

BaCe_{1-x-y}Zr_xM_yO₃ (M = Y, Gd) Proton Conductors for Solid Oxide Cells

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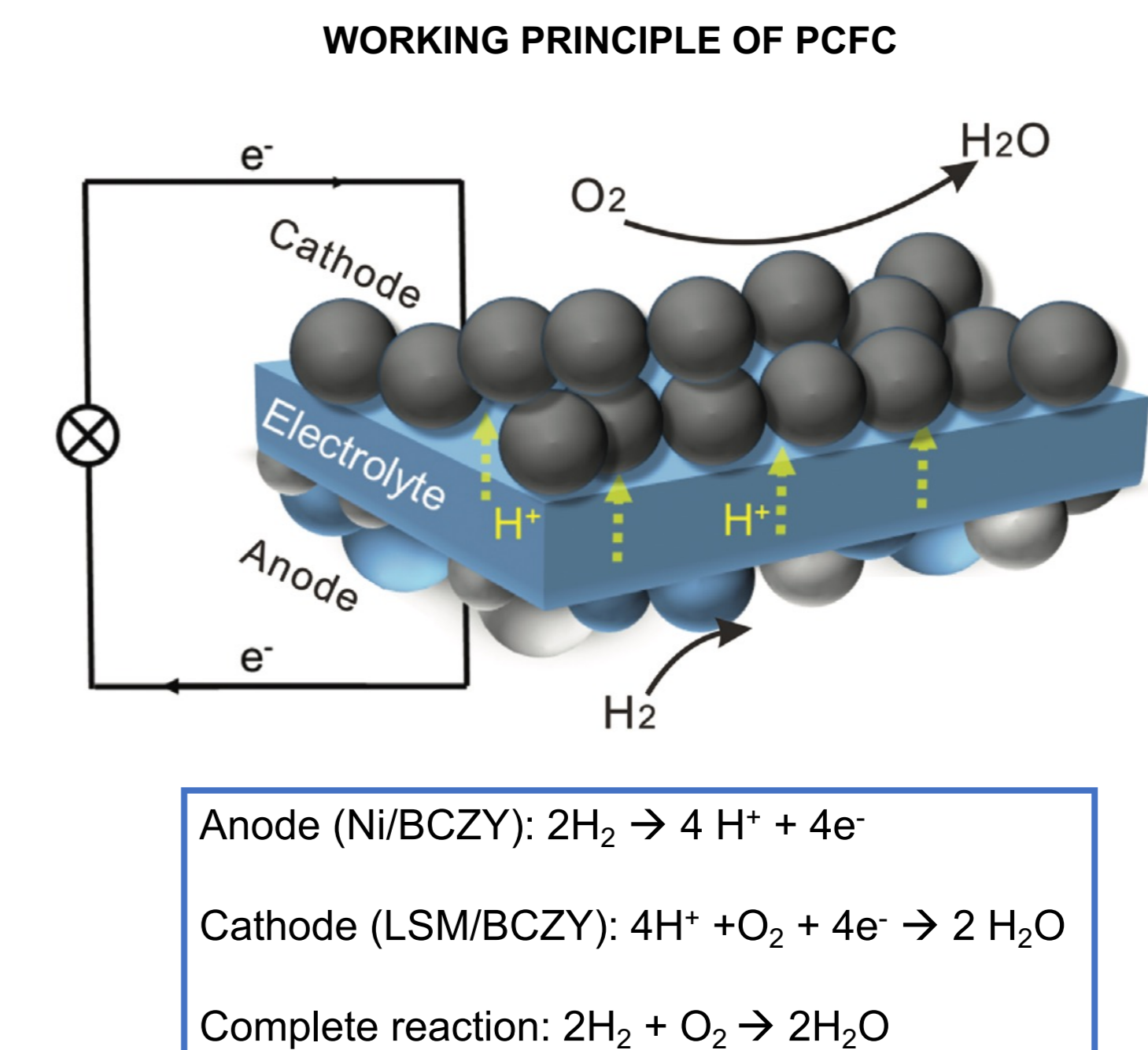
