Supporting Information

$^{19}F/^{119}Sn/^{207}Pb$ NMR Studies on Ion Dynamics in Tetragonal $PbSnF_4$; Spectroscopic Evidence for Defect-Driven Conductivity

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Table S1. Crystal and Refinement Parameters for β-$PbSnF_4$

Crystal system	Tetragonal
Space group	*P*4/*nmm*
Unit cell dimensions	a = 4.23629(10) Å
	c = 11.45875(55) Å
Volume	205.6408(121)
Z	2
Calculated density	6.490736 g/cm^3
R factors	R_p = 0.06366
	R_{wp} = 0.09572
	R_{ex} = 0.02835
	R_F^2 = 0.08988
# of profile points used	1791

Table S2. Structural Parameters for β-$PbSnF_4$

atom	x	y	z	U_{iso}
Pb	0.750000	0.750000	0.37861(58)	0.020279
Sn	0.250000	0.250000	0.13375(75)	0.011331
F1	0.750000	0.250000	0.20838(135)	0.247351
F2	0.750000	0.250000	0.50000	0.021116
F3	0.250000	0.250000	0.31554(105)	0.189801

Table S3. Anisotropic Thermal Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	0.01870	0.01870	0.02343	0.00000	0.00000	0.00000
Sn	0.01676	0.01676	0.00047	0.00000	0.00000	0.00000
F1	0.02306	0.35947	0.35952	0.00000	0.00000	0.00000
F2	0.01152	0.01152	0.04032	0.00000	0.00000	0.00000
F3	0.25740	0.25740	0.05460	0.00000	0.00000	0.00000

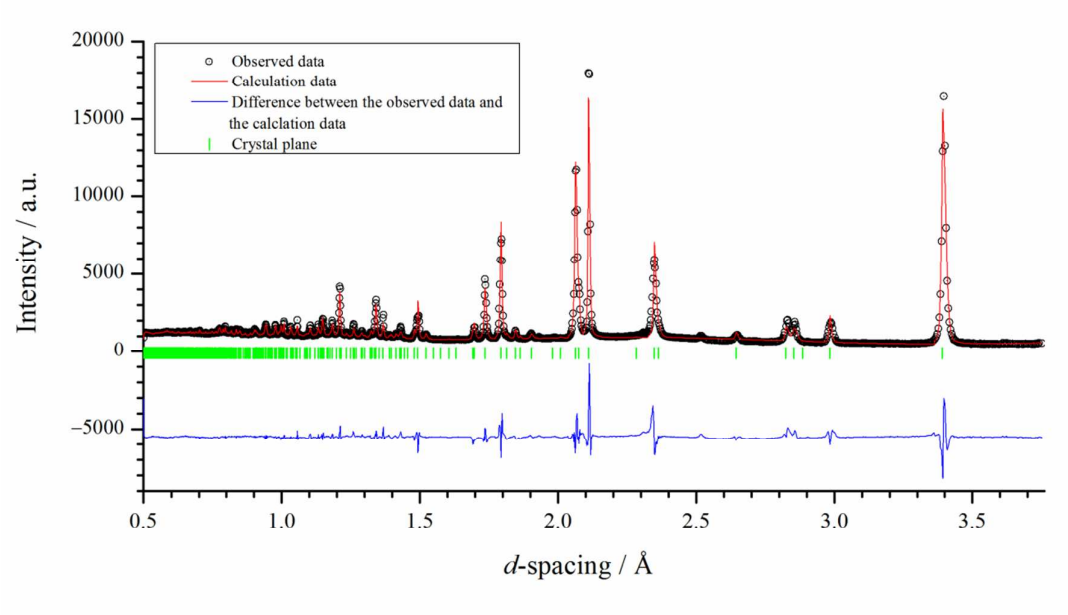

Figure S1. Fitted neutron diffraction profile for β-$PbSnF_4$.

