

## Studies on dielectric behaviour of an oxygen ion conducting ceramic – $\text{CaMnO}_{3-\delta}$

Namita Pandey, Awalendra K Thakur\* & R N P Choudhary

Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur 721302, India

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An oxygen deficient ceramic oxide having perovskite structure has been prepared by the conventional solid state reaction method. X-ray diffraction studies have confirmed the sample formation in single phase polycrystalline form. The scanning electron micrographs have confirmed polycrystalline texture of the material along with indications of porous microstructure. The temperature dependence of the dielectric properties (permittivity/loss tangent) in the sub-ambient and ambient temperature region suggests the possibility of a strong dipolar ordering. The appearance of maxima in both the permittivity and loss factor pattern at a very close temperature range ( $\epsilon_{\text{max}} \sim 1879$  at  $29^\circ\text{C}$ ,  $\tan \delta_{\text{max}} \sim 9.7$  at  $35^\circ\text{C}$  at a common frequency of 10 kHz) supports the presence of dipolar interaction in  $\text{CaMnO}_{3-\delta}$ . It has been attributed to a strong interaction of the oxide ion-oxygen vacancy pair in the crystal lattice of an oxygen deficient perovskite ( $\text{CaMnO}_{3-\delta}$ ) that in turn reduces the net mobility of oxygen ion at lower temperatures and imparts it a higher dielectric permittivity as well as high loss factor close to room temperature. A decrease in the permittivity and monotonous increase in loss factor with rise in temperature above the ambient value suggest a thermally activated weakening of the dipolar ordering in the system. In view of a very high value of loss factor at and above room temperature, it would be premature to conclude the existence of ferroelectric ordering in the material system just by the presence of a peak in both the permittivity and loss factor pattern.

The development, analysis and evaluation of oxygen ion conducting ceramic membranes having the characteristic features of oxygen permeation, high mobility of oxide ions through it, structural, thermal and phase stability are considered to be essential prerequisites for their suitability in devices such as in solid oxide fuel cell, gas sensors and oxygen pumps. Recently a new trend for developing oxide ion conducting ceramics, by way of creating oxygen defect (anion deficiency) in the lattice itself, is emerging rapidly. Ceramics with such a defect concentration can be expected to facilitate easier oxygen transport through such a membrane by an effective control of external parameters such as oxygen partial pressure. However, developing an oxygen deficient ceramic membrane having inherent defect in its lattice with structural, thermal, chemical and electrical stability is very challenging. Secondly, the measurement and analysis of electrical properties of such a material system demands a meticulous planning in the electrode selection and in maintaining appropriate experimental conditions such as temperature and oxygen partial pressure.

In oxygen ion conductors, the electrical conduction occurs predominantly due to mobility of oxide ions through the crystal lattice arising as a result of hopping of the  $\text{O}^{2-}$  ion from one site to another within the lattice. Such type of charge conduction is basically a thermally activated process involving energy dissipation in the form of absorption from the heat source or from an external applied electrical field or from both (i.e. the dissipation of electrical thermal energy). The mechanism of oxygen transport occurring in the ceramic membrane due to diffusion (migration) of oxide ion via vacancies (lattice defect) in the form of oxygen ion-vacancy pair, i.e.,  $\text{O}_2 + 2e^- \rightarrow \text{O}^{2-} + \overset{\infty}{V}_\text{o}$  may be treated as analogous to dipolar system with an equivalent positive charge on  $\overset{\infty}{V}_\text{o}$ . Such a dipole gets strongly affected under the action of external applied field resulting in induced dipolar reorientation and may be expected to affect charge transport within the crystal lattice of the material. Hence, the property needs to be measured and analyzed very carefully in order to understand the mechanism of oxygen ion transport in oxygen deficient ceramic oxide. Various mechanisms have been proposed to analyze the oxygen ion transport

\*For correspondence (E-mail: akt@phy.iitkgp.ernet.in)

and the idea based on diffusion of “oxygen ion-vacancy pair” is considered to be a reasonable one. This mechanism appears to be analogous to “reoriented dipoles” in a dielectric system such that  $O^{2-}$  ions and oxygen vacancies ( $V_o$ ) act as polarons. This situation necessitates an analysis of the dielectric relaxation properties of oxide ion conducting systems in order to understand the basic physics involved in the ion transport behaviour.

