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Evaluation of Yttrium doped Barium Cerate-zirconate protonic electrolyte materials for Innovative Dual membrane Solid oxide fuel cells.

Solid oxide fuel cell (SOFC) is a technology for production of electricity by electro-chemical oxidation of hydrogen with oxygen to produce water. The cell works on principle of oxidation of H_2 to H^+ at anode and reduction of oxygen to O^{2-} at cathode separated by a solid electrolyte for transfer of the ions. The proton and oxide ion combine to form water as a product after transfer of either H^+ of O^{2-} ion across the electrolyte. The electronic mass balance is obtained by flow of electrons through the outer circuit. The oxide ion proton conductors based on doped barium cerate system appear a feasible alternate as electrolyte for Intermediate Temperature SOFCs, operational at 500-700 °C.

Following research activities were carried out for the above mentioned application during the STM stay of Dr. Salil Varma at Institute for Energetics and Interphases, CNR Genova Centre.

1. Evaluation of Ba-Ce-Zr-Y oxide as prospective electrolyte material for proton conducting SOFCs

$BaCeO_3$ is reported to be excellent proton conductor in 400-600 °C temperature range, but suffers from chemical stability issues. Compared to this $BaZrO_3$ provides excellent chemical stability with very limited protonic conductivity. Work was been initiated at BARC for studies on $BaCe_{8-x}Zr_xY_{0.2}O_3$ series of compounds to derive a composition with requisite stability and ionic conductivity. Based on initial experiments, it has been observed that cubic $BaCeO_3$ phase is stabilized for value of x upto 0.4 and also the relevant compositions of $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_3$ (BCZY) exhibit the ionic conductivity comparable to that exhibited by $BaCeO_3$, This composition also demonstrates required stability in reducing, oxidising, moist and carbon dioxide. The physico-chemical properties observed for these compositions make them ideal candidate for their application as electrolyte in proton conducting ITSOFC [1].

1.1 Preparation of $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_3$.

The above mentioned composition was prepared by oxalate co-precipitation route. For this purpose, solutions of nitrate salts of barium, cerium, zirconium and yttrium were mixed in stoichiometric ratio and then this solution was added to oxalic acid solution to carry out simultaneous co-precipitation. The precipitate obtained was filtered, dried and then decomposed at 850 ^{o}C. The obtained powder was pelletized and calcined at 1400 ^{o}C for 48 h with intermittent grinding and pelletising.

1.2 Characterization of BCZY

The sample prepared were characterized by XRD for the phase composition. The XRD patterns recorded after 24 h and 48 h of calcinations at 1400 ^{o}C temperature exhibit cubic phase, matching with $BaCeO_3$-$BaZrO_3$ solid solution [1]. A minor impurity phase corresponding to orthorhombic phase of this composition also exists, as depicted in Fig 1a.

