Figure 1. The Rietveld refinement of the PXRD langbeinite-structured $NH_4Zr_2(PO_4)_3$.
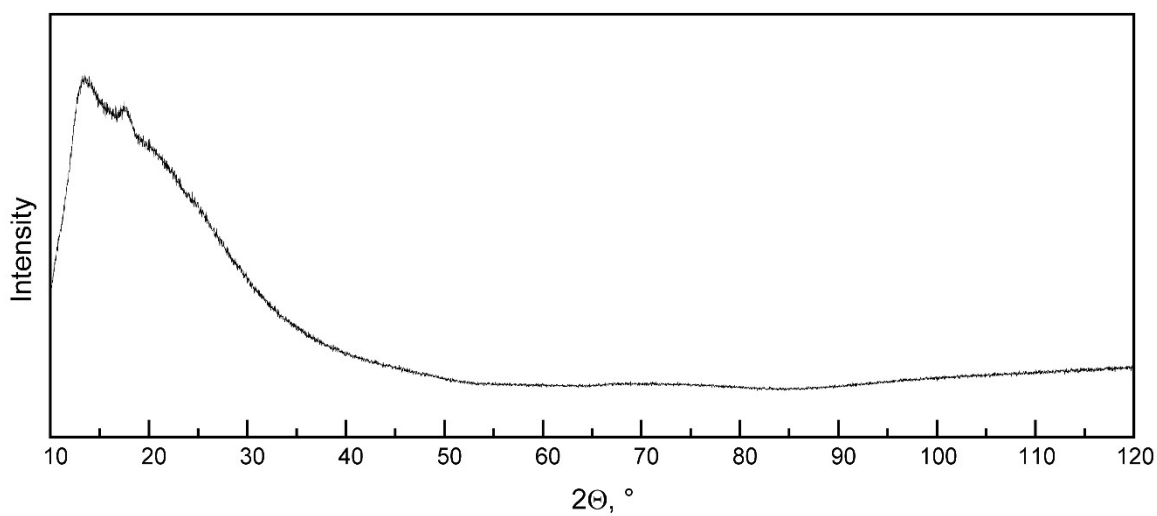

Figure 2. XRD pattern of an empty inert sample holder.

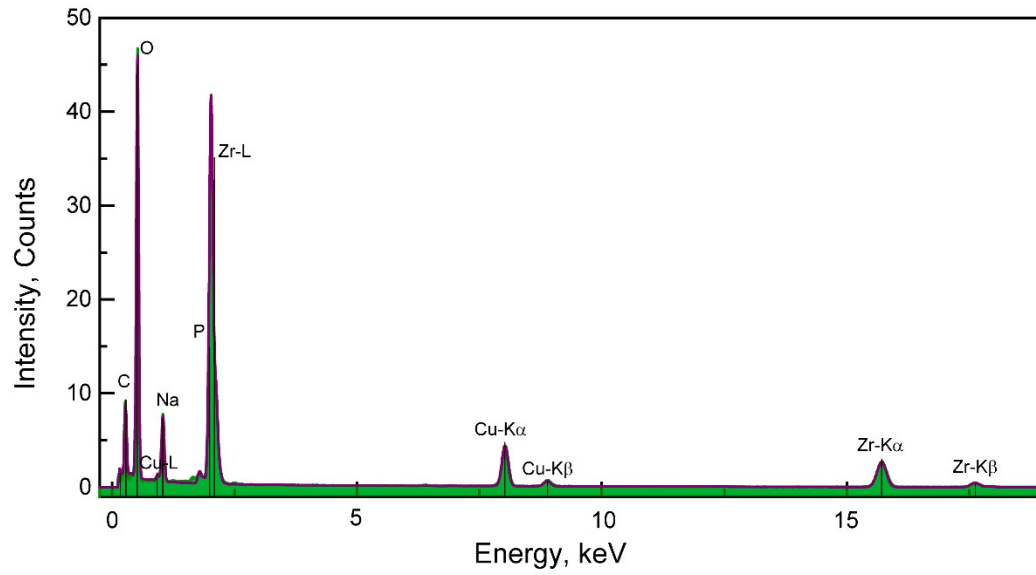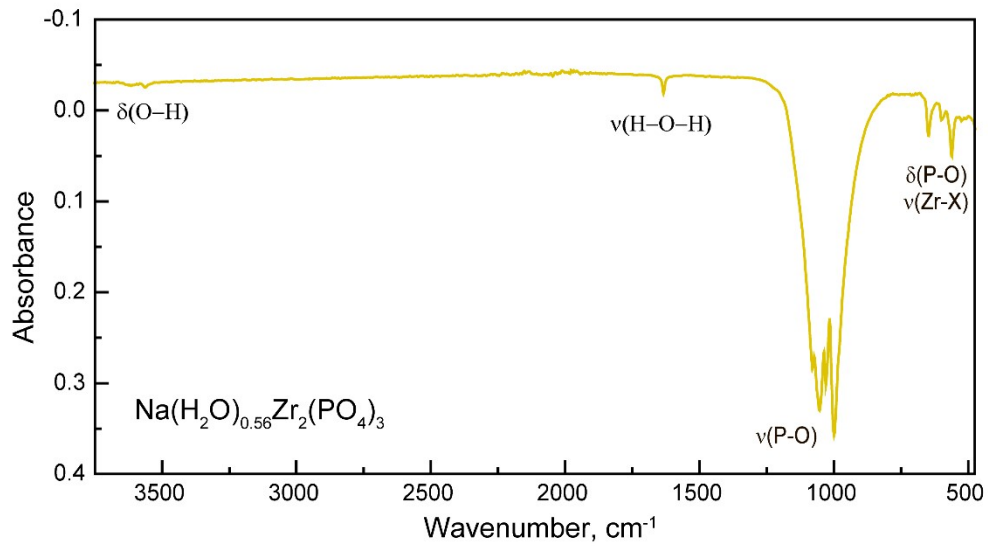Figure 3. STEM-EDX spectra of $NaZr_2(PO_4)_3$.

