Chapter 3

Studies on A-A'-M-M'-O (A=Na or K; A'=Ca or Sr; M= Ti or Zr; M' = Nb or Ta) system

The oxide ion conductors in the system A-A'-M-M'-O (A=Na or K; A'=Ca or Sr; M= Ti or Zr; M'= Nb or Ta) were prepared by solid state reaction method. Phase identification by X-ray powder diffraction shows they have perovskite type structure. The effects of microstructure on the properties were studied using scanning electron microscopy (SEM). Ionic conductivity of the oxides was measured using ac impedance spectroscopy as a function of temperature ranging from 300-750°C.
3.1 Introduction

Inorganic oxides having high ionic conductivity are currently of great importance, primarily because of their possible application as solid electrolytes in solid oxide fuel cells (SOFC) [1]. They have a wide variety of other applications also like oxygen sensors [2] and pumps [3] as well as membranes for oxygen separation [4]. Currently, yttria stabilized zirconia (YSZ) is commonly used as an electrolyte in the conventional SOFCs [5]. However, it is associated with some limitations such as high operating temperature (1073-1273K), relatively low ionic conductivity below 1000°C, problems about long term stability of the cells, etc. Lowering the operating temperature can reduce some of these problems.

Therefore, there is intense research going on worldwide to find new materials having high ionic conductivity at lower operating temperatures. Some useful materials have already been developed in a few different systems such as samarium doped ceria (SDC) [6], rare earth gallates [7] and lanthanum molybdate, La$_2$Mo$_2$O$_9$ [8] and NaBi$_3$V$_2$O$_{10}$ [9].

Perovskite structured oxide ion conducting compositions with conductivities high enough for consideration are developed recently. Perovskite type oxides have two sites for aliovalent doping and thus creating vacancies in oxygen sublattice, which help the migration of oxygen ions through the lattice [10-12]. Lanthanum gallate is one candidate for application as electrolyte in SOFCs [13, 14]. Doubly doped (Sr and Mg) LaGaO$_3$ based perovskite system exhibits oxide ion conductivity higher than that of YSZ at 800°C [15-17]. In the present study, high ionic conductivity in new perovskite type oxides: A-A'-M-M'-O (A=Na or K; A'=Ca or Sr; M= Ti or Zr; M'= Nb or Ta) is reported.

3.2 Experimental

High temperature solid state reaction technique is used for the preparation of the oxides in the A-A'-M-M'-O (A=Na or K; A'=Ca or Sr; M= Ti or Zr; M'= Nb or Ta) systems. High purity chemicals Na$_2$CO$_3$ (99%, NICE), K$_2$CO$_3$(99+%, Acros Organics), CaCO$_3$ (99+%, Acros Organics), SrCO$_3$ (98.5%, OTTO KEMI), Ta$_2$O$_5$ (99.9%,
Acros Organics), TiO$_2$ (99%, Merck) ZrO$_2$ (99%, Acros Organics) and Nb$_2$O$_5$(Sigma-Aldrich Chemicals) were wet mixed with acetone as the wetting medium in an agate mortar and dried in an air oven at 100°C for 1 hr. The process of grinding and heating was repeated thrice to get a homogeneous mixture.

The samples of NaA'TiM$_6$O$_6$ (A' = Ca or Sr; M' = Nb or Ta) were calcined at 1300°C in platinum crucible for 12 hrs. Calcined powders were ground well and uniaxially pressed into compacts of 10mm diameter and 2.5mm thickness using hydraulic press by applying a pressure of 2.5 tons. Then the pellets were sintered at 1450°C for 6 hrs.

NaA'ZrM'_6O$_6$ (A' = Ca or Sr; M' = Nb or Ta) samples were calcined at 1300°C for 12 hr. The calcined powder was uniaxially pressed into pellets of 10mm diameter and 2.5mm thickness using hydraulic press by applying a pressure of 2.5 tons. Then the pellets were sintered at 1450°C for 12 hr.