But, the dielectric analyses of ionic conductors need special attention and care to be taken to get true picture of the dielectric properties. It is because ionic conduction causes a serious problem arising due to a number of factors such as ion migration at low frequencies, contribution to the permittivity due to mobile ions and electrode polarization due to electrochemical double layer formation at the interfaces<sup>1-3</sup>. These contributions mostly mask the effect of dielectric properties making it difficult to detect dipolar contribution. The major dielectric function in such a situation is usually expressed as;

$$\epsilon'' = \epsilon''_{dipolar} + \frac{\sigma_{dc}}{\omega\epsilon_0} \quad \dots (1)$$

where,  $\epsilon''$  is the complex permittivity due the dipolar reorientation and due to the ionic transport,  $\epsilon''_{dipolar}$  is the complex permittivity due to only the dipolar contribution,  $\sigma_{dc}$  is the dc conductivity due to the bulk contribution,  $\omega$  is the frequency applied,  $\epsilon_0$  is the permittivity in the air or vacuum medium.

The 2<sup>nd</sup> term dominates at low and moderate frequencies and hence correction is essentially required to eliminate/minimize the error. The correct formulation can be expressed as:

$$\epsilon''_{corrected} = \epsilon''_{dipolar} = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)} - \frac{\sigma_{dc}}{\omega\epsilon_0} \quad \dots (2)$$

The present paper reports the results of an experimental investigation on the dielectric behaviour of an oxide ion conducting ceramic  $CaMnO_{3-\delta}$  having inherent oxygen vacancies along chains perpendicular to a-b plane associated with  $Mn^{3+}$  ion having square pyramidal structure with coordination number 5. The simplest form of such a vacancy distribution<sup>4</sup> in a crystal lattice may be depicted as Fig. 1.

The oxygen vacancy in the crystal lattice represents the unoccupied site, having positive charge equivalent to those occupied by the oxygen ions, having negative charge.

## Experimental Procedure

The material sample  $CaMnO_{3-\delta}$  ( $\delta=0.5$ ) under investigation has been prepared by solid state reaction route with an appropriate stoichiometric ratio of precursor materials  $CaCO_3$  (99.2% Loba) and  $Mn_2O_3$  (99.5% Alfa Aesar). The sample physical mixture of starting materials were mixed in dry and wet (methanol) conditions to achieve homogeneity. Subsequently the sample physical mixture was calcined in air at temperature of 1200°C for 12 h. The calcinations process was repeated under similar conditions to ensure that no un-reacted precursors are left into the calcined sample. Next the calcined sample was ground thoroughly to obtain fine powders of the materials and the pellets were prepared by cold pressing at a pressure of 4.5 MPa. The sintering of cold pressed pellet was carried out at 1300°C for 12 h. The sintered pellet was polished to make their faces flat and parallel and coated with conductive silver paste followed by drying at 150°C for 2 h prior to electrical measurements.

The formation of material was confirmed by X-ray diffraction experiment carried out at room temperature in the diffraction angle range ( $10 \leq 2\theta \leq 90^\circ$ ) with  $Cu-K_\alpha$  ( $\lambda=1.5418\text{\AA}$ ) radiation using Philips X'pert X-ray diffractometer [Model:1710]. The surface morphology has been observed using scanning electron microscopy (SEM Model: CAMSCAN-2 JEOL). The sample was coated with gold under vacuum prior to scanning electron microscope. The dielectric properties (permittivity and loss) was measured in the frequency range of 100 Hz-1 MHz using HIOKI LCR Hi-Testor (3522-50) over a

