NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (4), P. 613–617

Dielectric relaxation and charge transport process in $PrCrO_3$ nano-ceramic

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PACS 61.05.cp, 77.22.Gm **DOI 10.17586/2220-8054-2016-7-4-613-617**

In this work we have investigated the frequency dependent dielectric properties of $PrCrO_3$ nano-ceramics using alternating current impedance spectroscopy. The material was synthesized by the sol–gel process. The Rietveld refinement of the X-ray diffraction data suggests single phase formation of the material with Pnma space group. The observed structure is substantiated by Raman spectrum of the sample. The ac conductivity follows the power law. The most probable relaxation frequencies at different temperatures were found to obey Arrhenius' law.

Keywords: Dielectric properties, sol-gel process, X-ray diffraction.

Received: 31 January 2016

1. Introduction

The rare-earth (R) transition-metal (M) oxides of perovskite structure with general formula RMO_3 have been the subject of investigation in recent years as they possess various interesting phenomena such as high temperature superconductivity, colossal magnetoresistance, and multiferroicity. Among these materials, rare–earth based orthochromites with general formula $RCrO_3$ have been investigated for their usefulness in several devices such as solid–oxide fuel cells and catalytic converters [1]. One of these orthochromites, $PrCrO_3$ (PCO), is an anti-ferromagnetic material with a Neel temperature of 237 K [2]. The Cr^{3+} spin structure is predominately G_x-type and a weak ferromagnetic moment lies along c-crystallographic axis at 4.2 K in PCO [2]. Prasad et al. [3] have investigated the relaxor ferroelectric like permittivity of bulk PCO ceramic having 30 nm grain size. Zhang et al. [4] have synthesized the cubic particle of orthorhombic PCO by hydrothermal process. Their results have showed that the molar ratio 1:1 of Pr and Cr can be obtained when the material is synthesized at 280 °C for 7 days using 8 M KOH solution.

The magnetic property of PCO is extensively studied, but to the best of our knowledge there is no report on the dielectric properties of PCO nano-ceramic till date. In the present work we have investigated the dielectric relaxation and ac conductivity of PCO nanoparticles synthesized by the sol-gel process.

2. Experimental

To prepare the PCO nano-ceramic, the metal nitrates with 1:1 molar ratio were dissolved in deionized water separately. Citric acid and ethylene glycol solution was added dropwise to the metal nitrates solution and stirred at 353 K for 6 h to form the gelled mass by auto combustion process. The dried gel was then calcined at 973 K in air for 4 h. The calcined sample was compressed into disc and sintered at 1023 K for 6 h. Scanning electron micrograph and energy dispersive X-ray spectrum were taken by a FEI QUANTA 200 scanning electron microscope. Transmission electron micrograph (TEM) was taken by TECNAI 200 kV transmission electron microscope. The X-ray diffraction (XRD) pattern of calcined PCO was taken by Rigaku Miniflex-II X-ray diffractometer. Raman spectrum was collected by Jobin-Yvon LABRAM-HR spectrometer using 488 nm line of an Ar-ion laser line. The frequency dependence capacitance and conductance of sintered pellet were measured by an LCR meter (Hioki) at frequencies ranging from 42 Hz to 1 MHz in temperature range from 303 – 673 K.

3. Results and disscussion

3.1. Structural Analysis

The Rietveld refinement of the room temperature XRD pattern of PCO with orthorhombic symmetry having Pnma (D_{16}^{2h}) space group using Full-prof code is shown in Fig. 1. The good agreement between the observed and calculated interplanar distances (d-values) of PCO indicates the single phase formation of the material in Pnma space group symmetry. The unit cell parameters, reliability factors, bond distances and bond angles obtained from

