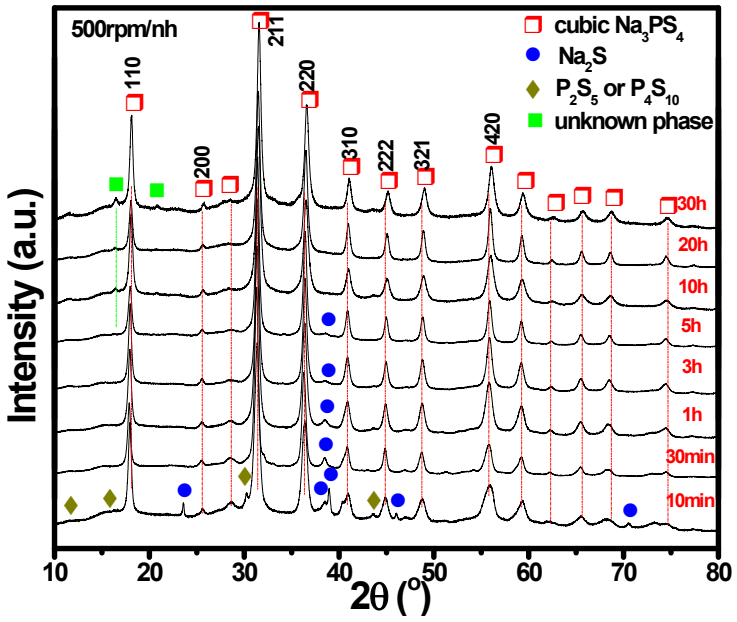
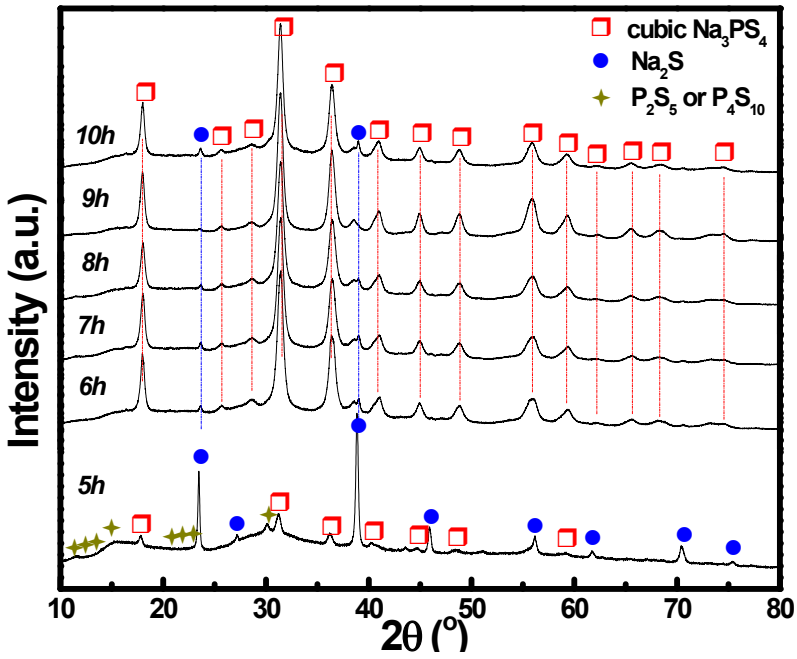
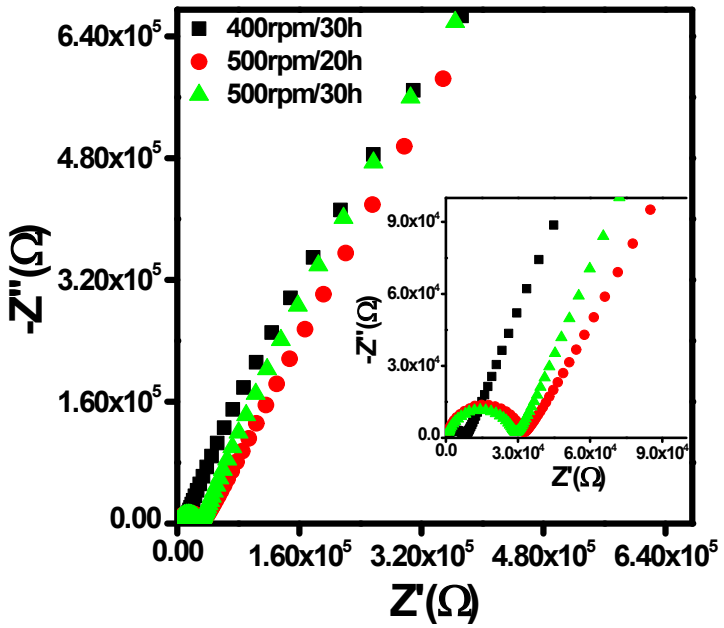