KSrTi Nb$_6$ sample was calcined at 1000°C for 3 hr and the calcined powder was pelletised using hydraulic press by applying a pressure of about 2.5 tons and sintered at 1300°C for 3 hr. The potassium compound shows some hygroscopic nature while preparation.

The crystalline phase of the samples was examined by powder X-ray diffraction method (XRD) with a Philips X-pert Pro X-ray diffractometer using Ni-filtered CuK$_\alpha$ radiation. The differential thermal analysis is carried out on the powdered samples using Shimadzu 50H Thermal Analyzer.

The surfaces of the polished and thermally etched (near the sintering temperature for 30 min) pellets were photographed using scanning electron microscope, JEOL JSM 5600LV to study grain morphology. For the electrical conductivity measurements the pellets were electroded with long silver leadwires using silver paste. The measurements were taken using Solatron 1260 Impedance Analyzer in the air and oxygen atmosphere.
3.3 Results and Discussion

3.3.1 $\text{AA}^\prime \text{T}i\text{M}^\prime \text{O}_6$ ($\text{A}=$Na or K; $\text{A}^\prime=$Ca or Sr; $\text{M}^\prime=$ Nb or Ta) system

3.3.1.1 XRD and Structure

Powder XRD patterns of the $\text{AA}^\prime \text{T}i\text{M}^\prime \text{O}_6$ ($\text{A}=$Na or K; $\text{A}^\prime=$Ca or Sr; $\text{M}^\prime=$ Nb or Ta) system is given in fig 3.1a-c. All the peaks in the patterns can be indexed on the basis of perovskite type structure. The XRD patterns of these compounds show the formation of a single phase pure perovskite type compound. The tolerance factor calculated for this system is ~1, the optimum tolerance factor to obtain the largest electrical conductivity in perovskite type oxides [18].

NaCaTiNbO$_6$ and NaCaTiTaO$_6$ give XRD patterns which can be indexed based on orthorhombic perovskite structure. The d spacing is in good agreement with the JCPDS powder diffraction file (PDF) No.51-133 [19]. The prominent peaks are (101), (200) and (220) reflections.

NaSrTiNbO$_6$, NaSrTiTaO$_6$ and KSrTiNbO$_6$ can be indexed on the basis of cubic perovskite structure. These patterns are similar to that of earlier reported XRD patterns of perovskite type compounds such as KTaO$_3$ and are in good agreement with the PDF No.38-1470 [20]. The strong diffraction peaks corresponds to (110), (100) and (200) planes. The lattice parameters of these oxides are given in table 3.1.
Fig. 3.1a X-ray diffraction pattern of the NaCaTiM'O_6 (M = Nb or Ta)

Fig. 3.1b X-ray diffraction pattern of the NaSrTiM'O_6 (M' = Nb or Ta)
3.3.1.2 Differential thermal analysis (DTA)

The DTA curves for the NaA'TiM'O₆ (A' = Ca or Sr; M' = Nb or Ta) system are shown in Fig. 3.2 a-d. DTA study of the new system is carried out to see whether there is any phase change occurs during heating. There is no phase change is observed in the DTA plots.
Fig. 3.2a DTA curve for NaCaTiNbO₆

Fig. 3.2b DTA curve for NaCaTiTaO₆
**Fig. 3.2c** DTA curve for NaSrTiNbO$_6$

**Fig. 3.2d** DTA curve for NaSrTiTaO$_6$
3.3.1.3 SEM and microstructure

The SEM microstructure of the polished thermally etched surfaces of the sintered pellets is shown in fig.3.3a-e. The samples show well sintered and well grown grains with minimum porosity except in the case of KSrTiNbO$_6$. The density calculated for these materials is in the range 4.6-4.9 g/cc. This can be confirmed from the microstructure. The average grain size of this material is 5µm. The micrographs reveal single phase morphology of the compounds without any secondary phase. The micrograph indicates that KSrTiNbO$_6$ is porous and this affected its conductivity value.
Fig. 3.3 SEM micrographs of AA'TiM'O₆
(A=Na or K; A'=Ca or Sr; M' = Nb or Ta) system

c. NaSrTiNbO₆

d. NaSrTiTaO₆

e. KSrTiNbO₆
3.3.1.4 Electrical conductivity studies

Conductivity in solids can be either electronic or ionic. Electronic conductivity is usually of the order of \(10^{-3}\) S/cm (semiconductors) to \(10^{10}\) S/cm (metals) and such materials will usually blackish. Ionic conductivity would be of the order of \(10^{-5} - 10^1\) S/cm and such materials would be usually colorless.