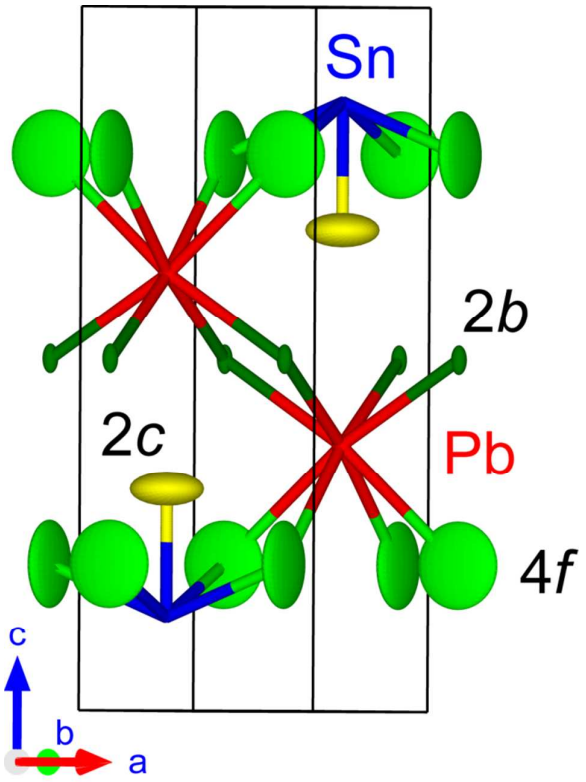

Figure S2. Thermal ellipsoid plots (30 % probability) of β-$PbSnF_4$ in the unit cell. *a*, *b*, and *c* denotes three crystallographic axes. Blue and red balls are Pb and Sn, respectively. The three F sites (2b, 2c, and 4f) are designated by dark green, yellow, and green ellipsoids, respectively.

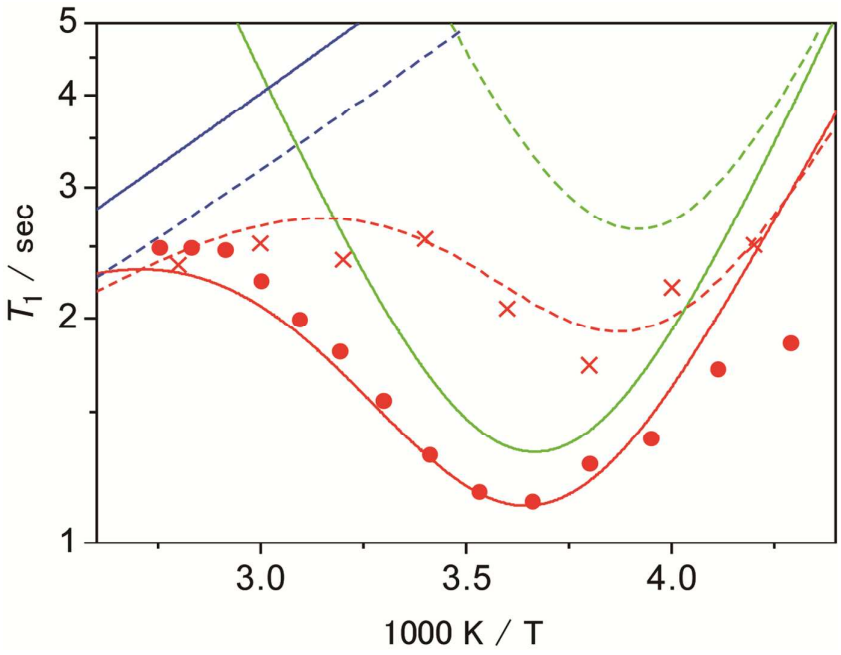

Figure S3. Contribution of the dipolar relaxation and the CSA relaxation to the temperature dependence of the ^{207}Pb spin-lattice relaxation time (T_1) for β-$PbSnF_4$. The filled circles denote the observed T_1 at 14 T and the cross at 7 T. The red solid and dotted curves through the data points are the calculated sum of the two relaxation rate, $(\frac{1}{T_1})_D + (\frac{1}{T_1})_{CSA}$, the blue curves are $(\frac{1}{T_1})_D$, and the red ones are $(\frac{1}{T_1})_{CSA}$. The solid lines are for 14 T and the dotted ones are for 7 T. Each rate function is given in the text, and the parameters for calculation were $A_D = 2.0 \times 10^8$ /s^{-2}, τ_0 and E_a for the dipolar fluctuation = 8×10^{-10} /s and 7.7 kJ/mol, respectively, and τ_0 and E_a for the CSA relaxation = 5×10^{-14} /s and 23 kJ/mol, respectively. A_{CSA} corresponds to $\Delta\sigma(1+\eta^2/3)^{-1/2}$ = 120 ppm with Eq. (6) in the text.