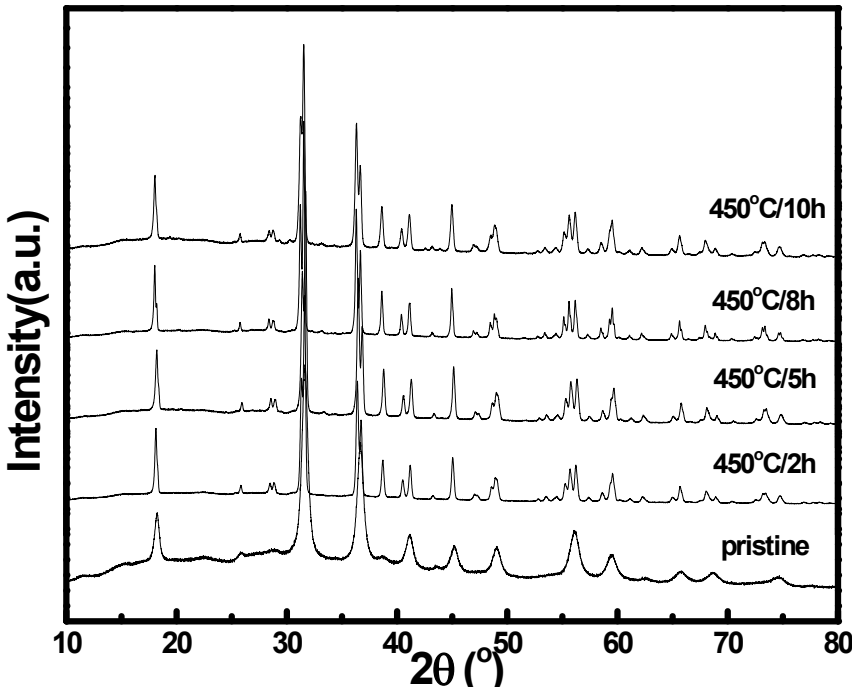
SI Figure S1. Powder XRD patterns of $75Na_2S$-$25P_2S_5$ samples synthesized by ball milling at rotation speed of 500 rpm for different milling time.



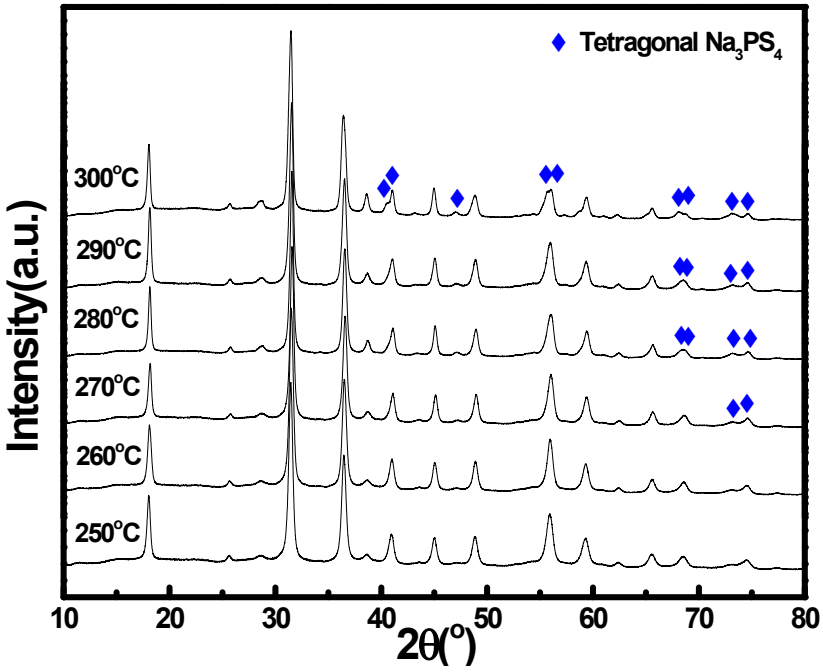
SI Figure S2. Powder XRD patterns of $75Na_2S$-$25P_2S_5$ samples synthesized by ball milling at rotation speed of 400 rpm from 5 to 10 h. (The samples milled 5 and 10 h have been depicted just for comparison)