The electrical conductivity of NaA'TiM_6 (A' =Ca or Sr; M' = Nb or Ta) system has been measured in the temperature range 300-750°C in air as well as oxygen atmosphere. The conductivity values at 700°C are given in table 3.2. The electrical conductivity at 700°C is in the order of \(10^4\) S/cm for all compounds except KSrTiNbO_6.

The Arrhenius plots of the conductivity, \(\sigma\) as a function of 1/T (T=absolute temperature) is shown in fig. 3.4a-e. The conductivity value obtained for the system in air atmosphere is higher than the value obtained in oxygen atmosphere. In oxygen deficient systems the conductivity takes place by the hopping of O\(^{2-}\) ions in the vacancies. Since, the number of vacancy decreases in oxygen atmosphere the rate of hopping of O\(^{2-}\) ions into vacancy sites also decreases [21]. Hence the ionic conductivity decreases in the oxygen atmosphere.

As can be seen from the figures, the curves are approximately linear indicating that \(\sigma\) nearly follows the Arrhenius type equation,

\[
\sigma = \sigma_0 \exp (-E_a/kT).
\]

In this relation, \(\sigma_0\) represents a pre exponential factor, \(E_a\) is the apparent activation energy of conduction process, \(k\) is the Boltzman’s constant and \(T\) is the absolute temperature.

The activation energy for conduction was calculated from the slope of the graph in the temperature range 500-600°C. Kilner and Brook [22] calculated that the intrinsic activation energy for the perovskite structure should be 0.8 ± 0.2 eV. The higher activation energy compared to fluorite structure is due to the smaller opening through which the oxide ion must pass in the perovskite structure. It is seen that activation energy of current carriers in strontium compound is more than the calcium substituted compounds. The reason for this may be that the larger cation Sr\(^{2+}\) increases the polarizability of ions to give the bonding character to be covalent [18]. Kreuer proposed
that the perovskite with Sr in A site absorb water in vacancies and stabilize oxide ion in the lattice [23].

The activation energy in the oxygen atmosphere is higher than that in the air atmosphere. This corresponds to the decrease in conductivity due to the decrease in rate of hopping of $O^{2-}$ ions in the vacancy sites in the system [24]. The systems with Ta show more activation energy. This may be due to the change in ionic radius of Nb and Ta.

The typical Cole-Cole plots of the Na$A'TiM'O_6$ ($A' =$Ca or Sr; $M' =$ Nb or Ta) system at different temperatures (600-700°C) are shown in fig.3.5a-i. The intersection of the semicircle on the low frequency side (right of the fig.) with abscissa was taken as the total resistance of the sample. There is only one semicircle is observed which corresponds to the grain conduction [25]. Frequency decreases with the increasing real component of impedance. For some of the compounds the plot doesn’t pass through the origin. This is because there are other arcs appear at higher frequencies and also $R_\infty > 0$. The presence of pores modifies the impedance plots by altering the diameter of the arcs [26]. The distortion of the semicircle at low frequency region (right of figure) is due to the material electrode interaction [27].
Fig. 3.4a \( \log \sigma \) vs \( 1000/T \) for NaCaTiNbO\(_6\) in air and oxygen atmosphere

Fig. 3.4b \( \log \sigma \) vs \( 1000/T \) for NaCaTiTaO\(_6\) in air and oxygen atmosphere
Fig. 3.4c log\(\sigma\) vs 1000/T for NaSrTiNbO\(_6\) in air and oxygen atmosphere

