Recent progress in the experimental and theoretical studies on the barium zirconate proton conductors: A review

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Abstract

There have been significant developments of solid-state-ion conducting energy materials and perovskite-based oxides those exhibit excellent proton conduction at intermediate temperatures. In contrast to high-temperature oxygen ion-conducting oxides or low-temperature proton-conducting polymers, perovskite oxides have obtained distinguished attention because of their diversified structural aspects and potential applications. Highly stable and conductive electrolytes with improved electrochemical and thermochemical properties are in great demand in numerous fields such as portable electronics and transport systems, energy storage, fuel cells, etc. This review focuses on recent development in the proton-conducting performance of BaZrO₃ (BZO) energy materials. This study aims to integrate the fundamentals of proton conducting BZO perovskites in the prospect of the recent development in materials science and computational engineering. Therefore, in the first half of this review, the basic overview of the BZO perovskites structure, fundamentals of working principles, fabrication, and processing methods underlying the successful development of these materials with superior performance is discussed. The second part principally concentrates on the significant improvement towards higher conductive BZO perovskite fabrication with the help of theoretical studies via density functional theory (DFT) based first-principles calculation and molecular dynamics (MD) simulation followed by the prominent applications in low-temperature solid oxide fuel cells. The presented information on in-depth analysis of the physical properties of barium zirconate from experimental and theoretical studies will guide aspirants in further conducting research in this field near future.

1. Introduction

The increasing global population and demand for a high-quality life leading to unparalleled industrialization instigate a higher level of energy demand around the globe. Moreover, recent global concern about sustainability and environmental pollution due to toxic by-products and worsening climate crisis, has propelled demand for sustainable and eco-friendly energy conversion methods. Among such efforts, fuel cells, especially solid oxide fuel cells (SOFCs) [1–6], are the prime energy conversion devices that got much interest in the last decades. The most common applications are proton-exchange membrane fuel cells (PEMFCs) [7–10], lithium batteries [11–14], flow batteries [15–18], and alkaline water electrolyzers [19–22], etc. The common fuel cell devices are operated at high temperatures (>1000 °C). This leads to critical problems includes but are not limited to high production costs, materials degradation, performance depletion, poor stability and life cycle, long start-up times. And limits the application potential in cases as examples portable power and transportation systems [23–30], electrochemical sensors [31–37], gas separations [38–43], and so on. To overcome these drawbacks, low or intermediate temperatures (IT) operated SOFCs gained much attention [38,43,44]. However, ion transfer resistivity of electrolytes at low temperatures is another concern as the perovskite functions via a thermally activated ion transport process. To reduce the electrolyte's resistivity and to improve the overall conductivity of the SOFCs, new electrolyte development with higher conductivity or thinner electrolyte films must gain exceptional interest [45,46].

Interestingly, proton-conducting ceramics and perovskite oxides have shown tremendous potential in proton conduction at intermediate temperatures (300-800 °C) in the presence of hydrogen and/or water vapor environment [47]. In the high-temperature proton conductor (HTPC) structure proton transport occurred via a

hopping method from one ion to the next, implies no restriction of proton conduction, and, therefore, makes very promising electrolytes for IT-SOFCs [38,43,44]. Researchers observed proton conduction at low temperatures (25-300 °C) owing to the advantages of low activation energy [43]. In contrast to classical oxygen-ion conductors, proton-conducting electrolytes allow complete utilization of hydrogen, produced from water at cathode, and avoid reducing the system's overall efficiency [43]. Among HTPC materials, BaCeO₃(BCO), SrCeO₃(SCO), BZO perovskites showed prominent potential. BCO and SCO exhibited poor stability and conductivity at high temperatures, whereas BZO showed excellent stability [48]. However, BZO exhibited lower conductivity due to high refractory nature, blocking nature of grain boundary, and poor sinterability. It is reported that the Y-doped barium zirconate (BZY) overcomes the poor sinterability and grain boundary resistance at intermediate temperatures [48].

In the current years, promising development on high-performance proton-conducting perovskites at low temperatures (<300 °C) or even room temperatures has been reported in the literature [43]. The low resistance of grain boundary and high conductivity results in developing stable thin films at low temperatures. Park *et al.* fabricated nanosized 10% Y-doped barium zirconate (BaZr_{0.9}Y_{0.1}O_{3-δ} or BZY10) and investigated the effect of grain boundary on proton conductivity at low temperatures (30-400 °C) [49]. The result showed high proton conductivity at very low temperatures (>100 °C), which can be ascribed due to the absorbed water at the interfaces of nanoscale grain boundaries. The nanosized grain structure consists of nanograins connected with the interfacial hydrated layer, which acts as the proton conduction pathway rather than transporting through the bulk systems [50].

The co-doping strategy also put forward the development towards high proton conductivity at intermediate temperatures [51]. An ideal proton-conducting perovskite should possess high conductivity and excellent chemical stability to widen its applications. During doping, impurities may arise in the BZY structure, either A-site [52], B-site [53], or both [3,54]. Several research groups have investigated the dopant's effects on conductivity, stability, proton trapping ability at the operating conditions. Dawson *et al.* observed stable BZO at both H₂O and CO₂ environments using DFT for Y and Sn co-doped BZO perovskites [55]. They also estimated the binding energy between dopants and protons to evaluate proton trapping ability in co-doped perovskites. Bjorheim *et al.* investigated dopant radium's effect on the entropy of the hydroxide group and oxygen vacancy formation [56]. These findings suggest that the vibrational formation entropy became negative with the increasing ionic radius of the dopants. In the case of hydration enthalpy, it became more negative with decreasing the dopants' ionic radius. Loken *et al.* analyzed the hydration enthalpy for Na-, K-, Rb- or Cs-doped BZO and observed this phenomenon [57].

MD simulations allowed to investigate the proton trapping ability of doped BZO. Kitamura *et al.* showed that Zn has more strong proton trapping ability compared to Y using MD simulations [58]. This phenomenon was hypothesized to occur due to the significant charges present in the dopants. A study conducted by Reddy *et al.* on the chemical stability of Y- or In-doped BCO-BZO solid systems and found In-doped systems were better stable at CO₂ and H₂O atmosphere after long-term exposure [43]. Kang *et al.* carried out a similar investigation on BZO doped with K, Rb, or Cs at A-sites [59]. The carbonate formation reaction was investigated using the DFT method and observed that K-doped BZO showed the highest stability and proton conductivity among all

the dopants. It is worth mentioning that there is a relationship between stability and conductivity during A-site doping and needs to do a trade-off, which can be estimated using DFT analysis [59].

The first section of this review focuses on the recent literature on experimental studies on BZO, especially the fundamental properties of BZO, like hydrogen solubility, hydrogen diffusivity, sinterability, chemical stability, grain size, grain boundary, activation energy, proton conductivity, mechanical properties, etc. The second section emphasizes the recent literature on DFT and MD based theoretical studies on BZO and discusses the insights obtained regarding BZO from such studies on structure, doping, defect characteristics, proton conduction, and thermodynamic parameters.

2. Overview Of Bzo Proton Conductor

The general chemical formula of high proton conductor perovskite-type oxides is $AB_{1-x}M_xO_{3-\delta}$, where trivalent dopant M is used to replace the tetravalent B site to create oxygen vacancies, which play the vital role for proton conduction in the lattice structure of ABO_3 perovskite [47]. **Fig. 1** shows the schematic presentation of the generation of an oxygen vacancy in the BZO perovskite.

The following equations [Eqs. (1) and (2) (using Kröger-Vink notation)] depict the oxygen vacancies formation and relation with dopants. The presence of oxygen vacancies is the main prerequisite for proton migration in oxide perovskites [47].

The proton formation as hydroxide defects occurred according to the following equations (Eq. (3)) in the presence of adsorbed water [38,43,47]. In Kröger-Vink notation of this reaction is as follows (Eq. (3)):

Proton migration through the lattice via the hopping process includes fast rotation and reorientation of the proton, which implies localization of proton in the vicinity of oxygen ion followed by transfer to the next ion [61,62]. The hopping or diffusion mechanism of the proton is depicted in **Fig. 2** [62].

Among all the proton-conducting perovskites, barium zirconate and barium cerate are the most prominent and widely studied oxides. The crystal structure of BZO, shorter and stronger Zr-O bonds, and the bond length distances between Zr-O and Ba-O made BZO more stable than Ce-O ones [47]. The BZY showed excellent performance in high bulk proton conductivity and thermo stability at the temperature range of 300-600 °C [43,63,64]. However, the overall proton conductivity is lower compared to cerates due to grain blocking effects [65]. These grain boundary blocking effects arise in BZY due to various factors such as impurities in precursors [66,67], dopants defects [68], poor sinterability [62], inappropriate processing temperatures [38,43], and chemical composition of grain boundary [69]. To widen the application areas of BZY perovskites, it is in great demand to overcome those drawbacks and enhance the proton conductivity and chemical stability for long term exposure at operating temperatures.

