Structure and electrical conductivity properties of K doped Sr$_{1-x}$K$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.75-\delta}$ complex perovskites

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Abstract

In the present study structural and electrical conductivity properties of complex perovskites with general formula Sr$_{1-x}$K$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.75-\delta}$ have been studied. Potassium is doped in the cuboctahedral Sr site Sr$_{1-x}$K$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.75-\delta}$ with different dopant concentrations such as $x = 0, 0.25, 0.50, 0.75$ and $1$. The structural and morphological properties of Sr$_{1-x}$K$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.75-\delta}$ were studied using Thermogravimetry (TG) analysis, x-ray diffraction (XRD) and Scanning electron microscopy (SEM). Electrochemical impedance spectroscopy (EIS) was performed to investigate the electrical properties. The effect of structural and morphological variations associated with the dopant concentration affecting the electrical conductivity behaviour of Sr$_{1-x}$K$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.75-\delta}$ complex perovskite oxides were studied in detail. The higher total conductivity was observed for 100% K doped ($x = 1, 3.10 \times 10^{-5}$ S cm$^{-1}$ at 800°C) and 25% K doped ($x = 0.25, 2.02 \times 10^{-5}$ S cm$^{-1}$ at 800°C) composition.

1. Introduction

Perovskites (general formula ABO$_3$) is a class of complex oxides that can incorporate large number of point defects such as oxygen vacancies and protons that compensate dopants or part of inherent off-stoichiometry. Among perovskites, complex perovskite of type A$_x$(B$_{1+y}$B$_2$$_{2-y}$)O$_{3-3x/2}$ where A, B = divalent alkaline earth metals and B' = pentavalent Nb, Ta is an important class of model materials for proton and oxide ion conduction [1, 2]. In such compositions when B and B' cation ratio is 1:2 (A$_x$B$_y$B'$_{3-y}$O$_{3}$), the material exhibits trigonal crystal structure with no structural oxygen vacancies, whereas the composition with 1:1 ordered (A$_x$B$_y$B'$_{3-y}$O$_{3}$) B cation sublattice exhibits a face centered cubic structure with inherent structural oxygen vacancies [2, 3]. In perovskite structure both A and B sub-lattices can adopt cations with different valence and size because of their high tolerance resulting in the formation of various types of superstructures [3, 4].

Perovskite materials that are capable of protonic and ionic conductivity are potential candidates for electrolytes in sensors, batteries, fuel cells, electrolysers etc [5–7]. Perovskite oxides with anionic vacancies (inherent or created by doping) behave as oxide ion conductors in dry atmosphere at higher temperatures and proton conductors in hydrated atmosphere at lower operating temperatures [8]. Until now however, only a few materials have been proposed as electrolytes for SOFC, most of them are simple perovskites suitably doped to get the required property such as: Sr doped LaGaO$_3$ [9, 10], (La,Sr)(Ga$_{1-x}$Mg$_x$)$_3$O$_{3-y}$, Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ [12] and La$_{0.8}$Sr$_{0.2}$Ga$_{1-x}$Mg$_x$O$_{1.8}$ [13]. Commonly used ceramic SOFC electrolytes are Scandium doped zirconia (SDZ), Gadolinium doped Ceria (GDC) and Bismuth Yttrium Oxide (BYO) [14], Gd$_2$O$_3$, Sm$_2$O$_3$ and Y$_2$O$_3$ [15]. Later other perovskite materials like in Al doped CaTiO$_3$ [16], CaTi$_{0.95}$Mg$_{0.05}$O$_3$ [16], La$_2$MoO$_4$ [17], Ba$_2$Ln$_2$O$_3$ [18], La$_2$GaMo$_4$O$_{12}$, La$_2$AlMo$_4$O$_{12}$, La$_2$InMo$_4$O$_{12}$ [19, 20], BaCeO$_3$ and BaZrO$_3$ [21–23], Ba$_3$Ca$_{1-x}$Nb$_{2-x}$O$_{9-3x/2}$ (BCN) [24], Sr$_2$Nb$_2$O$_7$, Sr$_2$NbO$_{4.5}$, Sr$_2$Nb$_2$O$_7$ (SCN) [27, 28], have been extensively studied.