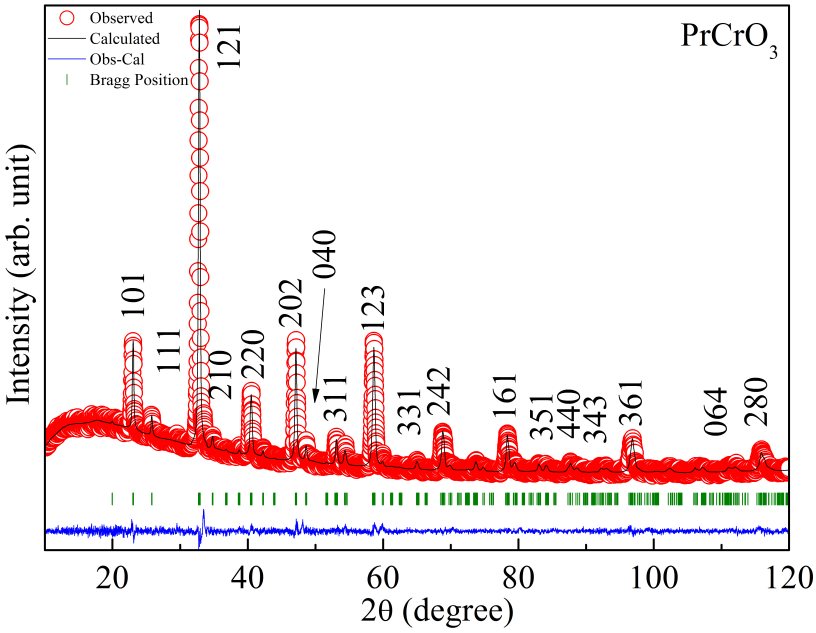


FIG. 1. Rietveld refinement of XRD profile of $PrCrO_3$ at room temperature

TABLE 1. Rietveld refinement data

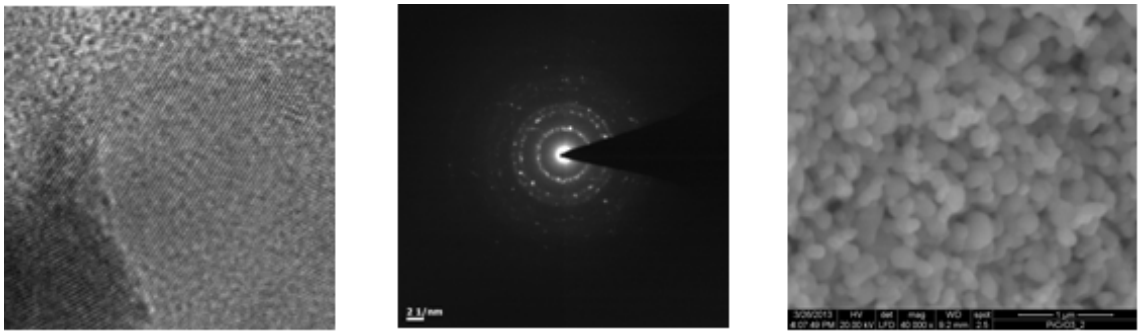
Lattice parameters (Å)	Bond length(Å)	Bond angle
$a = 5.4721(5)$	$\langle \mathrm{Pr-OI} \rangle = 2.79$, $\langle \mathrm{Pr-OII} \rangle = 2.29$	$\mathrm{Cr-OI-Cr} = 154.3\ ^\circ$
$b = 7.7107(5)$	$\langle \mathrm{Cr-OI} \rangle$ 1.99, $\langle \mathrm{Cr-OII} \rangle = 1.96$	$\mathrm{Cr-OII-Cr} = 161.1\ ^\circ$
$c = 5.4445(5)$	$R_P = 3.76$, $R_{wp} = 4.93$, $R_{exp} = 5.23$, $\chi^2 = 0.891$	

Atom	x	y	z	Multiplicity	B_{iso} (Å^2)
Pr	0.5357(3)	0.25	0.4946(9)	4	0.429
Cr	0.25	0	0	4	0.087
OI	−0.0184(4)	0.25	0.5945(8)	4	0.705
OII	0.2891(7)	0.0235(5)	0.72077(7)	8	0.972

Rietveld refinement are given in Table 1. The mean size of coherent scattering regions, as calculated from the XRD data, was found to be 100 nm.

The high resolution TEM (HRTEM) image and selected area electron diffraction (SAED) pattern of PCO are shown in Fig. 2. The HRTEM image presented in Fig. 2(a) shows the well resolved lattice fringes of nanoparticles. The SAED pattern shows strong spots in regular positions indicating that particles are well crystalline in nature. The SEM image as shown in Fig. 2(c) indicates the compactness of the grains. The average grain size is found to be 92 nm. EDAX analysis shows that the atomic percentage of Pr, Cr and O in PCO is 19.09 %, 15.27 % and 65.64 % respectively.