3. Experimental Studies On Bzo Proton Conductor

The preparation of powders and the subsequent electrolyte fabrication process plays a crucial role in any material's final performance. For BZO, among various synthesis parameters, the addition of transitional metals as dopants and sintering aid during fabrication affects the final composition and particle grain size. Moreover, these parameters influence chemical mechanical stability and, most, proton conductivity's behavior. Therefore, recent literature works are summarized and reviewed in the following subsections by focusing on the above aspects. At the end of this section, a quick view of hydrogen solubility on BZO is also presented.

3.1 Doping

Doping with metal ions is a familiar technique to increase the proton conductivity of BZO. In the midst of them, BZY is reported to have high proton conductivity, especially at a temperature below 700 °C [70]. To find an ideal yttrium doping concentration, the influence of dopant concentration on BZY was studied by Han *et al.* [71]. The studied powders having compositions of $\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-\delta}$, where $x = 0.1-0.25$ were prepared using the solid-state reaction (SSR) method [72,73]. The scanning electron microscope (SEM) images of powders (sintered at 1600°C for 24 h in the presence of oxygen) revealed that the 10 to 15 mole % yttrium doped BZY have bimodal microstructure. Moreover, samples containing 14 and 15 mole % of Y^{3+} have larger grains compare to ones having 10-13 mole % Y^{3+} . The trend of increasing grain size continued up to 16 mole % of Y^{3+} and uniform grain size is achieved for BZY having 16-25 mole % yttrium. A similar trend was observed from the total conductivity measurements at wet H_2 ($= 0.05 \text{ atm}$). The total conductivity of BZY material increases with the increasing Y^{3+} concentration from 10 to 20 mole %. However, for samples containing a Y^{3+} concentration of 20 - 25 mole %, total conductivity remains almost unchanged. More importantly, 20 mole % Y^{3+} -doped BaZrO_3 showed total conductivity at 500 °C, an essential property for intermediate temperature operated solid oxide fuel cells. The observed influence of yttrium concentration is attributed to the lowering of grain boundaries resistance with increasing doping concentration. This phenomenon is further confirmed by Iguchi *et al.* [74] as the as-synthesized BZY samples having 5-15 mole % of yttrium doping showed similar characteristics. The activation energy of 1.03, 0.71, and 0.48 eV were measured for samples of 5, 10, and 15 mole % Y^{3+} -dopants, respectively.

Kato *et al.* investigated the influence of partial Ba substitution by Ca and Sr in $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ materials leading to the final composite composition of $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ and $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (where $x = 0.05-0.4$), respectively [75]. Notably, all the composites were produced using the SSR method. Although the sintering ability is improved with Ca and Sr insertion on BZY, the total transport number decreases with the increasing Sr concentration in the ceramic, which results from the decrease of bulk and apparent grain-boundary conductivities.

Similarly, co-doping of Sm^{3+} and Y^{3+} on BZO is reported by Zhu and co-workers [76]. A citrate-nitrate combustion route was applied to synthesize $\text{BaZr}_{0.8}\text{Y}_{0.2-x}\text{Sm}_x\text{O}_{3-\delta}$ composite samples. The dilatometry study, conducted in the temperature range of 50-1550 °C, reveals that the sintering shrinkage of co-doped materials improves with the increasing concentration of Sm^{3+} . However, the total electrical conductivity decreases with

the increment of Sm^{3+} concentration. The larger ionic radius of Sm^{3+} which is comparable to Y^{3+} may be the main reason as the dopants with smaller ionic radii have more stable proton bonds to oxygen at the first neighbor of dopant. Thus, the activation energy of proton conductivity at the grain boundary increases and a higher proton migration resistance developed through the grain boundary. Recently, Kuroha *et al.* (2020) [77] reported the effect of Nickel (Ni) addition (Ni = 0 to 0.4) in a 20% In-doped barium zirconate ($\text{BaZr}_{0.8}\text{In}_{0.2}\text{O}_{3-\delta}$ or BZI20) electrolyte of a tubular fuel cell. The tubular cell's electrolyte surface morphology was investigated by SEM that discovered a highly dense crack-free surface. Due to the increase of Ni-content, the proton diffusivity, electrical conductivity, and density of the samples were decreased, while proton concentration was unchanged. The reason behind the decrement of conductivity might be correlated to the dissolution of Ni in the BZI20 electrolyte.

3.2 Grain size

Like doping concentration, the grain size of ceramic powders influences the proton conductivity. Yamazaki *et al.* studied the grain size influence for polycrystalline sintered BZY20 pellets. The precursor powder was synthesized using the wet-chemical method [78]. The variation of sintering temperature results in different grain size boundaries. 1.2 μm average distance between grain boundaries was achieved for sintering temperature below 1150 $^{\circ}\text{C}$, where for sintering at 1150 -1200 $^{\circ}\text{C}$ reduced the distance to 0.5 μm , which further reduced to 0.44 μm at 1600 $^{\circ}\text{C}$. The effective grain boundaries conductivity of samples from sintering temperature 850 and 1600 $^{\circ}\text{C}$ were calculated using AC impedance spectroscopy and found to be 2.5-3.2 times (depending on measured temperature) larger for larger grain size. The lower density of grain boundaries is the reason behind the enhancement of the effective grain boundary conductivity and the total conductivity. Where, at 450 $^{\circ}\text{C}$, the total conductivity of 1.2 μm grain size samples reached $\sim 70\%$ of the grain interior-dominated conductivity, while 0.44 μm grains size gained only 56 % of grain interior-dominated conductivity even at 600 $^{\circ}\text{C}$. Iguchi *et al.* [79] investigated the grain growth and grain boundary distribution of $\text{BaZr}_{0.95}\text{Y}_{0.05}\text{O}_3$ and observed that the sample preparation method did not affect grain structures and grain boundaries distributions, but the duration of sintering influenced the grain growth (**Fig. 3**). Grain size impact on BZY10 materials conductivity was studied by Jarry *et al.* [80]. The samples' manufacturing process was varied, spark plasma sintering was applied as a sintering technique, and SSR methods followed by sintering with and without sintering aid was applied to produce BZY10 samples having a grain size of 0.3 - 5.0 μm . Noteworthy that all the prepared samples exhibited a similar chemical composition in bulk and grain region. Ambient pressure (AP) X-ray photoelectron spectroscopy (XPS) was applied to study the hydration of the prepared samples and reported that the hydroxylation contribution increases with grain size and is higher at the surface. There was a direct observable correlation among the grain size, grain boundaries, and OH^- concentration. When the OH^- concentration increases, the larger grain size-based grain boundaries effectively adsorbed more water for the increment of grain size. It was observed that OH^- concentration increases at the surface of BZY10 but decreases as AP-XPS analysis depth increases from the sample surface. Hence it is proposed to be one of the contributing factors of higher proton conductivity for the existence of larger grain size in materials. The obtained results concluded that larger grains may enhance the hydration, which raise the catalytic activity of oxidation in a cell.

3.3 Sintering aid

Although at intermediate temperature ($\sim 500^\circ\text{C}$), BZY shows good mechanical and chemical stability with moderate proton conductivity, to improve the overall performance it is necessary to operate such fuel cell electrolyte materials at a higher temperature (like $\geq 800^\circ\text{C}$). Besides, BZY requires a higher sintering temperature ($\sim 1800^\circ\text{C}$) to fabricate [81]. In such cases, sintering aid materials like Co, Ni, etc. were applied to overcome the sintering issues [82]. Sample preparation and uses of sintering aids also have influences on total conductivity [83]. Therefore, to fabricate the BZY electrolyte, the sintering temperature must be considered to develop a cost-effective method. As an example, Ricote *et al.* reported that the high temperature treated BZY (sintered at 1720°C while annealed at 2200°C) having grain size distribution of $1\text{--}10\ \mu\text{m}$ acquire 3 times higher total conductivity at 600°C (measured at 5% H_2 , 0.03 atm H_2O) than materials sintered at 1600°C using NiO as sintering aid exhibiting grain size distribution of $1\text{--}6\ \mu\text{m}$ [83]. The ratio of grain boundary resistance to bulk resistance of the heat-treated sample is half compared to samples sintered using NiO. As a result, the grain boundary activation energy was calculated to be 0.84 eV for the NiO-sintered aid product. Sintering aid plays a key role in reducing the sintering temperature and the synthesis of densified ceramic powders. The uses of CuO, and ZnO as sintering aids for the synthesis of BZY20 ceramics was reported by Kosasang *et al.* [84]. With the use of 1 wt. % ZnO as a sintering aid, a homogenous particle grain size of $0.5\ \mu\text{m}$ was achieved where $1\ \mu\text{m}$ grain-sized particles were visualized using 1 wt.% CuO. In performance comparison, the ceramic powders prepared with CuO as a sintering abetment have better total proton conductivity than ZnO ones. This is due to the high grain boundary conductivities for the sample with CuO ones where bulk grain boundary conductivity is similar to the ZnO ones. Aktas *et al.* studied the impact of BaO as a sintering aid on $\text{BaZr}_{0.92}\text{Y}_{0.08}\text{O}_{3-\delta}$ ceramics earlier [85]. The powders were synthesized by mechanical mixing of BZY powders with BaO followed by the high-temperature sintering process. With the increasing amount of BaO, the final grain size of ceramic powder decreases, whereas grain boundary activation energy increases. This scenario was viewed for the presence of secondary phase at the grain boundary of BaO crystals.