Sr$_2$Nb$_2$O$_7$ is a type of perovskite oxide reported to be good proton conductor with reasonable conductivity ($\sim 10^{-4}$ S cm$^{-1}$) [25] and can be used as promising material for sensors and SOFCs [28].
However, it has been reported that these materials lack long-term stability. Ba$_2$Ca$_{1.5}$Nb$_2$O$_7$-δ (BCN) is another extensively studied proton conductor [4, 22, 24 and 29–31]. Our recent study on K doped BCN revealed its denser structure, decrease in large grain boundary contributions to the total conductivity with enhanced basicity and better stability [3, 29 and 32]. Partial substitution of monovalent K in the position of divalent host A site atoms (Ba) enhanced the number of oxygen vacancies thereby enhanced the number of active sites for oxide ion conductivity [4 and 32].

In the present study, Sr$^{2+}$ is partially substituted by K$^+$ in the 1:1 ordered Sr$_{1−x}$K$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.75−δ}$ perovskite. Complex perovskites with nominal compositions for different degree of substitutions such as Sr$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.75}$ (SSN) for $x = 0$, Sr$_{0.75}$K$_{0.25}$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.625}$ (SKSN25) for $x = 0.25$, Sr$_{0.50}$K$_{0.50}$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.5}$ (SKSN50) for $x = 0.50$, Sr$_{0.25}$K$_{0.75}$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.375}$ (SKSN75) for $x = 0.75$ and K$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.25}$ (SKSN100) for $x = 1$ are synthesised by solid state reaction method. Their thermal, structural and morphological characteristics associated to the total conductivity and stability is investigated. The 1:1 ordered double perovskite crystal structure of such composition already has two inherent structural oxygen vacancies. Further substituting Sr$^{2+}$ by K$^+$ will increase the number of oxygen vacancies thereby increasing the number of active sites for ionic conduction. As proven by Bhella et al [32] it is also expected that K$^+$ substitution will enhance the stability of the perovskite. Although Sr$_x$Nb$_2$O$_{11}$ and Sr$_x$Nb$_2$O$_9$ are well-investigated materials, a study of its behavior with monovalent element doping has not been reported yet.

2. Experimental details

2.1. Materials and methods
The precursors SrCO$_3$, K$_2$CO$_3$ and Nb$_2$O$_5$, all from Sigma Aldrich with 99.999% purity were preheated up to 150°C. Stoichiometric amounts of the preheated precursors corresponding to each composition mentioned in table 1 were ball milled separately using tungsten carbide bowl with a ball to powder weight ratio of 10:1 for 20 h. Wet milling was carried out with toluene as process control agent. Wet milled samples were collected and dried in hot air oven. The dried samples were subjected to Thermogravimetry (TG) analyses to identify the phase formation temperature. Based on the information obtained from TG analyses the milled samples were calcined at suitable temperatures and subjected to x-ray diffraction (XRD) analyses to check the phase purity. After phase purity of the samples was confirmed, the powders were pressed into individual pellets of different composition and sintered at 1200 °C for 5 h to study their electrical properties using electrochemical impedance spectroscopy. The dopant concentration in Sr$_{1−x}$K$_x$(Sr$_{0.50}$Nb$_{0.50}$)O$_{2.75−δ}$ was varied as $x = 0, 0.25, 0.50, 0.75$ and $1$ (expected oxygen vacancies are 0.25, 0.375, 0.50, 0.65 and 0.75 per formula unit respectively) with nominal compositions as given in table 1. The entire set of compositions is named as SKSN perovskite series.

2.2. Characterization techniques
2.2.1. Thermal analysis and calcination
Thermal analysis (Thermogravimetry) of the ball milled precursors was carried out using NETZSCH STA 449 F3 Jupiter simultaneous thermal analyser. Baseline correction was performed for the alumina crucibles in dry air atmosphere (mixture of nitrogen and oxygen) from room temperature to 1200 °C at a heating rate of 20 °C min$^{-1}$ before each sample analysis. Based on the results from thermal analysis the samples were calcined at 1000 °C for 2 h using a high temperature muffle furnace in clean alumina crucibles.

