Scheelite type $\text{Sr}_{1-x}\text{Ba}_x\text{WO}_4$ ($x = 0.1, 0.2, 0.3$) for possible application in Solid Oxide Fuel Cell electrolytes

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Polycrystalline scheelite type $\text{Sr}_{1-x}\text{Ba}_x\text{WO}_4$ ($x = 0.1, 0.2 & 0.3$) materials were synthesized by the solid state sintering method and studied with respect to phase stability and ionic conductivity under condition of technological relevance for SOFC applications. All compounds crystallized in the single phase of tetragonal scheelite structure with the space group of $I4_1/a$. Room temperature X-ray diffraction and subsequent Rietveld analysis confirms its symmetry, space group and structural parameters. SEM illustrates the highly dense compounds. Significant mass change was observed to prove the proton uptake at higher temperature by TG-DSC. All compound shows lower conductivity compared to the traditional BCZY perovskite structured materials. SBW with $x = 0.3$ exhibit the highest ionic conductivity among all compounds under wet argon condition which is $1.9 \times 10^{-6}$ S cm$^{-1}$ at 1000 °C. Since this scheelite type compounds show significant conductivity, the new series of SBW could serve in IT-SOFC as proton conducting electrolyte.

The use of renewable energy and energy conversion and storage have become increasingly important due to the huge demand of energy supply in modern society and emerging ecological concerns in a way which is environmental friendly and low cost. Fuel cells, especially solid oxide fuel cells (SOFC), proton exchange membrane fuel cells, supercapacitors, Li-ion batteries, acousto-optic filter, solid state lasers, photo-catalysts and solar cells etc. are the wide range of technological applications for the energy conversion and storage devices. The performance of these devices depends intimately on the properties of their materials.

Because of the high efficiency, fuel flexibility and low pollutant emission, SOFC becomes to be a boundless blessing in alternative energy sector for upcoming generation. Oxygen ion conduction requires high activation temperature, which are incompatible with low or intermediate temperature operation. Proton conducting materials can be thermally activated at lower temperatures than oxygen ion conducting ones. At intermediate temperature range (400–700 °C), some perovskite type oxides shows low activation energy and high proton conductivity in H$_2$ and H$_2$O atmospheres. Further development of protonic solid oxide fuel cells operating at intermediate temperature (IT, 400–700 °C) is still important technological challenge. The IT-SOFC has proved to be cost effective over conventional high temperature solid oxide fuel cells (HT-SOFC), as IT-SOFC can be manufactured more economically using less expensive stack interconnect materials. High-temperature proton conductors have, in general, been found to be oxides with oxygen deficiency in the form of oxygen vacancies, where protons dissolve as hydroxide defects in the oxide at the expense of the vacancies.

Getting the best proton conducting electrolyte material with a highly chemical stability is a great challenge. Synthesis of a highly dense ceramic proton conducting electrolyte materials at low sintering temperature is another major challenge as well. Acceptor doped perovskites are examples of oxides containing both oxygen vacancies and protons. Some of the Ba and Sr containing perovskites exhibit state-of-the-art proton conductivity of about 0.01 S cm$^{-1}$ (e.g. BaCe$_{0.9}$Y$_{0.1}$O$_{3-\delta}$). Meanwhile, BaCeO$_3$ and BaZrO$_3$ based materials exhibit a high

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The patterns can be indexed as single phase scheelite type tetragonal symmetry in the I41/a space group. Figure 2 shows the refinement of XRD pattern of SBW1 by Rietveld refinement. The patterns reveal that the Bragg reflections shift to the lower 2θ angle which leads to decrease the unit cell volume because of smaller unit cell volume by doping bigger atomic element (Ba) to smaller atomic element (Sr).

According to the Vegard’s law, the difference in ionic radii causes the increase in cell volume. Figure 2 shows the refinement of XRD pattern of SBW1 by Rietveld refinement. The patterns reveal that the Bragg reflections shift to the lower 2θ angle which leads to decrease the unit cell volume because of smaller unit cell volume by doping bigger atomic element (Ba) to smaller atomic element (Sr).

