

Supplementary Materials

Stoichiometric Tuning of Lattice Flexibility and Na Diffusion in NaAlSiO₄: Quasielastic Neutron Scattering Experiment and Ab-initio Molecular Dynamics Simulations

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Sample Synthesis and Characterization:

The samples were characterized by fitting the observed powder XRD data for N-NASO and L-NASO with the structural details reported by Zhao et al.¹ for nepheline type NaAlSiO_4 (Space group: $P6_3$) and trigonal low carnegieite type NaAlSiO_4 (Space group: $P3_2$), respectively (Fig S1). The unit cell parameters and profile parameters were only refined. In differential thermal analyses study on L-NASO, an endothermic peak around 658°C (931 K) was observed which is closely similar to that reported by Zhao et al.¹ for L-NASO to H-NASO structural transition (Fig S2).

Figure-S1. Rietveld refinement plots of the powder x-ray diffraction patterns of N-NASO (Space Group: $P6_3$) and L-NASO (Space Group: $P3_2$). The χ^2 values for refinement for N-NASO and L-NASO are 4.29 and 1.85 respectively.

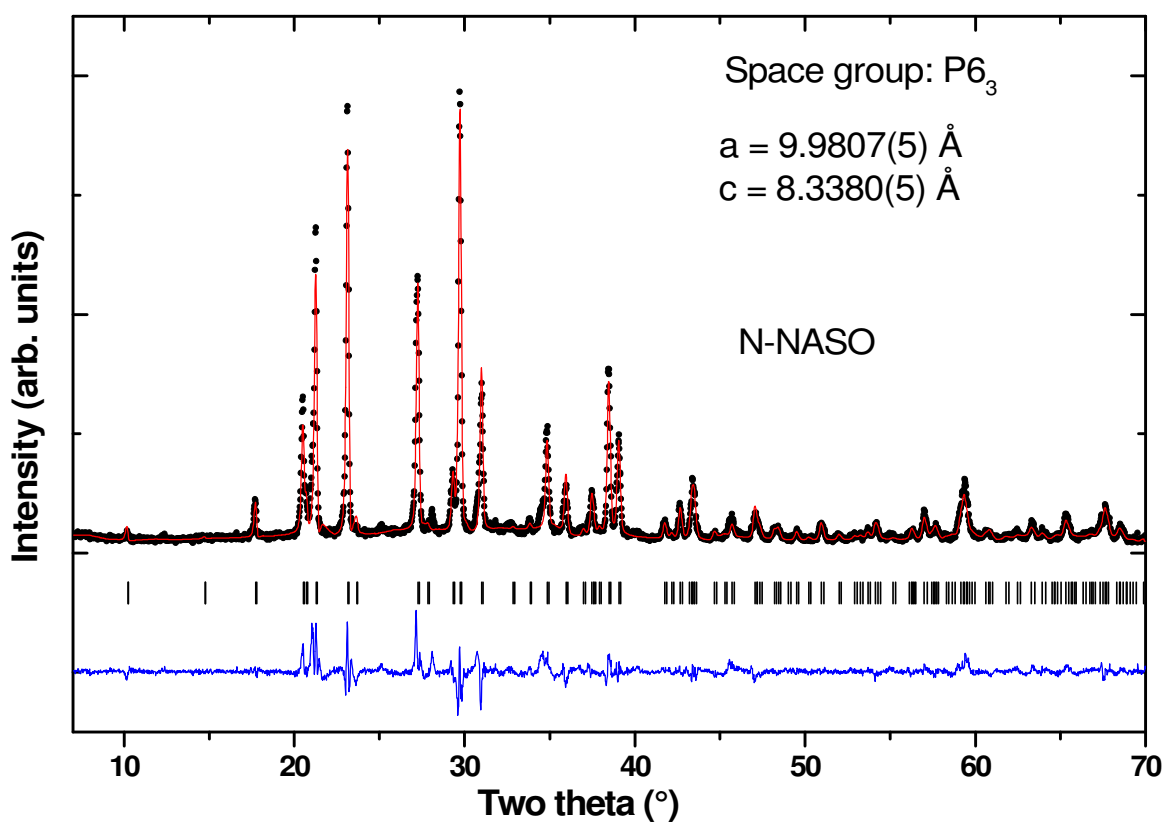
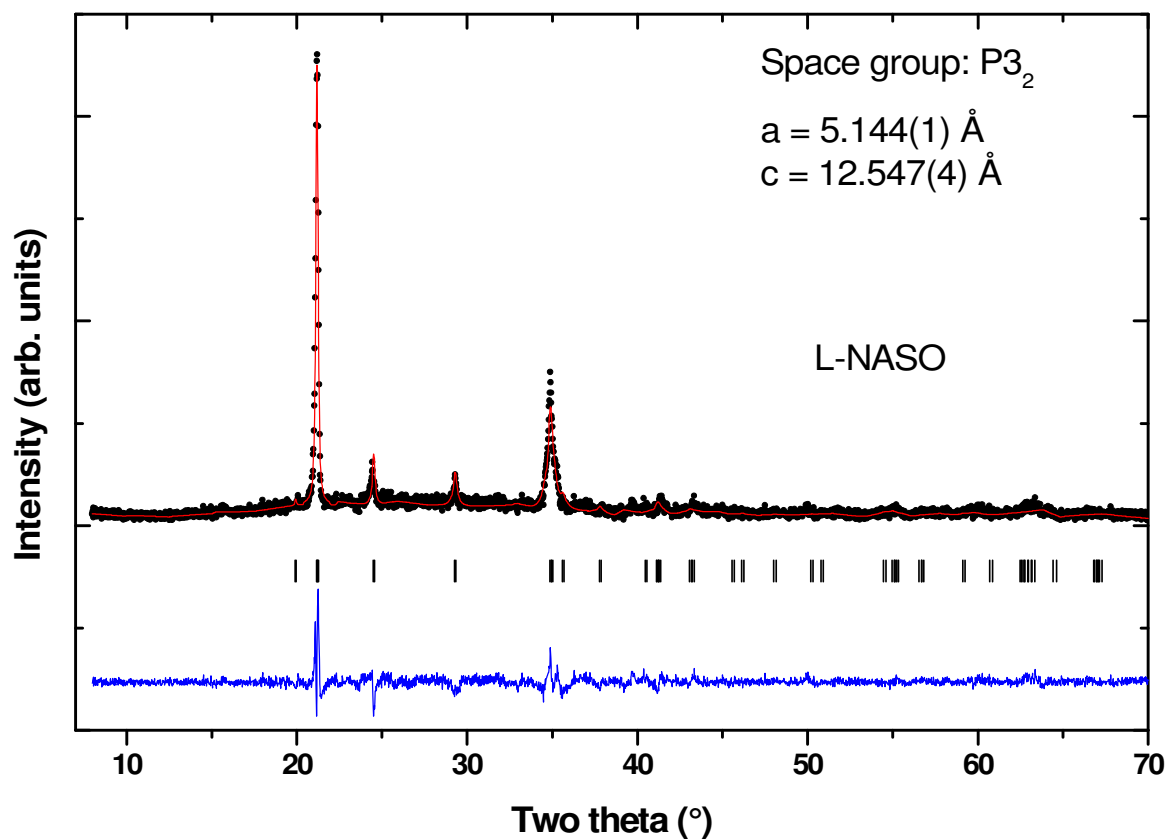