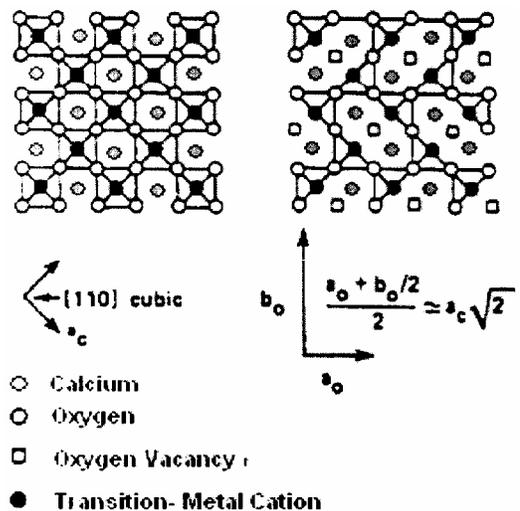


Fig. 1—Schematic crystal structures of (a) stoichiometric  $CaMnO_3$  and (b) oxygen deficient  $CaMnO_{3-\delta}$

varying range of temperature ±100°C in order to observe the dipolar (oxide ion O<sup>2-</sup>-oxygen vacancy V<sub>o</sub><sup>∞</sup> pair) interaction and its response to temperature.

**Results and Discussion**

**X-ray diffraction (XRD) studies**

The X-ray diffraction studies have been carried out to confirm the formation of material CaMnO<sub>3-δ</sub> under the reported conditions. The experimental pattern recorded at room temperature is shown in Fig. 2. The diffractogram shows sharp single peaks of varying intensities having clearly distinct features than that of the precursor materials confirming formation of the sample-CaMnO<sub>3-δ</sub> in polycrystalline form in the present studies. A significant splitting in all the XRD peaks has been noticed. This may be attributed to the oxygen deficiency in the crystal lattice resulting in the creation of oxygen vacancy (unoccupied sites equivalent to those occupied by lattice oxygen). This observation agrees well with the reports available in literatures. A preliminary structural analysis suggests an orthorhombic crystal structure with lattice parameters *a*= 5.4253 Å, *b*=10.3650 Å, *c*= 3.3857 Å. This is different from those of the standard perovskite type CaMnO<sub>3</sub> without any oxygen deficiency. A comparison of lattice parameters for CaMnO<sub>3</sub> *a* = 5.279, *b* = 7.448, *c* = 5.264 and CaMnO<sub>3-δ</sub> suggests that the latter has been distorted perovskite due to lattice contraction<sup>(5, 6)</sup>. The XRD result has been used to estimate sample density and porosity. The theoretically (XRD) and bulk (measured) density have been estimated to be 4.33 g/cm<sup>3</sup> and 3.369g/cm<sup>3</sup> respectively. The comparison of these two gives us an estimate of porosity in the sintered pellet which works out to be 22%.

**Scanning electron microscopy analysis**

The surface microstructure of the sintered pellets has been observed in the scanning electron micrograph shown in Fig. 3.

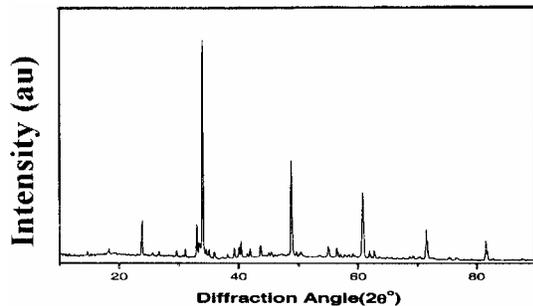


Fig. 2— X-ray diffractogram of CaMnO<sub>2.5</sub> at room temperature, calcined at 1200°C for 12 h

The micrograph reveals a polycrystalline texture comprising of well defined grains separated by grain boundaries. The average grain size is found to be in the range of 5-10 μm has been estimated. A significant presence of voids is also noticed in the micrograph suggesting porous microstructure in the sample sintered at 1300°C. This observation recorded from SEM micrograph is in good agreement with the XRD results of the material sample.

