Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Table S1. Activation energy, pre-exponential factor, and conductivity for bulk, grain boundary (g.b.), and total conductivity of $CsPb_{0.9}K_{0.1}F_{2.9}$

	Temperature range T / K	Activation energy E_a / kJ mol^{-1}	Preexponential factor log(A_0 / S cm^{-1} K)	$\sigma_{298\ K}$ / S cm^{-1}
bulk	173–203	31.8(5)	6.98(13)	-
	248–318	7.92(9)	1.356(17)	3.1×10^{-3}
g.b.	173–318	40.0(2)	7.86(4)	2.3×10^{-2}
total	173–233	37.62(17)	7.200(5)	-
	298–348	10.89(4)	1.821(7)	2.7×10^{-3}

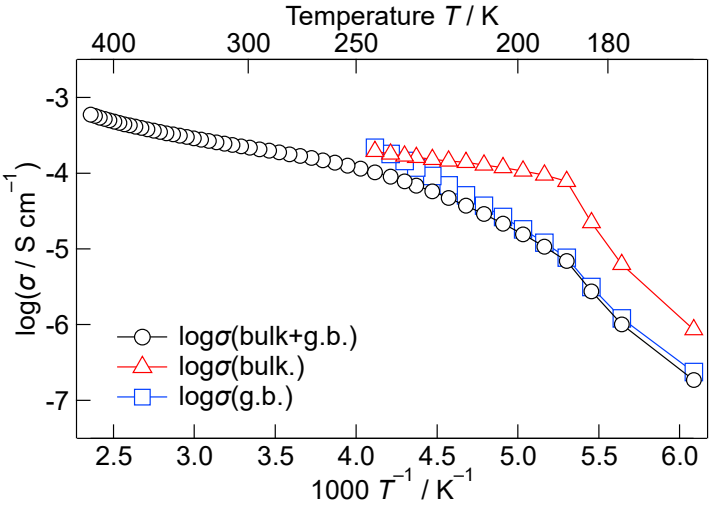

Figure S1. Arrhenius plot of the ionic conductivities of $CsPbF_3$. Bulk, grain boundary (g.b.), and total conductivities are shown as red triangle, blue square, and black circle, respectively.

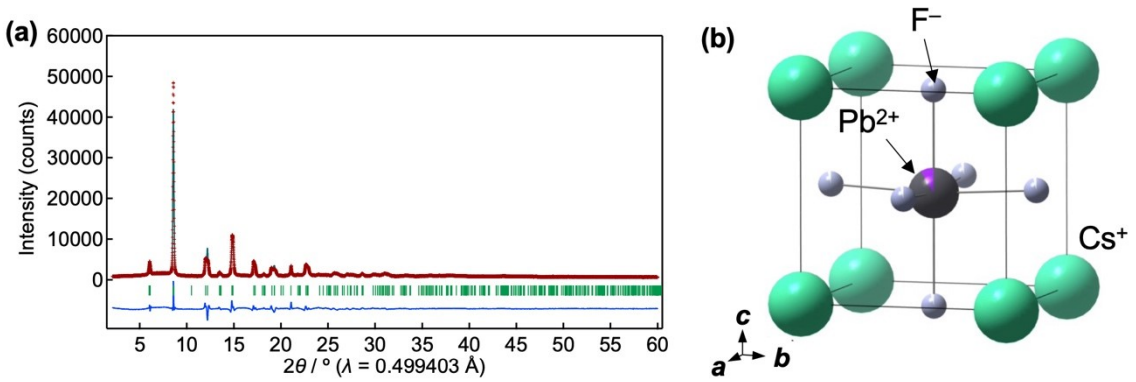

Figure S2. (a) Rietveld refinement result for the synchrotron XRD data of $CsPb_{0.9}K_{0.1}F_{2.9}$ at 200 K. Red point, black line, blue line, and green symbol represent the observed intensities, calculated intensities, difference curves, and positions of the Bragg reflections of tetragonal $CsPb_{0.9}K_{0.1}F_{2.9}$. (b) Refined structure of tetragonal $CsPb_{0.9}K_{0.1}F_{2.9}$ at 200 K. Green, black, purple, and grey balls represent Cs, Pb, K, and F atoms, respectively.

Table S2. Rietveld refinement results from synchrotron XRD data for $CsPb_{0.9}K_{0.1}F_{2.9}$ at 200 K

Atom	Site	*g*	*x*	*y*	*z*	B_{iso} / Å^2
Cs^+	1*a*	1.000(2)	0	0	0	0.3
Pb^{2+}	1*b*	0.906(3)	0.5	0.5	0.4735(14)	0.3
K^+	1*b*	=1–*g*(Pb^{2+})	0.5	0.5	=*z*(Pb^{2+})	0.3
F^-	1*b*	0.9667	0.5	0.5	–0.049(14)	5
F^-	2*c*	0.9667	0	0.5	0.5	5

Unit cell: tetragonal *P*4*mm*(99); $a = b = 4.71016(18)$ Å, $c = 4.7845(3)$ Å, $V = 109.4670(7)$ Å^3; $R_{wp} = 11.4\%$, $R_p = 8.3\%$, $R_F = 2.5\%$, S = 4.0

