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Synthesis, crystal structure, DFT, and photovoltaic studies of $BaCeCuS_3$

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Electronic Supplementary Information (ESI)

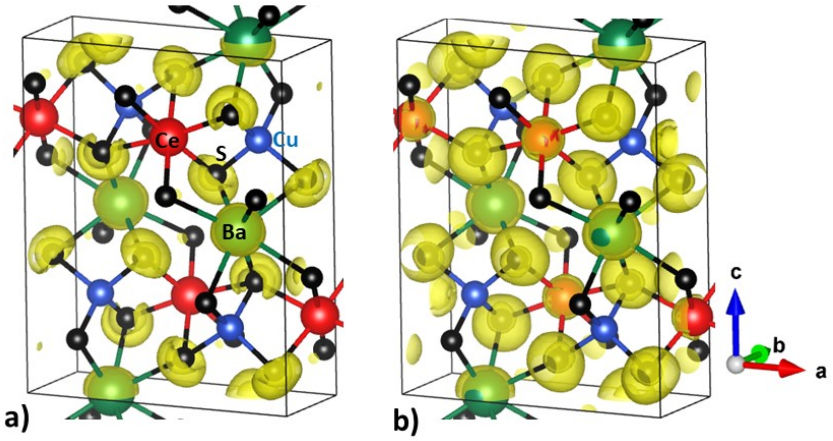

Fig SI1: The 3D iso-surfaces of the electron localization function (ELF) for $BaCeCuS_3$ with **(a)** $ELF = 0.80$ and **(b)** $ELF = 0.75$**.** The yellow cloud indicates the density of transferred charge.

Table SI1 Atomic displacement parameters ($Å^2$) for the $BaCeCuS_3$ structure.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
$BaCeCuS_3$						
Ba1	0.02149(19)	0.01205(16)	0.01333(17)	0.000	−0.00111(13)	0.000
Ce1	0.00723(14)	0.00772(14)	0.01306(15)	0.000	0.00010(10)	0.000
Cu1	0.0126(3)	0.0215(4)	0.0157(4)	0.000	0.0008(3)	0.000
S1	0.0111(6)	0.0101(5)	0.0108(6)	0.000	0.0009(5)	0.000
S2	0.0084(5)	0.0096(5)	0.0115(6)	0.000	−0.0004(4)	0.000
S3	0.0133(6)	0.0108(5)	0.0110(6)	0.000	−0.0003(5)	0.000