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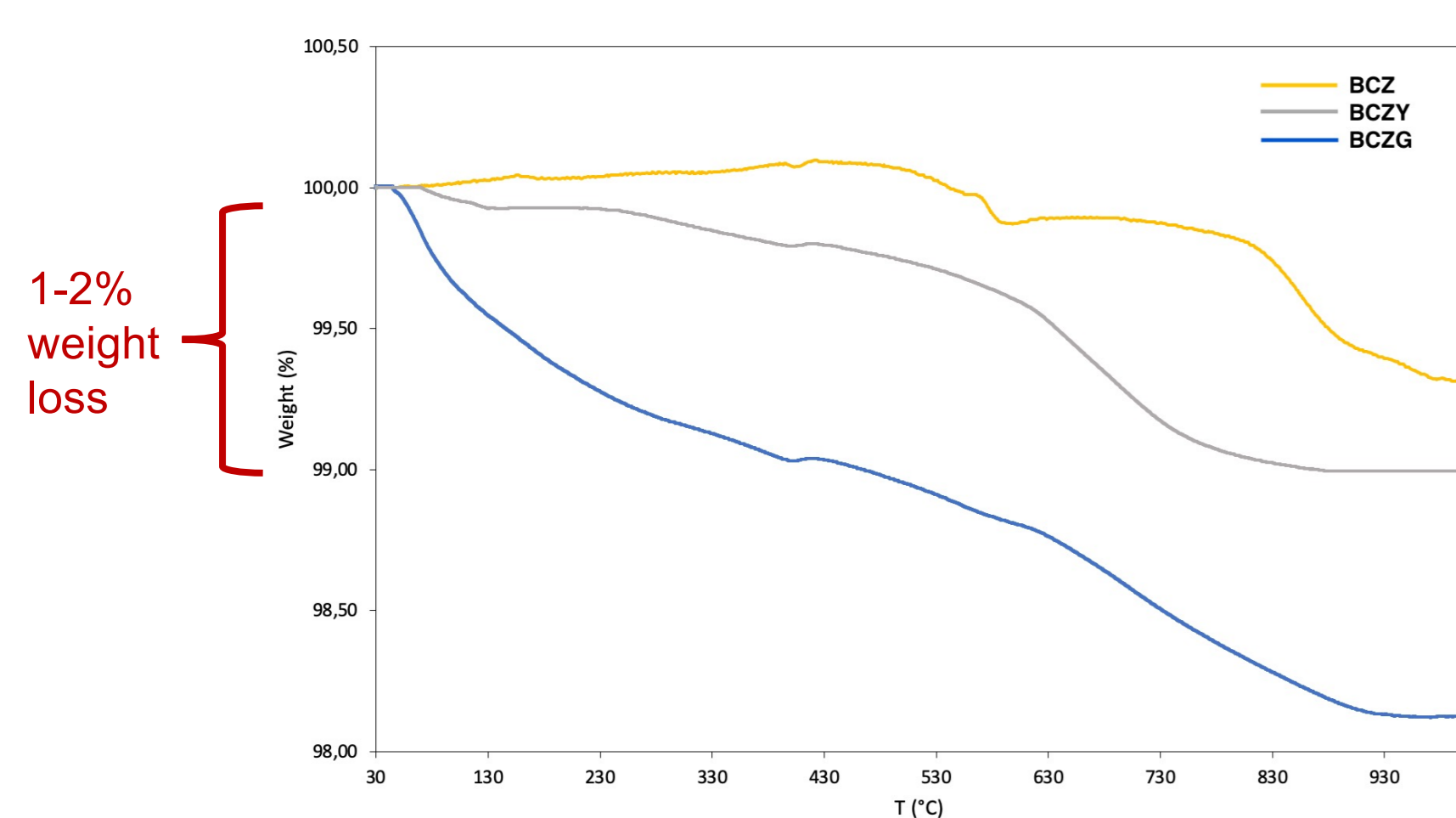
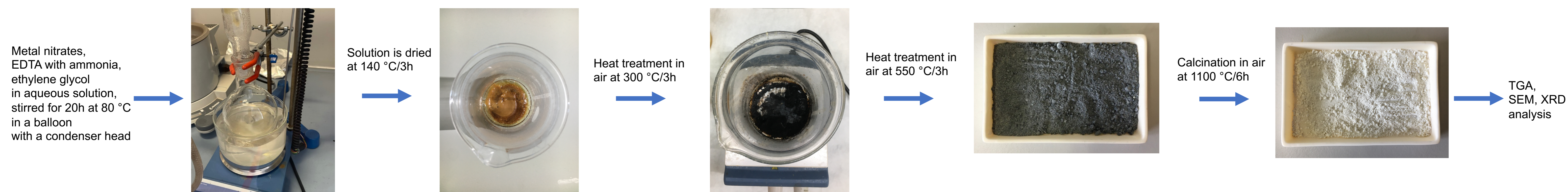
Introduction