Recently, alternative proton-conducting materials like acceptor-doped rare-earth materials, MTO4, where M = La, Ca, Sr, Ba, Y, Nd, Gd and T = Nb, W, Mo, Mn have been suggested that offer high CO2 tolerances based on the scheelite structure31–36. Proton conductivity dominates under wet conditions up to temperatures around 1,000°C with a contribution of p-type electronic conduction, significant under oxidizing conditions above 800°C. LaNbO4-based materials exhibit moderate conductivity while being almost pure proton conductors, and for their stability in CO2-containing atmosphere and water vapour environment31,37. The highest proton conductivity recorded so far is the material LaNbO4 when it contains minor A-site acceptor substitutions, such as Ca0.6Sr0.4WO4 and BaWO4 at 800°C36. It was reported that photoluminescence intensity of mixed tungstate Ca0.6Sr0.4WO4 is higher than for individual tungstate35.

Among all scheelite crystals, BaWO4 is the most efficient crystal for the development of Raman lasers40. The calculations also show BaWO4 to be a direct band gap crystal having less dispersive valence and conduction bands and in contrast to other Scheelites crystals. These scheelite-type oxides exhibit a high oxide ion conduction, e.g., Pb0.05Sm0.95WO4 shows a conductivity of ~2 × 10−1 Scm−1 at 800°C, which is comparable to that of YSZ (3.6 × 10−2 Scm−1 at 800°C)30,41. Ca and Ba doped SrWO4 scheelite material were prepared by solid solution and standard wet milling ceramic preparation method and used as optical and photovoltaic applications38–41. No work has been reported to use these materials fuel cell devices.

In the current study, Ba doped with SrWO4 in A-site of this scheelite composition in order to get sufficient highly density electrolyte material used in SOFC devices. High density coupling with high conductivity will make this material very useful for SOFCs applications. The new mixed ion conducting scheelite Sr1−xBaxWO4 (SBW) (x = 0, 0.1, 0.2, 0.3), later mentioned as SBW1 (for x = 0.1), SBW2 (for x = 0.2) and SBW3 (for x = 0.3), were prepared by solid state sintering method and examined by using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric-differential scanning calorimetry (TG-DSC), Fourier transform infrared (FTIR) and Electrochemical impedance spectroscopy (EIS).

**Result and Discussion**

**X-ray powder diffraction.** Figure 1 shows the X-ray diffraction patterns of all SBW compounds (x = 0.1, 0.2 & 0.3) sintered at 1000°C. In this composition, Strontium (Sr) and Barium (Ba) were A-site components and Tungsten (W) was B-site components, which was fully occupied. Sr2+ (ionic radius = 1.44 Å) was replaced by Ba2+ (ionic radius = 1.61 Å) as dopant for making A-site 100% occupied. The XRD was carried out as prepared samples. The XRD patterns of all compositions show crystalline nature of the ceramics. No additional or intermediate phases were detected. This suggests that the complete solubility of Ba in the SrWO4 crystal lattice at 1000°C. Earlier studies on these materials the sintering temperature is higher than this study42,44.

The patterns reveal that the Bragg reflections shift to the lower 2θ angle which leads to decrease the unit cell volume because of smaller unit cell volume by doping bigger atomic element (Ba) to smaller atomic element (Sr). The patterns can be indexed as single phase scheelite type tetragonal symmetry in the I41/a space group. Figure 2 shows the refinement of XRD pattern of SBW1 by Rietveld refinement. Unit cell parameters, densities, volumes and Rietveld refinement factors (R-factors) are listed in Table 1. These scheelites crystallize in the tetragonal symmetry in the I41/a space group. Figure 2 shows the Rietveld refinement profile of SBW1; 3D schematic diagram of the tetragonal structure drawn by using Diamond software has been shown in insert. In the scheelite-type ABO4 structure with octahedral A cations (Sr/Ba) coordinated with eight oxygen atoms and tetrahedral B cations (W) were connected with four oxygen atoms, which are common binary oxides in both natural and synthetic systems.