We have studied the Raman spectrum of PCO to get a better understanding of the crystal structure and its consequence on the vibrational features of the material. The room temperature Raman spectrum of PCO as shown in Fig. 3 (Symbols are the experimental points) is typically matched with the Raman spectrum of perovskite having orthorhombic crystal structure. According to group theory, the orthorhombic Pnma structure has 24 Raman active modes ($7A_g$ + $5B_{1g}$ + $7B_{2g}$ + $5B_{3g}$) at the zone center. The antiphase tilt of the adjacent CrO_6 octahedra and the antiparallel displacements of Pr cations activate the Raman modes. The sum of 20 Lorentzian lines (violet solid lines in Fig. 3) is used to fit the experimental data. For the clarity of the figure, the frequency range is divided into two parts. Very weak intensity peaks are neglected during the Lorentzian fitting of the experimental data and thus a lesser number of peaks are obtained than the theoretical prediction.



(a) (b) (c)

FIG. 2. HRTEM (a), SAED pattern (b) and SEM image (c) of $PrCrO_3$

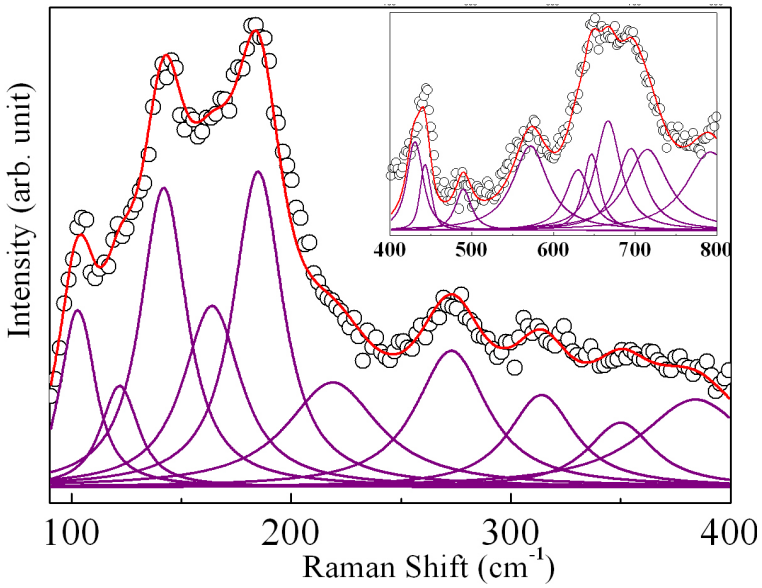


FIG. 3. Raman spectrum of $PrCrO_3$ at room temperature

3.2. Ac conductivity and dielectric relaxation

The angular frequency ($\omega = 2\pi\nu$) dependent log-log plots of ac conductivity (σ_{ac}) for PCO at different temperature are shown in Fig. 4. At each temperature, the conductivity decreases with decreasing frequency and becomes independent of frequency in the low frequency region. The extrapolation of this region towards $\omega = 0$ gives dc conductivity (σ_{dc}) which is attributed to the long range translational motion of the charge carriers. In this low frequency region, the electric field cannot perturb the hopping conduction mechanism of charged particles and hence, the conductance is approximately equal to the dc value. As the temperature is increased, the dc part of the conductivity spectra shifts to higher frequency side. The large value of dc conductivity at the higher temperature range with respect to the value in the lower temperature range indicates the generation of large number of thermally activated charge carriers in the experimental temperature range. The conductivity begins to increase after the frequency exceeds the critical frequency called hopping frequency (ω_H). The conductivity spectra of PCO follow the power law [5] as shown by the solid lines in Fig. 4. The temperature dependence of σ_{dc} obtained from the fitting of the experimental data to the power law at different temperatures follows Arrhenius' law (inset of Fig. 4) with an activation energy of 0.32 eV. The activation energy value indicates that polaron hopping may be responsible for conduction processes in PCO.