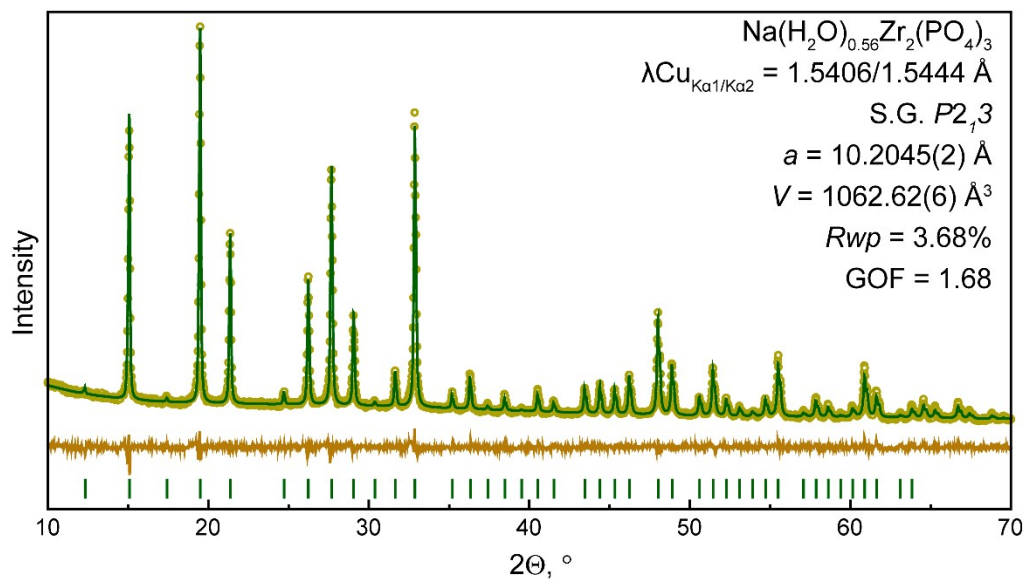Figure 4. FTIR spectra of the $Na(H_2O)_{0.56}Zr_2(PO_4)_3$-langbeinite stored under air atmosphere.