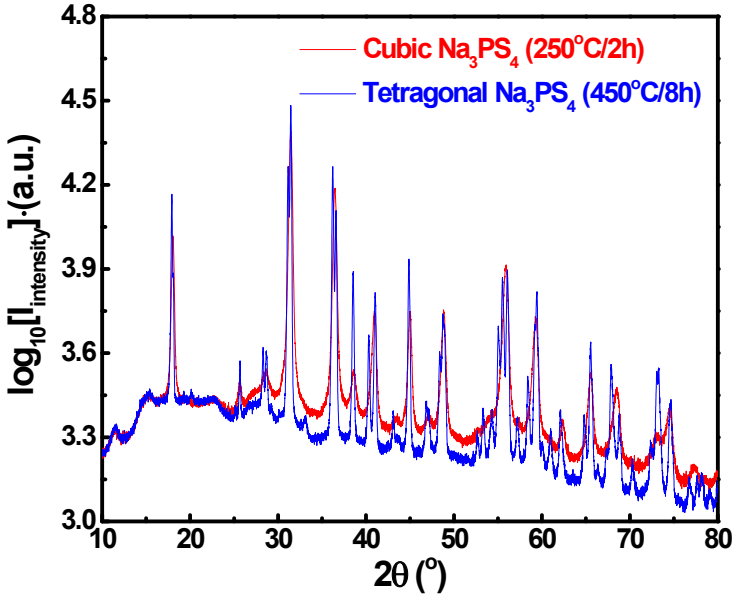
SI Figure S3. Complex impedance plots for the final mixture ball milled with 400 rpm at 30 h and 500 rpm at 20 and 30 h.



SI Figure S4. The XRD patterns of the sample annealed at 450 °C for different durations (2, 5, 8, and 10 h).

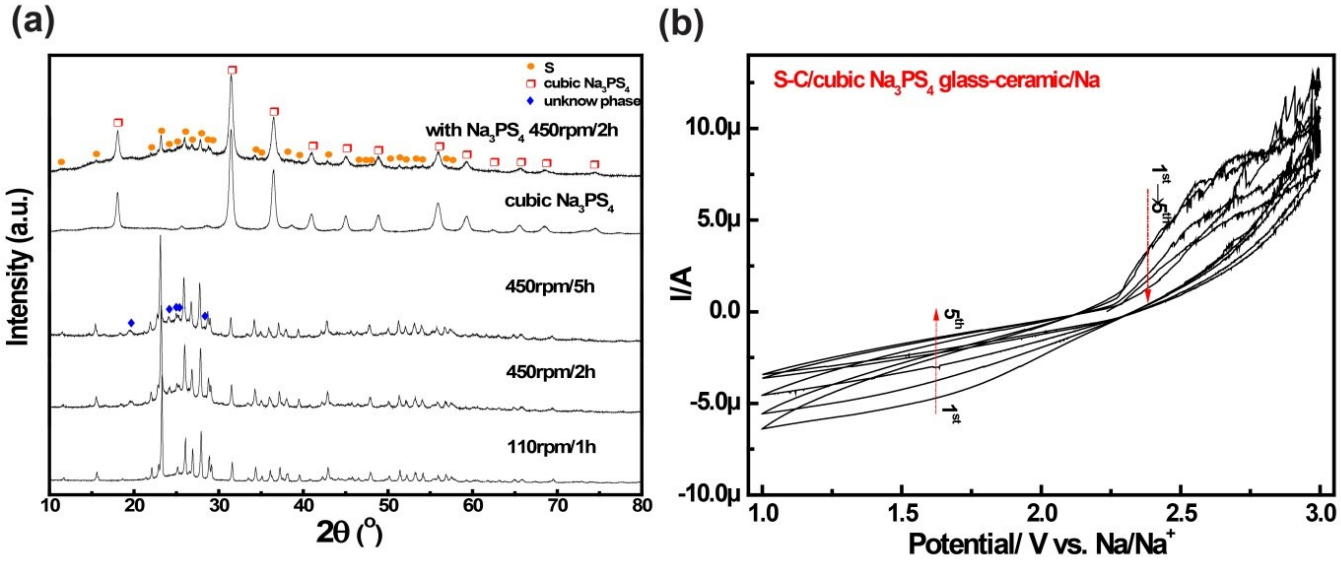


SI Figure S5. The XRD patterns of the sample annealed at 250, 260, 270, 280, 290 and 300 °C for 2 h and then quenched. The patterns of the sample annealed at 250 and 300 °C were just exhibited for comparison.

