Composition and temperature dependent structural investigation of the perovskite-type sodium-ion solid electrolyte series $Na_{1/2-x}La_{1/2-x}Sr_{2x}ZrO_3$

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Background

- Several highly publicised cases of exploding mobile phones due to highly flammable organic electrolytes have highlighted critical safety concerns for widespread use of lithium-ion batteries.
- To address these safety issues, the flammable electrolyte can be replaced by solid electrolytes to form all-solid-state batteries(ASSBs). Perovskite-type structures are promising candidates for solid electrolytes. In addition, due to the high cost of lithium, replacing lithium with the more abundant and cheaper sodium is highly advantageous.
- A new series of perovskite-type sodium electrolytes was recently synthesised by Zhao *et al*. [1]. The reported cubic symmetry described by the space group P_{213} is unusual for a perovskite-type structure with this composition both theoretical end members $Na_{1/2}La_{1/2}ZrO_3$ and $SrZrO_3$ have orthorhombic symmetry.

Laboratory X-ray powder diffraction of the $Na_{1/2-x}La_{1/2-x}Sr_{2x}ZrO_3$ Series

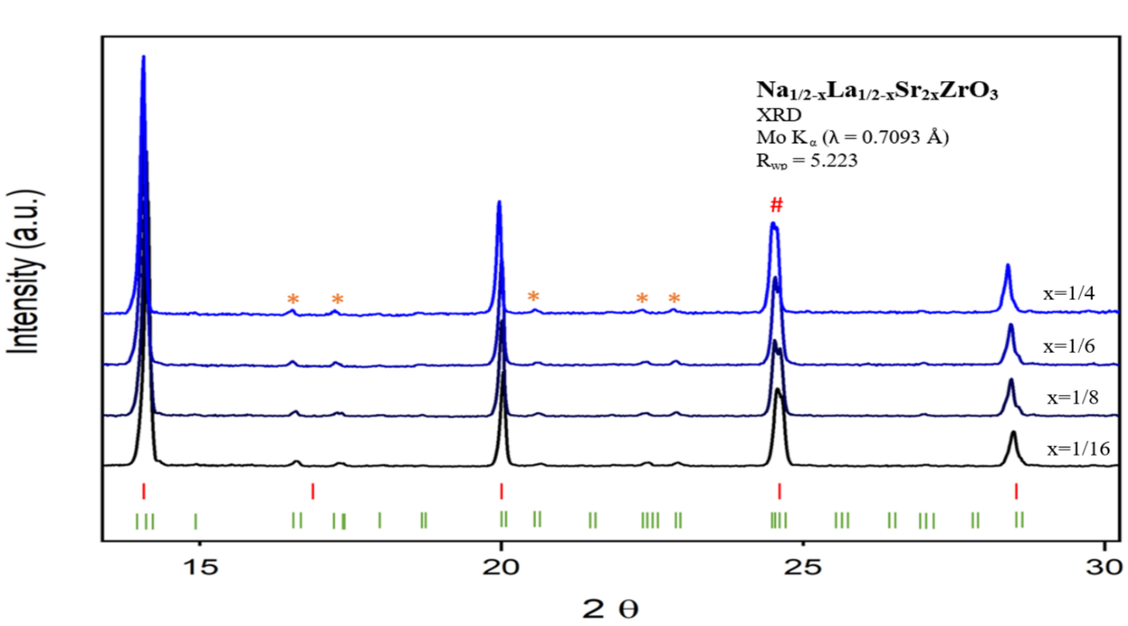


Figure 1: XRPD patterns of the $Na_{1/2-x}La_{1/2-x}Sr_{2x}ZrO_3$ series showing signs of splitting marked by (#) and weak reflections (*). The red peak markers indicate Bragg reflections expected for a cubic perovskite and the green peak markers indicate the Bragg reflections consistent with the orthorhombic space group Pbnm.

- XRPD patterns of the series collected at ambient temperature showed peak splitting as well as a number of very weak reflections (Figure 1).
- The XRPD data for all members of the series to an orthorhombic symmetry described by the same space group *Pbnm*. This is in agreement with the symmetry of the theoretical end member $SrZrO_3$.
- The presence of weak reflections between ~ 15° and ~24° 2θ was found to be characteristic of the orthorhombic symmetry for a perovskite structure, rather than impurity phases as previously reported [1].