Figure-S2. Differential thermal analyses (DTA) trace of L-NASO recorded while heating (heating rate 10°C/min) the sample in flowing oxygen atmosphere. The high temperature transition of L-NASO to H-NASO occurs at about 658 °C (931 K).

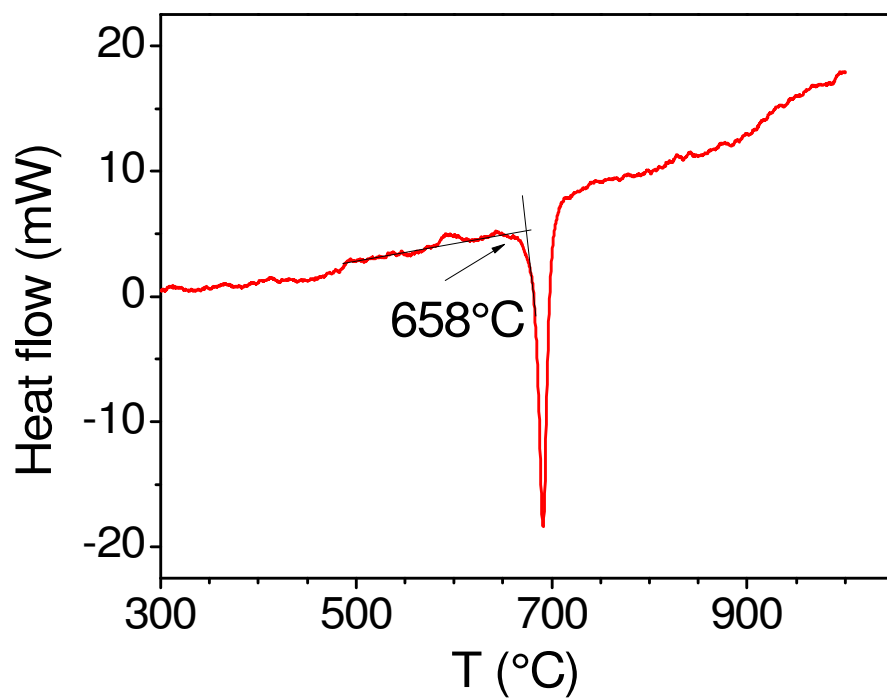


FIG S3 (Color online). The measured $S(Q, E)$ at a selected $Q = 1.0 \text{ \AA}^{-1}$, and its fit to one Lorentzian peak and one delta function convoluted with the resolution function and linear background. Upper panel: L-NASO (700 K and 900 K) and H-NASO (1100 K and 1243 K). Lower panel: N-NASO.