![Figure 1. Room temperature XRD patterns of Sr1−xBaxWO4 (x = 0.1, 0.2 & 0.3).](source)
**Scanning electron microscopy.** SEM experiment was carried out to observe the microstructure morphology of the SBW compounds. Figure 3(a–c) shows the surface microstructure of SBW series and Fig. 4 shows the cross-section SEM of SBW1. The surfaces of the samples were smooth and crack free. The grains were connected to each other and well developed making high density materials. The cross-sectional image shows less grain boundaries and less-porous. No trace of secondary or liquid phase was found at the grain boundary region. The grain sizes were also large and compact. These characteristics indicate that non-porous high-density feature of these materials can meet up the required aspect of solid electrolyte. Table 1 show that the relative densities of the samples were around 91 to 95%. The grain sizes of all compositions were around 1–10 µm. In term of protonic conductivity large grain offers less grain boundary resistance which is good for electrolyte. It can be noticed that the increasing Ba concentration in replacement of Sr leads to the decreasing of the density. Figure 5 represents the
pattern of compositions by X-ray analysis. Each chemical element has unique electron movement that performs as energy. The figure can be described the intensity of all SBW1 elements. Carbon peaks are also there because of the carbon coating on the samples surface. The element compositions of all three compounds are shown in Table 2 with formula source and EDX source. The results from EDX are reasonably comparable to formula values, because X-ray is effective media to direct the elements of compounds accurately. The uses of X-ray exist in XRD and EDX, this confirm that it is the efficient media to identify the elements of material.

Thermogravimetric analysis. To investigate the hydration behavior through weight loss/gain, thermogravimetric analysis of the samples was performed in the temperature range 25°C–1000°C. Figure 6 shows the TGA curves (a) in dried and (b) in hydrated environment for x = 0.1, 0.2 and 0.3, respectively under N2. The flow rate was 20 ml/min and the measured sensitivity for all sample compounds were between 0.28–0.58 uV/mW. The weight change was monitored with increasing temperature. During heating, the mass gain started at low temperature (around 30°C) and got highest at 100°C which is related to the water uptake from surroundings. In the
intermediate temperature range (i.e. 100–600 °C), approximately 60% of theoretically possible protonic defects [OH\(^{\ddagger}\)] were filled in the intermediate temperature range, which is similar to the result of Ahmed et al.\(^{45}\).

All solid oxide proton conductors supposed to hold hydrogen in the intermediate temperature range where \(H^+\) can conduct following Grotthuss mechanism\(^{46}\). The observed maximum mass loss was \(\approx 0.43\%\) for \(x = 0.1\), \(0.89\%\) for \(x = 0.2\) and \(0.16\%\) for \(x = 0.3\) respectively in dried environment. In hydrated environment, initial mass loss occurred from 25 °C to 400 °C. After 400 °C to 500 °C, a mass gain (0.08% for \(x = 0.1\), 0.01% for \(x = 0.2\) and 0.005% for \(x = 0.3\)) occurred due to proton absorption, which leads to significant increase the proton content. A mass loss again occurred due to loss of proton at higher temperature. Since hydrogen makes O-H bonds with oxygen, it needs oxygen vacancy. Ba\(^{2+}\) doping in replacement of Sr\(^{2+}\) at the A-site creates less oxygen vacancies and facilitates the protonic conduction. From neutron diffraction experiments the location of protons can be observed in the structure\(^{47,48}\). After hydration and running under \(H_2\) environment, the XRD was carried out to check the phase stability. Figure 7 shows the XRD curves of SBW1 before and after \(H_2\) test and hydration process. There was no phase change under \(H_2\) and hydration\(^{49}\).