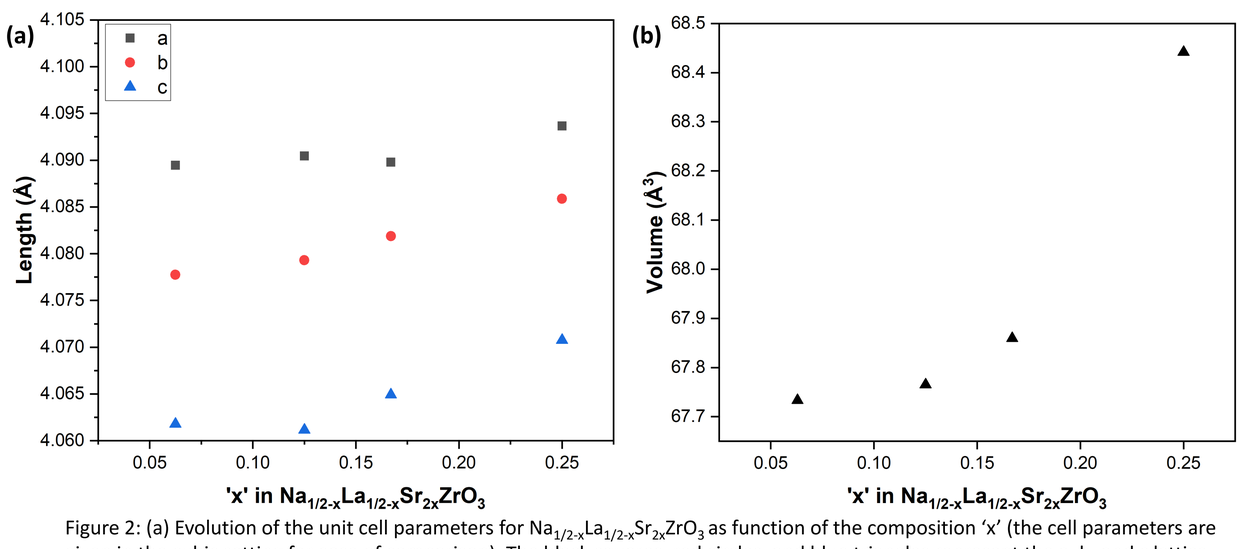


Figure 2: (a) Evolution of the unit cell parameters for $Na_{1/2-x}La_{1/2-x}Sr_{2x}ZrO_3$ as function of the composition 'x' (the cell parameters are given in the cubic setting for ease of comparison). The black squares, red circles, and blue triangles represent the a, b, and c lattice parameters, respectively, refined in this project from XRPD data. (b) Evolution of unit cell volume with composition 'x'. The error bars in both (a) and (b) are smaller than the symbols.

- The unit cell parameters of the orthorhombic *Pbnm* perovskite can be described in terms of the ideal cubic perovskite given by $\sim\sqrt{2}a_p \times \sim\sqrt{2}a_p \times \sim 2a_p$ where a_p is the length of an ideal cubic perovskite unit cell. Unit cell parameters extracted from Rietveld refinement for each member of the series were converted to the pseudo-cubic values for ease of comparison. The unit cell volume (Figure 2b) showed a trend with increasing Sr^{2+} substitution, the lattice parameters showed (Figure 2a) a less clear trend. This is contrary to the linearly trend reported by Zhao *et al*.