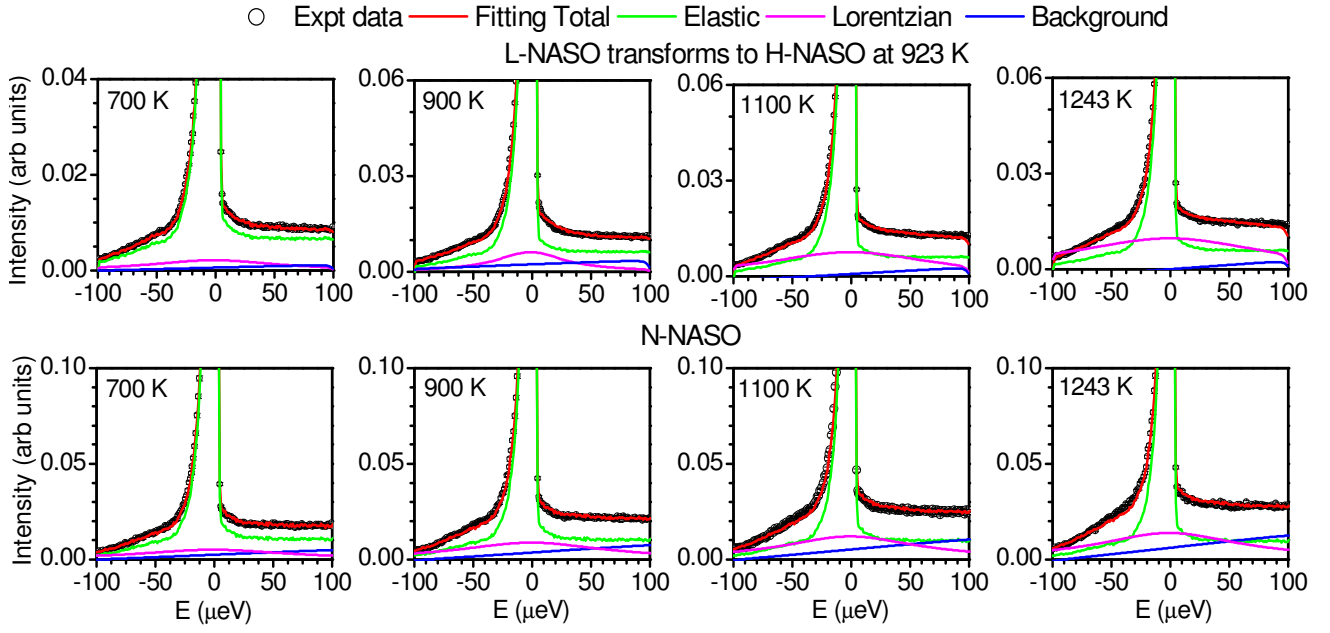
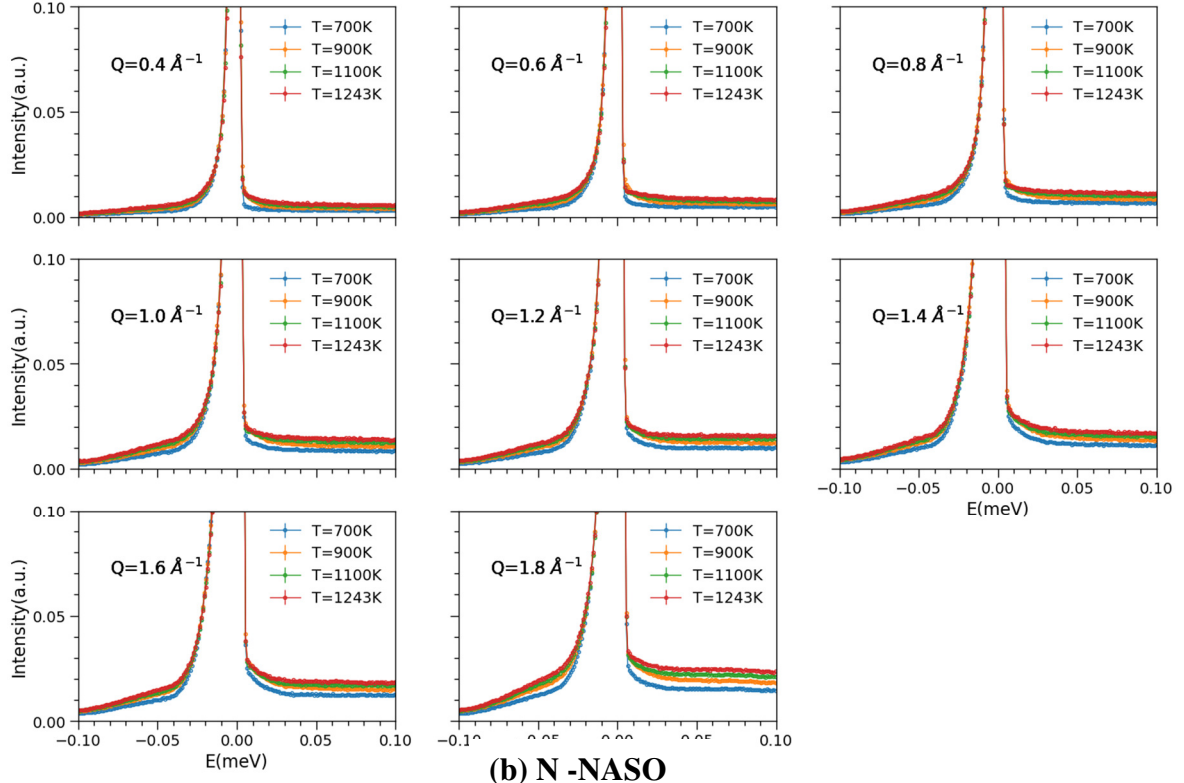


FIG S4 (Color online). The measured QENS spectra of (a) L-NASO and (b) N-NASOs as a function of temperature, above 923K L-NASO transforms to H-NASO.

(a) L-NASO and H-NASO



(b) N -NASO

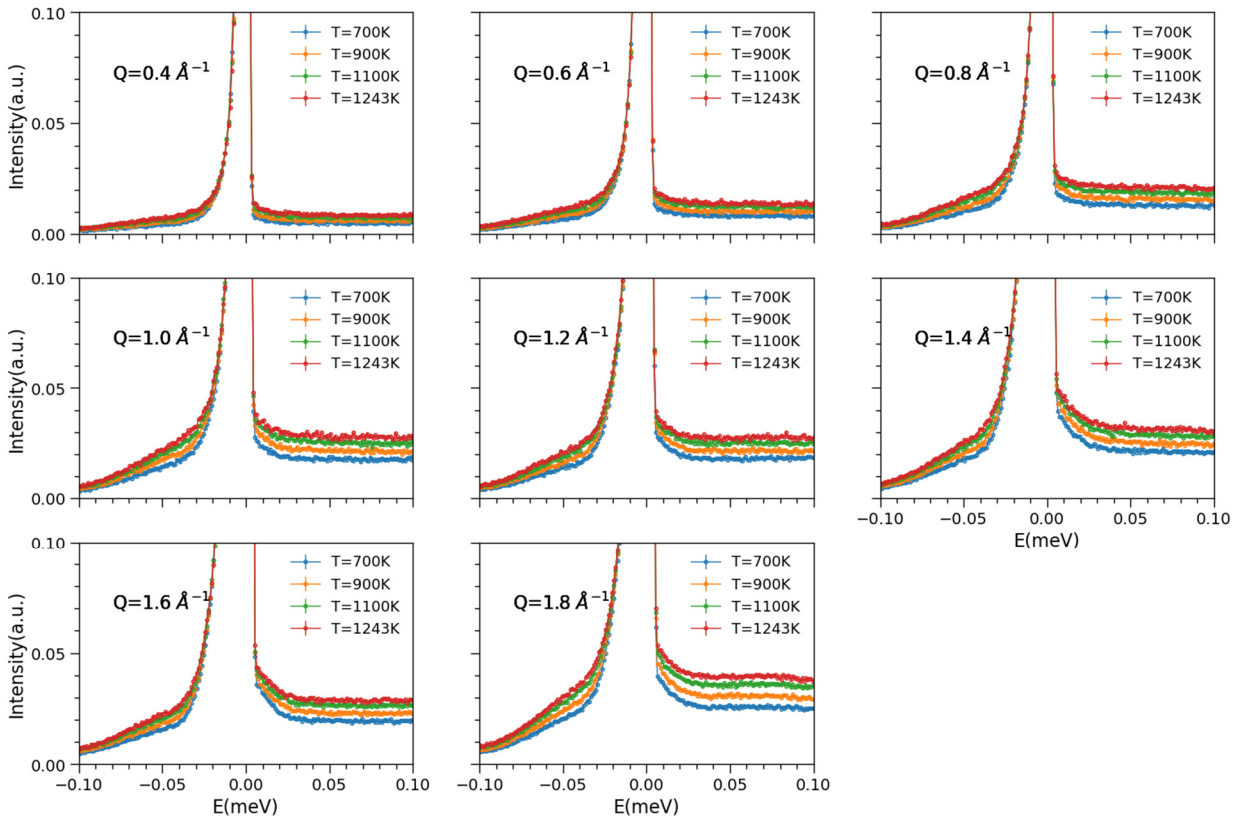


FIG S5 (Color online) The Q-dependent variation of the area of elastic peak (delta function) and Lorentzian estimated by fitting to $S(Q, E)$. The room temperature data were used as the resolution function.