2.2.2. Structural analysis
The calcined and sintered samples were subjected to x-ray diffraction (XRD) analysis using X’Pert PANalytical diffractometer to confirm the phase purity and to know the crystal structure. The XRD data was collected at room temperature using Cu-Kα radiation with a step size of 0.05° in the range between 20° to 80°. Rietveld refinement and profile fitting was carried out on the experimental XRD data using X’ pert High score plus version 4.8 software in accordance to the crystal structures available in ICCD database.

2.2.3. Morphological analysis
Surface morphology and elemental analyses of the sintered pellets were studied through scanning electron microscopy (SEM) (JEOL-JSM 6390, Japan) at an accelerating voltage of 30 kV. Densities of the as prepared pellets were calculated from the sample mass and volume. Liquid displacement method (Archimedes’ technique) was used to determine the density and porosity of sintered pellets. Theoretical densities of the sintered pellets were calculated using the formula mentioned below;

$$\text{Theoretical density (} \rho_{\text{th}} \text{)} = \sum \frac{\text{Number of atoms in an unit cell} \times \text{Atomic weight of element}}{\text{Volume of unit cell calculated from XRD} \times \text{Avagadro number}} \text{ g/cm}^3$$ (1)
Table 1. Parameters obtained from structural analysis of SKSN perovskite series after sintering.

| S. No | Potassium content (x) | Nominal Composition and its abbreviation | PCPDF No. | Space group & Bravais lattice | Refined cell dimension (Å) |
|-------|-----------------------|------------------------------------------|-----------|-------------------------------|----------------------------|
| 1.    | 0                     | Sr(Sr0.50Nb0.50)O2.75 SSN                 | PDF# 739070 | Fm3m (225) Face Centered Cubic | a≈b≈c≈8.289               |
| 2.    | 0.25                  | Sr0.75K0.25(Sr0.50Nb0.50)O2.625 - SKSN 25 | PDF# 739070 | Fm3m (225) Face Centered Cubic | a≈b≈c≈8.294               |
| 3.    | 0.50                  | Sr0.50K0.50(Sr0.50Nb0.50)O2.5 - SKSN 50   | PDF# 739070 | Fm3m (225) Face Centered Cubic | a≈b≈c≈8.290               |
| 4.    | 0.75                  | Sr0.25K0.75(Sr0.50Nb0.50)O2.375 - SKSN 75 | PDF# 790649 | P4/mmm (123) Primitive tetragonal | a≈b≈4.158, c≈12.20       |
| 5.    | 1                     | K(Sr0.50Nb0.50)O2.25 SKSN 100             | PDF# 790649 | P4/mmm (123) Primitive tetragonal | a≈b≈4.167, c≈12.24       |
To know the porosity of pellets using liquid absorption method, the initial weight of sintered pellet was noted, and then the pellets were dipped in Hexane for around 10 min. The dipped pellets are weighed and the difference in mass was noted. Using the formula given below the porosity of the pellets was calculated;

\[
\text{Porosity} = \frac{\Delta w}{\text{Volume of the pellet} \times \text{bulk density}} \times 100\% \tag{4}
\]

\(\Delta w\) = Initial weight-final weight of the samples.

2.2.4. Electrochemical Impedance spectroscopy (EIS) analysis

The total conductivity measurements of all the samples were carried out using impedance analyzer, AUTOLAB, ECO CHEMIE, Netherlands from 10Hz−10MHz in the temperature range 100 °C to 800 °C in dry air atmosphere at ~0.21 atm. The total conductivity of the samples is determined from the intercepts of the semicircle on the real axis by using the following relationship:

\[
\sigma = \frac{l}{RA} \text{S cm}^{-1} \tag{5}
\]

where \(l/A\) is the geometrical factor, \(l\) is the thickness, \(A\) is the area of the sample and \(R\) is the total resistance which is indicated by the intercept of the semicircle on the real axis. The data analysis was performed using the Autolab software Frequency Response analyzer (FRA) 4.9 version. Equivalent circuit fitting of the experimental data were done using Electrochemical (EC lab) V10.40 and Z-view version 2.1b software.