**FT-IR.** The FT-IR spectra (Fig. 8) of SBW ceramics measured in the wave number region of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). The characteristic strong and broad absorption bands have two vibration modes around 920 cm\(^{-1}\) (SBW1), 922 cm\(^{-1}\) (SBW2), and 923 cm\(^{-1}\) (SBW3) were assigned to O-W-O anti-symmetry stretching vibrations in [WO\(_4\)] tetrahedron. A sharp but less intense absorption peaks at 1370 cm\(^{-1}\) (SBW2) and 1372 cm\(^{-1}\) (SBW3) have appeared, which arises due to symmetric bending vibrations in the [WO\(_4\)] tetrahedron. As the concentration of Ba increases in the samples from \(x = 0.1\) to \(x = 0.3\), the absorption band becomes more prominent in SBW3 sample as compare to other samples. Adsorbed water molecules on the surface of the sample at 1710 cm\(^{-1}\), 1713 cm\(^{-1}\), and 1714 cm\(^{-1}\) were also detected for SBW1, SBW2, and SBW3 respectively. The photo catalytic activity and proton conductivity were closely related to the number of -OH groups present on the surface of catalyst because the photo generated holes (h\(^{+}\)) react with water and generate, OH radicals, which can oxidize the organic pollutants. Therefore, an increase in the number of surface -OH groups could improve the proton conductivity.

Figure 6. TGA plot of (a) dried and (b) hydrated \(Sr_{1-x}Ba_xWO_4\) (\(x = 0.1, 0.2 \& 0.3\)).

Figure 7. XRD before and after \(H_2\) and after hydration of SBW1.
Electrochemical impedance spectroscopy. The ionic conduction properties of the SBW series were investigated using AC impedance spectroscopy. Figure 9 shows impedance spectrum of SBW3 recorded at 1000 °C in dry and wet Ar and wet H₂ condition with bulk and grain boundary (GB) response. A model used to estimate the GB and bulk resistance of the sample compositions. The electrode interface response was excluded from the fitting and the total resistance was the sum of the GB and bulk resistance. In dry Ar, more than one semicircle was observed up to 700 °C in the prepared samples which indicates the existence of GB resistance. The bulk resistance was obtained from the intercept of impedance curve and the real axis (Z' axis) at high frequency. It was difficult to separate bulk resistance from grain boundary resistance above 700 °C although two equivalent circuits was used in series (see Fig. 9 inset). In high temperatures sometimes we need to add inductance at high frequency region to fit the impedance curve with equivalent circuit.

The observed capacitance in the high frequency range was in between 10^{−12}−10^{−8} F and in the intermediate frequency range was in between 10^{−8}−10^{−6} F which provide the bulk/grain-boundary and sample/electrode response, respectively.50,51.

The total conductivities of all 3 samples (x = 0.1, 0.2, 0.3) in wet and dry Ar and wet H₂ atmosphere is shown in Fig. 10. The total conductivity values were 2.01 × 10^{−8}, 9.33 × 10^{−8} and 1.1 × 10^{−7} S cm⁻¹ for SBW1, 3.8 × 10^{−8}, 1.92 × 10^{−7} and 9.69 × 10^{−8} S cm⁻¹ for SBW2 and 2.09 × 10^{−8}, 3.05 × 10^{−7} and 8.3 × 10^{−8} S cm⁻¹ for SBW3, respectively, under dry Ar, wet Ar and wet H₂ atmosphere. The total (bulk + GB) conductivity increases with the increase of Ba^{2+} dopant i.e. with the decrease of Sr^{2+} content. Conductivity increases in wet Ar in comparison to dry Ar significantly, which indicates the dominant proton conductivity in these samples. The highest conductivity was 1.9 × 10^{−6} S cm⁻¹ for SBW3 at 1000 °C in wet Ar condition. Mixed oxide ion, proton and electron conduction is common in ceramics which can be used as semiconductors, storage materials, fuel cell electrodes
and batteries, catalysts and separation membranes. The mixed conduction also depends on the selectivity i.e. the type of conductivity is domination. Moreover, this property depends on the structure and the composition of the materials. In SBW1, protonic conduction was dominating over oxide ion and electron conduction52. The mobile ions in these materials are oxide ions and/or protons, sometimes accompanied with electronic conduction53. Though the ionic conductivities were lower than typical electrolytes, considering other properties like high density and stability in wet atmosphere we can preliminary select it as a candidate and need to improve its conductivity by modifying its microstructure or doping at A-site of B-site. Table 3 shows the comprehensive comparison of SBW3 with that of the other typical electrolytes. In wet Ar atmosphere, the activation energies (Ea) for the total conductivity were 1.4 eV, 1.03 and 1.07 eV for x = 0.1, 0.2 and 0.3, respectively. Normally all proton conductors show some oxide ion conduction at temperature higher than 700 °C. It could be good to prove/separate conduction type by hydrogen concentration cells. According to the calculation of Irvine et al.51 and calculation of activation energy, it is possible to understand the nature of the conductivity.