Proton conductors with perovskite structure (ABO₃) have been intensively investigated because of their potential applications in solid oxide fuel and electrolysis cells (SOC), hydrogen separation membranes, catalysts, etc. Perovskites in the last period, attracted a lot of attention as they are versatile materials that can be easily prepared through simple synthesis methods and present different geometrical stable structures especially when doped. These materials are excellent candidates as electrolyte materials in Proton Conducting Fuel Cells (PCFC) offering several advantages over traditional Solid Oxide Fuel Cells (SOFC). They maintain high performances and efficiencies while reducing the operating temperature of several degrees (T < 700 °C), as proton conducting electrolytes have lower activation energy to H⁺ transport (0.3-0.6 eV). Moreover, they provide good flexibility in reversible mode (electrolysis and combustion) and high-water partial pressures at the cathode, avoiding fuel dilution and downstream separation. Perovskite ceramic oxides of the family of BaCeO₃ and BaZrO₃ are among the classes of electrolyte materials for PCFC as they show high proton conductivity and good chemical stability, respectively, especially when doped with rare earth cations as yttrium or gadolinium. Doped cerate-zirconate electrolyte with general structure BaCe_{1-x-y}Zr_xM_yO₃ (M = rare earth cation), allow to reach a good compromise between stability and conductivity by modifying the Zr/Cr ratio and dopants (in literature are reported values of ionic conductivity of 1-2*10⁻² S/cm [2] [4] and 1.84*10⁻² S/cm [3] with yttrium and gadolinium doping and low Zr content, respectively). In this work, BaCe_{1-x-y}Zr_xM_yO₃ perovskites powders (M = Y, Gd) have been synthesized through a modified Pechini sol-gel process [2] with the aim of evaluating the chemical composition, purity, morphology and ionic conduction properties of these materials to be integrated as electrolyte in complete fuel cell. Powders obtained with this process, were characterized by X-ray diffraction (XRD), Thermogravimetric Analysis (TGA) and Scanning Electron Microscope (SEM). Pellets (d=2,5 cm) were fabricated with an isostatic press at 3-4 tons and sintered in air and ambient pressure varying the temperature between 1250-1450°C and dwell time to reach the best compactness, densification and homogeneity.



Sol-gel synthesis and characterization of BaCe_{1-x-y}Zr_xM_yO₃ (M = Y, Gd)