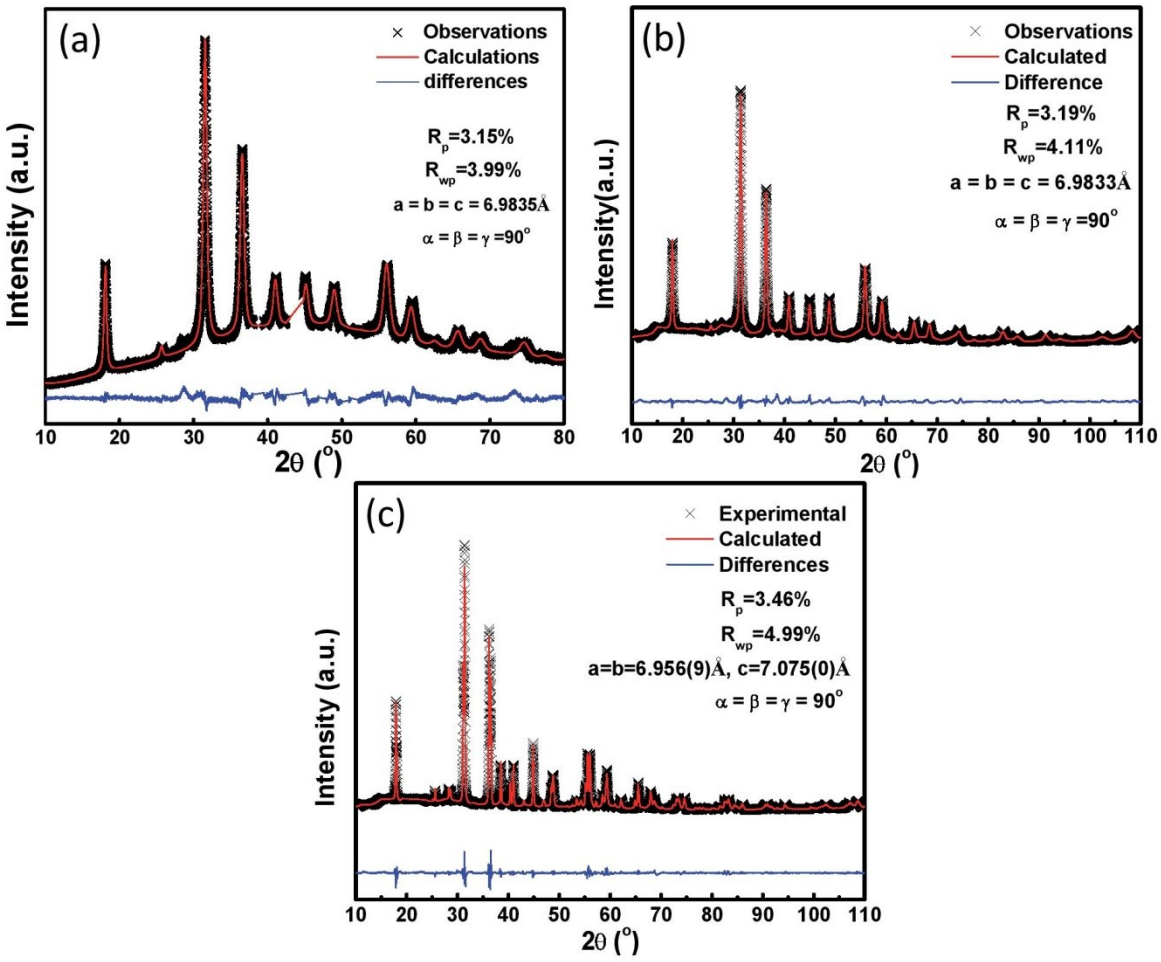


SI Figure S6. XRD patterns of the final cubic and tetragonal Na_3PS_4 materials at room temperature. The XRD patterns can be quantitatively be compared because