Neutron powder diffraction of $Na_{1/4}La_{1/4}Sr_{1/2}ZrO_3$

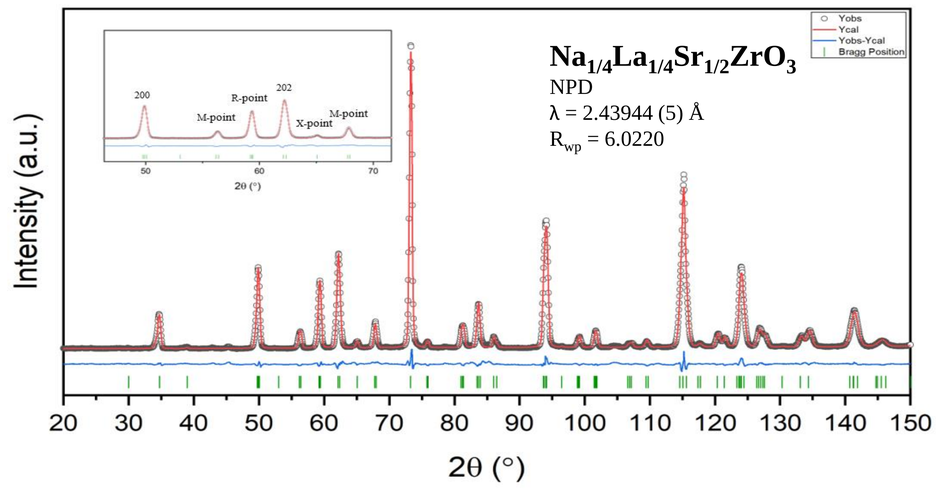
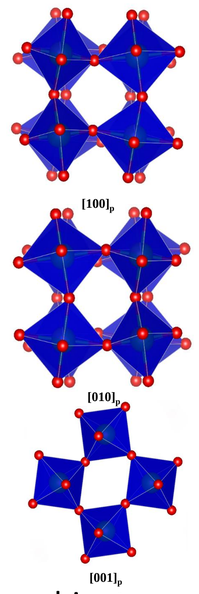
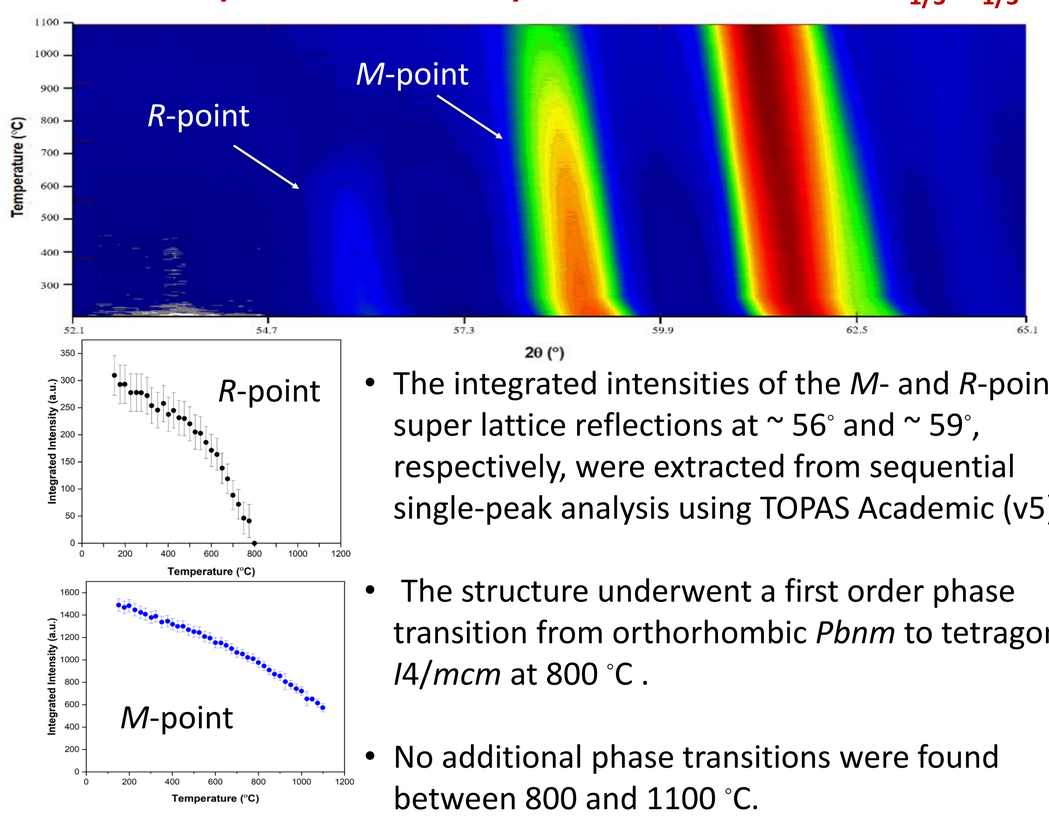


Figure 3: Neutron powder diffraction of $Na_{1/4}La_{1/4}Sr_{1/2}ZrO_3$ at room temperature from ECHINDA



- NPD data collected from ECHDINA for all members of the series at ambient temperature showed the presence of *R*-point and *M*-point superlattice reflections, with h, k, l = odd odd even and odd even even indices, respectively, indicative of the presence of both in- and out-of-phase tilting of the BO_6 octahedra.
- This is consistent with XPRD data analysis. All members of the series were found to have out-of-phase tilting of the BO_6 octahedra about the $[100]_p$ and $[010]_p$ axes with an in-phase tilt along the $[001]_p$ axis of the pseudo-cubic perovskite.

Variable Temperature Neutron powder diffraction of $Na_{1/3}La_{1/3}Sr_{1/3}ZrO_3$



- The integrated intensities of the *M*- and *R*-point super lattice reflections at ~ 56° and ~ 59°, respectively, were extracted from sequential single-peak analysis using TOPAS Academic (v5).
- The structure underwent a first order phase transition from orthorhombic *Pbnm* to tetragonal *I*4/*mcm* at 800 °C .
- No additional phase transitions were found between 800 and 1100 °C.

Conclusions and future works

- $Na_{1/2-x}La_{1/2-x}Sr_{2x}ZrO_3$ sodium perovskite-type electrolyte series has an orthorhombic *Pbnm* symmetry rather than a cubic symmetry at room temperature.
- The progressive replacement of Na^+ and La^{3+} with the larger Sr^{2+} cation on the *A*-site resulted in a continuous increase of the unit cell parameters.
- Through the analysis of integrated intensities, the structure of $Na_{1/3}La_{1/3}Sr_{1/3}ZrO_3$ was found to undergo a phase transition from orthorhombic *Pbnm* ($a^- a^- c^+$) to tetragonal *I*4/*mcm* ($a^0 a^0 c^-$) at 800 °C.

References

[1] Zhao, Yanzhang; Liu, Zhanying; Xu, Jiaxin; Zhang, Tengfei; Zhang, Fang; Zhang, Xiaogang (2019). Synthesis and characterization of a new perovskite-type solid-state electrolyte of Na1/3La1/3Sr1/3ZrO3 for all-solid-state sodium-ion batteries. *Journal of Alloys and Compounds*, **783,** 219-225.