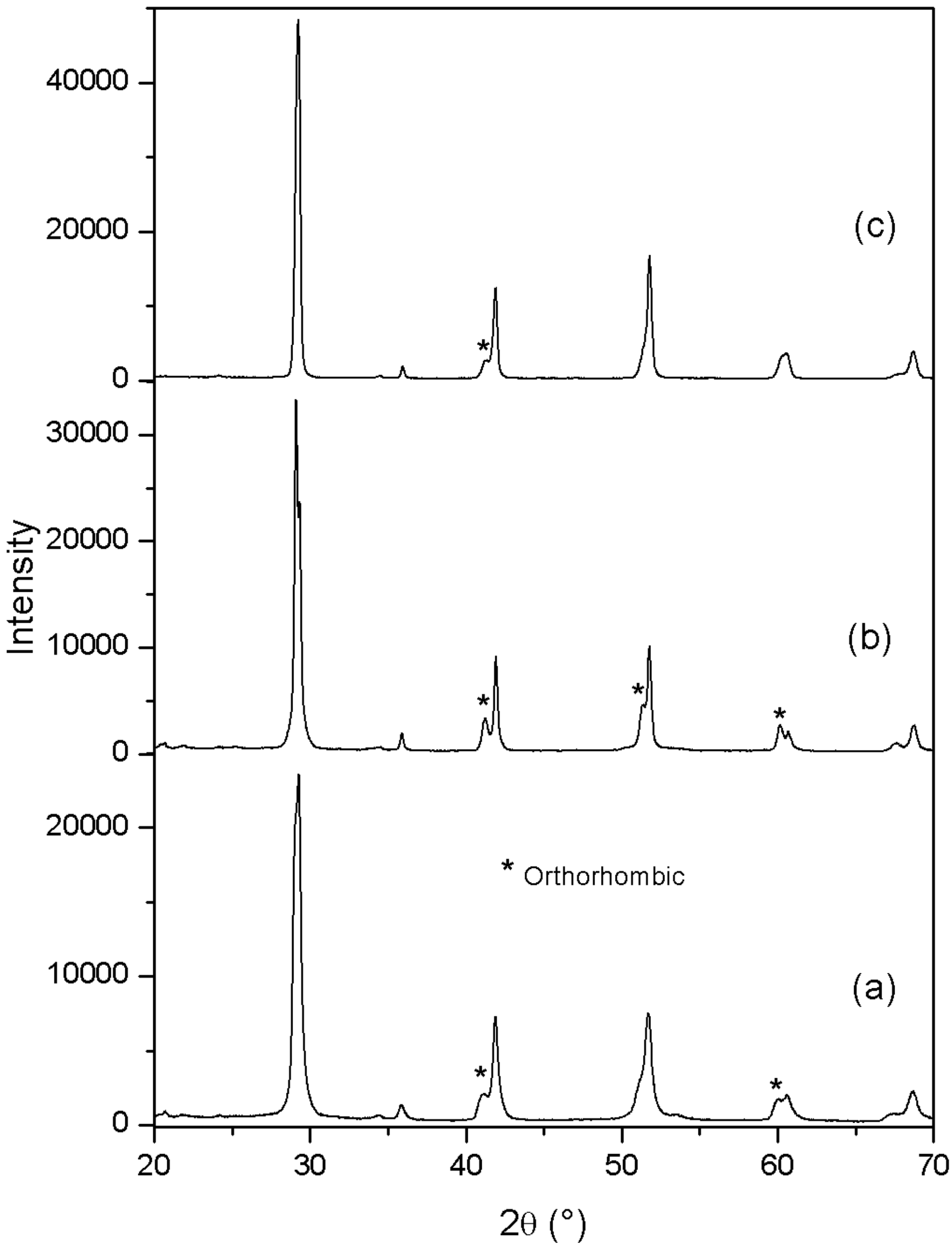

Fig. 1: XRD Pattern of (a) As-synthesized, (b) inner phase of sintered BCZY and (c) outer phase of sintered BCZY.

The BET Surface area of this sample was evaluated employing N_2 adsorption technique and is found to be 0.7 m^2/gm, suggesting for highly compacted material.

Scanning electron microscopy was employed to understand morphology of the BCZY sample. The SEM micrographs suggest for presence of two type of morphologies, namely smaller particles with dendrite like structures and bigger well sintered particles with cuboid like structure, as shown in Fig. 2. From SEM micrographs, it can be observed that the dendrites grow by filling up of the space, to form the cuboid shape particles. Back electron diffraction imaging does not show any contrast between these two particle, hence it appears that they are for similar composition.