Decreasing of Sr$^{2+}$ content in SBW series the activation energy reduces from 1.4 eV to 1.03 eV. The change may be related to the fergusonite – scheelite phase transition, which also occurs within this temperature region. It has been suggested that the change in charge carrier species might be responsible for the difference in activation energy in the scheelite systems. Recent article reported that the activation energy was increased with reduced ionic radius among the LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases; at low temperature, the PrNb$_{0.92}$W$_{0.08}$O$_{4.04}$ showed the lowest Ea (1.34 eV) while LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ and NdNb$_{0.92}$W$_{0.08}$O$_{4.04}$ had a similar value (1.56 eV)54. The variation in activation energy with composition might result from the difference in ionic radius.

Methods

Structural measurements. All three compounds, Sr$_{1-x}$Ba$_x$WO$_4$ (x = 0.1, 0.2 & 0.3), were prepared by solid state reaction method. Stoichiometric amount of BaCO$_3$, SrCO$_3$ and WO$_3$ were mixed in a mortar pestle and grinded using ethanol for proper mixing. The finely ground dried powders were calcined at 700 °C for 10 h with a heating rate of 2 °C min$^{-1}$. Uniaxial hydraulic press was utilized to make 13 mm diameter pellets using 5 ton pressure and subsequently sintered at 900 °C in air for 10 h. The heating and cooling rates were 2 °C min$^{-1}$ and 5 °C min$^{-1}$, respectively. The final sintering temperature is 1000 °C in air for 10h. The phase characterization was examined by X-ray powder diffraction using Bruker axs-D8 advance diffractometer (CuK$\alpha_1$, $\lambda$ = 1.5406 Å) in

| Electrolyte | Ionic Conductivities Scm$^{-1}$ | Temperature (°C) | Reference |
|-------------|---------------------------------|------------------|-----------|
| SBW1        | $1.1 \times 10^{-7}$           | 800              | This work |
| SBW2        | $1.92 \times 10^{-7}$          | 800              | This work |
| SBW3        | $1.9 \times 10^{-6}$           | 1000             | This work |
| BCZ        | $1.79 \times 10^{-10}$ - $2.86 \times 10^{-12}$ | 300              | 56         |
| YSZ        | $2.28 \times 10^{-10}$         | 600              | 57         |
| LSGM       | $3.6 \times 10^{-14}$          | 800              | 58         |
| SDC        | $1.62 \times 10^{-10}$         | 941              | 59         |
| GDC        | $1.02 \times 10^{-10}$         | 941              | 59         |

Table 3. Comprehensive comparison of ionic conductivity of typical electrolytes with this work.
the 20 range from 10° to 100°. The 60 sec/step counting time and 0.01° step size was used for data collection. The FullProf software was used to refine the obtained data by the Rietveld method35. The morphological characteristic of the prepared electrolytes were examined using FE-SEM (JSM-7610F). Sample chamber evacuated before collecting SEM images.