Table SI2 All the bond angles (in degrees) in $BaCeCuS_3$

$S2^{i}$—Ba1—$S2^{ii}$	81.54 (4)	$S3^{viii}$—Ce1—$Ce1^{v}$	43.37 (2)
$S2^{i}$—Ba1—$S3^{ii}$	134.76 (3)	$S1^{ix}$—Ce1—$Ce1^{v}$	44.13 (2)
$S2^{ii}$—Ba1—$S3^{ii}$	82.70 (3)	$S1^{x}$—Ce1—$Ce1^{v}$	135.87 (2)
$S2^{i}$—Ba1—$S3^{i}$	82.70 (3)	$Cu1^{vii}$—Ce1—$Ce1^{v}$	127.412 (9)
$S2^{ii}$—Ba1—$S3^{i}$	134.76 (3)	$Cu1^{viii}$—Ce1—$Ce1^{v}$	52.589 (9)
$S3^{ii}$—Ba1—$S3^{i}$	79.07 (3)	$Cu1^{ix}$—Ce1—$Ce1^{v}$	52.883 (9)
$S2^{i}$—Ba1—$S1^{i}$	92.20 (3)	$Cu1^{x}$—Ce1—$Ce1^{v}$	127.116 (9)
$S2^{ii}$—Ba1—$S1^{i}$	150.38 (3)	$S2^{vi}$—Ce1—$Ce1^{iv}$	90.0
$S3^{ii}$—Ba1—$S1^{i}$	120.17 (3)	S2—Ce1—$Ce1^{iv}$	90.0
$S3^{i}$—Ba1—$S1^{i}$	72.09 (3)	$S3^{vii}$—Ce1—$Ce1^{iv}$	43.37 (2)
$S2^{i}$—Ba1—$S1^{ii}$	150.38 (3)	$S3^{viii}$—Ce1—$Ce1^{iv}$	136.63 (2)
$S2^{ii}$—Ba1—$S1^{ii}$	92.20 (3)	$S1^{ix}$—Ce1—$Ce1^{iv}$	135.87 (2)
$S3^{ii}$—Ba1—$S1^{ii}$	72.09 (3)	$S1^{x}$—Ce1—$Ce1^{iv}$	44.13 (2)
$S3^{i}$—Ba1—$S1^{ii}$	120.17 (3)	$Cu1^{vii}$—Ce1—$Ce1^{iv}$	52.589 (9)
$S1^{i}$—Ba1—$S1^{ii}$	79.03 (3)	$Cu1^{viii}$—Ce1—$Ce1^{iv}$	127.412 (9)
$S2^{i}$—Ba1—$S1^{iii}$	75.41 (3)	$Cu1^{ix}$—Ce1—$Ce1^{iv}$	127.116 (9)
$S2^{ii}$—Ba1—$S1^{iii}$	75.41 (3)	$Cu1^{x}$—Ce1—$Ce1^{iv}$	52.883 (9)
$S3^{ii}$—Ba1—$S1^{iii}$	139.386 (18)	$Ce1^{v}$—Ce1—$Ce1^{iv}$	180.0
$S3^{i}$—Ba1—$S1^{iii}$	139.386 (18)	S1—Cu1—S3	108.10 (6)
$S1^{i}$—Ba1—$S1^{iii}$	74.99 (3)	S1—Cu1—$S2^{ii}$	108.60 (4)
$S1^{ii}$—Ba1—$S1^{iii}$	74.99 (3)	S3—Cu1—$S2^{ii}$	108.88 (4)
$S2^{i}$—Ba1—$Cu1^{ii}$	169.52 (3)	S1—Cu1—$S2^{i}$	108.60 (4)
$S2^{ii}$—Ba1—$Cu1^{ii}$	104.08 (2)	S3—Cu1—$S2^{i}$	108.88 (4)
$S3^{ii}$—Ba1—$Cu1^{ii}$	39.54 (3)	$S2^{ii}$—Cu1—$S2^{i}$	113.63 (6)
$S3^{i}$—Ba1—$Cu1^{ii}$	87.14 (2)	S1—Cu1—$Ce1^{i}$	134.96 (2)
$S1^{i}$—Ba1—$Cu1^{ii}$	87.08 (2)	S3—Cu1—$Ce1^{i}$	55.64 (3)
$S1^{ii}$—Ba1—$Cu1^{ii}$	39.47 (3)	$S2^{ii}$—Cu1—$Ce1^{i}$	116.38 (4)
$S1^{iii}$—Ba1—$Cu1^{ii}$	114.38 (2)	$S2^{i}$—Cu1—$Ce1^{i}$	55.07 (3)
$S2^{i}$—Ba1—$Cu1^{i}$	104.08 (2)	S1—Cu1—$Ce1^{ii}$	134.96 (2)