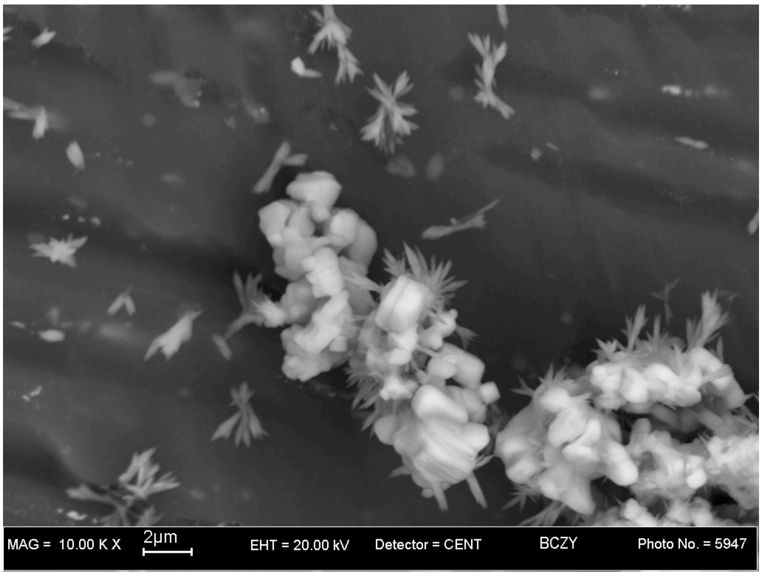

Fig. 2: SEM micrograph for BCZY sample.

1.3 TMA measurements

The thermo-mechanical analysis was carried to determine the temperature required for the sintering of the prepared BCZY sample. A pellet of about 10 mm diameter and 25 mm mm height was prepared by isostatic pressing. A pellet of 10 m diameter and 6 mm height was cut from this pellet for TMA measurement. In TMA, the pellet was heated under air atmosphere for temperature up to 1700 ^{o}C. The change in length is observed with multi-step reduction in height. The first step sintering is found to initiate from 1480 ^{o}C, followed by another at 1530 ^{o}C and another at 1600 ^{o}C. There is sharp increase in dimension at 1650 ^{o}C, followed by further decrease.