3. Results and discussions

3.1. Thermogravimetry (TG) analysis

Figure 1 shows the TG plots of 20 h ball milled precursors corresponding to individual compositions of SKSN perovskite series. The TG curve corresponding to undoped SSN composition shows several stages of weight loss. The first stage of weight loss between room temperature to 200 °C is due to the loss of the adsorbed moisture and structural water from the ball-milled precursors. The second stage of weight loss around 650 °C is due to the removal of carbonaceous species present in the materials. The third stage of weight loss (800–1000 °C) is attributed to the final phase formation. It is observed that not all the doped compositions exhibit any standard weight loss profile. This may be due to the heterogeneous mixing of starting precursors. Based on the thermal analysis and previous literature data [25] all the K doped SSN samples are calcined at 1000 °C for 2 h and checked for phase purity.
3.2. X-ray diffraction (XRD) analysis

Figures 2(a) & (b) shows the XRD patterns of sintered (1200 °C, 5 h) SKSN perovskite series. The patterns are indexed based on Joint Committee on Powder Diffraction Standards (JCPDS) database. The diffractograms of SSN, SKSN 25 and SKSN 50 indicate simple cubic crystal structure and the patterns are indexed according to PCPDF #739070. This is in congruence with the reported structural data for similar perovskites [33]. SKSN 75 and SKSN 100 indicate tetragonal symmetry and the patterns are indexed according to PCPDF #790649. The cell parameters are refined from profile fitting using X’Pert High Score plus software. It is observed that the compositions with lower dopant concentrations retain the same cubic crystal structure as the undoped SSN. However, at higher dopant concentrations (SKSN 75 and SKSN 100) change in crystal structure from cubic to tetragonal is observed as shown in figure 2(b). This may be due to the substitution of dopant cations along certain preferred crystallographic positions in the unit cell. It should be noted that when a significant number of dopant cations are substituted in the Sr site the parent crystal lattice experiences distortion resulting in the modification of its symmetry and crystal structure. The ionic radius of K\(^{+}\) (1.78 Å) is higher when compared to Sr\(^{2+}\) (1.44 Å) [34]. Therefore significant lattice expansion is expected and observed for higher dopant concentrations (refer table 1). The change in crystal structure from cubic to tetragonal and change in cell volume can significantly affect the electrical properties.

3.3. Scanning electron microscopy (SEM) analysis

Figure 3 shows the SEM images taken from the vertical cross sections of sintered pellets of SKSN perovskite series. SEM images show different microstructures for all the samples. The each pellet appears to be composed of particles of different morphology and sizes. The surface of the undoped composition in figure 3(a) appears to be less densified with distinct pores compared to the doped SKSN perovskite samples. Figure 3(b) shows the SEM images of SKSN 25 with distinct grain and grain boundaries. It is observed that, initial lower degree of potassium substitution enhanced the densification. The SEM images of SKSN 50 and SKSN 75 (x = 0.50 and 0.75) is shown in figures 3(c) & (d). On increasing the potassium concentration beyond 25%, the surface of the pellets
appear to disintegrate which is reflected in the decreasing density and increasing porosity of these compositions as described in Table 2. 100% K doped SKSN composition showed higher densification when compared to all other doped and undoped compositions as shown in Figure 3(e). The densification and porosity significantly influence the electrical behaviour of the studied compositions. The highly densified sample is expected to exhibit high electrical conducting behaviour due to the free and rapid mobility of the carriers.