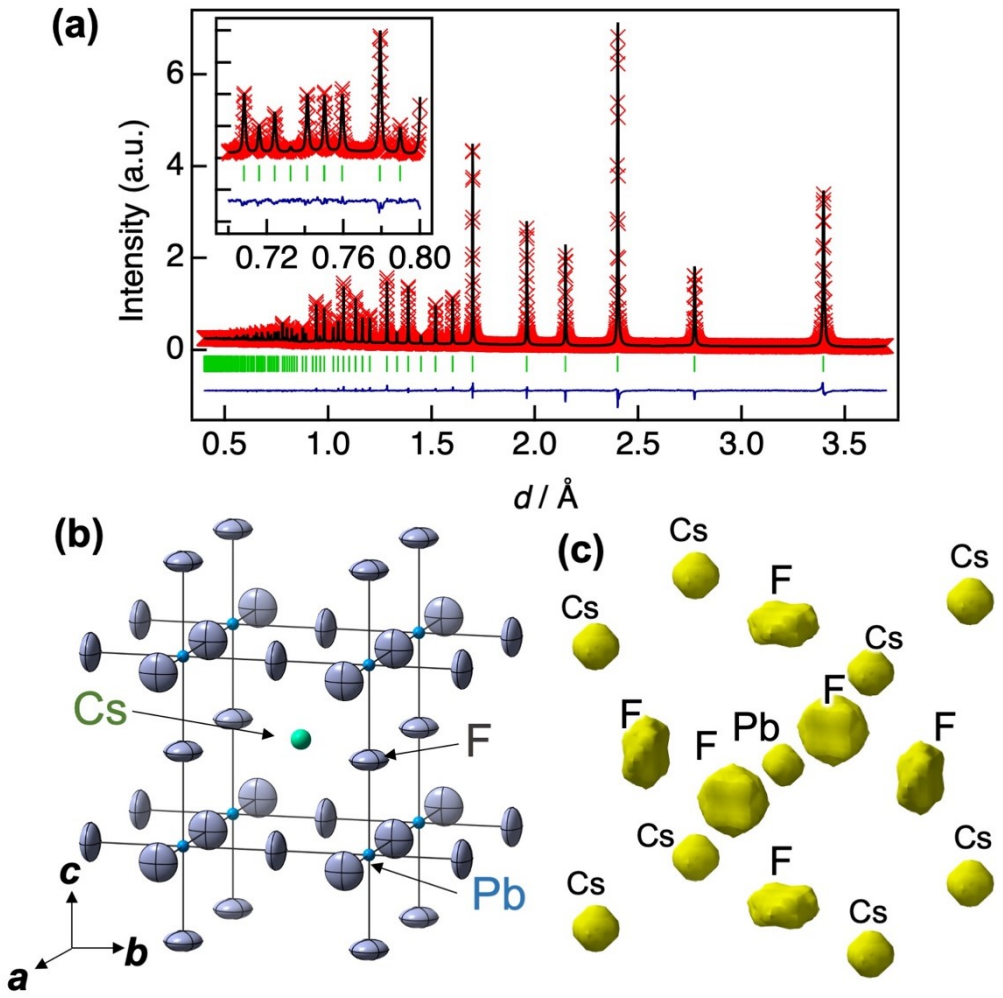

Figure S3. (a) Rietveld refinement result for neutron diffraction data of $CsPbF_3$ at 298 K. Red crosses, black line, blue line, and green marks represent the observed intensity, the calculated intensity, the difference curve, and the positions of the Bragg reflections of cubic- $CsPbF_3$, respectively. (b) The refined structure of $CsPbF_3$. Green, blue, and grey balls represent Cs, Pb, and F atoms, respectively. Thermal ellipsoids are shown with a probability level of 50%. (c) Three-dimensional isosurface of nuclear scattering length density of $CsPbF_3$ obtained from MEM analysis. The yellow isosurfaces correspond to positive nuclear scattering length density at 3 fm $Å^{-3}$

Table S3. Rietveld refinement results from the neutron diffraction data of $CsPbF_3$ at 298 K

Atom	Site	*g*	*x*	*y*	*z*	U_{eq} / Å^2	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2
Cs	1*b*	1	0.5	0.5	0.5	0.02859(9)	0.02859(9)	$=U_{11}$(Cs)	$=U_{11}$(Cs)
Pb	1*a*	1	0	0	0	0.01095(6)	0.01095(6)	$=U_{11}$(Pb)	$=U_{11}$(Pb)
F	3*d*	1	0.5	0	0	0.07620(13)	0.0276(2)	0.1005(2)	$=U_{22}$(F)

Unit cell: cubic *Pm*-3*m* (221); $a = b = c = 4.803166(4)$ Å, R_{wp} =3.36%, R_e = 1.87%, R_p = 2.76%, R_B =2.85%, R_F = 5.64%, goodness of fit $S = R_{wp}/R_e = 1.80$.

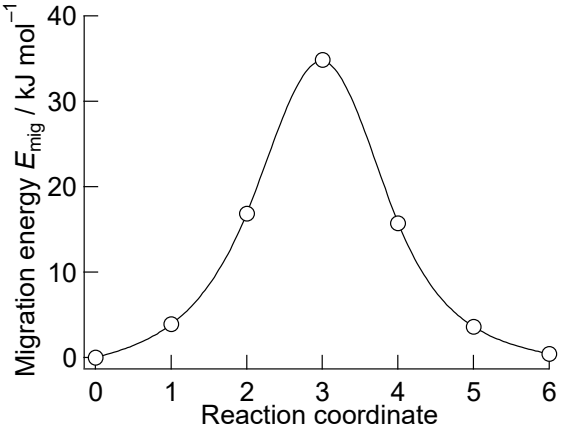

Figure S4. Migration energy of fluoride ions in $CsSrF_3$