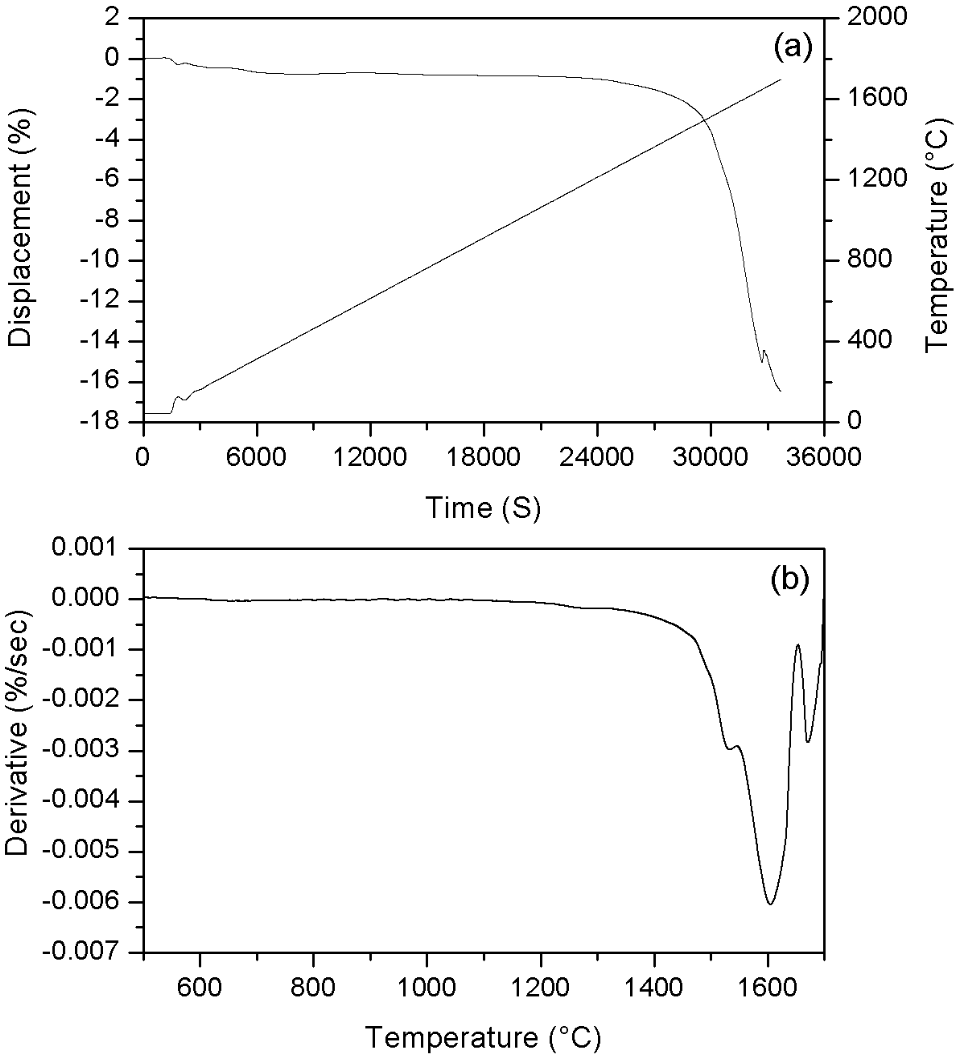

Fig. 3: TMA Plot for BCZY sample for (a) Displacement vs time and (b) Derivative vs temperature.

The XRD pattern, for sample after the TMA analysis exhibits presence of cubic BCZY phase along with the orthorhombic impurity of BCZY and another small phase of cubic zirconia.

The morphology of the sintered pellet exhibited multiple phases and features with some highly sintered phases with very little porosity and some less sintered and porous phases. There is also variation in composition with the more sintered phases exhibit non-uniform distribution of barium phases. This can happen due to volatility/mobility of barium at such high temperatures. The loss of barium will also explain for the separation of Zirconia phase, as observed from XRD.

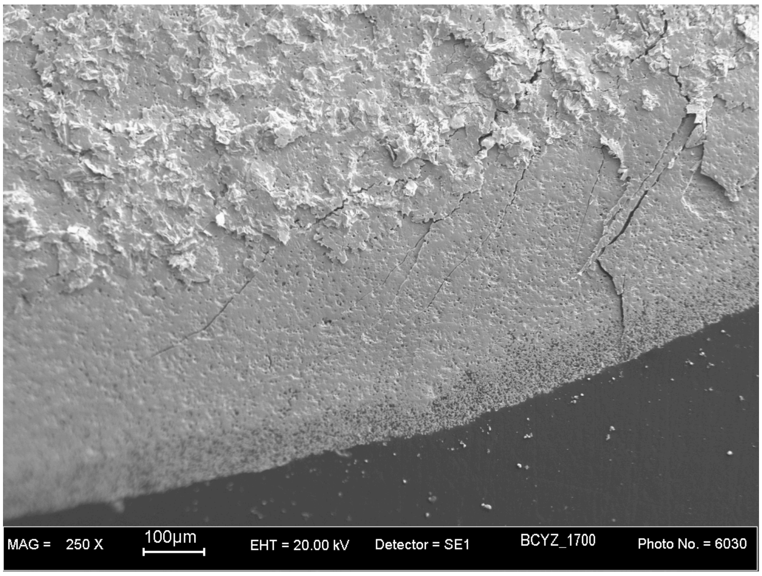

Fig. 4: SEM micrograph of BCZY pellet after TMA measurement.

Considering the above mentioned observations it could be concluded that 1620 ^{o}C will be ideal sintering temperature for this sample.

1.4 Sintering of BCZY

The Pellet of BCZY prepared by Iso-static pressing was sintered at 1620 ^{o}C for 4 h. The pellet obtained after the sintering was found to be of dark grey and cracked coating on outside, with white and dense material inside. The sintering was inhomogeneous and the two phases obtained were separated out for their characterisation to understand the genesis of this behaviour.