In Fig. 5 the frequency dependent dielectric constant (ε') and loss tangent ($\tan\delta$) of PCO as a function of temperature are shown. The observed peaks in $\tan\delta$ can be explained according to the fact that a strong correlation between the conduction mechanism and the dielectric behavior exists in PCO. For a thermally activated relaxation

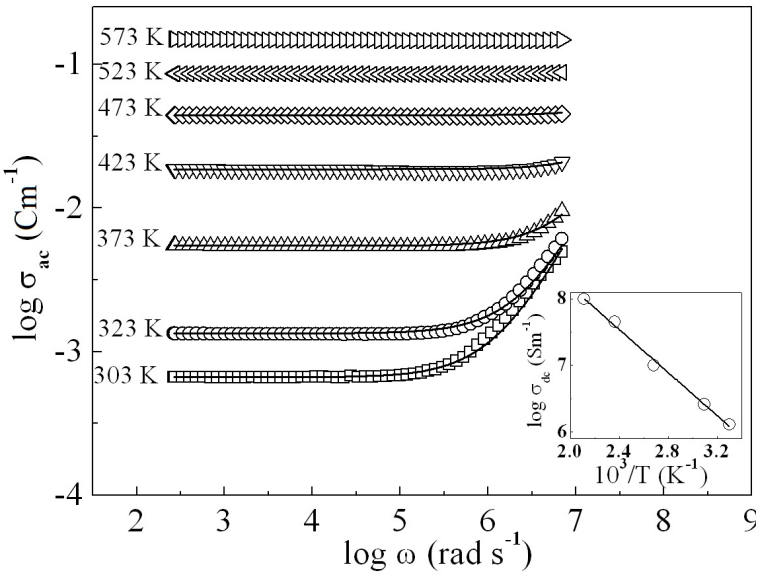


FIG. 4. Frequency dependent Ac conductivity. Inset is the temperature dependence of σ_{dc}

process, the relaxation time τ has the form $\tau_0 \exp(E/k_BT)$, where E and k_B are the activation energy for the relaxation process and the Boltzmann constant, respectively. Then the resonant condition is $\omega_{\max}\tau_0 \exp(E/k_BT) = 1$, where $\omega_{\max}$ is the frequency at which $\tan\delta$ has its maximum value. The temperature dependence of the most probable relaxation frequency ($\omega_{\max}$) follows Arrhenius' law (inset of Fig. 5), and a straight line fit to the experimental data gives an activation energy of 0.319 eV. This activation energy is equal to the activation energy obtained for the temperature dependence of σ_{dc}. This suggests that the dielectric loss in PCO is due to the conduction of charge carriers.

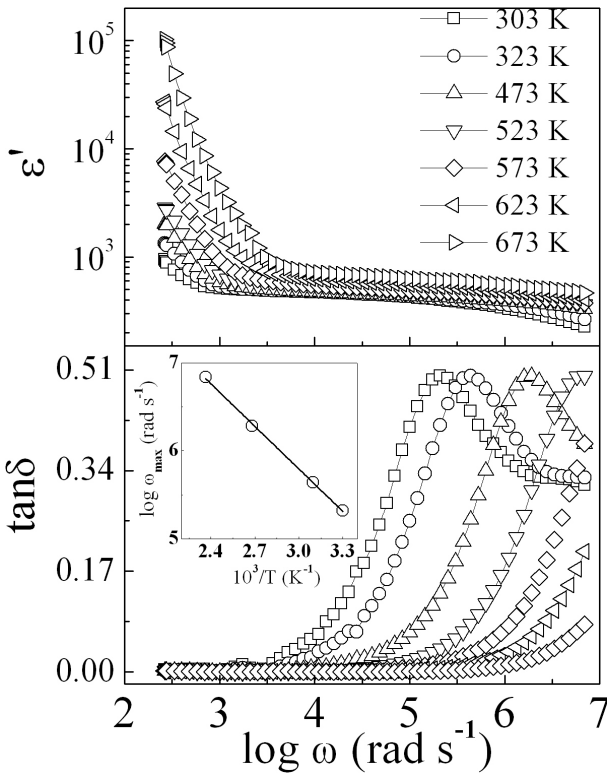


FIG. 5. Frequency dependence of ε' and $\tan\delta$. Inset is the Arrhenius plot of $\omega_{\max}$

4. Conclusions

The Rietveld refinement of XRD profile suggests the single phase formation of PCO with Pnma space group. The Raman spectrum fitted with 20 Lorentzian lines substantiates the orthorhombic crystal structure of PCO with space group Pnma. The dielectric properties of the sample have been investigated as a function of frequency and temperature. The frequency-dependent conductivity spectra follow the power law. The activation energy for charge carrier transport is found to be 0.32 eV, which indicates that polaron hopping plays the main role for the dielectric relaxation in PCO.

Acknowledgements

Alo Dutta thanks to Department of Science & Technology of India for providing the financial support through DST Fast Track Project under Grant No. SB/FTP/PS–175/2013.

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