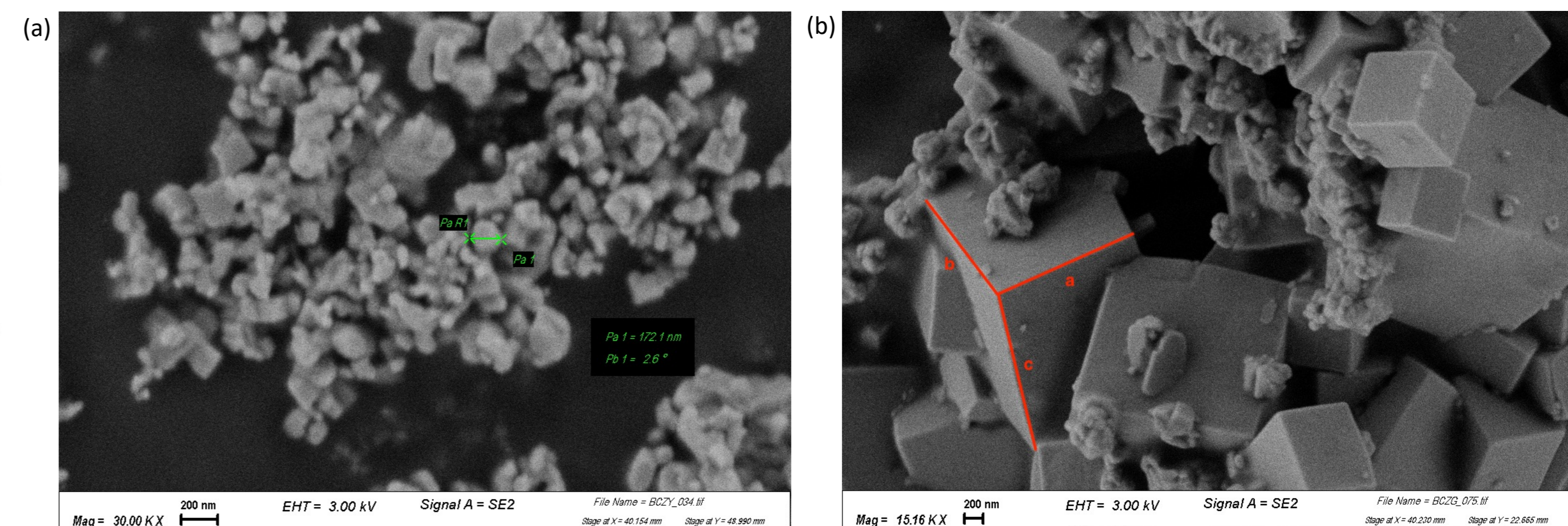
In the sol-gel modified Pechini process [2] a stoichiometric quantity of metal nitrate precursor was dissolved in distilled water. An aqueous solution of EDTA with Ammonium (pH 9) was added to promote metal cations complexation, followed by the addition of the other metal nitrates and the polymerizing agent, ethylene glycol. The recovered gel underwent heat treatment to decompose the organic content and the residual of the unreacted precursors. The obtained powder was calcined at 1100 °C in air. This procedure was used to prepare BaCe_{0.8}Zr_{0.2}O₃ (BCZ powder without doping) and comparing it with BaCe_{0.6}Zr_{0.2}Y_{0.2}O₃ (BCZY) and BaCe_{0.6}Zr_{0.2}Gd_{0.2}O₃ (BCZG) powders.



TG analysis of calcined BCZ, BCZY, BCZG powders. A weight reduction of 1-2% can be observed for BCZY and BCZG. The small weight loss seen in the calcined powder is related to traces of nitrate and carbonates still present, evaporating at higher temperatures, as reported in the literature [3].