To investigate the possible inter-diffusion between metal and perovskite ceramics, some research groups incorporated transition metals (Mn, Fe, Co, etc.) as sintering boost into BZY electrolyte by calcination process from the cathode materials ($\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ [86], $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ [87], $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ [88], etc.) of an electrolyzer or fuel cell during cell fabrication. However, the impact of the possible inter-diffusion of transition metals into the BZY by the calcination process remains ambiguous, as it may produce an unexpected reduction of cell performance. Han *et al.* (2020) [89] studied the electrochemical and structural properties of the BZY20 proton-conducting electrolyte with individual doping of transition metals like iron (Fe), manganese (Mn), Nickel (Ni), and cobalt (Co) prepared by conventional SSR method instead of calcination process. The X-ray absorption near-edge structure spectroscopy (XANES) analysis was used to determine the success of Fe, Mn, Ni, and Co incorporation into the BZY20 perovskite crystal structure. The transported proton number was measured by the electromotive force (EMF) analysis in the temperature range of 500°C to 700°C in the wet reducing (H_2) atmosphere and in the wet oxidizing (O_2) atmosphere, respectively. The results showed that the incorporation of transitional metals like Co improves the sintering capability, though the proton concentration, transported proton number, and proton conductivity was decreased even after the incorporation of all transitional elements, i.e., Fe, Mn, Ni, or Co. In another study, Han *et al.* (2018) [69]

investigated BZY20 electrolyte materials using ZnO, NiO, and CuO as sintering additives. The experiment showed similar results, i.e., though ZnO, NiO, and CuO improved the sintering ability of BZY20, a significant reduction of proton conduction and resultant increment of hole conduction deteriorates the cell performance. Besides, as the concentration of Zn, Ni, and Cu in the BZY20 crystal increases, the proton conductivity decreases. Therefore, a post-annealing (at 700 °C for 48 h) on the Ni, Cu, and Zn-doped BZY20 was performed in a reducing hydrogen atmosphere for the removal of Ni, Cu, or Zn content from BZY20. Though the post-annealing can remove the ZnO, NiO, and/or CuO sintering additives in some cases, nevertheless the kinetics of the process was very slow. Chen *et al.* (2019) [90] reported the feasibility of formulating dense BZY polycrystalline electrolytes with low amounts of NiO (0.2%) and low sintering temperatures (1500°C). Their approach improves the Ba evaporation issue, grain size distribution, and relative density. However, NiO addition negatively impacts electronic leakage of BZY10 ceramics in humid oxidizing environments due to misdiagnosis of proton ceramic fuel cell (PCFC) cathode material's electrocatalytic activity and reduced faradaic efficiency of proton ceramic electrolysis cells (PCECs). Therefore, care must be taken during incorporation of such metals (Mn, Fe, Co, Ni, Cu, Zn etc.) as sintering aid to achieve higher cell performance.

3.4 Composites and thin films

BZO perovskite found another promising application as a component of polymer-based composites. In general, polymer-based membranes are commonly used in PEMFC [91]. For such an application, Nafion is a conventional polymer material, in which polytetrafluoroethylene backbone and the sulfonic acid functional group provides the physical and proton transport sites, respectively [92]. However, proton conductivity properties of Nafion decreases at a temperature above 80 °C, therefore as an alternative other polymers, i.e., poly(ether ether ketone), poly(phenylene), poly(ether sulfone), and poly(arylene ether) having higher proton conductivity ($>60 \text{ mS cm}^{-1}$ at 80°C) has drawn attention [93,94]. To improve the proton conductivity at a higher temperature and relative humidity, the incorporation of doped BZO was studied [95,96]. A perovskite oxide composition of BZY10 nanoparticle was incorporated in sulfonated poly(ether ether ketone) (SPEEK) polymer [97]. In their work, the amounts of nanoparticles, as well as the degree of sulfonation, were varied to optimize the performance of SPEEK based nanocomposite membrane. As a result, the chemical, mechanical, and thermal stability of composites improved with nanoparticle incorporation. Proton conductivity of the composite membrane increased initially with the incorporation of nanoparticles, however, after the application of 1.8 wt. % of nanoparticle in the matrix, the proton conductivity decreased. The reason is mentioned to be the agglomeration of nanoparticles, narrowing of proton conductivity channels, and rearrangements of the hydrogen bond between -OH groups of nanoparticles and -SO₃H group of SPEEK [98]. The doping of Y³⁺ into BZO plays a vital role in the increase of proton conductivity as dopant sites act as water uptake sites and 'proton traps'. In comparison with pristine SPEEK and incorporated SPEEK-BZY10 composite the maximum power density of fuel cell performance increases from 0.16 to 0.43 Wcm⁻² at 80 °C. A similar positive influence of BZY10 nanoparticles in the case of incorporation with the sulfonated poly (1,4-phenylene ether-ether sulfone) (SPEES) membrane is stated by Hooshyari *et al.*[99]. The chemical and mechanical stability increases compared to the pure polymer membrane. In terms of membrane performance of 9 wt. % doping of BZY10 nanoparticles in SPEES-based nanocomposite, an overall proton conductivity of 117 mS cm⁻¹, and

considerable fuel cell performance of 0.61 Wcm^{-2} was found at 80°C . In that study, pure SPESS polymer membranes proton conductivity was reported to be 81 mS cm^{-1} at 80°C and 95 % RH.

Afterward, Aruta et al. study the positive impact of Y^{3+} doping proton conductivity of BZO perovskite materials by fabricating thin films of BZY10 on oxide substrate [100]. With the help of hard X-ray photoelectron spectroscopy (HAXPES), scanning transmission electron microscopy (STEM), and DFT calculations, they investigated the thin film structure and explained the cause of the improved proton transport properties of Y^{3+} -doped BZO on NdGO_3 substrate. The distorted perovskite structure of NdGO_3 compared to the cubic structure of Y-doped BZO, during Pulsed Laser Deposition (PLD), influences the film to grow with an in-plane compressing strain of about 8 %. The developed strain was the driving force for the Y^{3+} dopants to substitute, preferably Ba^{2+} sites, compare to Zr^{4+} sites in the crystal structure. The HAXRPES investigations and DFT calculations further verified this scenario. Due to the smaller size of Y^{3+} compare to Ba^{2+} , Y^{3+} substitutions for Ba^{2+} increased the number of fast proton transport pathways by lowering the proton transfer barriers (activation energy required for the migration step) that result in the improved proton conductivity in doped perovskite materials, hence, the films deposited in their studied composite. Furthermore, the PLD deposition rate and choice of substrates on the formation of BZY10 thin film and resulting proton conductivity were studied by Bae *et al.* [101]. Ceramic material was prepared following mechanochemical, where MgO and sapphire substrates were used. In both substrates, the slow deposition rate consequences highly dispersed films with lower grain boundaries compared to higher deposition rates. The proton conductivity is higher in thin films deposited applying a slow deposition rate due to the decrease in insulating grain-boundaries' density. In comparison between MgO and sapphire substrate, thin films grown on the sapphire substrate shows lower proton conductivity due to higher Ba deficiency in the final deposited layer.

Recently, Exner *et al.* (2020) [102] proposed a novel method known as powder aerosol deposition (PAD) [103–106] to produce highly dense BZY20 film to analyze the electrical, optical, and mechanical behavior at high temperatures (800°C to 1000°C). Uniform and crack free PAD films with dense microstructure were observed from the SEM micrographs. Bulk sintered samples were also prepared for a direct comparison of mechanical properties with PAD films. Vickers' microhardness test confirms that the hardness of films was about 2.4 times higher than the sintered bulk samples. Film crystallites size was about 9 times lower than that of the mixed powder, and finally, the XRD, SEM, and hardness test results confirm that the PAD film is suitable for electrical studied [105,107–112]. At lower temperature (400°C) film sample showed a lower conductivity of $2.5 \times 10^{-8} \text{ S/cm}$, which is 3.5 order lower than the bulk one. On the other hand, at higher temperatures (800°C to 1000°C), almost similar conductivity ($2 \times 10^{-2} \text{ S/cm}$) was observed both in bulk and film samples. BZY20 revealed more than 0.9 ionic transfer numbers even at high temperatures ($\sim 800^\circ\text{C}$) it suggests that BZY20 is favorable for proton conduction above 700°C . By the feasibility study, the PAD film functionality as a membrane was confirmed after successful deposition of PAD-BZY20 film onto the porous NiO electrode. As the film exhibits the higher conductivity in the high-temperature region (800°C to 1000°C), it may be assumed that the PAD film is beneficial as a functional film in the electrochemical membrane devices in high-temperature operation.