Fig. 3.4d log\(\sigma\) vs 1000/T for NaSrTiTaO\(_5\) in air and oxygen atmosphere
Fig. 3.4e log $\sigma$ vs $1000/T$ for KSrTiNbO$_6$ in air atmosphere

Fig. 3.5a Cole-Cole plot for NaCaTiNbO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C
Fig. 3.5b Cole-Cole plot for NaCaTiNbO$_6$ at 700°C in (a) oxygen and (b) air atmosphere

Fig. 3.5c Cole-Cole plot for NaCaTiTaO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C
Fig. 3.5d Cole-Cole plot for NaCaTiTaO$_6$ at 700°C in (a) oxygen and (b) air atmosphere.

Fig. 3.5e Cole-Cole plot for NaSrTiNbO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C.
Fig. 3.5f Cole-Cole plot for NaSrTiNbO$_6$ at 700°C in (a) air and (b) oxygen atmosphere.

Fig. 3.5g Cole-Cole plot for NaSrTiTaO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C.
Fig. 3.5h Cole-Cole plot for NaSrTiTaO$_6$ at 700°C in (a) air and (b) oxygen atmosphere

Fig. 3.5i Cole-Cole plot for KSrTiNbO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C
Table 3.1
Crystal system and lattice parameters of AA′TiM′O₆ (A′=Na or K; A′=Ca or Sr; M′ = Nb or Ta) system

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystal System</th>
<th>Lattice parameter (Å)</th>
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<td>a</td>
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<tr>
<td>NaCaTiTaO₆</td>
<td>Orthorhombic</td>
<td>5.432</td>
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<td>NaSrTiTaO₆</td>
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<td>NaSrTiNbO₆</td>
<td>Cubic</td>
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<td>KSrTiNbO₆</td>
<td>Cubic</td>
<td>3.925</td>
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Table 3.2
Comparison of conductivity and activation energy of NaA′TiM′O₆ (A′=Ca or Sr; M′ = Nb or Ta) compounds at 700°C

<table>
<thead>
<tr>
<th>Composition</th>
<th>Conductivity (air) (S cm⁻¹)</th>
<th>Conductivity (O₂) (S cm⁻¹)</th>
<th>Activation energy (air) (eV)</th>
<th>Activation energy (O₂) (eV)</th>
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<tr>
<td>NaCaTiNbO₆</td>
<td>1.61x10⁻⁴</td>
<td>1.43x10⁻⁴</td>
<td>1.068</td>
<td>1.171</td>
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<tr>
<td>NaCaTiTaO₆</td>
<td>1.49x10⁻⁴</td>
<td>1.37x10⁻⁴</td>
<td>1.241</td>
<td>1.269</td>
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<tr>
<td>NaSrTiNbO₆</td>
<td>3.77x10⁻⁴</td>
<td>3.21x10⁻⁴</td>
<td>1.083</td>
<td>1.180</td>
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<tr>
<td>NaSrTiTaO₆</td>
<td>2.03x10⁻⁴</td>
<td>1.99x10⁻⁴</td>
<td>1.262</td>
<td>1.310</td>
</tr>
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</table>
3.3.2 NaA'ZrM'O₆ (A' = Ca or Sr; M' = Nb or Ta) system

3.3.2.1 XRD studies

XRD patterns of NaA'ZrM'O₆ (A' = Ca or Sr; M' = Nb or Ta) system is shown in fig.3.3.6a-c. The patterns are similar to that obtained in the earlier system; the peaks are not sharp. The patterns of NaCaZrNbO₆ and NaCaZrTaO₆ are indexed on the basis of orthorhombic perovskite structure. The d spacing is in good agreement with the PDF No.51-133 [19] and prominent planes are (101), (200) and (220).

NaSrZrNbO₆ and NaSrZrTaO₆ can be indexed on the basis of cubic perovskite structure and are in good agreement with the PDF No.38-1470 [20]. The strong diffraction peaks corresponds to (110), (100) and (200) planes. The lattice parameters of these oxides are given in table 3.3.