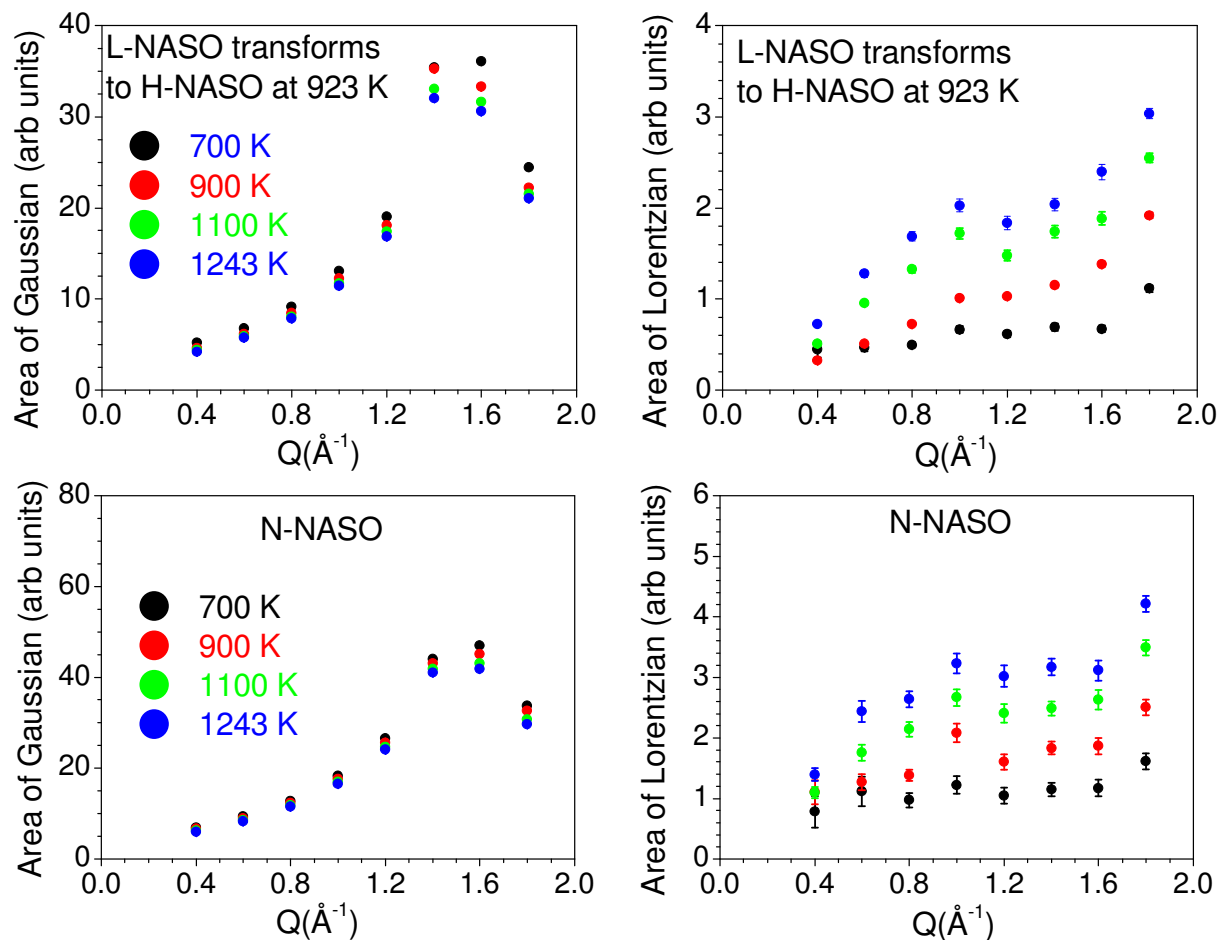


FIG S6 (Color online) The Q -dependent variation of half-width at half maximum (HWHM) of Lorentzian peak extracted from measured $S(Q, E)$. Upper panel: L-NASO (700 K and 900 K) and H-NASO (1100 K and 1243 K), L-NASO is transformed to H-NASO at 923 K. Lower panel: N-NASO. The data are fitted to the C-E model (red line) of jump-diffusion for L-NASO (900 K) and H-NASO (1100 K and 1243 K). Other data are fitted to a horizontal line indicating localized diffusion.