**Dielectric properties**

The variation of the dielectric properties (permittivity and tangent loss) as a function of temperature has been studied to investigate the nature of interaction in the oxygen ion-oxygen vacancy/air an external combination under the action of electric field as the constant parameter and the temperature as the variable parameter at different frequencies. The pattern of permittivity variation as a function of temperature is shown in Fig. 4. The pattern shows

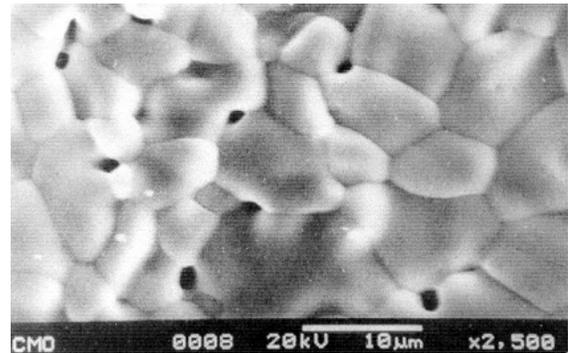


Fig. 3 —Scanning electron micrograph of CaMnO<sub>3-δ</sub> sintered at 1300°C

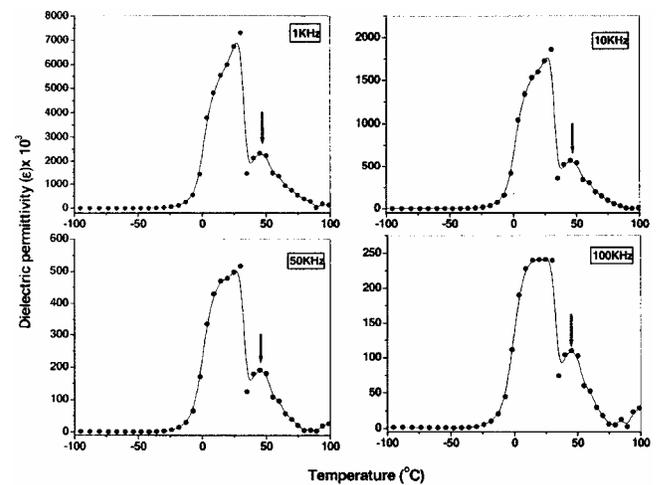


Fig. 4—the variation of relative dielectric permittivity versus temperature from -100°C to 100°C at different frequencies of 1 kHz, 10 kHz, 50 kHz and 100 kHz

almost constant value of permittivity (~20) up to -40°C irrespective of frequency. Such a low value of relative permittivity in the sub-ambient region (-40°C) is suggestive of absence of any significant dipolar interaction under the influence of applied electric field at such a low temperature. As the temperature increases above -40°C permittivity gradually starts increasing and shoots up to a very high value ( $\epsilon_{\max}$ ) at temperature of approximately 27-29°C as recorded in Table 1 irrespective of frequency. However further rise in temperature causes a drastic fall with the appearance of another small maximum at the same place at 44-46°C beyond which permittivity fall monotonically. The first (predominant) maxima in the permittivity versus  $T$  plot occurring at 27°C may be attributed to a very strong dipolar ordering into the system under ambient temperature/condition and may be related to non-linear (ferroelectric to paraelectric) phase transition arising due to strong dipolar interaction among cationic and anionic species in the crystal lattice. This seems logical in view of the results obtained for the variation of loss tangent factors ( $\tan \delta$ ) as a function of temperature shown in Fig. 5.

Table 1—The peak position appearing in the relative permittivity with respect to temperature (Fig. 4)

Frequency	Permittivity ( $\epsilon$ )				Dielectric Loss	
	$\epsilon_{\max}$	$T_c$ (°C)	$\epsilon_{\max}$	$T_c$ (°C)	$D_{\max}$	$T_c$ (°C)
1 kHz	7253	29	2388	46	—	—
10 kHz	1879	29	579	46	9.7	35
50 kHz	511	29	188	46	5.64	35
100 kHz	243	29	111	46	4.92	35