![X-ray diffraction pattern of NaCaZrM'O₆ (M' = Nb or Ta)](image)

**Fig. 3.6a** X-ray diffraction pattern of NaCaZrM'O₆ (M' = Nb or Ta)
3.3.2.2. Differential thermal analysis (DTA)

The DTA curves for the NaA'ZrM'O₆ (A' = Ca or Sr; M' = Nb or Ta) were shown in fig. 3.7 a-d. The system is studied for determination of any phase change during heating. There is no phase change is observed for this system.
Fig. 3.7a DTA curve for NaCaZrNbO$_6$

Fig. 3.7b DTA curve for NaCaZrTaO$_6$
Fig. 3.7c DTA curve for NaSrZrNbO$_6$

Fig. 3.7d DTA curve for NaSrZrTaO$_6$
3.3.2.3. SEM and Microstructure

The SEM micrographs of the system NaA'ZrM'O₆ (A' = Ca or Sr; M' = Nb or Ta) were given in fig.3.3.8 a-d. The density measured for NaCaZrM'O₆ (M' = Nb or Ta) system is in the range 4.9 g/cc and for the other system, NaSrZrM'O₆ (M' = Nb or Ta), it is in the range 4.2 g/cc. The micrograph confirms these results. The SEM micrograph of NaCaZrTaO₆ shows pores within the grains. The micrograph indicates that NaSrZrTaO₆ is porous and this affected its conductivity value. The average grain size is in the range 1-3 µm.
a. NaCaZrNbO₆
b. NaCaZrTaO₆
c. NaSrZrNbO₆
d. NaSrZrTaO₆

Fig. 3.8 SEM micrographs of NaA'ZrM'O₆
(A' = Ca or Sr; M' = Nb or Ta) system
3.3.2.4 Electrical conductivity studies

The electrical conductivity of the system NaA'ZrM'O₆ (A' =Ca or Sr; M' = Nb or Ta) has been measured by impedance analyzer over a frequency range 100mHz-10MHz in the air as well as oxygen atmosphere. The measurement temperature range was between 300-750°C. Fig.3.9 a-d shows Arrhenius plots of conductivity for NaA'ZrM'O₆ (A' =Ca or Sr; M' = Nb or Ta) system. The graph obtained is almost straight line indicating that the conductivity obeys the Arrhenius equation. It can be seen from the Arrhenius plots that the electrical conductivity increases linearly with rising temperature and no abrupt conductivity change is observed. The conductivity values at 700°C are given in table 3.4.

The conductivity values obtained for the system in oxygen atmosphere is less than the values obtained in air atmosphere. This is due to the decrease in the rate of diffusion of O²⁻ ions into the vacancy due to the decrease in the number of vacancy in oxygen atmosphere [24].

The activation energy for conduction was calculated from the slope of the graph in the temperature range 500-600°C. The activation energy of the system in oxygen atmosphere is higher than that in air. This is expected from the decrease in ionic conductivity.

The conductivity is a function of the elements in the structure, the size of the elements and the degree of order or disorder in the structure. Sammells et al. [28, 29] observed that there is a strong correlation between the conductivity and the size of the critical radius. The critical radius refers to the radius of the smallest area through which the oxide ion O²⁻ must pass.

The degree of distortion seems to be the most important parameter controlling the oxide ion conductivity and the distortion seems in turn to be closely related to the degree of deviation from matching ionic radii of the cation dopants that are used to introduce the oxide vacancies [30]. The charge of the B ion (in this case Ti⁴⁺, Zr⁴⁺, Nb⁵⁺ and Ta⁵⁺) is also seems to be important in the ABO₃ perovskites.
The typical Cole-Cole plots of the NaA'TiM'O₆ (A'=Ca or Sr; M' = Nb or Ta) system at different temperatures (600-700°C) are shown in fig.3.10a-h. The intersection of the semicircle on the low frequency side (right of the fig.) with abscissa was taken as the total resistance of the sample. There is only one semicircle which corresponds to the grain conduction. The Cole-Cole plot of NaCaZrTaO₆, does not pass through the origin, since Rₒ₀>0. Presence of pores modifies the impedance plot by altering the diameter of the arcs [26].