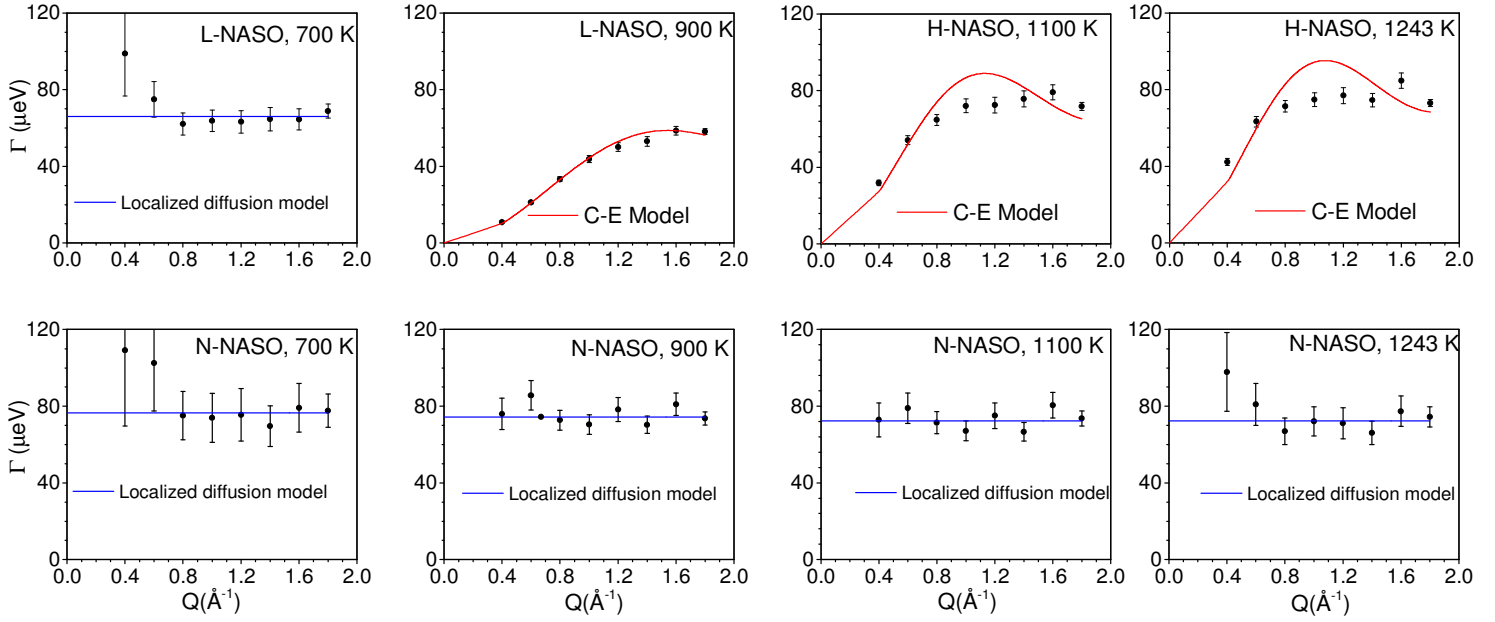


FIG S7 (Color online). The AIMD calculated pair distribution functions of various pairs of atoms in the L-NASO, H-NASO, and N-NASO phases.

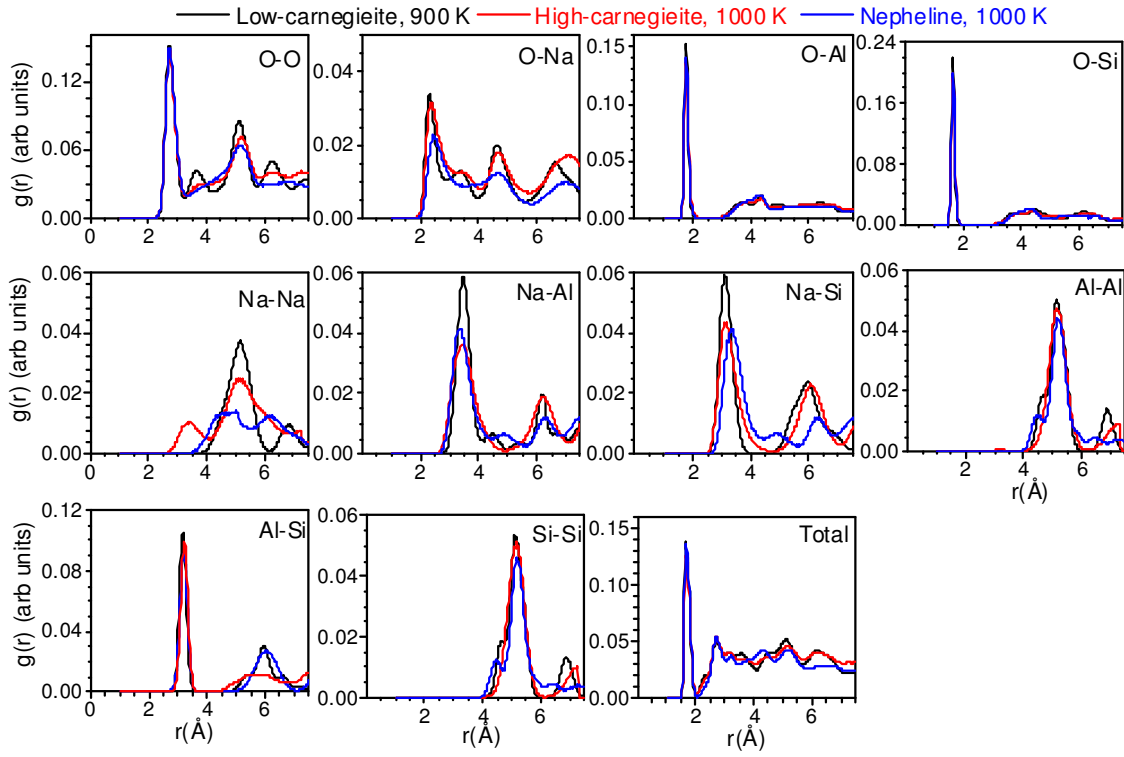


FIG S8 (Color online). The calculated MSD ($\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle$) of Na, Al, Si and O in atoms in the L-NASO(low- carnegieite; Trigonal, $P3_2$) phase, (b) H-NASO (high-carnegieite; cubic, F-43m) (c) N-NASO phase, (d) the calculated MSD of Na at $2a$ (Na1) and $6c$ sites (Na2) in N-NASO and (e) MSD component of Na1 along x, y and z- axis in N-NASO. It shows only Na1 is diffusing along the z- axis.

