

A Full Interionic Potential for $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ Superionic Conductors

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Computer simulation is not being as widely applied to the study of inorganic solids due to the lack of interionic potentials that describe the properties accurately. A large class of inorganic solids consist of interconnected tetrahedra or octahedra or both. An interionic potential is proposed for one class of such solids viz., the Nasicons ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$), that is shown to reproduce the structure and conductivity correctly.

Superionic conductors (SIC) are an important class of materials which find enormous technological applications, for example in batteries. These are solids with high ionic conductivities, comparable to those of molten salts. The field has attracted considerable experimental and theoretical attention in the past three decades.¹ A better understanding of the ionic motion is important to design solids with better conductivity. For this, a knowledge of the microscopic detail is essential. Computer simulation techniques can provide such atomic-level details which are otherwise difficult to obtain experimentally. A prerequisite for carrying out simulations is a reliable and accurate interionic potential. Previously there have been such attempts to develop interionic potential to study SIC, notably, by Vashishta and Rahman² for AgI and Walker and Catlow³ for sodium β -alumina.

After the discovery of $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ by Hong⁴ and Goodenough et al.⁵ these materials attracted considerable attention as excellent candidates for solid electrolytes. Hong⁴ showed that $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ is an excellent ionic conductor above 443 K with its conductivity comparable to that of Na- β -alumina. They also exhibit low thermal expansion and are industrially useful materials. They have an open framework structure, consisting of corner-linked ZrO_6 octahedra and $(\text{Si}/\text{P})\text{O}_4$ tetrahedra, with a high density of alkali-ion sites. The framework $\text{Zr}_2(\text{Si}/\text{P})_3\text{O}_{12}$ is highly stable and at the same time flexible. The high flexibility allows it to incorporate alkali ions of different sizes (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+), and some of these allow for a continuous variation in the composition, x . The presence of five different ions, the relatively high structural complexity of $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, and the interplay between a number of factors make these materials more complex than other SICs such as AgI or Na- β -alumina. One simplifying assumption is to treat the framework of ZrO_6 octahedra and $(\text{Si}/\text{P})\text{O}_4$ tetrahedra as rigid, so that only a potential between the alkali ion and framework ions would be required. In fact, recently we proposed such a potential for $\text{LiZr}_2(\text{PO}_4)_3$.⁶ However, such an interionic potential cannot model the material completely since it cannot give us information about certain crucial aspects. For example, the changes in lattice parameter or the rotation of the polyhedra with composition (which have been observed experimentally⁷) and their possible effect on ion mobility cannot be investigated. This contribution reports a full interionic pair potential for $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ consisting of interactions between all pairs of ions. It is then employed in variable shape—constant pressure—constant

Table 1. Interaction Potential Parameters for X–O Where X = Na, Zr, Si, P, and O^a

species X	q_X (e)	σ_X (Å)	A_{X-O} (eV)	C_{X-O} (eV Å ⁶)	n_{X-O}
Na	0.702	1.13	0.1716	0.000	9
Zr	2.808	0.86	1.2126	11.917	9
Si	2.808	0.40	2.8059	11.529	9
P	3.510	0.31	3.6158	9.279	9
O	-1.404	1.21	0.3252	47.999	7

^a $A_{\text{Na-Na}} = 5$ eV, $n_{\text{Na-Na}} = 11$ and all the other A_{i-j} 's and C_{i-j} 's that are not listed above are assumed to be zero.

temperature (NPT) Monte Carlo (MC) and microcanonical (NVE) molecular dynamics (MD) simulations. It is seen that the potential predicts lattice parameter and conductivity in agreement with experiment over the entire range of composition, $0 \leq x \leq 3$.

We have employed a pair potential with form similar to that proposed earlier by Rahman and co-workers² for simulating the SIC phase of AgI:

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + \frac{A_{ij}(\sigma_i + \sigma_j)^{n_{ij}}}{r_{ij}^{n_{ij}}} - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where q_i is the charge and σ_i is the ionic radii of the i th ion. A_{ij} and C_{ij} are the overlap repulsive energy and dispersion energy of ion pairs i and j . The σ of the interionic potential in eq 1 is taken from Huheey.⁸ The parameters of the potential are determined by fitting to the structure⁹ and conductivity⁷ at $x = 2$ at $T \approx 600$ K. These parameters are given in Table 1.

Simulations have been performed in the rhombohedral $R\bar{3}c$ space group for all the compositions. Variable-shape NPT-MC simulations with six degrees of freedom for the cell were carried out.^{10,11} The initial configuration for these runs were the X-ray diffraction structure of Boilot et al.⁹ These simulations yield the volume, cell parameters, and atomic positions under a given set of external conditions. Microcanonical (NVE) MD simulations are then carried out with the starting configuration and cell parameters given by the NPT-MC simulations to obtain dynamical properties such as conductivity. All simulations have been performed at four different compositions, $x = 0, 1, 2$, and 3.

Size of the simulated system is $3 \times 3 \times 1$ unit cells. Properties are calculated for 10^4 MC steps after devoting 5000 steps for proper equilibration of the system. Displacement of the size and shape of the simulation cell are attempted every four MC moves. Each MC move consists of an attempt to move all the particles (Na, Zr, P, Si, and O) once, chosen sequentially. Note that X-ray studies are unable to distinguish between the Si and P positions.^{7,9} Their positions were fixed such that they are evenly distributed in the unit cell for $x = 1$ and 2 to start with.