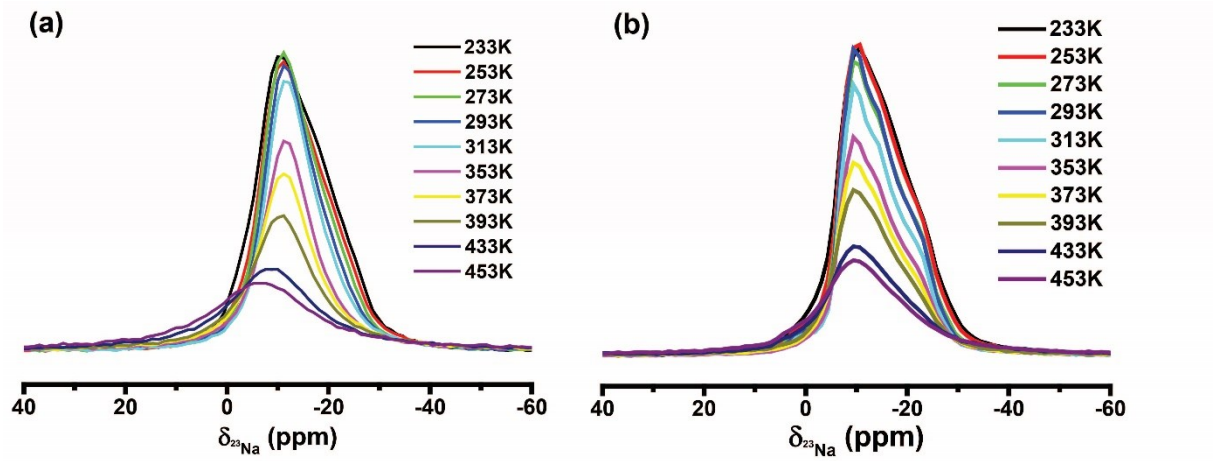
the patterns were collected with the same holder, on the same amount of material, with the same X-ray footprint and with the same exposure time. The higher background starting at approximately 25° 2θ for the cubic material, annealed at 250 °C for 2 hours, compared to the tetragonal material, annealed at 450 °C for 8 hours, indicates a significantly larger amorphous fraction in the cubic Na_3PS_4 material.



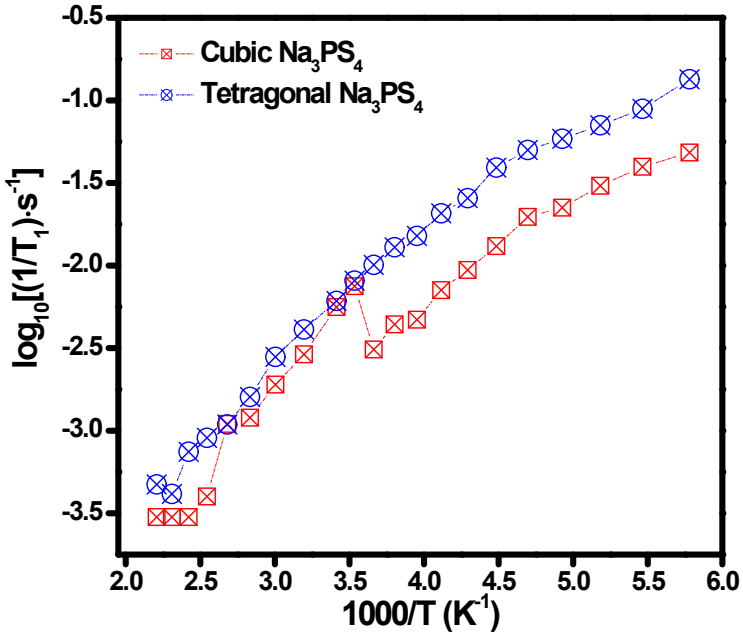
SI Figure S7. (a) The XRD patterns of sulphur with carbon and cubic the Na_3PS_4 glass-ceramic after different mechanical milling conditions. The XRD pattern of the as-prepared cubic Na_3PS_4 after 250 °C/2 h is also shown for comparison. (b) Cyclic voltammetry tests of the all-solid-state cells with the cubic Na_3PS_4, S-C composite electrode and Na-metal negative electrode at a scanning rate of 0.05 mVs^{-1} between 1.0 V and 3.0 V at room temperature.