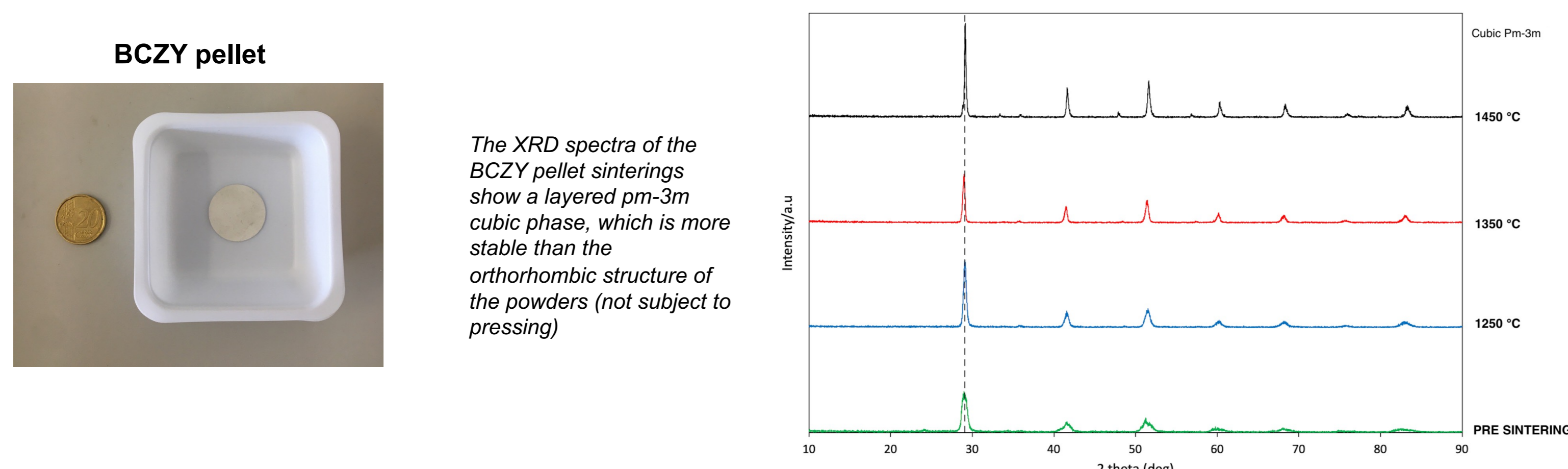
The XRD spectra of BCZ, BCZY and BCZG show that by including the dopant in the structure the peaks shift to the left with the increase of the ionic radius and thus the lattice parameters. The crystalline structure change from cubic pm-3m for BCZ to orthorhombic Imma for BCZY and BCZG.



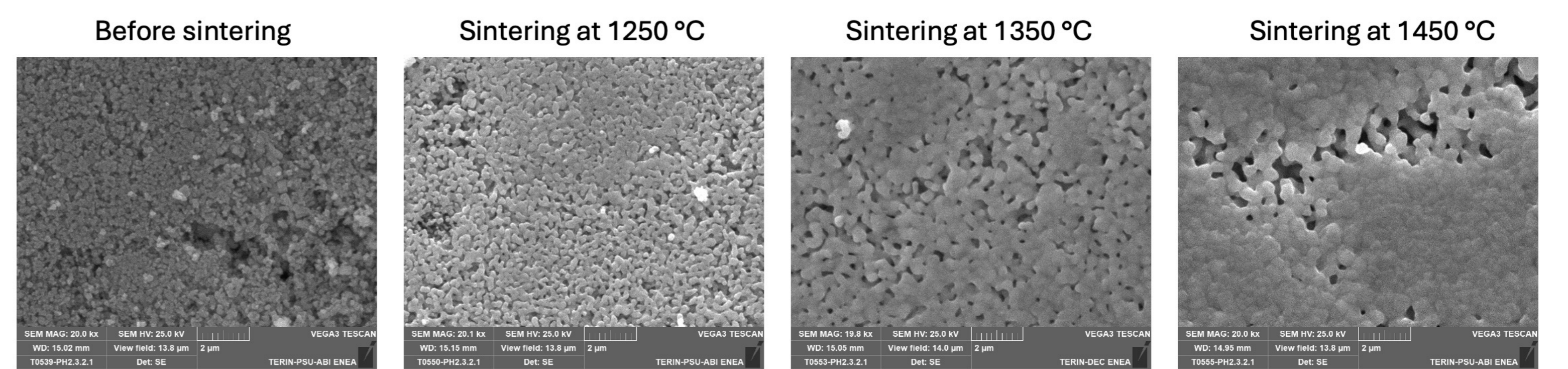
SEM images of BCZY(a) and BCZG(b) powders after calcination with an orthorhombic structure clearly visible in (b) (a≠b≠c). The crystal structure change from cubic to orthorhombic when a dopant is added to BCZ, inducing lattice deformation. Aggregated nanoparticles are in the order of 200 nm for BCZY and in the order of μm for BCZG.