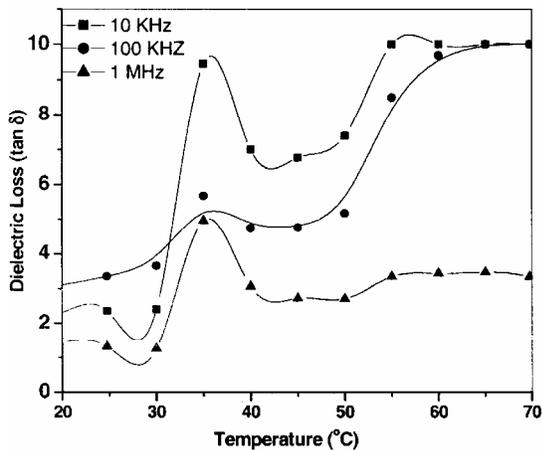


Fig. 5— The variation of dielectric loss or tangential loss versus temperature over the range of 20°C to 70°C. 1 kHz, 10 kHz, and 100 kHz

The  $\tan \delta$  versus temperature plot shows a peak appearing at approximately 34°C which is very close to the temperature for the primary maxima in permittivity versus  $T$  plot (Fig. 4). Both the permittivity and loss peaks appear at almost the same temperature irrespective of the frequency. However, their magnitude decreases with rise in frequency. A comparative value for both is given in the Table 1. A relative decrease in the magnitude of the loss with increase in frequency is suggestive of weakening of the dipolar ordering in the material system at the transition temperature at of 45°C ( $\pm 1^\circ\text{C}$ ) with a significant lowering value of permittivity in comparison to that observed for  $\epsilon_{\max}$  at 29°C suggests the presence of transient ordering in the system. It may be related to interaction of oxygen vacancy-oxide ion pair in the crystal lattice. It seems logical because no such feature has appeared in the loss pattern versus temperature. This interaction appears to be dynamic in nature suggested by the drastic lowering in permittivity and loss factor with increase in frequency at a given temperature (Table 1).

This may be related to the formation of a transient dipole between oxide ion in the lattice and oxygen vacancy (unoccupied site) pair positive during the mobility of oxide ion from one unoccupied site to another.

In order to confirm this hypothesis the relaxation time at various temperatures have been estimated and observed as a function of temperature. The pattern of variation is shown in Fig. 6 ( $\tau$  versus  $1000/T$ ). A typical Arrhenius behaviour suggests the ion migration in the material system is thermally activated process<sup>7,8</sup> requiring some threshold energy for mobility from one available site to another in the lattice.

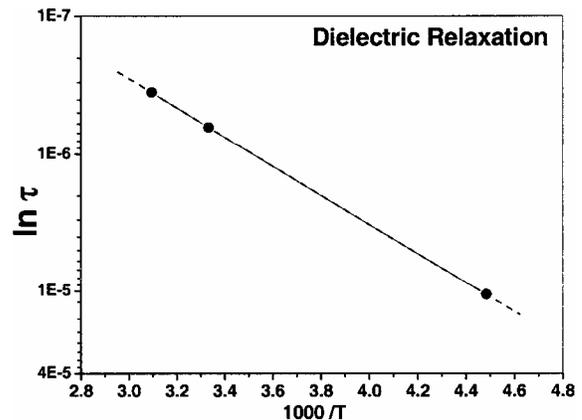


Fig. 6— Dielectric Relaxation time ( $\tau$ ) versus  $1000/T$  to calculate the activation energy

The estimated value of activation energy works out to be ~0.33 eV. This seems to be low at a first glance to make oxide ion transport feasible. But the present system is a distorted perovskite having inherent oxygen vacancy and porous microstructure as revealed in XRD analysis and SEM micrograph. The presence of oxygen vacancy itself within the system may get activated at a relatively lower value of 0.33 eV facilitating O<sup>2-</sup> ion hopping from one available site to another. However, this requires further investigation to understand the underlying mechanism.

### Conclusions

An oxygen deficient ceramic oxide has been prepared using standard solid state reaction route. The material formation in single phase has been confirmed. XRD analysis has revealed a distorted perovskite structure with an orthorhombic unit cell. The SEM micrograph has shown confirmed the polycrystalline texture with the significant porosity.

The dielectric results confirm ferroelectric phase transition at room temperature beyond which the defect concentration in the lattice (oxide ion-oxygen vacancy pair) became active and mobile. The mobility of oxygen ion from one vacancy site to another produces a transient dipole.

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