The XRD pattern for the outer grey layer, as shown in Fig. 1b, exhibits increase in orthorhombic phase, while the inner white phase exhibits decrease in orthorhombic phase. Otherwise, there is now generation of any impurity phase.

The particle morphology was evaluated employing scanning electron microscopy. The particles obtained after the sintering are found to be of same size as for as-synthesized samples but are more homogenous, with complete absence of dendrite like structures. Hence, the heating at 1600 °C results only in homogenisation of particle morphology with particles of 2-4 µm size.

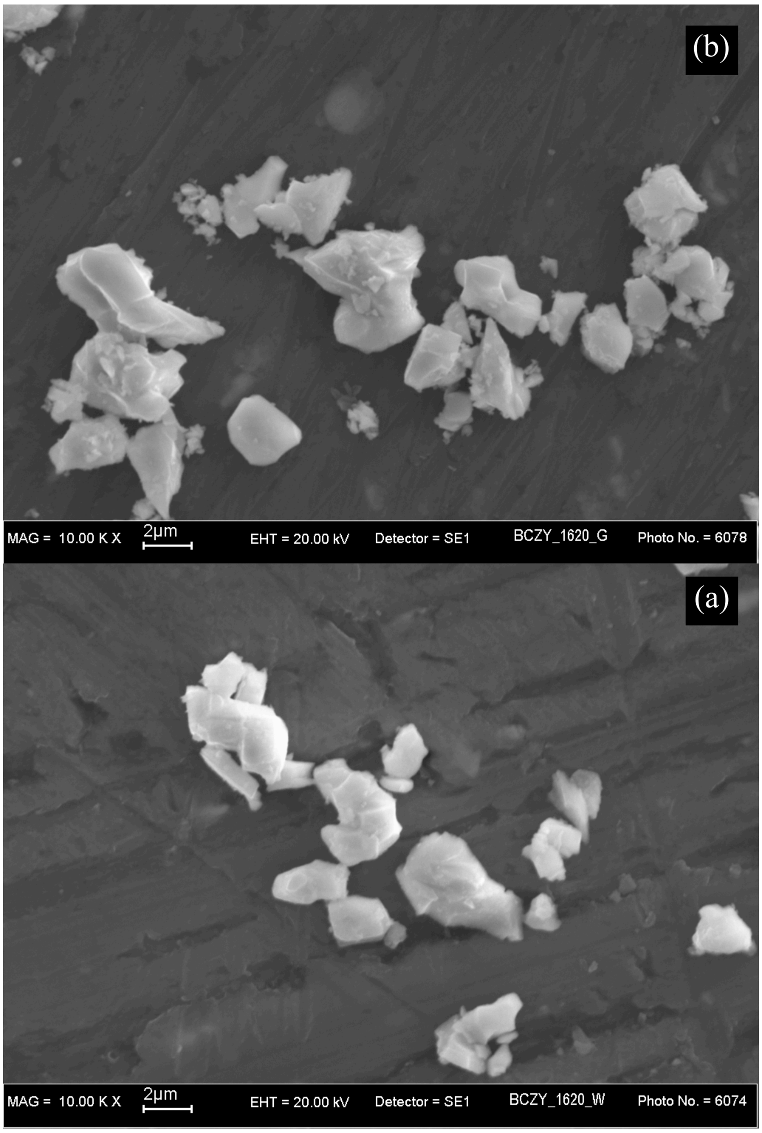

Fig. 5: SEM of the particles after sintering of BCZY sample, (a) white inner phase and (b) grey outer layer.

2 Conclusions and future research plans

BCZY samples prepared by oxalate co-precipitation route exhibit cubic phase with orthorhombic impurity. The particles exhibit in-homogeneous morphology and Dilatometric measurement infers for multistep sintering. The powder sintered at 1620 °C exhibit presence of homogeneous particles but with particles of about 2-4 µm.

The future plan of research will be to make these samples with modified oxalate co-precipitation route and by Pechini method for controlled morphology and phase purity. This should result in lower temperature sintering of these compounds.