S2^{ii}—Ba1—Cu1^{i}	169.52 (3)	S3—Cu1—Ce1^{ii}	55.64 (3)
S3^{ii}—Ba1—Cu1^{i}	87.14 (2)	S2^{ii}—Cu1—Ce1^{ii}	55.07 (3)
S3^{i}—Ba1—Cu1^{i}	39.54 (3)	S2^{i}—Cu1—Ce1^{ii}	116.38 (4)
S1^{i}—Ba1—Cu1^{i}	39.47 (3)	Ce1^{i}—Cu1—Ce1^{ii}	74.822 (19)
S1^{ii}—Ba1—Cu1^{i}	87.08 (2)	S1—Cu1—Ce1^{ix}	56.13 (3)
S1^{iii}—Ba1—Cu1^{i}	114.38 (2)	S3—Cu1—Ce1^{ix}	135.67 (2)
Cu1^{ii}—Ba1—Cu1^{i}	69.030 (19)	S2^{ii}—Cu1—Ce1^{ix}	54.49 (3)
S2^{i}—Ba1—Cu1	40.810 (19)	S2^{i}—Cu1—Ce1^{ix}	115.41 (4)
S2^{ii}—Ba1—Cu1	40.810 (19)	Ce1^{i}—Cu1—Ce1^{ix}	165.31 (3)
S3^{ii}—Ba1—Cu1	113.88 (3)	Ce1^{ii}—Cu1—Ce1^{ix}	103.537 (11)
S3^{i}—Ba1—Cu1	113.88 (3)	S1—Cu1—Ce1^{x}	56.13 (3)
S1^{i}—Ba1—Cu1	125.55 (2)	S3—Cu1—Ce1^{x}	135.67 (2)
S1^{ii}—Ba1—Cu1	125.55 (2)	S2^{ii}—Cu1—Ce1^{x}	115.41 (4)
S1^{iii}—Ba1—Cu1	68.52 (3)	S2^{i}—Cu1—Ce1^{x}	54.49 (3)
Cu1^{ii}—Ba1—Cu1	144.563 (10)	Ce1^{i}—Cu1—Ce1^{x}	103.537 (11)
Cu1^{i}—Ba1—Cu1	144.563 (10)	Ce1^{ii}—Cu1—Ce1^{x}	165.31 (3)
S2^{i}—Ba1—Ba1^{iv}	49.233 (18)	Ce1^{ix}—Cu1—Ce1^{x}	74.234 (18)
S2^{ii}—Ba1—Ba1^{iv}	130.768 (18)	S1—Cu1—Ba1^{vii}	61.09 (3)
S3^{ii}—Ba1—Ba1^{iv}	129.534 (17)	S3—Cu1—Ba1^{vii}	61.05 (3)
S3^{i}—Ba1—Ba1^{iv}	50.467 (17)	S2^{ii}—Cu1—Ba1^{vii}	157.70 (4)
S1^{i}—Ba1—Ba1^{iv}	50.484 (16)	S2^{i}—Cu1—Ba1^{vii}	88.67 (3)
S1^{ii}—Ba1—Ba1^{iv}	129.514 (16)	Ce1^{i}—Cu1—Ba1^{vii}	75.832 (13)
S1^{iii}—Ba1—Ba1^{iv}	90.0	Ce1^{ii}—Cu1—Ba1^{vii}	116.34 (2)
Cu1^{ii}—Ba1—Ba1^{iv}	124.514 (10)	Ce1^{ix}—Cu1—Ba1^{vii}	116.95 (2)
Cu1^{i}—Ba1—Ba1^{iv}	55.485 (10)	Ce1^{x}—Cu1—Ba1^{vii}	76.661 (13)
Cu1—Ba1—Ba1^{iv}	90.0	S1—Cu1—Ba1^{viii}	61.09 (3)
S2^{i}—Ba1—Ba1^{v}	130.768 (18)	S3—Cu1—Ba1^{viii}	61.05 (3)
S2^{ii}—Ba1—Ba1^{v}	49.233 (18)	S2^{ii}—Cu1—Ba1^{viii}	88.67 (3)
S3^{ii}—Ba1—Ba1^{v}	50.467 (17)	S2^{i}—Cu1—Ba1^{viii}	157.70 (4)
S3^{i}—Ba1—Ba1^{v}	129.534 (17)	Ce1^{i}—Cu1—Ba1^{viii}	116.34 (2)