3.5 BZO as fuel cell electrolyte materials

BZO has much potential as fuel cell electrolytes due to its improved chemical stability. However, BZO has a lower power output compared to barium cerate. Therefore, numerous research efforts were focused on the co-doping of rare-earth metals on BZO to increase the power density and chemical stability. In short, the most common synthesis technique was the SSRs method. Followed by combustion, sol-gel, spray pyrolysis, citric acid (CA) – ethylenediaminetetraacetic acid(EDTA), etc. methods, different types of techniques like– dry-pressing, uniaxially-pressing, co-pressing, tape-casting, solution casting, PLD, etc. were applied for electrolyte fabrication. Furthermore, for calcination, the temperature range of 600-1400 °C and the holding time in the range of 2 to 6 h was applied. For example, Xie *et al.* (2018) [113] used 1100 °C and 3 h for calcination. On the other hand, Wallis *et al.* (2020) [114] used the spark plasma sintering method as it reduces the sintering temperature significantly (elapsed 20 minutes only). The relative density of the electrolyte depends on the composition, fabrication process, and temperature. For example, Zhu and S. Wang (2019) [76] pointed out that using Sm³⁺ doping improves the sintering activity, thus increased the density. Chen *et al.* (2019) [90] found out that using Bi doping relative density increases from 82% to 95%. In this section, based on the recent research works, a tabulated summary containing the composition of BZO, their preparation method, and relative density is presented in **Table 1** [15,76,77,90,99,113,115–140].

Table 1: A summary of the preparation parameters of the BZO-based electrolyte for fuel cell fabrication.

Electrolyte materials composition	Synthesis method	Fabrication method	Calcined temperature (°C)/time (h)	Sintering temperature (°C)/time (h)	Relative density (%)	Ref
BaZr _{0.8} Y _{0.2} O _{3-δ}	Citrate-nitrate combustion	Dry-pressed	1250/3	1600/5	79.32	[76]
BaZr _{0.8} Y _{0.15} Sm _{0.05} O _{3-δ}				1450/10	86.76	
BaZr _{0.8} Y _{0.1} Sm _{0.1} O _{3-δ}				1600/5	87.09	
BaZr _{0.8} Y _{0.05} Sm _{0.15} O _{3-δ}				1600/5	89.22	
BaZr _{0.8} Sm _{0.2} O _{3-δ}				1600/5	91.36	
BaZr _{0.75} In _{0.2} Bi _{0.05} O _{3-δ}	Citric acid - EDTA	Dry-pressed	1000/3	1500/10	95	[137]
BaZr _{0.8} Y _{0.15} Ca _{0.05} O _{3-δ}	Citrate-nitrate combustion	Dry-pressed	1200/3	1600/10	-	[138]
BaZr _{0.8} Y _{0.20} O _{3-δ}						
BaZr _{0.8} Y _{0.2-x} Sm _x O _{3-δ}						
BaZr _{0.8} Y _{0.2} O _{3-δ}	-	PLD	-	-	-	[139]
BaZr _{0.8} Y _{0.2} O _{3-δ}	Wet chemical	Co-pressing and co-sintering	1100/6	1400/6	-	[140]
BaZr _{0.8} Y _{0.2} O _{3-δ}						
BaZr _{0.8} Y _{0.2} O _{3-δ}	Micro-machining process	PLD/MBE	-	-	-	[115]
BaZr _{0.8} Y _{0.2} O _{3-δ}	Wet chemical	Painted on surface	1250/5	1400/5	-	[116]
BaZr _{0.6} Fe _{0.2} Y _{0.2} O _{3-δ}						
BaZr _{0.4} Fe _{0.4} Y _{0.2} O _{3-δ}						
BaZr _{0.2} Fe _{0.6} Y _{0.2} O _{3-δ}						
BaZr ₀ Fe _{0.8} Y _{0.2} O _{3-δ}						
BaZr _{0.8} Y _{0.2} O _{3-δ}	SSRS (with Ball-milled precursor powder)	Uniaxially pressed	-	1435-1535/5-25	56 - 94	[117]
BaZr _{0.8} Y _{0.2} O _{3-δ}	SSRS (with Planetary	Uniaxially pressed	-	1435-1535/5-25	94 - 95	

	Ball-milled precursor powder)					
BaZr _{0.8} Y _{0.2} O _{3-δ}	Combustion	-	150/1	1150/4	-	[118]
BaZr _{0.8} Gd _{0.2} O _{3-δ}						
BaZr _{0.8} Sm _{0.2} O _{3-δ}						
BaZr _{0.8} Gd _{0.2} O _{3-δ}	Citric acid - EDTA	Dry-pressing	1100/3	-	-	[113]
BaZr _{0.8} Gd _{0.18} Zn _{0.02} O _{3-δ}				1300/10	~41	
BaZr _{0.8} Gd _{0.16} Zn _{0.04} O _{3-δ}				1400/10	~91	
BaZr _{0.8} Gd _{0.14} Zn _{0.06} O _{3-δ}				1500/10	91.33	
BaZr _{0.9} Y _{0.1} O _{3-δ}	Combustion-based wet-chemical route	Uniaxially pressed	600-800/2	1500-1600/12	95	[90]
BaZr _{0.8} Y _{0.2} O _{3-δ}	SSRS	-	600/-	1450/ -	-	[119]
BaZr _{0.8} In _{0.2} O _{3-δ}	Glycine-nitrate combustion	Cold isostatic pressing	900/10	1600/10	98	[77]
BaZr _{0.8} Y _{0.2} O ₃	Citric acid - EDTA	-	1100/10	1450/5	-	[120]
BaZr _{0.9} Y _{0.1} O _{3-δ}	Sol-gel	Co-pressing	1000 or 1200/5	1000 or 1200/5	-	[121]
BaZr _{0.4} Ce _{0.4} Y _{0.2} O _{3-δ}	SSRS	Spin coating	1400/-	1400/8	97	[122]
BaZr _{0.6} Ce _{0.2} Y _{0.2} O _{3-δ}				1400/12		
(BaZr _{0.8} Y _{0.2} O _{3-δ}) - (BaCe _{0.8} Y _{0.2} O _{3-δ})	Sol-gel	-	1050/3	1450/5	-	[123]
BaZr _{0.85} Y _{0.15} O _{3-δ}	-	Pulsed laser deposition	-	1450/10	-	[124]
BaZr _{0.9} Y _{0.1} O _{2.95}	SSRS	-	-	1700/6	-	[125]
BaCe _{0.2} Zr _{0.7} Y _{0.1} O _{2.95}					-	
BaZr _{0.5} Ce _{0.3} Y _{0.2} O _{3-δ} + NiO (before calcination)	Solid-state reaction	-	-	1600/10	97	[126]

BaZr _{0.5} Ce _{0.3} Y _{0.2} O _{3-δ}			-	1600/24	96.4	
BaZr _{0.5} Ce _{0.3} Y _{0.2} O _{3-δ} + NiO (after calcination)			-	1600/10	96.4	
BaZrO ₃ + ¹³⁴ BaO	Spray pyrolysis	-	-	1600/10	>97%	[127]
BaZrO ₃ + ⁹⁶ ZrO						
BaZr _{0.9} Y _{0.1} O _{2.95} (Exsolve composite)	Spray-pyrolysis	-	900/4	1600/10	-	[128]
BaZr _{0.9} Y _{0.1} O _{2.95}			1000/3		-	
BaZr _{0.9} Y _{0.1} O _{3-δ}	Sonochemical	-	-	1400/20	84	[129]
		-	-	1450/20	90	
				1500/20	95	
BaZrO _{3-δ}	Solid state reaction	-	-	1600/24	96	[130]
BaZr _{0.98} Y _{0.02} O _{3-δ}		-	-		96	
BaZr _{0.95} Y _{0.05} O _{3-δ}		-	-		98	
BaZr _{0.9} Y _{0.1} O _{3-δ}		-	-		93	
BaZr _{0.85} Y _{0.15} O _{3-δ}					92	
BaZr _{0.80} Y _{0.2} O _{3-δ}		-	-		96	
BaZr _{0.75} Y _{0.25} O _{3-δ}		-	-		96	
BaZr _{0.7} Y _{0.3} O _{3-δ}		-	-		96	
BaZrO ₃	Combustion	Co-pressing	1100/6	1400/6	-	[131]
BaZr _{0.8} Y _{0.2} O _{3-δ}	Combustion	Co-pressing	1100/6	1200/3	-	[15]
BaZr _{0.75} Y _{0.2} Pr _{0.05} O _{3-δ}	Sol-gel	Co-pressing	600/3	1650/10	-	[132]
BaZr _{0.8} Y _{0.2} O _{3-δ}	Combustion	Tape casting	1100/3	1450/6	-	[133]
BaZr _{0.9} Y _{0.1} O _{3-δ}	Gel polymerization	Solution-casting	1000/3	-	-	[99]
BaZr _{0.8} Y _{0.2} O _{3-δ}	Solid-state reaction	Co-pressed	750/3	1600/24	-	[134]
BaZr _{0.8} Y _{0.2} O _{3-δ}	SSRS	Tape-	800 or	1500/10	87	[135]

		casting	1000/2			
BaZr _{0.8} Y _{0.2} O _{3-δ}	Combustion	Spin-coated	1100/3	1400/6	-	[136]