![Cole-Cole plots](image)

**Fig.3.9a** log $\sigma$ vs 1000/T for NaCaZrNbO₆ in air and oxygen atmosphere
Fig. 3.9b log $\sigma$ vs $1000/T$ for NaCaZrTaO$_6$ in air and oxygen atmosphere

Fig. 3.9c log $\sigma$ vs $1000/T$ for NaSrZrNbO$_6$ in air and oxygen atmosphere
Fig. 3.9d log $\sigma$ vs $1000/T$ for NaSrZrTaO$_6$ in air and oxygen atmosphere

Fig. 3.10a Cole-Cole plot for NaCaZrNbO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C
Fig. 3.10b Cole-Cole plot for NaCaZrNbO$_6$ at 700°C in (a) oxygen and (b) air atmosphere

Fig. 3.10c Cole-Cole plot for NaCaZrTaO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C
Fig. 3.10d Cole-Cole plot for NaCaZrTaO$_6$ at 700°C in (a) oxygen and (b) air atmosphere.

Fig. 3.10e Cole-Cole plot for NaSrZrNbO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C.
Fig. 3.10f Cole-Cole plot for NaSrZrNbO$_6$ at 700°C in (a) oxygen and (b) air atmosphere.

Fig. 3.10g Cole-Cole plot for NaSrZrTaO$_6$ in air atmosphere (a) 600°C (b) 650°C and (c) 700°C.
**Fig. 3.10h** Cole-Cole plot for NaSrZrTaO$_6$ at 700°C in (a) air and (b) oxygen atmosphere

**Table 3.3**

Comparison of conductivity and activation energy of NaA$'$ZrM$'$O$_6$ (A$'$=Ca or Sr; M$'$ = Nb or Ta) compounds at 700°C

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<td>a</td>
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<tr>
<td>NaCaZrTaO$_6$</td>
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<td>NaCaZrNbO$_6$</td>
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<td>NaSrZrNbO$_6$</td>
<td>Cubic</td>
<td>3.946</td>
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Comparison of conductivity and activation energy of NaA'ZrM'O_6 (A'=Ca or Sr; M' = Nb or Ta) compounds at 700°C

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<th>Conductivity (O_2) (S cm⁻¹)</th>
<th>Activation energy (air) (eV)</th>
<th>Activation energy (O_2) (eV)</th>
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<tbody>
<tr>
<td>NaCaZrNbO_6</td>
<td>3.62 x 10⁻³</td>
<td>2.73 x 10⁻⁵</td>
<td>1.858</td>
<td>2.124</td>
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<tr>
<td>NaCaZrTaO_6</td>
<td>1.78 x 10⁻³</td>
<td>1.17 x 10⁻³</td>
<td>2.157</td>
<td>2.201</td>
</tr>
<tr>
<td>NaSrZrNbO_6</td>
<td>2.56 x 10⁻³</td>
<td>2.31 x 10⁻³</td>
<td>1.893</td>
<td>2.198</td>
</tr>
<tr>
<td>NaSrZrTaO_6</td>
<td>1.22 x 10⁻⁴</td>
<td>1.09 x 10⁻⁴</td>
<td>2.321</td>
<td>2.524</td>
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3.4 Conclusion

The A-A'-M-M'-O (A=Na or K; A'=Ca or Sr; M= Ti or Zr; M'= Nb or Ta) systems were prepared and electrical properties were studied. The X-ray diffraction study shows the formation of perovskite structured compounds with single phase. The high value of ionic conductivity is obtained for the NaA'ZrM'O_6 (A'=Ca or Sr; M' = Nb or Ta) system, except NaSrZrTaO_6 compound. The conducting species in this system is the O²⁻ ions. From the ionic conductivity studies, it can be concluded that this systems, especially Zr substituted compounds, are potential candidates as solid electrolytes.
Reference

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