**TGA and FT-IT measurements.** The weight change with increasing temperature was conducted by thermogravimetric analysis. The samples were introduced to hydration furnace in in wet N\textsubscript{2} atmosphere. N\textsubscript{2} gas was passed through water to make it wet which gives about 3–5% H\textsubscript{2}O to flow with N\textsubscript{2} gas. The hydration steps were at 800, 600, 400, and 200 and 150 °C with residence time of 2, 2, 48, 2, and 55 h, respectively. The samples were heated at 200°C/h until 800°C and cooled at 10°C/h to 150°C. The hydrated samples were investigated by a NETZSCH thermogravimetric analyzer. Nitrogen flowed constantly in the TGA at 20 mL/min. Fourier transform infrared (FTIR) spectra were recorded by PerkinElmer Spectrometer for diffuse infrared spectroscopy in air at room temperature. Powder samples were subtracted with a run with optically transparent KBr, as a reference.

**Electrochemical measurements.** The electrochemical properties were examined using a Solartron electrochemical impedance analyzer with frequency response analyzer connected to the fuel cell using ProboStat (NorECs, Norway). The impedance data was collected in the frequency range from 1 mHz to 6 MHz using applied sine wave amplitude of 1 V rms. Platinum electrodes were used on both sides of the sample (13 mm diameter and 0.5 cm2 electrode area) for the impedance measurements. Impedance data were collected from 1000 to 150°C with the steps of 50°C under dry and wet Ar atmosphere in cooling cycle. Ar gas passed through 2 beds of P\textsubscript{2}O\textsubscript{5} desiccant to find dry Ar whereas Ar gas flowed through water at 22 °C (p(H\textsubscript{2}O) = 0.026 atm) to find wet Ar atmosphere. After reaching each temperature, 30 minutes isothermal time was given to ensure stability before recording impedance spectra. Z-View (Scribner Associates Inc.) refinement program was used to fit and analyze the experimental impedance data. The brick-layer model of grain boundaries was assigned to represent the electrical response of the sample compositions. Each curve from the experimental data interpreted a parallel sequence of a resistance (R) and a constant-phase element (CPE). The resistance could not be extracted reliably due to high impedance at lower temperature (200°C).

**Conclusion**

In this research study, the main focus was to develop scheelite type Sr\textsubscript{1–x}Ba\textsubscript{x}WO\textsubscript{4} (x = 0.1, 0.2 & 0.3) electrolytes for SOFC applications. SBW electrolytes were successfully synthesized by solid state sintering method and characterized by using XRD, SEM, TGA and EIS. Fullprof software was used to analyze XRD data in the Rietveld method which showed a tetragonal scheelite structure in the H\textsubscript{4}/a space group. The unit cell parameter increases with Ba-doping. SEM morphological images showed a high density and non-porous materials which is important for electrolyte application. Ba doping increases the grain size. TGA analysis showed a significant proton uptake at the intermediate temperature range. In terms of conductivity, all compound shows low ionic conductivity. SBW3 exhibited the ionic conductivity of 1.9 × 10\textsuperscript{−6} S cm\textsuperscript{−1} at 1000°C under wet argon condition. From the obtained results it indicates that these kinds of materials have a very good microstructure and significant conductivity with good stability which can be applied as electrolyte materials for IT-SOFCs.

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Author Contributions
The research was conceived by A.K.A., S.E. and A.A. A.A. and J.Z. prepared the materials and performed XRD experiments; A.A. S.M.H.R. and M.A.I. performed the electrochemical and SEM experiments; supervision and technical assistance to the experiments was provided by A.K.A., J.Z. and S.E. A.A., A.K.A. and S.M.H.R. performed the data analysis; A.A. drafted the manuscript. All Authors contributed to the final version of the manuscript.

Additional Information
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