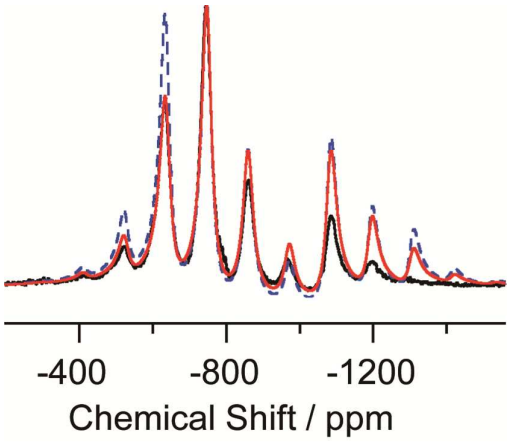

Figure S4. Observed (black) and calculated (red and blue-dotted) ^{119}Sn MAS spectra of β-$PbSnF_4$ taken at 25 ˚C with the MAS frequency of 25 kHz. The CSA parameters obtained from the static spectrum at -40 ˚C (σ_{11} = -534 ppm, σ_{22} = -633 ppm, and σ_{33} = -1412 ppm) were used to calculate the spectrum given in the blue-dotted line. The spectrum given in the red line was calculated with these CSA parameters and the 4-site motion of the σ_{33} axis schematically illustrated in Fig. 2(b) with the apex angle of 34^o and the rate > 10^7 Hz. Apodization by an exponential broadening function (7 kHz) was applied to the calculated FID data before Fourier transformation.

It is notable that the calculated static lineshape (the blue-dotted line) is not consistent with the observed one, while the agreement is better for the calculated one with including motion (the red line). Due most probably to the neglect of the Hahn-echo process in calculation, the observed intensities of the spinning sidebands at the lower-frequency sides are smaller than those calculated one appreciably. As it is difficult to incorporate the Hahn-echo process, molecular motion, and MAS into the simulation program, we have not tried to fit the MAS spectra

.

Some details about simulation algorism

Simulated ^{119}Sn NMR spectra were produced with FORTRAN original programs [1,2]. For the wobbling motion, 4-site jump was assumed. NMR frequency at site *i* was calculated as [3,4]

$$\omega_{CSi} = \sqrt{\frac{2}{3}} \sum_{n,m=-2}^{2} D_{n0}^{(2)}(\psi,\theta,\phi) D_{mn}^{(2)}(\alpha_i,\beta_i,\gamma_i) \rho_{2m}^{CS}, \quad (1)$$

$$\rho_{20}^{CS} = \sqrt{\frac{3}{2}}\left(\sigma_{33} - \frac{1}{3}\mathrm{Tr}\hat{\sigma}\right), \quad \rho_{2\pm2}^{CS} = \frac{1}{2}\left(\sigma_{11} - \sigma_{22}\right), \quad (2)$$

where $D_{mn}^{(2)}(\Omega)$ is the second-order Wigner rotation matrix. $(\alpha_i,\beta_i,\gamma_i)$ and (ψ,θ,ϕ) are the Euler angles for transformation from the principal axes of the chemical shift tensor to the molecular axes and from the molecular axes to the laboratory axes, respectively.

The echo signal $G(t,\theta,\phi)$ is written as

$$G(t,\theta,\phi) = \mathbf{1}\cdot\hat{\mathbf{B}}\exp(\hat{\mathbf{A}}t)\exp(\hat{\mathbf{A}}\tau)\exp(\hat{\mathbf{A}}^{*}\tau)\cdot\mathbf{P}, \quad (3)$$

where $\hat{\mathbf{A}}$ is the matrix with the elements $i\omega_i$ - k_{ii} on the diagonal and k_{ij} off the diagonal. k_{ij} is the jumping rate between site *i* and *j*. $\hat{\mathbf{B}}$ and $\mathbf{P}$ are the matrix for finite pulse width and a vector of site populations, respectively. $\mathbf{1}$ is a vector written as $\mathbf{1} = (1,1,1,1)$.