Sintering study and characterization

The calcined powders were mixed with PVP (Polyvinylpyrrolidone) as plastifying agent and ethanol to increase densification of the powders and particles sintering. Powders with PVP were grinded with a mortar and dried to remove ethanol. Powders were die pressed with an uniaxial pressure of 3-4 tons. The obtained pellets of BCZY and BCZG (2,5 cm of diameter) were sintered in a high temperature furnace at different temperatures in order to reach the best compactness and densification. First attempts were made on yttrium doped pellets (BCZY), sintered at different temperatures.

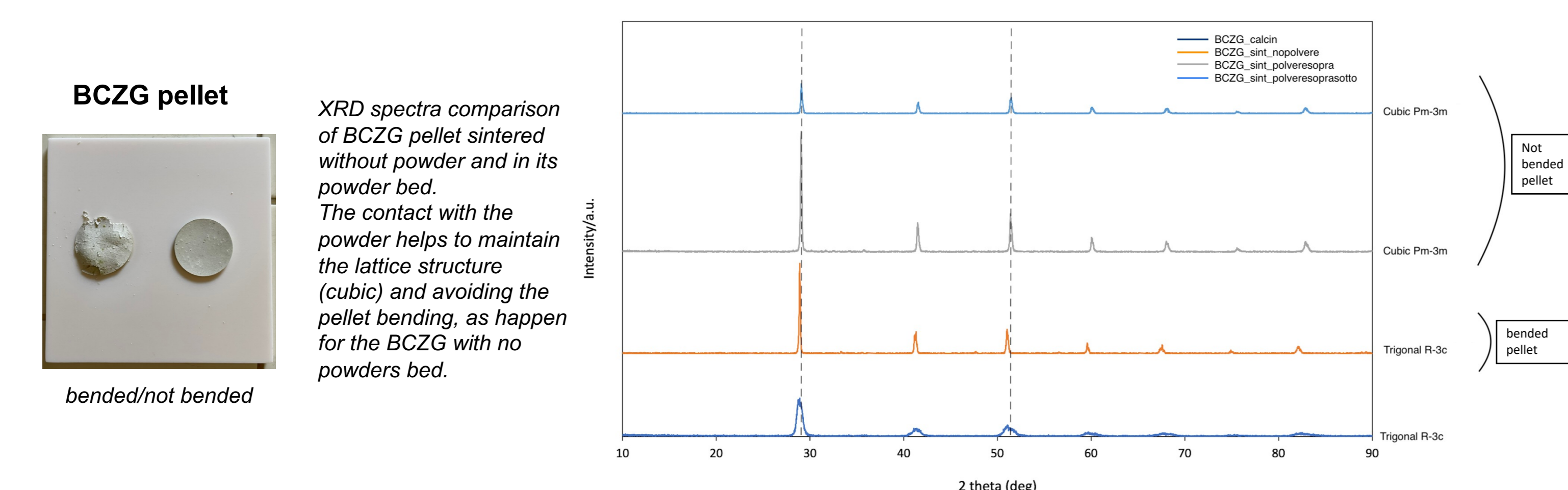


The XRD spectra of the BCZY pellet sinterings show a layered pm-3m cubic phase, which is more stable than the orthorhombic structure of the powders (not subject to pressing)