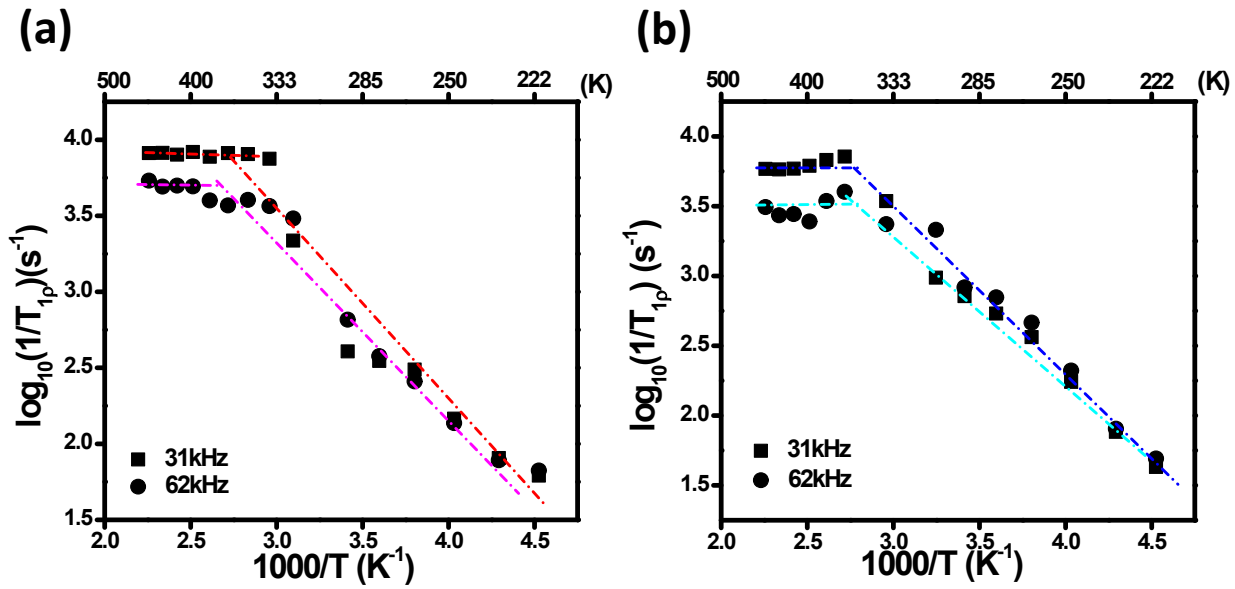
SI Figure S8. XRD refinement of cubic Na_3PS_4 at (a) 223 K, (b) 293 K and (c) of tetragonal Na_3PS_4 at 293 K (c).



SI Figure S9. An overlay of ^{23}Na spectra of the (a) cubic and (b) tetragonal Na_3PS_4 measured under MAS at 9.4 T at a spinning frequency of 12.5 kHz in the temperature window of 233 K- 453 K.



SI Figure S10. The T_1 relaxation times for tetragonal and cubic Na_3PS_4 probed by MAS NMR.



SI Figure S11. Temperature dependence of the ^{23}Na NMR SLR rates ($1/T_{1\rho}$) in the rotating-frame of reference of cubic (a) and tetragonal (b) Na_3PS_4 glass-ceramics. $T_{1\rho}$'s were measured at $\omega_1/2\pi$ values of 31 and 62 kHz respectively. The black, red and green dash line in the figure indicated the fitting result of the $T_{1\rho}$ of the cubic Na_3PS_4 glass-ceramics. Static solid state NMR measurements were performed on a Varian 600 spectrometer (B_0=14.1 T) for which the ^{23}Na resonance frequency amounts 158.746 MHz. The $\pi/2$ pulse length was determined to be 9 μs with an RF field strength of 62 kHz. Chemical shifts were referenced with respect to a 0.1 M NaCl solution. The air sensitive materials were sealed in a custom-made Teflon tube in an Argon filled glove box (H_2O, O_2 < 0.3 ppm). Variable temperature measurements were performed using a 5 mm static goniometer probe from -50 °C to +175 °C.

Table 1. Refined structure data of cubic Na_3PS_4 at 223 K.

Sample	Atom (ox.)	Fractional coordinates				Occupancy	Uiso
		x	y	z			
Na_3PS_4	Na1	0.5	0.5	0	6	0.9348	0.09962
	Na2	0.75	0.5	0	12	0.0330	0.09962
	P	0	0	0	2	1.0000	0.03439
	S	0.1670	0.1670	0.1670	8	1.0000	0.03868