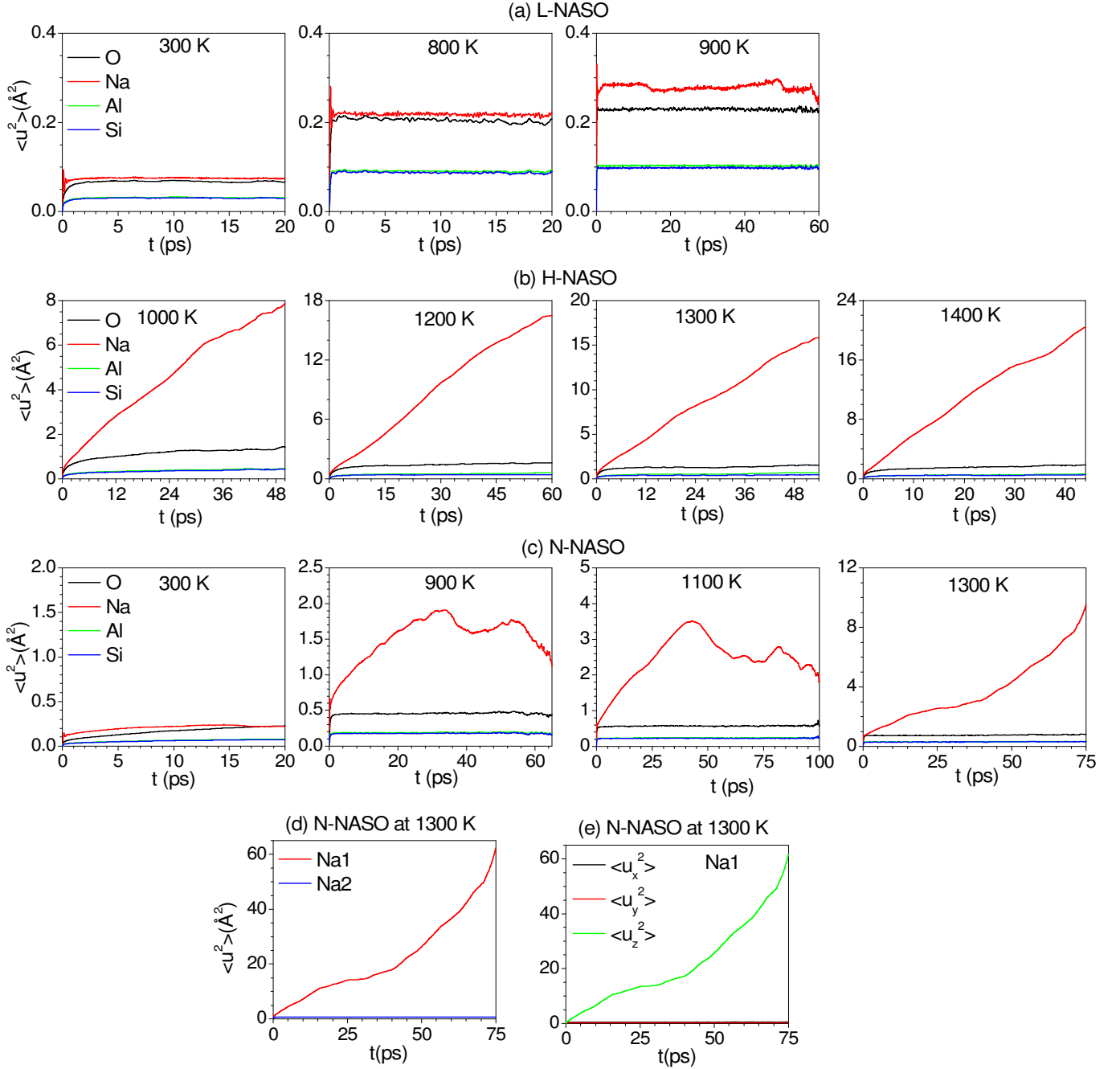


FIG S9 The calculated MSD ($\langle u^2 \rangle$) of Na atoms and the estimated error from three independent AIMD simulations at elevated temperature. The error bars shown are one standard deviation, as calculated following Ref^[2,3].

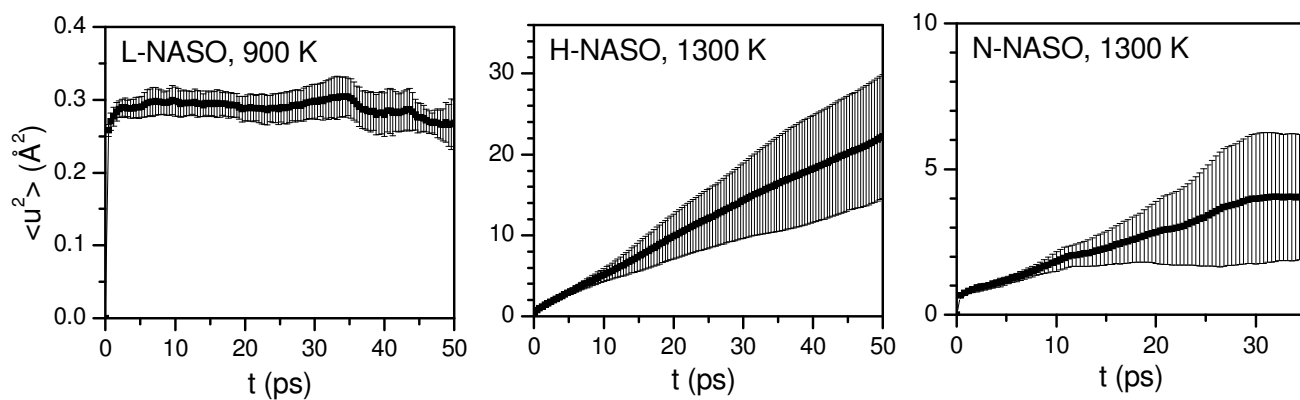


FIG S10 (Color online). (a) The calculated diffusion coefficients in the H-NASO phase using AIMD simulations and the fit to estimate the activation energy barrier (E_a). The correlation time for the calculation of the diffusion coefficient is chosen to be 40 ps. (b) The calculated free energy (F) at 1300 K from Na probability distribution between two nearest Na-sites (at Na1 and Na2) in H-NASO. For H-NASO ($\text{Na}_{1.14}\text{AlSiO}_4$; cubic, F-43m) Na occupies the $4d$ (Na1 site) and $4b$ (Na2 site) with 100 % and ~14% occupancies, respectively.