**Table 2.** Porosity and density of SKSN perovskite series after sintering.

| Composition | Porosity (%) | Experimental ($\rho_{ex}$) | Theoretical ($\rho_{th}$) | Relative Density % |
|-------------|--------------|----------------------------|--------------------------|-------------------|
| SSN         | 36.4%        | 3.13                       | 4.171                    | 75                |
| SKSN 25     | 23%          | 4.32                       | 5.043                    | 85.6              |
| SKSN 50     | 28%          | 3.75                       | 4.674                    | 80.2              |
| SKSN 75     | 32.4%        | 2.12                       | 2.695                    | 78                |
| SKSN 100    | 13.8%        | 2.79                       | 2.947                    | 94                |

Figure 3. SEM images of surface of the sintered pellets of a. SSN b. SKSN 25, c. SKSN 50, d. SKSN 75 and e. SKSN 100.
3.4. Impedance analysis

Figures 4(a)–(e) shows the $Z''$ versus $Z'$ plots obtained for pure and K substituted SSN perovskite. Shapes of the impedance plots are reproducible. The nature of the semicircles indicates that each is the resultant of two overlapped semicircles corresponding to grain and grain boundary contributions to the total conductivity.

Figure 4(a) shows the impedance plots of undoped SSN composition at different temperatures. It is observed from the plot that it is a single semicircle with the absence of intermediate frequency arc corresponding to the
grain boundary contribution. This indicates that the semicircle obtained for SSN composition corresponds only to the bulk contribution of the total conductivity.

Figures 4(b)–(e) shows the impedance plots of K doped SKSN compositions. All plots of the K doped SKSN perovskite series show single semicircle along with the intermediate frequency arc corresponding to the grain boundary contribution. Among the doped series, only SKSN 75 composition showed complete semicircle at higher frequency region as shown in the enlarged images. In the plots of SKSN 25, SKSN 50 and SKSN 100 a fragment of semicircle is missing in the higher frequency region. This clearly shows that in doped compositions, the majority contribution to the total conductivity is from grain boundaries compared to bulk.

Figure 5 shows the Arrhenius plots of total electrical conductivity of SKSN perovskite series with varying potassium concentration. Here the conductivity values are plotted against $1000 / T$ factor and the slope is calculated by linearly fitting the curve using origin pro software. From the obtained slope the activation energy is calculated using the following equation:

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (6)

where $\sigma_0$ is the pre-exponential factor, $E_a$ is the activation energy, $k$ is the Boltzman constant and $T$ is the absolute temperature. The average thickness of each SKSN pellet was 0.27 cm. The variation in total conductivity with respect to dopant concentration at various measured temperatures is depicted in figure 6. The activation energies calculated using the slopes of the individual Arrhenius plots of SKSN perovskite series are listed in table 3.

From figures 5 & 6 it can be observed that total conductivity increases with increasing dopant concentration for most of the compositions. The conductivity obtained for doped compositions is higher than the undoped SSN. Lower values of total conductivity were observed for undoped SSN and compositions having potassium dopant concentration with $x = 0.50$ and 0.75. This could be attributed to the microstructure of the pellets after sintering. SEM micrographs of SSN, SKSN 50 and SKSN 75 indicate smaller grains. This means the portion of the grain boundaries in these compositions is larger. Larger portion of the grain boundaries offer more resistance for the carrier migration in the material. In addition, the enhancement in conductivity for SKSN 25 may be due to the presence of significant number of free moving ions. Further K doping in SKSN 50 and SKSN 75 compositions the conductivity decreased possibly due to the interaction of Sr atoms with the oxygen vacancies thus trapping the free movement of ions. Though the oxygen vacancies are more in these compositions compared to SKSN 25 the conductivity is reduced due to the blocking of the free moving ions. SKSN 100 composition showed the highest total conductivity among the doped series in which the A site strontium is completely replaced by K ions which overcome the Sr atoms interaction with the oxygen vacancies. Also the presence of excess oxygen vacancies and rapid mobility of potassium ions enhanced the total conductivity in SKSN 100 composition. The variation in the cell volume influenced in carrier mobility thus the conductivity properties varied for each composition. It is also evident from SEM images that SSN, SKSN 50 and SKSN 75 samples have low densification with high porosity compared to SKSN 25 and SKSN 100 which also influenced their electrical behaviour.
The obtained conductivity of doped and undoped SKSN compositions are in the order of SKSN100 > SKSN25 > SKSN50 > SKSN75 > SSN. As of our knowledge there is no report on potassium doped SSN compositions and its electrical properties.