S1^{i}—Ba1—Ba1^{v}	129.514 (16)	Ce1^{ii}—Cu1—Ba1^{viii}	75.832 (13)
S1^{ii}—Ba1—Ba1^{v}	50.484 (16)	Ce1^{ix}—Cu1—Ba1^{viii}	76.661 (13)
S1^{iii}—Ba1—Ba1^{v}	90.0	Ce1^{x}—Cu1—Ba1^{viii}	116.95 (2)
Cu1^{ii}—Ba1—Ba1^{v}	55.485 (10)	Ba1^{vii}—Cu1—Ba1^{viii}	69.030 (19)
Cu1^{i}—Ba1—Ba1^{v}	124.514 (10)	S1—Cu1—Ba1	129.30 (4)
Cu1—Ba1—Ba1^{v}	90.0	S3—Cu1—Ba1	122.60 (4)
Ba1^{iv}—Ba1—Ba1^{v}	180.0	S2^{ii}—Cu1—Ba1	56.89 (3)
S2^{vi}—Ce1—S2	173.75 (2)	S2^{i}—Cu1—Ba1	56.89 (3)
S2^{vi}—Ce1—S3^{vii}	96.69 (4)	Ce1^{i}—Cu1—Ba1	80.399 (16)
S2—Ce1—S3^{vii}	87.59 (4)	Ce1^{ii}—Cu1—Ba1	80.399 (16)
S2^{vi}—Ce1—S3^{viii}	96.69 (4)	Ce1^{ix}—Cu1—Ba1	84.927 (17)
S2—Ce1—S3^{viii}	87.59 (3)	Ce1^{x}—Cu1—Ba1	84.927 (17)
S3^{vii}—Ce1—S3^{viii}	93.27 (4)	Ba1^{vii}—Cu1—Ba1	145.341 (10)
S2^{vi}—Ce1—S1^{ix}	86.79 (3)	Ba1^{viii}—Cu1—Ba1	145.341 (10)
S2—Ce1—S1^{ix}	88.87 (3)	Cu1—S1—Ce1^{ix}	81.01 (4)
S3^{vii}—Ce1—S1^{ix}	176.36 (4)	Cu1—S1—Ce1^{x}	81.01 (4)
S3^{viii}—Ce1—S1^{ix}	87.38 (3)	Ce1^{ix}—S1—Ce1^{x}	91.75 (4)
S2^{vi}—Ce1—S1^{x}	86.79 (3)	Cu1—S1—Ba1^{vii}	79.43 (4)
S2—Ce1—S1^{x}	88.87 (3)	Ce1^{ix}—S1—Ba1^{vii}	159.46 (5)
S3^{vii}—Ce1—S1^{x}	87.38 (3)	Ce1^{x}—S1—Ba1^{vii}	91.316 (15)
S3^{viii}—Ce1—S1^{x}	176.36 (4)	Cu1—S1—Ba1^{viii}	79.43 (4)
S1^{ix}—Ce1—S1^{x}	91.75 (4)	Ce1^{ix}—S1—Ba1^{viii}	91.316 (15)
S2^{vi}—Ce1—Cu1^{vii}	137.492 (18)	Ce1^{x}—S1—Ba1^{viii}	159.46 (5)
S2—Ce1—Cu1^{vii}	45.524 (19)	Ba1^{vii}—S1—Ba1^{viii}	79.03 (3)
S3^{vii}—Ce1—Cu1^{vii}	43.31 (3)	Cu1—S1—Ba1^{xi}	174.14 (6)
S3^{viii}—Ce1—Cu1^{vii}	98.96 (3)	Ce1^{ix}—S1—Ba1^{xi}	94.95 (3)
S1^{ix}—Ce1—Cu1^{vii}	133.05 (3)	Ce1^{x}—S1—Ba1^{xi}	94.95 (3)
S1^{x}—Ce1—Cu1^{vii}	79.08 (3)	Ba1^{vii}—S1—Ba1^{xi}	105.00 (3)
S2^{vi}—Ce1—Cu1^{viii}	137.492 (18)	Ba1^{viii}—S1—Ba1^{xi}	105.00 (3)
S2—Ce1—Cu1^{viii}	45.524 (19)	Cu1^{vii}—S2—Cu1^{viii}	113.63 (6)

