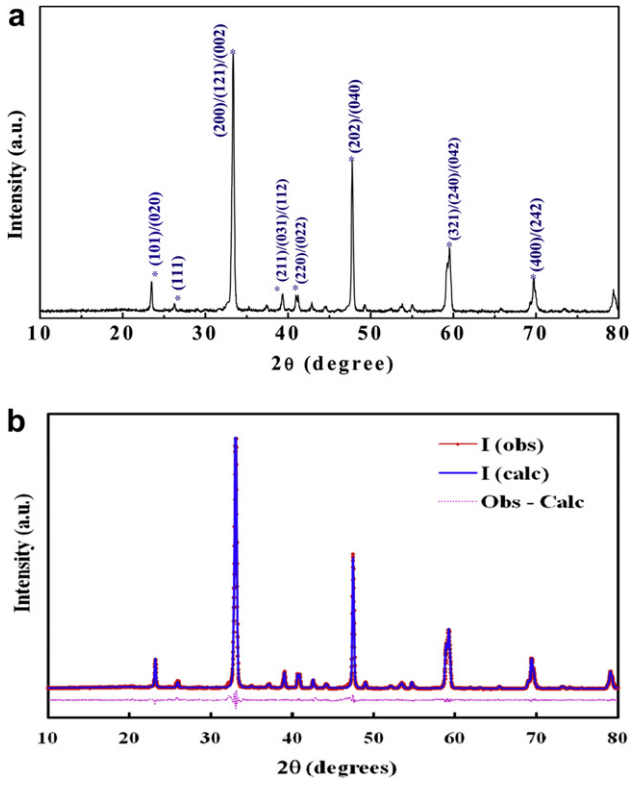

Fig. 1. (a) XRD pattern of calcium titanate at RT, (b) Rietveld refined XRD pattern of $CaTiO_3$.

where K is a constant ~ 0.89, λ is the characteristic X-ray wavelength (1.54 Å), B is the FWHM in radians and θ is the Bragg's angle. The average size thus obtained was 32 nm for the (121) peak.

In Rietveld refinement a structural model is required that has an approximation for the actual structure. In this method, the entire spectrum, including the background intensity, is considered to be a single discrete function against which a multi parameter model must be fitted. In Rietveld refinement we need to minimize the function Δ [14], given by

$$\Delta = \sum_i w_i\{I_{iO} - I_{iC}\}^2 \tag{2}$$

where, w_i the weight parameters given by $(1/w_i) = \sigma_i^2$, σ_i being the standard deviation associated with the intensity at each $2\theta_i$ value, I_{iO} and I_{iC} are observed and calculated intensities for diffraction angle $2\theta_i$. In order to achieve convergence and to make the refinement more quantitative, agreement indices or residuals are defined. The profile residual, R_p [14],

$$R_p = \frac{\sum_i |I_{iO} - I_{iC}|}{\sum_i I_{iO}} \tag{3}$$

and the weighted profile R_{wp} [14],

$$R_{wp} = \left[\frac{\sum_i w_i (I_{iO} - I_{iC})^2}{\sum_i w_i I_{iO}^2}\right]^{\frac{1}{2}} \tag{4}$$

are used to obtain convergence and this leads to the value of goodness of fit parameter, χ^2 approaching 1 [14].

A Si (640c) powder as a standard sample was used to correct the zero-point shift for the measured diffraction data. The initial Rietveld refinement was performed considering systemic errors into account as zero-point shift, then the unit cell and background parameters were refined. To further improve the fitting, the peak profile parameters (location, intensity, peak asymmetry and FWHM), isotropic thermal parameters, lattice parameters, scale factor, occupancy and atomic functional positions were refined. The refinement was done with the Pbnm space group for the orthorhombic perovskite structure. A good agreement was obtained between the experimental relative intensities and the simulated intensities from the model. The background was corrected using a Chebyschev polynomial of the first kind and the diffraction peak profiles were fitted by pseudo-Voigt function. Refined structural parameters along with the R-factors are listed in Table 1 and the bond lengths and bond angles are listed in Table 2.

The octahedra TiO_6 is deformed from the one in the regular cubic space group. In $CaTiO_3$ the Ti–O2 bond along the semi minor axis {O2 (B)} of the equatorial plane of the octahedron is shortened by 0.7% relative to the Ti–O bond (1.953 Å) in the ideal TiO_6 octahedron of $SrTiO_3$ [15]. The bond angle Ti–O1–Ti is the tilting angle of the octahedron relative to the plane 001 and Ti–O2–Ti is the rotating angle around the c-axis, both of these angles are less than 180° (Table 2) demonstrating rotation of the polyhedral TiO_6. The

Table 1
Refined structural parameters for $CaTiO_3$.

Structural model	Cell parameters	Sites	Positional coordinates			R factor
			x	y	z	
Pbnm	$a = 5.3870$ Å	Ca	0.006	0.032	0.250	$R_p = 4.16$
(Orthorhombic)	$b = 5.4351$ Å	Ti	0.000	0.500	0.000	$R_{wp} = 5.55$
	$c = 7.6442$ Å	O1	0.572	−0.018	0.250	$\chi^2 = 1.68$
	V = 223.814 Å^3	O2	0.285	0.289	0.038	$R_f^2 = 3.60$