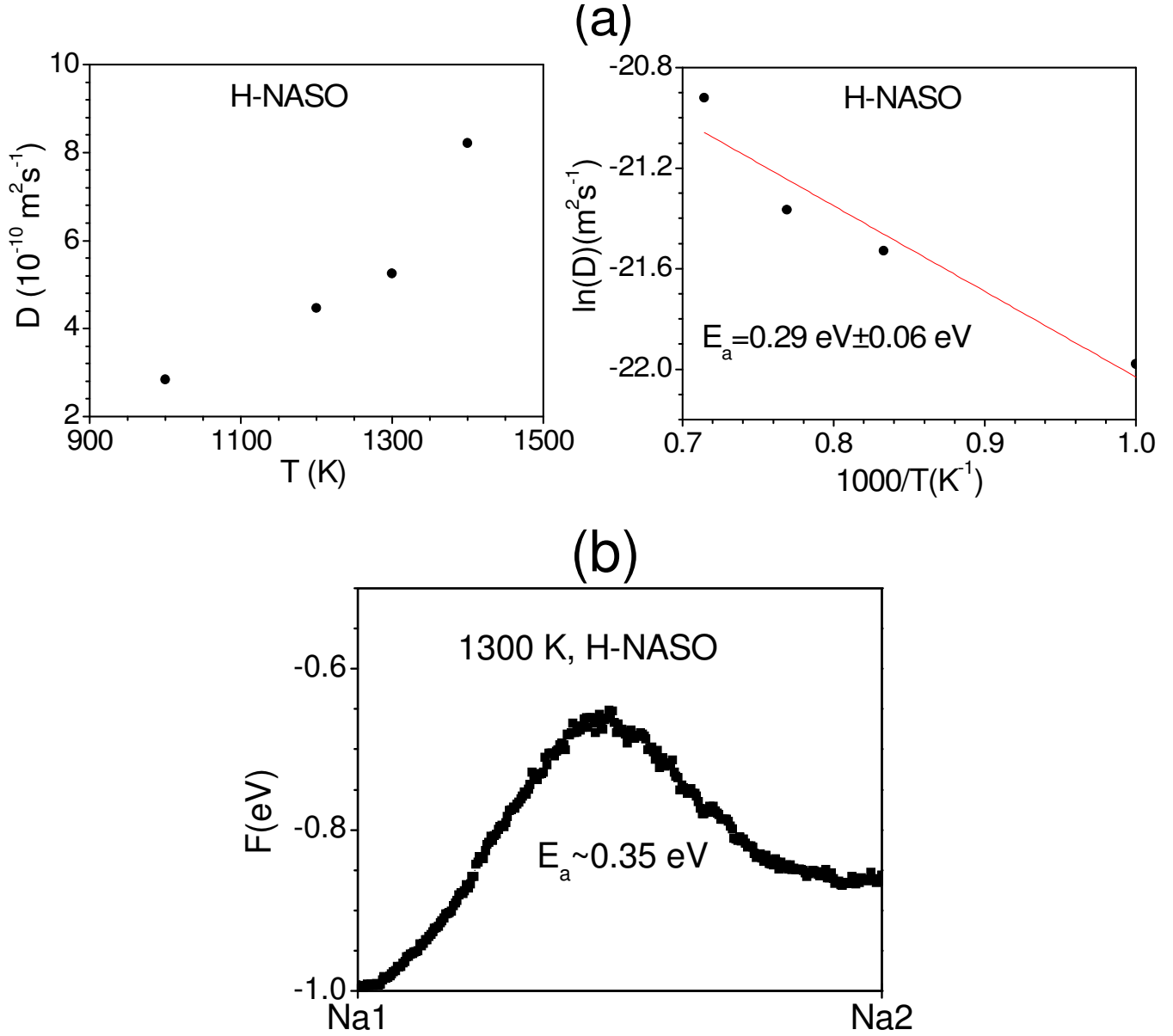


FIG S11 (Color online). The calculated MSD ($\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle$) of Na, O, Si and Al in the H-NASO phase without Na excess at $4b$ Wyckoff site.

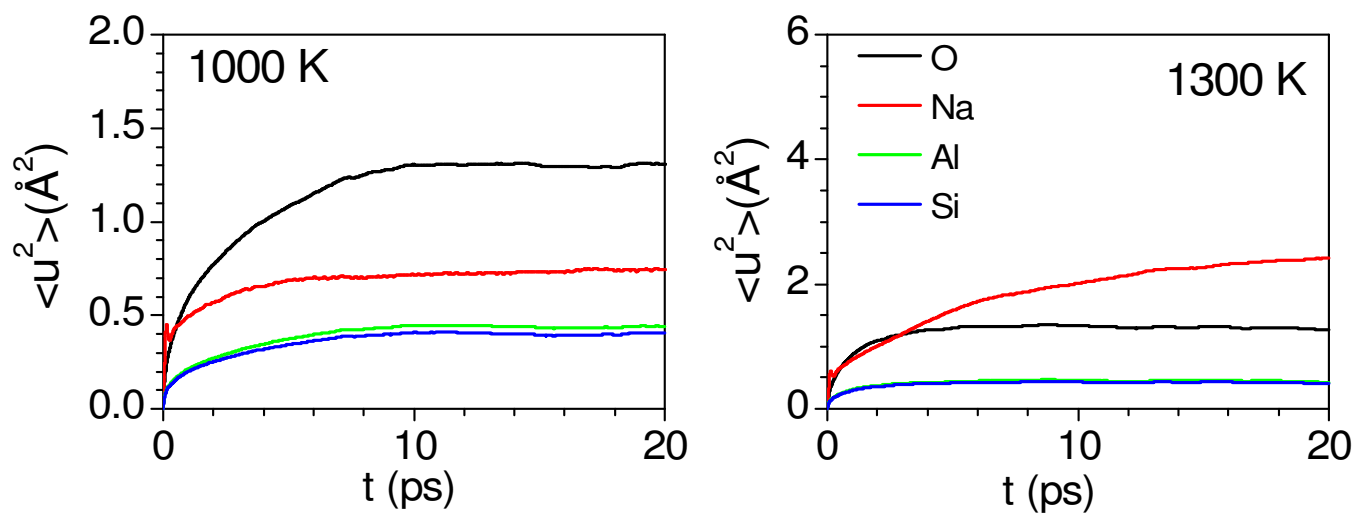


FIG S12 (Color online) Computed trajectories of selected Na atoms in the low-carnegieite (L-NASO; trigonal, $P3_2$), high-carnegieite (H-NASO; cubic, $F-43m$), and nepheline (N-NASO; hexagonal, $P6_3$) phases. Red, blue, violet, and green spheres represent oxygen, sodium, aluminum, and silicon atoms, respectively, at their lattice sites. Green color dots show the time-dependent positions of the selected sodium atoms. The numbers below each frame indicate the temperature of the simulation and the duration of the trajectory of Na, respectively.