3.6 Stability and conductivity

Although there are some problems like sintering ability, mechanical stability, and chemical stability [141,142], owing to the higher proton conductivity at intermediate temperature (~500 °C), but both BCO and BZO are potential materials for the electrochemical fuel cell devices. Though barium zirconate shows higher chemical stability in the CO₂ atmosphere than the barium cerate [143,144], it is important to study the synergistic effect of chemical and mechanical stability on barium zirconate after CO₂ attack. Recently, Rokas *et al.* (2016) [145] studied the chemical and mechanical stability (Vickers hardness and fracture toughness) on the sintered highly dense BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.95} and BaZr_{1-x}Y_xO_{3-x/2} (x = 0 to 0.2) proton-conducting perovskite oxides after CO₂ exposure at different temperatures (500 °C to 750 °C). Ba-deficient BaCO₃ surface was appeared upto 1 mm in depth due to CO₂ attack, and an explicit Y-content and grain size dependency observed. EDS line scanning confirmed the decreased Ba- but increased Zr- and Y-content at the CO₂ exposed BZY10 surface. Due to the increase of CO₂ exposure temperatures, the Vicker's hardness was unchanged, but with the increase of exposure temperature (in the range of 550 °C–750 °C), the fracture toughness was decreased due to the increase of lateral cracks and induced stress at the surface. On account of the CO₂ reaction, grain boundaries become weak, which resulted in reduced fracture toughness. SEM micrographs showed that the reduction of fracture toughness does not affect the amount of large BaCO₃ crystal formation on the sample surface. Although the formation of BaCO₃ does not potentially affect the hardness of the experimental sample, the overall mechanical performance was reduced for the generation of micro-cracking on the surface of the sample after the attack of CO₂. Therefore, care must be taken when BZO-ceramics would be used in the CO₂ containing atmosphere.

Conductivity values of BZY10 show 2 order of magnitude difference, measured by various research groups [71,130,146–150]. The reasons for this discrepancy are the variation of sintering temperatures and times, sintering methods, and conductivity measuring atmospheres, etc. [71,130,147–150]. Another reason might be the changes of Y³⁺ mole % caused by the variation of sintering conditions [148], but this phenomenon needs further investigation for clarification [146]. For example, due to the variation of sample synthesis techniques, sintering processes, and sintering conditions, Ba-deficiency was observed, which reduce the conductivity of BZY10 [141,151]. To clarify the discrepancy of literature cited conductivity values of BZY10, recently, Han *et al.* (2019) [146] reported the correlation between the conductivity data with the structural parameters like crystallites size and perovskite phases of sintered BZY10. Experimental results revealed that the BZY10 has bimodal microstructures, i.e., a mixture of two different perovskite phases instead of a single phase with different Y-content values regardless of the sintering time. Lattice constant shows similar variation like Y content change, and the phase fraction of both perovskite phases were very close to 50 wt.%. For samples with over 40 h of sintering, Ba-vacancies were observed due to the small deficiency of Ba-content. These Ba-

vacancies might be responsible for the reduction of bulk and grain boundary conductivities for the long time sintered BZY10. Zhu *et al.* reported a comparative study on the sinterability, crystal structure, chemical stability, and electrical conductivity between the BZY20 and $\text{BaZr}_{0.8}\text{Y}_{0.15}\text{Ca}_{0.05}\text{O}_{3-\delta}$ (BZYC5) ceramics. The results show better grain growth, sinterability, chemical stability, and electrical conductivity for the BZYC5 than the BZY sample (Fig. 4) [138].

3.7 Hydrogen solubility and diffusivity

The proton-conducting oxides have a potential application in the fusion reactor's isotope separation systems [15,103,152–159], hydrogen pump for tritium purification and recovery [160–165], and also as hydrogen sensors [31–37] and fuel cells [5–10]. Therefore, to advance in practical usage of oxide proton conductors as functional materials, it is essential to understand the hydrogen behavior in the proton-conducting materials, such as the amount of dissolution and internal diffusion of hydrogen [166–170]. Nevertheless, solubility and diffusivity data are limited and somewhat scattered for oxide materials. The authors of the current manuscript mentioned in their early studies that [60,171], the hydrogen solubility and diffusivity can be measured and calculated by using a tritium tracer method, for instance, a tritium imaging plate (TIP) [167–169,171,172] for the BZY10, $\text{BaZr}_{0.955}\text{Y}_{0.03}\text{Co}_{0.015}\text{O}_{3-\delta}$ (BZYC) [171], and $\text{CaZr}_{0.90}\text{In}_{0.10}\text{O}_{3-\delta}$ (CZI) [60]. In this method, the samples were vacuum-annealed at 1273 K for 1 h, and then samples were exposed for a different duration from 15 min to 16 h at various exposure temperatures of 623 to 1273 K in a 1.3 kPa HT (the tritium and hydrogen ratio was 10^{-4}) [171] or DTO (the tritium and deuterium ratio was 10^{-3}) [60] tritium atmospheres. The concentration of tritium (C_T) is higher in the edge and outer surface for non-cobalt samples (BZY) than the cobalt-containing sample (BZYC). However, opposite C_T results ($C_T(\text{BZYC}) > C_T(\text{BZY})$) were observed inside the samples (cross-sectional IP images) under the same exposure condition. Temperature independent hydrogen solubility ($S_{\text{BZY}} \sim 10^{-4}$ H/M) was found for HT exposed BZY sample was obtained from the Arrhenius plot. One order higher solubility ($S_{\text{BZYC}} \sim 10^{-3}$ H/M) was observed for the BZYC. Hydrogen diffusivity (D) of BZYC ($\sim 10^{-11}$ m²/s) is higher than the diffusivity of BZY ($\sim 10^{-12}$ m²/s), and a trend of increase of D was noticed with the increase of exposure temperature. Both higher solubility and diffusivity were observed for BZYC as compared with BZY (Fig. 5). This may be due to cobalt participant in the BZO perovskite as a catalyst in the HT reaction ($\text{HT} \rightarrow \text{H} + \text{T}$) during HT exposure. The hydrogen (H) solubility and diffusivity in CZI was lower than that of BZY and BZYC, and the activation energy of H-diffusion for CZI was approximately double of that for BZY and BZYC [60]. Therefore, a small amount of cobalt doping (1.5%) may play a vital role in enhancing the electrochemical activity of the proton conducting BZO.

4. Theoretical Studies On Bzo Proton Conductor

In obtaining insight into the structural properties, and characteristic attributes of perovskite materials, computational approaches play an instrumental role. Two important approaches in this regard are the first principles DFT study and MD simulation mode. While DFT uses functionals from the quantum mechanical consideration to determine properties of the system of interest, MD simulation provides a dynamic evolution of physical movement in a system of atoms or molecules. The discussions of DFT and MD simulation are gravely relevant to the current review. These methods provide critical insight regarding BZO, which, in some

cases, deem unapproachable or too inconvenient by experimental studies. Therefore, these computational approaches can be effectively used to complement experimental studies or validate specific experimental findings.

DFT and MD studies have investigated numerous attributes of BZO, such as their structure, surface properties, mechanical properties, proton transport mechanism, defect characteristics, formation energetics, optical properties, thermodynamic parameters, and its behavior at doped state. In this review the aforementioned attributes are deeply investigated employing DFT and MD simulation methods are summarized in **Table 2**, with the significant reference numbers and remarkable studies [6,55,56,59,62,100,149,150,173–210]:

Table 2: The properties, characteristics, attributes, and aspects studied or substantiated by MD and DFT for BaZrO₃.

Oxide	Study on	Ref. (for DFT)	Ref. (for MD)
BaZrO ₃	Structure, doping	[59,100,173,174,192,200]	[179,185–189]
	Defect characteristics	[173,207]	[149,150,190,191,193]
	Proton conduction	[62,175–179,208–210]	[6,194–199]
	Surface property	[180,181]	[201]
	Thermodynamic property	[55,56,182–184]	[202–206]

4.1 DFT studies

BZO is considered as a verily potential candidate for fuel cell applications, especially in its composite configuration, as admitted in recent studies [211]. Numerous DFT studies were performed on BZO to highlight its structural, thermodynamic, and proton transport aspects, especially in a doped state [212], as dopants invoke structural distortions and affect the proton transportability.

The ground-state structure of BZO was investigated by the neutron scattering experiment and First Principles (FP) calculations. It reveals that unstable phonon mode is a transition phenomenon, which is associated with rotations of ZrO₆ octahedra. These calculations, dependent on the exchange-correlation functionals, suggested the stable cubic perovskite structure of BZO [173].

FP calculations suggested that different types of doping affect the proton conduction significantly in a different manner. For example, B-site doped BZO shows that Ga-doping provides the highest chemical stability, whereas La-doping leads the maximum proton conduction [59,174]. This section highlights how DFT studies contribute to extract critical insight regarding BZO in appropriate detail. The abundance of such research works substantiates the strength of BZO as a proton-transporting perovskite candidate and its applicability in related fields.