Velocity form of Verlet algorithm with an integration time step $\Delta t = 2.5$ fs is found to yield good energy conservation. An equilibration of over 400 ps was followed by a production run of

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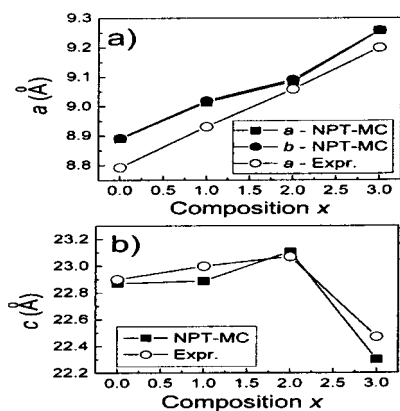


Figure 1. Variation of the (a) a and (b) c of the rhombohedral cell with x , in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ using the proposed interionic potential (see eq 1 and Table 1). Experimental values for a and c obtained from X-ray^{12,13} and neutron diffraction are also shown.¹⁴

400 ps. Properties were computed from the positions and velocities stored every 20 fs.

These materials show complex anisotropic thermal expansivities as often a strongly positive value along the c -axis while the value is near zero or even negative along the a -axis. Also when the alkali ion is substituted with bigger ions, such as, for example, Na^+ by K^+ , the c parameter is found to increase while a decreases. However an aspect of considerable importance in the context of the high Na^+ ion mobility in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ is the anomalous variation of the c parameter, with a maximum around $x = 2$, and the monotonic increase of the a parameter of the framework when composition, x , increases from 0 to 3.⁷ The former is found to be associated with a similar anomalous variation in the conductivity, where the maximum is found close to $x = 2$.⁷

Variable-shape NPT-MC and NVE-MD simulations were carried out at $x = 0, 1, 2$, and 3 using the interionic potential (eq 1) and the optimized parameters listed in Table 1. The potential energy of interaction $\langle U \rangle$ in units of eV/ion as well as the average temperature of the simulation obtained from the NVE-MD run are: at $x = 0$, $\langle T \rangle = 600.3$, $\langle U \rangle = -24.25$; at $x = 1$, $\langle T \rangle = 593.2$, $\langle U \rangle = -21.55$; at $x = 2$, $\langle T \rangle = 604.1$, $\langle U \rangle = -19.14$; at $x = 3$, $\langle T \rangle = 604.7\text{K}$, $\langle U \rangle = -16.96$ eV/ion. To see if the variations in lattice parameter, especially, the anomalous variation of the c parameter is predicted correctly by the potential, the average a , b , and c were computed from the NPT-MC runs for different values of x . The results are shown in Figure 1. Also shown are the experimental points from the X-ray^{12,13} and neutron diffraction measurements.¹⁴ The computed values obtained are in good agreement with the experimental results. In particular, the maximum in c near $x = 2$ is correctly reproduced by the simulations. The three cell angles α and β were close to 90° and γ close to 120° within the error in the calculation, thereby suggesting that the potential is predicting the cell parameters accurately.

The importance of the Nasicons arise from their ionic conductivity. The conductivity at $x = 2$ is larger than the conductivity exhibited by the Li^+ -substituted compound. NVE-MD simulations with rhombohedral periodic boundary conditions were then performed. The value of the lattice parameters were those obtained from the NPT-MC simulations. Figure 2 shows the dependence of the conductivity, σ_c , on x obtained from these simulations. The conductivity obtained from MD agrees well with that from experiment reported by Boilot et al.⁷ The deviation of the MD conductivity at lower values of x seems to arise from the slow relaxation of the ions. Much longer MD runs may be required to

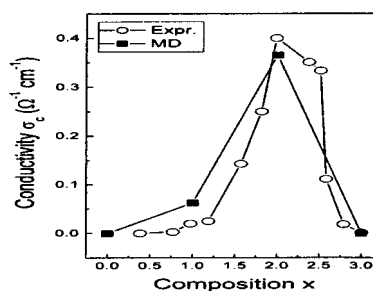


Figure 2. Conductivity, σ_c , variation, as a function of composition, x , predicted by the proposed interionic potential and estimated from MD simulation is compared with the experiments of Boilot et al.⁷

obtain accurate estimates of conductivity at small x since the hop from site to site are infrequent at lower values of x .

These results demonstrate that the proposed potential predicts both the structural properties and conductivity of the $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ system correctly. The availability of a complete potential enables one to simulate these solids and compute microscopic properties of interest. They open up many possibilities. For example, these potentials with suitable modification may be used for the whole range of solids $\text{MZr}_2\text{P}_3\text{O}_{12}$, where $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$, and Cs^+ . The temperature- and pressure dependence of their properties can also be studied. The observed maximum in conductivity near $x = 2$ has been suggested to be due to opening up of bottleneck by Baur et al.¹⁴ and Kohler and Schulz,¹⁵ while the increased repulsion between the Na^+ ions is held responsible by Boilot et al.⁷ Through more careful simulations, it should be possible to estimate the contributions to the conductivity from these two sources. Further, it is possible to obtain microscopic details relating to ionic motion as well as changes in framework from these simulations.

Organic and biomolecules are routinely simulated using force fields that have been derived over the past decade or two. The present study reports an accurate potential for the first time on a complex inorganic solid. With the availability of accurate potentials, it should be possible to carry out large-scale simulations on inorganic solids in a similar fashion.

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