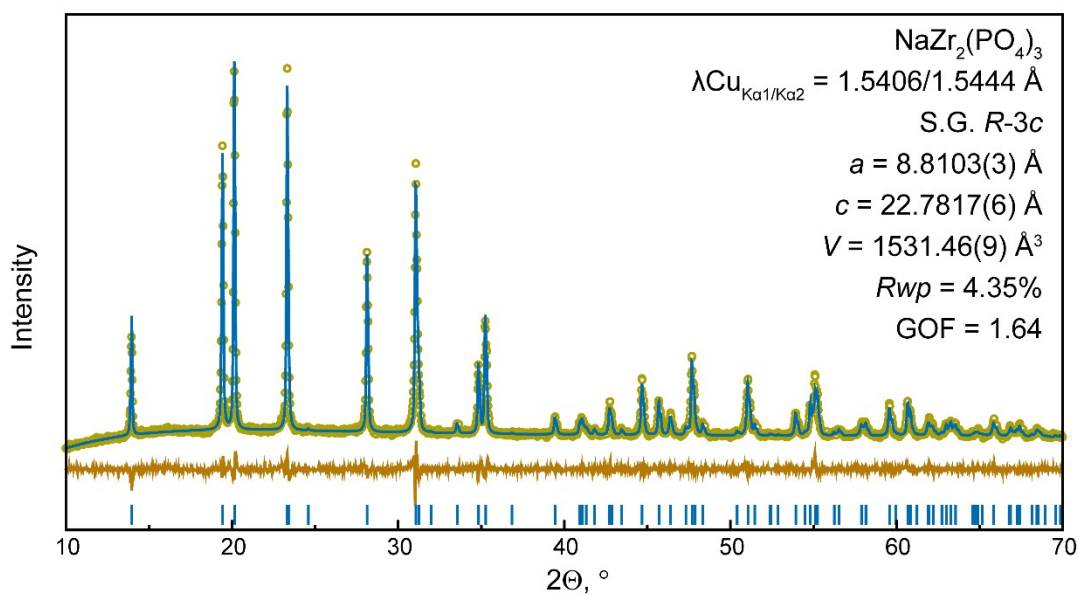Figure 5. The Rietveld refinement of PXRD for langbeinite-structured $Na(H_2O)_{0.56}Zr_2(PO_4)_3$

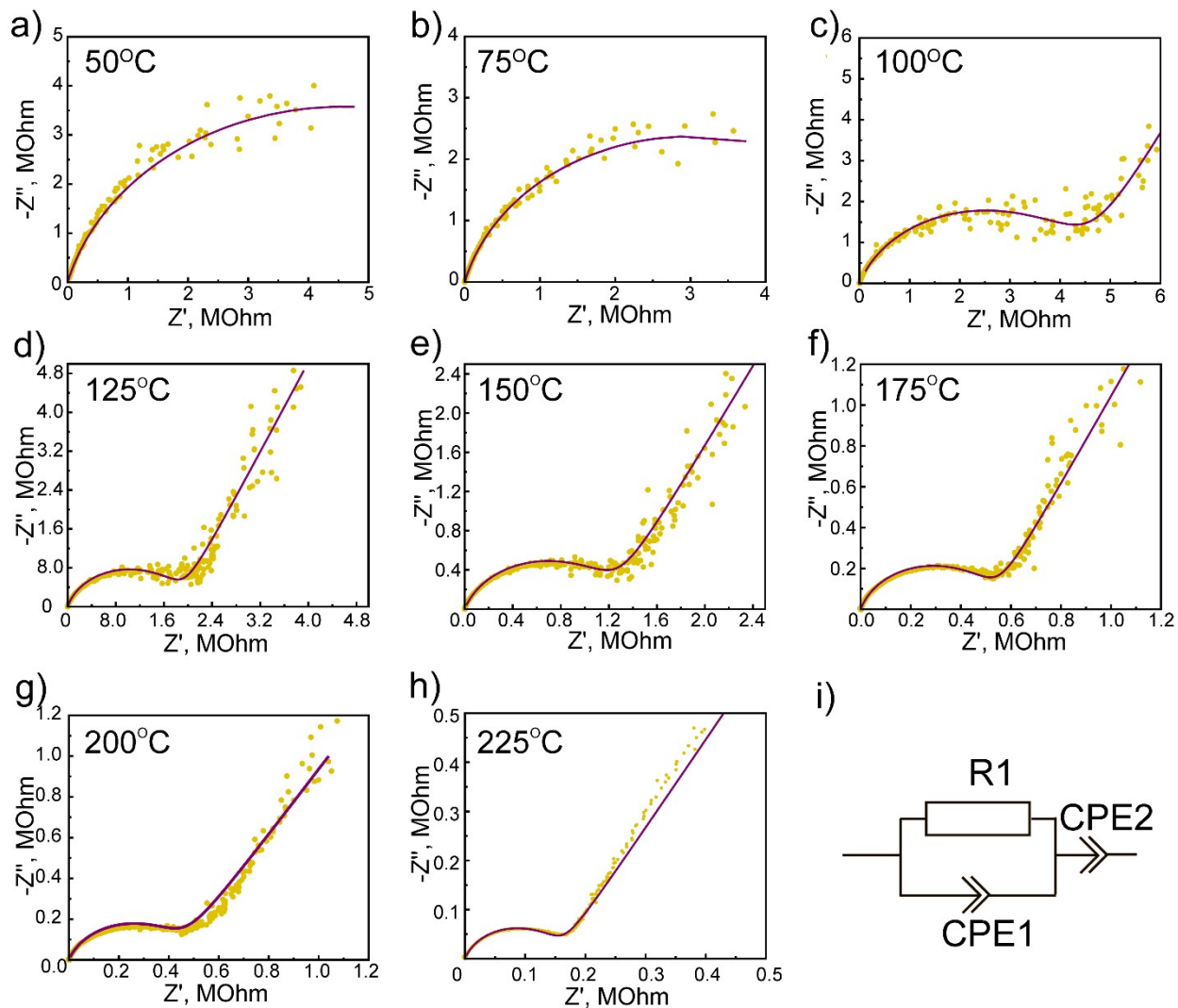Figure 6. The Rietveld refinement of PXRD NaSICON-structured $NaZr_2(PO_4)_3$