A combination of XPS, STEM, and DFT calculations show that BZY can accommodate a substantial Y dopant while providing lesser scope for other cations (Zr^{4+} and Ba^{2+}) [100]. The most critical insight of this study is the mechanism of the fast proton transport pathway– which is connected to the rich regions due to Y-substitutions, as they provide a negligible energy barrier for proton transportation. Therefore, it is evident that the ultrathin strain film's structural and conductivity properties are controlled by epitaxial strain. Acceptor dopants' ability to affect proton mobility is substantiated in a separate DFT study, which suggests similar attractive interaction between the proton and substituting trivalent dopants such as Ga, Sc, In, Y, and Gd – leading to structural stability [192]. However, the DFT calculations underestimate the experimental values of the required energy for proton migration. Furthermore, the study attempts to compensate for this aspect by implementing a jump-diffusion model, showing that DFT can be a useful tool for creating a reliable model for such perovskite materials. Solely from the oxygen vacancy perspective, the energetically favorable oxygen vacancy distribution was studied for BCO and BZO and the comparison shows that the vacancies tend to prefer Zr, while they prefer the dopant with the increase of Ce in the solid solution [200]. Therefore, it is substantiated that doping can invoke significant structural optimization in the geometry of BZO, which can be explained via DFT investigation. For example, one FP DFT study has shown the optimized configurations of ions in BZO(**Fig. 6**) [177].

While considering structural aspects, the defects and local distortions must be included in the discussion in perovskites, as they are directly related to proton mobility [213]. Defect engineering is always mentioned as a suitable approach to manipulate proton conductivity of perovskites such as SrZrO_3 (SZO), CaZrO_3 (CZO), and BZO [207]. Proton conductivity, as a thermally activated phenomenon, is dependent on the percentage of doping (as it increases localized lattice distortion), and surpassing a threshold point, or incorporating a grain boundary defect those frameworks can significantly vary the conductivity [173]. This study suggests that the proton conductivity can be improved pronouncedly by embodying dopant-lattice polaronic interaction, and this approach can be extended to other perovskite materials as well. The positive effect of manipulating dopant percentage (tested with 6.25% and 12.5% Y dopant), which results in local distortion in the structure and hence effect in proton conduction, was substantiated by multiple studies based on DFT calculations [214]. Aside from the dopant percentage, non-stoichiometry can affect the proton conductivity, as suggested by manual incorporation of planar and spherical defects by heat treatment– results in a lesser value of activation energy for proton transport [208]. This study strengthens previously suggested mechanisms of improving proton transport by decreasing dopant-lattice interaction [173,215]. For specific insight on the tilt grain boundary effect, Kim *et al.* [216], utilize space charge layer and structural disorder to incorporate proton and oxygen vacancies into the system. Based on segregation energies, the energy barriers for proton transport are calculated. Also, the applicability of BZO as an electrochemical device is justified in a separate grain boundary study, which suggests that BZO and BCO show high grain boundary resistance [217], which means their proton conductivity is limited by grain boundaries in a polycrystalline state, which can be quantified by the space-charge potential. Space-charge modeling in this study also shows that proton formation energies can be different in separate perovskite material in bulk form based on hydrogen bond formation. Focusing on grain boundary segregation, another study substantiated the space-charge formation due to defect segregation [218]. Furthermore, co-adsorption of H_2O and CO_2 study along with the space-charge attribute of BZO have shown that space-charge formation and adsorbate interaction contribute to defining defect concentrations [219]. For a specific study on defect chemistry and solubility of perovskites, DFT calculations

have played an instrumental role. It showed that metal (Ni) can be absorbed in the structure identified by grain boundary [220].

To explain high proton mobility in BZO and create a link between macroscopic proton conductivity and microscopic proton motion, nanoscale percolation has been taken into account, which shows that at low concentration, acceptors can trap protons and hence limit their mobility – while at higher concentration, they tend to create percolation pathways by leading the opposite effect [209]. Proton transfer in BZO has also been considered from a lattice perspective, and it suggests that structural defect can originate from the deformation of oxygen octahedra, which can introduce self-trapping distortion and reorganization of the compound [221]. Intuitively, ion rotation and proton transfer vary according to the availability of ion vacancies, and the associated parameters can be extracted by DFT study to obtain relative energy information due to lattice deformation (**Fig. 7**) [62].

Furthermore, kinetic Monte Carlo (KMC) associated with DFT calculations has shown that proton conduction can be hampered by the presence of other protons [210], as suggested by calculation of proton transporting energy barriers at high temperature in doped BZO. It is relevant to mention that oxidation and hole conductivity can be affected by polaronic contribution in the doped state of BZO perovskite [175]. By implementing local and semi-local exchange-correlation functionals along with hybrid functionals, the polaronic contributions in conductivity can be quantified, and energetically favorable self-trapped holes can be identified in the structure, which is prone to delocalization at high temperature, showing consistency with earlier modeling [176]. Moreover, 50% In-doped BZO study using DFT showed that dopant-proton interaction does not affect the diffusion of protons due to the presence of the percolation paths of dopants, which facilitate dopant transport throughout the lattice [179]. The In-doped study has also explored the effect of doping in affecting the proton conduction [177], and the Sc-doped study has discovered hydration energy [222]. As the dopants of BZO are discussed in detail in the previous section, these aspects are not repeated here.

Plane-wave based DFT calculation demonstrate that the proton diffusion coefficient is affected by applied strain in ABO_3 perovskite structure [223], and the enhanced proton diffusion is explained by the formation of preferable proton transport path due to compressive strain in the structure. To analyze the proton diffusion mechanism in the cubic perovskite structure at high temperature, first-principles MD simulation was performed, which showed that proton diffusion could be enhanced under the application of compressive condition due to the formation of preferential diffusion path (which can be attributed to charge redistribution under this condition). However, there is no evidence of enhancing diffusion from the application of tensile strain or relaxed bulk condition [223]. Specifically, the proton-oxygen pair correlation is highly affected by the compressive strain. Analyzing electronic and structural parameters from a plane wave-based DFT calculation by incorporating Car–Parrinello MD, it is obtained that applied strain leads to a nonlinear effect on proton diffusion constant. A separate study suggested that “A-site” ion vacancy can positively affect the proton conduction in BZY that reduces the barrier for proton diffusion by accounting for the proton conduction mechanism and hydroxide ion rotation [62]. **Fig. 8** shows that the hydroxide ion gets reoriented during rotation and H-O interaction processes, and the bond length also changes due to the larger space provided by the A-site ion vacancy. Due to specific benchmarking of proton diffusion, this study provides important insights on proton diffusion as well as designing proton conductors [62].

Also, alkali metals (Na, K, Rb, and Cs) were found to be efficient acceptor dopants in BZO because of its comparable or lower energy barriers for proton transport than that of Y-dopants, which suggest an unlike DFT study [178]. Specifically, the high-temperature attribute of BZO has been addressed in multiple studies, which show that BZO is impressively stable at high temperatures due to phonon contributions [224,225], which further validates its applicability in such a field. Interestingly, the DFT study has explored a novel structural aspect, is the electrostatic potential of BZO in its doped state. Spectroscopy studies suggest that Ba vacancy at the grain boundary contributes to the potential well, while DFT justifies that statement by demonstrating reduced atomic density at the grain boundary region [226].

It is relevant to mention that surface energy for different surfaces and interfaces of ABO_3 perovskites are calculated by the *ab initio* method [180], which found that (001) surface energies for zirconates are almost always smaller than the (011) and (111) surface energies, suggesting inward relaxation in (001) surface, and the interface bandgap in the surface depends more strongly upon the upper augmented layer than the substrate augmented layer. Moreover, the formation volume of point defects in BZO is studied by DFT in terms of the defect strain tensor, which suggested that vacancy and hydroxide ion radii are smaller than the oxygen ion radius. These calculations have also been successful in calculating dopant ionic radius agreeable with experiments [181]. Interfacial proton migration in BZO is separately studied in another work, which suggests a curved pathway for proton transport through the ZrO_2 -terminated (100) surface, where the energy barrier can be significantly reduced by the addition of carbonate ion [227]. Having an agreement with experimental results on BZ-molten carbonate electrolyte [228], this study suggests an enhanced facile interfacial proton migration between the electrolyte phases. To enhance the transport properties of electrochemical materials, charge-carrier interface studies are carried out well. This scenario suggests that heterogeneous doping can decrease the energy barrier for the transport of protons [229]. This observation is particularly important for designing novel nanostructured composite material.