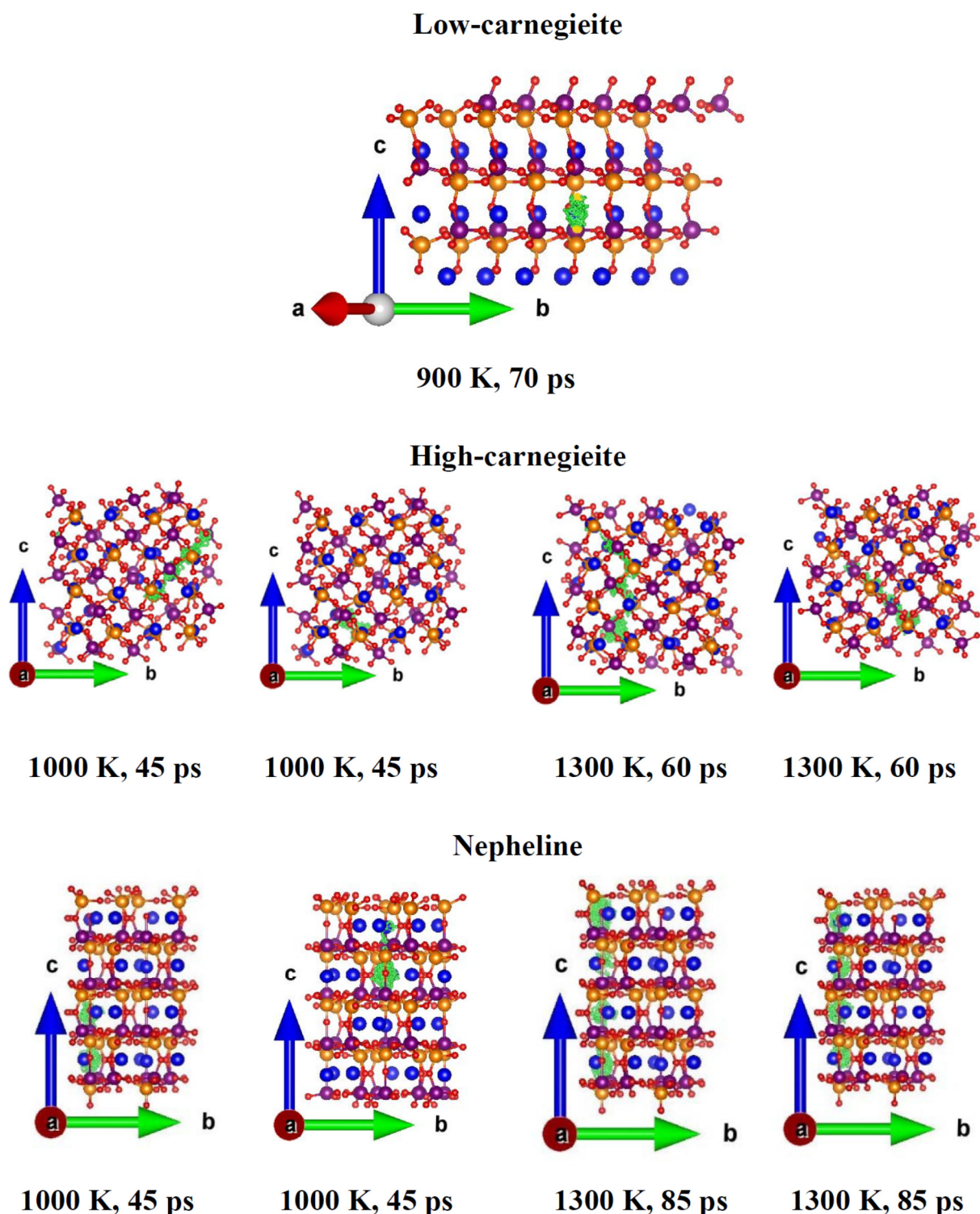
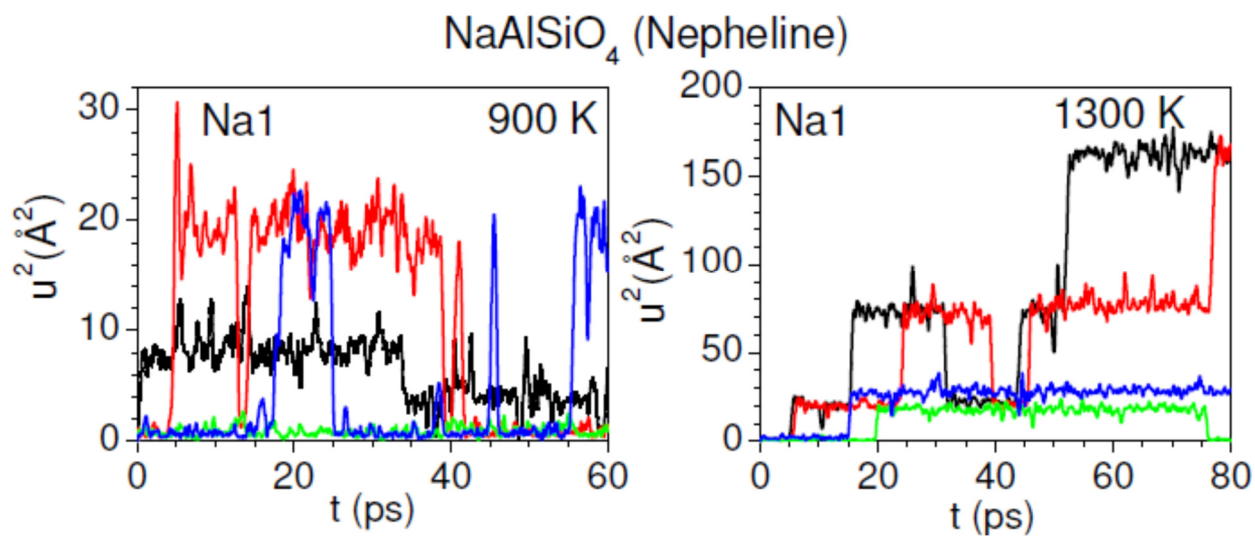


FIG S13 (Color online). The calculated squared displacement of Na atoms (at $2a$ site) in the nepheline (N-NASO; hexagonal, $P6_3$) phase.



1. M. Zhao, Z. Xia, M. S. Molokeev, L. Ning and Q. Liu, *Chemistry of Materials*, 2017, **29**, 6552-6559.
2. X. He, Y. Zhu, A. Epstein and Y. Mo, *npj Computational Materials*, 2018, **4**, 18.
3. C. Kim, O. Borodin and G. E. Karniadakis, *Journal of Computational Physics*, 2015, **302**, 485-508.