Figure 7. Nyquist plots obtained at different temperatures for $NaZr_2(PO_4)_3$ (a – h), yellow circles – experimental data, purple line – calculated data, and equivalent circuit used for data fitting (i).

Table S1. Fitting parameters of EIS data.

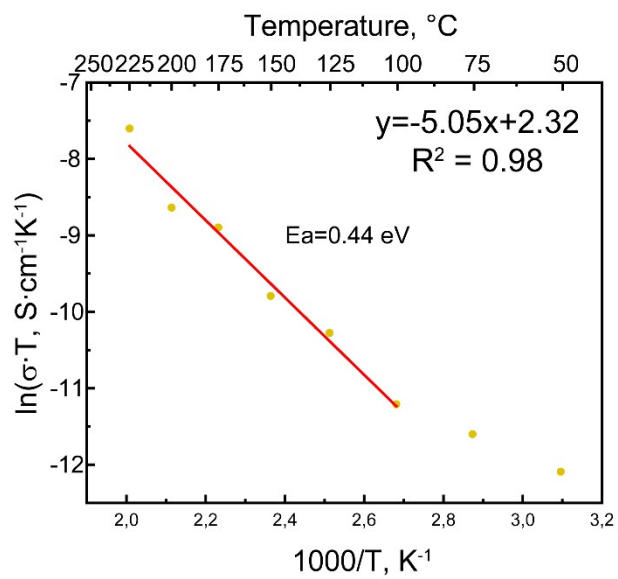| Temperature, $^{\circ}$C	R1, Ohm	Q1, $Fs^{(\alpha-1)}$	$\alpha 1$	Q2, $Fs^{(\alpha-1)}$	$\alpha 2$	Conductivity, S/cm
225	153353	1.43×10^{-9}	0.804	1.27×10^{-7}	0.677	1.04×10^{-6}
200	424974	1.46×10^{-9}	0.794	8.76×10^{-8}	0.647	3.75×10^{-7}
175	521246	9.90×10^{-10}	0.812	6.63×10^{-8}	0.724	3.05×10^{-7}
150	1.21×10^{6}	1.00×10^{-10}	0.802	4.96×10^{-8}	0.712	1.32×10^{-7}
125	1.84×10^{6}	7.04×10^{-10}	0.832	4.10×10^{-8}	0.741	8.65×10^{-8}
100	4.38×10^{6}	7.95×10^{-10}	0.803	3.33×10^{-8}	0.720	3.63×10^{-8}
75	6.05×10^{6}	4.60×10^{-10}	0.847			2.63×10^{-8}
50	9.17×10^{6}	4.41×10^{-10}	0.843			1.74×10^{-8}

Figure 8. The Arrhenius plot of the Na^+ ion conductivity of $NaZr_2(PO_4)_3$