Aside from the structural attributes, first principles (FP) phonon calculations have also attempted to address the thermodynamic properties of doped BZO. For example, hydration and defect property analysis has shown that the stable structure of BZO perovskite is cubic and that the vibrational formation entropy for oxygen vacancy is significantly higher than that of the protonic defect [56]. That defect characteristic specifically contributes to the formation of entropy, while being dependent on the size of dopants ion. The entropic calculations fairly agree with earlier experimentations [182,183] as well. The hydration ability and proton conduction were investigated for Y and Sn co-doped BZO by Dawson *et al.*, suggesting that BZO is indeed a potential material for electrode applications [55]. This study investigates the effect of all available defect sites and their contributions to analyze the hydration ability. The previous studies have shown, the most similar favorable and exothermic pathway for hydration when the location is in Y's vicinity. The synergy study of Sn and Y doping substantiated the applicability of BZO in the next-generation solid oxide fuel cells [228]. Defect formation based on thermodynamic modeling has facilitated the calculation of formation energy in BZO with different dopants, which showed that most dopants could substitute Zr without sacrificing favorable conditions energetically [230].

As a continued discussion on the thermodynamic properties of BZO, a notable DFT study is on high-temperature modeling [184]. Apart from strengthening its potency at high-temperature applications, this study shows that BZO possesses moderate mechanical properties and low thermal conductivity, making it

competitive with other silicates and ceramic materials. Notably, this study makes about 20% loss of Young's modulus at high temperature with a significant decrease in thermal conductivity. A high-temperature tracer diffusion study has also been performed, which facilitated the calculation of grain boundary diffusion [127].

4.2 MD studies

BZO is one of the highly explored perovskite materials for the analysis of MD studies that might deem as a useful method. Numerous *ab initio*, classical MD, and DFT studies have investigated its cogency and attributes as a robust proton-conducting oxide. For example, detailed thesis work on BCO and BZO has explored computational modeling of them. The calculations discovered relevant parameters connected to the local protonic environment and proton transfer phenomena, especially in the doped state, which were previously inaccessible to experimental maneuvers [231]. Although *ab initio* simulations have extracted some insight regarding microscopic processes of dissociative adsorption of hydrogen on structure surface [201], MD simulations performed with reactive force field have articulated temperature-dependent change of geometrical parameters. This part of the study has provided information regarding how a proton can dictate BZY structural features, even when far from a doping site. The specific modeling of D-BZ, D-YB, and D-2YB reveals a comparison between the radial distribution functions of protonated and unprotonated (single and double) structures. The simulation results predict that avoiding Y-clustering can improve proton transport in such compounds. Another independent MD simulation study by the same author on Y-doped BZO has shown that classical MD can analyze the Y-doping effect within the framework of the cubic formation of BZO and yttrium induces mutation in the oxygen sites in the vicinity of the local geometry [185]. Besides, topologically different oxygen sites can provide inkling on thermodynamically favorable proton-hopping paths, and further emphasizes the importance of avoiding Y-clustering to prevent protonic traps.

MD simulation on Y-doped BZO has been applied to illustrate the fast oxygen transport phenomenon because of its excellent ion conductivity as well as chemical activity. Through incorporating reactive force field potentials, the oxygen vacancies, doping effect, and edge dislocations have been explored for the BZO system with or without edge dislocations, and calculations on radial distribution function, expansion coefficient, and ionic self-diffusion coefficient. The MD calculations on the aforementioned entities have been carried out employing the dependencies of temperature and doping percentage [186]. These results manifest that a mole fraction of yttrium can increase oxygen transport which can be characterized by the oxygen transport coefficient. Also, due to the formation of double-bottle diffusion channels and the resulting regeneration of oxygen polyhedrons, dislocations can accelerate oxygen ion diffusion. Therefore, line defects can be considered in future studies to enhance ion conductivity at low temperatures.

Recently, different types of doping effects have been attempted on BZO, such as In and Sc-doping to find out local proton coordination [232], local structure [179], and vibration dynamics [233], which were studied by the same research group. The proton coordination study can be performed with a combination of experimental and plane-wave based DFT framework. Induced charge density due to the proton's introduction can be visualized by **Fig. 9**, which shows that there could be a significant difference between the charge distribution of stoichiometric and protonated bulk [223]. However, *ab initio* MD simulation on a hydrated sample of BZO shows that it is possible for overlapping INS spectra of protons to exist in the local structural environment,

clarified by O-H bend, O-H stretch, and higher-order transitions. This study also presents an argument that due to the presence of percolation paths throughout the lattice structure, proton diffusion does not necessarily get affected by dopant-proton interaction. MD simulations have provided independent insights on structural and thermodynamic aspects of BZO, but reactive force field parameters have been developed for studying electrode-electrolyte interfaces. These parameters have facilitated to re-calculate of the primary energy barrier for proton diffusion in BZY that manifests a very consistent experimental value [234]. Local distortion and dynamics were further explored by DFT-based MD simulations [213]. To further visualize the success of DFT-based MD studies to determine the proton diffusion coefficient, one may refer to the temperature-dependent proton diffusion coefficient for BZO (**Fig. 10(a)**) and the comparison with experimental values (**Fig. 10(b)**) [195,235,236].

Further study suggests the proton-trapping phenomenon in dopant state that invoked from the same perspective with the extended outlook. To achieve a self-intermediate scattering function for small and large momentum values, which facilitates validation against neutron scattering experiments has been investigated [194]. The thermal expansion coefficient results match well with experimental data up to 1200K, although the lattice parameter was overestimated, which was consistent with earlier observation [6,195]. The slightly doped lattice observation showed a little distortion from a cubic to tetragonal structure, which was validated by earlier experimentation [196], but for higher doping concentration, the orthorhombic structure did not sustain. Again, this study proved the reliability of the reactive force field (ReaxFF) potential to analyze such perovskite attributes by MD simulations and substantiated doping effect in BZO. However, the lattice parameter overestimation suggested that the ReaxFF model can be improved when BZO is modeled for too soft material.

Quantum Mechanical (QM) studies were carried out for different perovskite materials to determine their comparative diffusion coefficients and activation energies for proton transport (only inter-octahedra proton transfer for BZO [197,198]. These findings substantiate the QM method on BZO, as calculated activation energy is agreeable with statistical uncertainty and can be explained by proton's repulsive interaction with cation (Zr) [199]. The results of such activation energy were further affirmed by a separate research group using the valence-bond approach and reactive force field MD simulation [195,237] (Refer to **Fig. 11**, which shows the diffusion trajectory of the proton). Furthermore, path integral MD simulations which incorporate quantum effects into the dynamic analysis showed a significant difference between the potential barrier and the minimum energy paths due to the quantum effect. Between these two the translational path shows a decrease of potential barrier with an increase of quantum effect, while for the reorientation motion path the effect reveals the opposite trend [238,239].

Moreover, a detailed MD simulation study was carried out on BZO to highlight its microscopic atomic behavior, interatomic separation, and thermal transport properties by simplifying the interatomic potentials into pairwise interactions [202]. This study calculated isothermal compressibility, thermal expansion coefficient, heat capacity, and thermal conductivity for this material over a range of normal to very high temperature and pressure, which are in good agreement with experimental findings. From a strict interaction perspective, the potential functions have been analyzed to obtain insight regarding binding potential. Peaks at the radial distribution functions at the reference temperature, which broaden in cases of higher temperatures, provide a hint regarding close packing or solid phase, but in the case of BZO, splitting of the peak is observed, which suggests asymmetry to some extent. Also, the coordination numbers suggest structural robustness, i.e.,

the ability to maintain the perovskite structure even at high temperatures. Summarizing the structural and thermodynamic results from MD simulation, one can easily declare that BZO maintains a cubic perovskite structure but has a larger lattice constant than SrTiO_3 (STO). The lattice parameter of BZO negligibly increases at high temperature, and molar volume increases with temperature. The calculated parameters agree with experimental results [187,188], substantiating the reliability of MD simulation. However, the linear thermal expansion coefficient varies slightly from the experimental value, staying in good harmony with the experiment at room temperature while deviating at high temperatures [240,241]. Comparing with STO material, BZO is slightly less expansible. The calculation on isothermal compressibility shows that BZO is less stiff than STO, which validates the experimental finding [240,242]. A remarkable agreement is found for heat capacity [203–206] and thermal conductivity result [204] of BZO at room temperature while showing agreement with different consequences at high temperatures. Furthermore, the results of similar related thermal conductivity agree better with the experiment than earlier semi-empirical MD simulation, suggesting a better definition of pair potentials in this study [243]. The lower Debye temperature of BZO also substantiates the less stiff attribute [244]. In short, this study mainly provides us confidence in MD simulations on perovskite structures, as this approach has successfully reproduced reliable thermodynamic parameters. In this regard, a separate group has also undertaken the analysis of BZO to establish the thermodynamic parameters by using MD simulation and the researchers have organized the obtained results in two different works – one analyzing BZO only [245], and the other comparing SZO with BZO [246]. The earlier one incorporates a newer representation of pair potentials for BZO, and they also calculated lattice parameters, thermal expansion coefficient, isothermal compressibility, heat capacity, and thermal conductivity within a broad temperature and pressure range. These findings, similar to the previous paragraph, assent with experimental findings. Furthermore, the latter group has been able to reproduce agreeable results by taking into account thermal expansion and isothermal compressibility of BZO. This reproducibility of MD simulations on BZO suggests that such perovskite materials, especially thermodynamics parameters, can be studied with reliability by this approach.