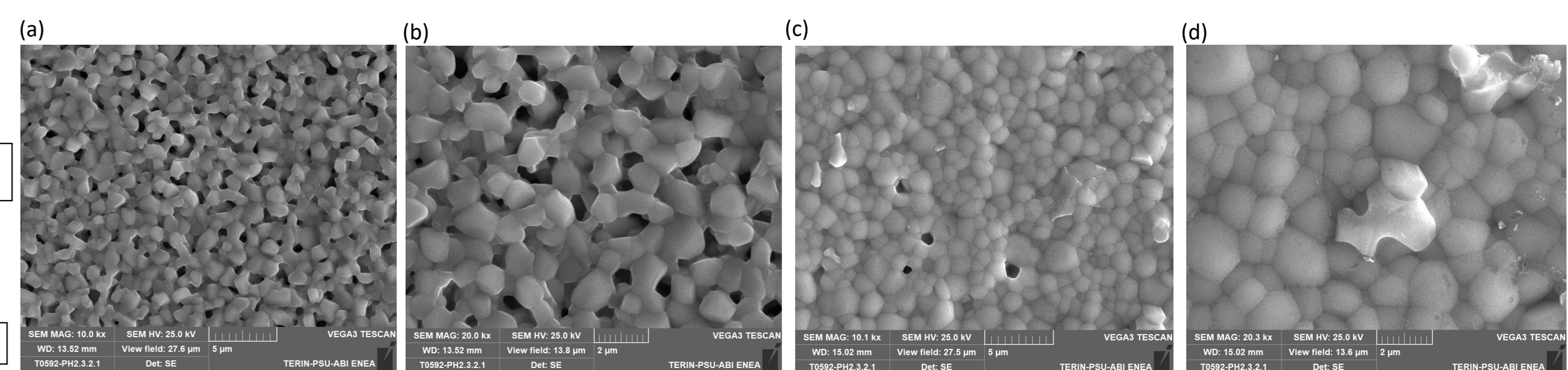


SEM images with a comparison between BCZY pellets before and after sintering at different temperatures. It can be observed that by increasing the sintering temperature, the degree of densification increases, there is more coalescence of particles which increase in size and the structure becomes more compact. 1450 °C is the best temperature.

BCZG was sintered directly at 1450 °C. Different trials were carried out by placing the BCZG pellet in a powder bed of the same stoichiometric composition, in order to increase electrolyte densification and avoiding the pellet bending due to thermal effect or Ba evaporation.



XRD spectra comparison of BCZG pellet sintered without powder and in its powder bed. The contact with the powder helps to maintain the lattice structure (cubic) and avoiding the pellet bending, as happen for the BCZG with no powders bed.



SEM images of BCZG pellet surface sintered without powder in contact ((a) and (b) at 10 kx and 20 kx respectively) and BCZG pellet surface in contact with powder of same composition ((c) and (d) at 10 kx and 20 kx respectively). It can be observed that the surface in contact with powder is more compact and there is more coalescence of grains.

Conclusions

- Perovskite oxides with stoichiometric composition of BaCe_{0.6}Zr_{0.2}Y_{0.2}O₃ (BCZY) and BaCe_{0.6}Zr_{0.2}Gd_{0.2}O₃ (BCZG) were synthesized through a modified Pechini reaction. The doped perovskite powder after calcination treatment shows an orthorhombic structure and nanometric size. When pressed in pellet and sintered at temperature as high as 1450 °C, a better compactness and densification is reached. The crystallinity of the two composition stabilizes to cubic structure and spacial group pm-3m.
- Different attempts have been carried out in order to improve the quality of sintering. By adding the same powder composition helps improving the homogeneity of the surface.

Outlooks

- Further attempts will be carried out trying to change other process parameters in particular introducing powders sieving in order to uniform the particles size before pressing the pellet and a milling step with ball miller. Furthermore, the sintering process will be optimised in agreement with the TGA to allow more uniform thermal effect.
- Once a compact and dense (>90%) electrolyte will be fabricated, Electrochemical Impedance Spectroscopy (EIS) measurements will be carried out to determine proton conductivities at different operating temperatures (300-700 °C) and in a 3-5% H₂/Ar humid atmosphere with a symmetrical cell set up.

Bibliography

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Acknowledgement

This research was funded by the European Union - NextGenerationEU from the Italian Ministry of Environment and Energy Security, POR H2 AdP MEES/ENEA with involvement of CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 "Ricerca e sviluppo sull'idrogeno", CUP: I83C22001170006