The signal of a powder sample was calculated by

$$G(t) = \int_0^{2\pi}\int_0^{2\pi} G(t,\theta,\phi)\sin\theta d\theta d\phi. \quad (4)$$

The simulation spectrum was obtained by Fourier transform of $G(t)$.

NMR frequency at site *i* for a sample under MAS is written as

$$\omega_{CSi} = \sqrt{\frac{2}{3}} \sum_{n,k,m=-2}^{2} D_{n0}^{(2)}(0,\theta_m,\omega_r t) D_{kn}^{(2)}(\alpha,\beta,\gamma) D_{mk}^{(2)}(\alpha_i,\beta_i,\gamma_i) \rho_{2m}^{CS}, \quad (5)$$

where $\theta_m (= \cos^{-1} 1/\sqrt{3})$ is the magic angle and ω_r is the sample spinning speed. $(\alpha_i,\beta_i,\gamma_i)$ and (α,β,γ) are the Euler angles for transformation from the principal axes of the chemical shift tensor to the molecular axes and from the molecular axes to the rotor axes, respectively.

The time evolution of the magnetization $M(t)$ is represented by [5]

$$M(t) = \hat{\mathbf{L}}(t) \cdot \mathbf{P}, \tag{6}$$

$$\hat{\mathbf{L}}(t) = T \exp\left[\int_0^t \hat{\mathbf{A}}(t') \mathrm{d}t' \right], \tag{7}$$

where T is the Dyson time-ordering operator.

Here, equal time increment Δt such that $t = n\Delta t$ is considered. By assuming time-independent $\hat{\mathbf{A}}(t)$ for a short period of time Δt, $\hat{\mathbf{L}}(t)$ is written as

$$\hat{\mathbf{L}}(t) = \hat{\mathbf{L}}(n\Delta t) = T \prod_{n'=1}^{n} \hat{\mathbf{S}}\left((n'-1)\Delta t\right) \exp\left[\hat{\mathbf{\Lambda}}((n'-1)\Delta t)\Delta t\right] \hat{\mathbf{S}}\left((n'-1)\Delta t\right)^{-1}, \tag{8}$$

$$\hat{\mathbf{\Lambda}}((n'-1)\Delta t) = \hat{\mathbf{S}}\left((n'-1)\Delta t\right)^{-1} \hat{\mathbf{A}}((n'-1)\Delta t) \hat{\mathbf{S}}\left((n'-1)\Delta t\right), \tag{9}$$

where $\hat{\mathbf{S}}\left((n'-1)\Delta t\right)$ is the matrix which transforms $\hat{\mathbf{A}}((n'-1)\Delta t)$ into a diagonal matrix $\hat{\mathbf{\Lambda}}((n'-1)\Delta t)$. When one rotor period is divided into n_{rot} equal periods Δt, the following relation is obtained

$$\exp\left[\hat{\mathbf{\Lambda}}((n_{\mathrm{rot}}+1)\Delta t)\Delta t\right] = \exp\left[\hat{\mathbf{\Lambda}}(\Delta t)\Delta t\right]. \tag{10}$$

Once $\hat{\mathbf{\Lambda}}((n'-1)\Delta t)$ and $\hat{\mathbf{S}}\left((n'-1)\Delta t\right)$ are estimated over one rotor period, $\hat{\mathbf{L}}(t)$ at subsequent times are calculated using these matrices and eq.(10). The NMR signal is given by

$$G(\alpha, \beta, \gamma, t) = \mathbf{1} \cdot \hat{\mathbf{B}} \cdot \hat{\mathbf{L}}(t) \cdot \mathbf{P} \tag{11}$$

The signal of a powder sample was calculated by

$$G(t) = \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} G(\alpha, \beta, \gamma, t) \sin\beta \mathrm{d}\alpha \mathrm{d}\beta \mathrm{d}\gamma. \tag{12}$$

The simulation spectrum was obtained by Fourier transform of $G(t)$. Note here that we did not take the Hahn-echo process in the MAS simulation and hence the fitting in Figure S4 was not satisfactorily.

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[3] Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: London, 1994.

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