Further MD analysis has investigated BZO from preference to cubic perovskite structure, distortion, intermediate structure perspectives, and has predicted phonon spectra to compare the stability of materials [189]. MD simulation can run at room temperature with similar structures that display as the outcome at room temperature, i.e., they can invoke free moving among degenerate structures, suggesting that this work attempts to analyze BZO by involving defects by manipulating the atom radii. However, this analysis explicitly admits the importance of studying dopant's role to enhance proton transport in such perovskite materials. The obtained radial distribution function implies that there is no observable distortion above room temperature, suggesting a phase transition and that larger system size can lead to the clustering of various types of distortions.

Moreover, a combination of MD simulations and the DFT method, indicate that in the grain boundary of BZO, proton and oxygen segregate to different grain boundaries clearly [190]. Combining the results from MD simulations and DFT, it can be summarized that for BZO, grain boundary segregation is significant to incorporate a positive core charge and electrostatic potential barriers, which has been demonstrated by experiments at different temperatures [149,150,191,193]. The defect-defect interaction can be attributed to the insensitivity of dopant concentration, but it is explained from the DFT perspective as well.

5. Conclusion

Improved proton-conducting energy materials are in great demand in various electrochemical and thermochemical processes, namely, hydrogen pumps and hydrogen sensors, portable electronics, transport systems, energy storage, fuel cells, and nuclear industry including off-gas capture and isotopic separations, among others. The poor sinterability, high sintering temperature (1700– 2100 °C) to promote desired microstructure and grain growth, defects due to dopants, and poor stability make it impractical for the aforementioned devices. During the last decades, the development of material science, microelectronics, and potential demand have forced the excessive development of solid-state-ion conducting ceramic materials, perovskite-based oxides that exhibited excellent proton conduction at low and/or intermediate temperatures. In the midst of all perovskites, BZO exhibited tremendous potential for good proton-conducting performance at low temperatures. This review has comprehensively discussed the working principle of BZO perovskites, the effect of processing, applications, and prospects of it. The rational selection of dopants and processing conditions govern the successful development of highly stable and conductive BZO electrolytes. The DFT and MD studies have validated multiple structural information, characteristics, and aspects of BZO are obtained from experimental studies that provided significant novel insights. Thus, the combination of experimental and theoretical studies on this review suggests that the zirconates are promising candidates for diversified applications such as proton conduction and diffusion, clean energy, optoelectronic, resistive random-access memory (RRAM), nanostructured composite material, and relevant elevated-temperature phenomena in the scientific community.

Nomenclature

Nomenclature			
AP	Ambient pressure	MD	Molecular dynamics
BCO	BaCeO ₃	PAD	Powder aerosol deposition
BZI20	20% In-doped barium zirconate	PCEC	Proton ceramic electrolysis cell
BZO	BaZrO ₃	PCFC	Proton ceramic fuel cell
BZY	Y-doped barium zirconate	PEMFC	Proton-exchange membrane fuel cell
BZY10	10% Y-doped barium zirconate	PLD	Pulsed laser deposition
BZY20	BaZr _{0.8} Y _{0.2} O _{3-δ}	QM	Quantum mechanical
BZYC	BaZr _{0.955} Y _{0.03} Co _{0.015} O _{3-δ}	ReaxFF	Reactive force field
BZYC5	BaZr _{0.8} Y _{0.15} Ca _{0.05} O _{3-δ}	RRAM	Resistive random-access memory
CA	Citric acid	SCO	SrCeO ₃
C_T	Concentration of tritium	SEM	Scanning electron microscope
CZO	CaZrO ₃	SOFC	Solid oxide fuel cell
D	Hydrogen diffusivity	SPEEK	Sulfonated poly(ether ether ketone)
DFT	Density functional theory	SPEES	Sulfonated poly (1,4-phenylene ether-ether sulfone)
EDTA	Ethylenediaminetetraacetic acid	SSR	Solid-state reaction
EMF	Electromotive force	STEM	Scanning transmission electron microscopy
FP	First principle	STO	SrTiO ₃
HAXPES	Hard X-ray photoelectron spectroscopy	SZO	SrZrO ₃
HTPC	High-temperature proton conductor	TIP	Tritium imaging plate
IT	Intermediate temperature	XANES	X-ray absorption near-edge structure spectroscopy
KMC	Kinetic Monte Carlo	XPS	X-ray photoelectron spectroscopy

Declarations

Conflicts of interest

The authors declare that they have no competing interests.

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Figures

Figure 1

Schematic of the generation of an oxygen vacancy by the substitution of two Zr⁴⁺ ions with two Y³⁺ ions in perovskite BaZrO₃ to form BaZr_{1-x}Y_xO_{3-α} [60].

Figure 2

Schematic representation of proton diffusion process in ABO₃ perovskite with (bottom row) and without (upper row) an A-site ion vacancy. Proton diffusion mechanism (upper left and bottom left figures). Hydroxide ion rotation and proton transfer mechanism (middle four figures). B-O-B bending motion mechanism (upper right and bottom right figures). Here red and brown balls represent the initial and final positions of the atoms, respectively. Reprinted with permission from Ref. [62].

Figure 3

(a) Grain orientation map for BaZr_{0.95}Y_{0.05}O₃ sample synthesized using the Pechini method (sintered 1800 °C, 1 h), (b) grain boundary character map (white line indicate lattice boundary), (c) Grain diameter distributions, (d) grain boundary character distributions. Reprinted with permission from Ref. [79].

Figure 4

SEM micrographs for the (a, c) top-view, and (b, d) cross-section of the BaZr_{0.8}Y_{0.2}O_{3-δ} (BZY20) and BaZr_{0.8}Y_{0.15}Ca_{0.05}O_{3-δ} (BZYC5) sintered pellets (1600 °C for 10 h), respectively. Total conductivities at (e) wet H₂, and (f) wet air for the BZY20 and BZYC5 pellets. Reprinted with permission from Ref. [138].

Figure 5

(a) IP images of the cross-sections and outer surfaces of the BZY and BZYC samples for different HT-exposure conditions (673-1073 K, 0.5-4 h), (b) IP images for tritium standard of ART-123 and MICROSCALE with radioactivity values. Color of red in the standard sample means higher tritium concentration, while blue means lower tritium concentration, (c) color spectrum of tritium concentration, (d) Arrhenius plot of the hydrogen solubilities for the BZY, BZYC [171], and CZI [60] samples, and (e) Arrhenius plot of the hydrogen diffusivities to compare the tritium diffusivity data for BZY, BZY, CZI that were obtained from the present studies [171] with the literature data of the proton diffusivity in BZY at 673–873 K, was reported by Kreuer [172]. Reproduce with permission from Ref. [60,171,172].

Figure 6

The possible optimization scheme of H and In ions in BZO, (a) optimization from position H(I), (b) optimization from position H(II), (c) optimization from H(I) and H(II) ions, where distances are shown in nanometer scale. Reprinted with permission from Ref. [177].

Figure 7

Difference in ion rotation and proton transfer in BZY systems (BZY: system without any ion vacancy, BZY-1Ba: system with one ion vacancy, and BZY-2Ba: system with two ion vacancies). Relative energy: (a) with the O-B-O bending angle during the outward O-B-O bending and A ion motions, (b) with the reorientation of the hydroxide ion in the AO plane, (c) with the O-B-O bending angle during lattice relaxation, (d) with the O-B-O bending angle during the inward O-B-O bending, (e) for OD -H- OA interactions, and (f) with the O-B-O bending angle during the recovery of the O-B-O bending motion. Here, local lattice deformation is presented by the inset figures. The red and brown balls represent the initial and final positions of the atoms, respectively. Reprinted with permission from Ref. [62].

Figure 8

The mechanism of how electronic density redistributes itself for (a) hydroxide ion reorientation and (b) OD-H-OA interactions to affect proton transport. Reproduce with permission from Ref. [62].

Figure 9

Difference in charge density due to the introduction of proton in BaZrO₃ bulk sample (a,c: relaxed state, and b,d: compressed state). Legend: Red: charge accumulation, Blue: charge depletion. Reprinted with permission from Ref. [223].

Figure 10

(a) Temperature-dependent proton diffusion coefficient in BaZrO₃, (b) Comparison of proton diffusion coefficient: MD vs. Experimental data. MD studies data on BaZr_{0.875}Y_{0.125}H_{0.125}O₃ are collected from Adri et al. [235], and data on experimental works of BaZr_{0.9}Y_{0.1}O_{3-δ} taken from Kreuer [172], and Karlsson et al. [236]. Reprinted with permission from Ref. [195].

Figure 11

Mechanism of proton diffusion (white spheres) at 1500 K in the BaZrO₃ lattice (smoothed and averaged over successive frames). Legend: O: Red, Ba: Green. It is clear that at square vertices, the oxygen atoms screen Zr

atoms, while on the square lattice oxygen atoms are placed near Y (light grey). Reproduce with permission from Ref. [195].