From table 3 it is observed that partially potassium substituted (SKSN 25) and fully substituted compositions (SKSN 100) exhibit the highest total conductivity. Highest total conductivity in these sample is attributed by the favourable mobility of structural oxygen ion/vacancy migrationalong with the additional oxygen vacancy sites generated due to doping. Though the oxygen vacancies are higher for SKSN 50 and 75 they do not favour high conductivity possibly due to the defect interactions. The oxyen vacancies formed by doping attracts the opposite charged dopant ions forming the defect associates which bind the mobile vacancies necessary for ion migration. The probability of formation of the defect associates may be higher for SKSN 50 and 75 compositions. Nevertheless, the higher total conductivity in SKSN 25 and SKSN 100 is attributed to favourable crystal structure, microstrutrual properties and lower activation energy ($E_a$) (table 3) which supports the conduction.

### 4. Conclusion

This study presents the effect of various concentrations of monovalent potassium in the position of divalent strontium on 1:1ordered $\text{Sr}_1-x\text{K}_x\text{Sr}_{0.50}\text{Nb}_{0.50}\text{O}_{2.75-\delta}$ synthesised by solid-state reaction route. Thermal analysis was performed to obtain the final perovskite phase formation temperature. Structural studies indicated a modification in crystal structure after sintering for compositions with higher dopant concentration. SEM images inferred that higher densification was achieved for SKSN 25 and SKSN 100 samples. These samples exhibited the highest total conductivity in air atmosphere than the other compositions. Doping K in SSN obstructs the structural oxygen ion/vacancy migration thus reducing the total conductivity in SKSN 50 and SKSN 75 compositions. The higher total conductivity obtained for SKSN 100 composition is $3.10 \times 10^{-5}$ S cm$^{-1}$ at 800 °C and SKSN 25 is $2.02 \times 10^{-5}$ S cm$^{-1}$ at 800 °C. The results reveal that doping K in SSN

### Table 3. Total conductivity values of SKSN perovskite series at different temperatures and their corresponding activation energies.

| Sample  | $\sigma_{tot}$ (S cm$^{-1}$) at various temperatures | $E_a$ (eV) |
|---------|---------------------------------------------------|------------|
|         | 650 °C | 700 °C | 750 °C | 800 °C |         |
| SSN     | $9.39 \times 10^{-8}$ | $1.64 \times 10^{-7}$ | $3.02 \times 10^{-7}$ | $7.83 \times 10^{-7}$ | $1.05$ |
| SKSN 25 | $4.74 \times 10^{-6}$ | $6.82 \times 10^{-6}$ | $1.31 \times 10^{-5}$ | $2.02 \times 10^{-5}$ | $0.55$ |
| SKSN 50 | $5.28 \times 10^{-7}$ | $3.36 \times 10^{-6}$ | $6.77 \times 10^{-6}$ | $1.82 \times 10^{-5}$ | $0.98$ |
| SKSN 75 | $1.59 \times 10^{-6}$ | $1.89 \times 10^{-6}$ | $2.89 \times 10^{-6}$ | $3.81 \times 10^{-6}$ | $0.45$ |
| SKSN 100| $1.70 \times 10^{-5}$ | $1.98 \times 10^{-5}$ | $2.36 \times 10^{-5}$ | $3.10 \times 10^{-5}$ | $0.31$ |

Figure 6. Variation of total conductivity with dopant concentration ($x$) in $\text{Sr}_{1-x}\text{K}_x\text{Sr}_{0.50}\text{Nb}_{0.50}\text{O}_{2.75-\delta}$ at different temperatures.
composition enhances the densification thereby improved the overall total conductivity by providing the additional number of oxygen vacancy sites for ion migration.

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