S3^{vii}—Ce1—Cu1^{viii}	98.96 (3)	Cu1^{vii}—S2—Ce1^{xii}	80.23 (4)
S3^{viii}—Ce1—Cu1^{viii}	43.31 (3)	Cu1^{viii}—S2—Ce1^{xii}	80.23 (4)
S1^{ix}—Ce1—Cu1^{viii}	79.08 (3)	Cu1^{vii}—S2—Ce1	79.40 (4)
S1^{x}—Ce1—Cu1^{viii}	133.05 (3)	Cu1^{viii}—S2—Ce1	79.40 (4)
Cu1^{vii}—Ce1—Cu1^{viii}	74.822 (18)	Ce1^{xii}—S2—Ce1	142.31 (5)
S2^{vi}—Ce1—Cu1^{ix}	45.282 (19)	Cu1^{vii}—S2—Ba1^{viii}	163.53 (5)
S2—Ce1—Cu1^{ix}	131.19 (2)	Cu1^{viii}—S2—Ba1^{viii}	82.30 (2)
S3^{vii}—Ce1—Cu1^{ix}	140.76 (3)	Ce1^{xii}—S2—Ba1^{viii}	107.77 (3)
S3^{viii}—Ce1—Cu1^{ix}	84.10 (3)	Ce1—S2—Ba1^{viii}	100.51 (3)
S1^{ix}—Ce1—Cu1^{ix}	42.86 (3)	Cu1^{vii}—S2—Ba1^{vii}	82.30 (2)
S1^{x}—Ce1—Cu1^{ix}	97.66 (3)	Cu1^{viii}—S2—Ba1^{vii}	163.53 (5)
Cu1^{vii}—Ce1—Cu1^{ix}	175.051 (11)	Ce1^{xii}—S2—Ba1^{vii}	107.77 (3)
Cu1^{viii}—Ce1—Cu1^{ix}	105.251 (11)	Ce1—S2—Ba1^{vii}	100.51 (3)
S2^{vi}—Ce1—Cu1^{x}	45.282 (19)	Ba1^{viii}—S2—Ba1^{vii}	81.53 (4)
S2—Ce1—Cu1^{x}	131.19 (2)	Cu1—S3—Ce1^{ii}	81.05 (4)
S3^{vii}—Ce1—Cu1^{x}	84.10 (3)	Cu1—S3—Ce1^{i}	81.05 (4)
S3^{viii}—Ce1—Cu1^{x}	140.76 (3)	Ce1^{ii}—S3—Ce1^{i}	93.27 (4)
S1^{ix}—Ce1—Cu1^{x}	97.66 (3)	Cu1—S3—Ba1^{viii}	79.41 (4)
S1^{x}—Ce1—Cu1^{x}	42.86 (3)	Ce1^{ii}—S3—Ba1^{viii}	90.552 (15)
Cu1^{vii}—Ce1—Cu1^{x}	105.251 (11)	Ce1^{i}—S3—Ba1^{viii}	159.25 (5)
Cu1^{viii}—Ce1—Cu1^{x}	175.051 (11)	Cu1—S3—Ba1^{vii}	79.41 (4)
Cu1^{ix}—Ce1—Cu1^{x}	74.234 (18)	Ce1^{ii}—S3—Ba1^{vii}	159.25 (5)
S2^{vi}—Ce1—Ce1^{v}	90.0	Ce1^{i}—S3—Ba1^{vii}	90.552 (15)
S2—Ce1—Ce1^{v}	90.0	Ba1^{viii}—S3—Ba1^{vii}	79.07 (3)
S3^{vii}—Ce1—Ce1^{v}	136.63 (2)		

Symmetry codes: (i) −*x*+1/2, *y*+1/2, *z*−1/2; (ii) −*x*+1/2, *y*−1/2, *z*−1/2; (iii) *x*+1/2, −*y*+1/2, −*z*+1/2; (iv) *x*, *y*+1, *z*; (v) *x*, *y*−1, *z*; (vi) *x*−1/2, −*y*+1/2, −*z*+3/2; (vii) −*x*+1/2, *y*+1/2, *z*+1/2; (viii) −*x*+1/2, *y*−1/2, *z*+1/2; (ix) −*x*, −*y*, −*z*+1; (x) −*x*, −*y*+1, −*z*+1; (xi) *x*−1/2, −*y*+1/2, −*z*+1/2; (xii) *x*+1/2, −*y*+1/2, −*z*+3/2.

Section SI1: Optical Properties

The optical parameters are computed from the complex dielectric function $\varepsilon(\omega) = \varepsilon^{'}(\omega) + \varepsilon^{''}(\omega)$. The imaginary part of the dielectric function $\varepsilon^{''}(\omega)$ is given in terms of electronic band structure as

$$\varepsilon_{ij}^{''}(\omega) = \frac{4\pi^2 e^2}{V} \lim_{q \to 0} \sum_{c,v,\vec{k}} 2w_{\vec{k}} \delta\left(\varepsilon_{c\vec{k}} - \varepsilon_{v\vec{k}} - \omega\right) \times \left\langle u_{c\vec{k}+\hat{e}_i q} \middle| u_{v\vec{k}} \right\rangle \left\langle u_{c\vec{k}+\hat{e}_j q} \middle| u_{v\vec{k}} \right\rangle^{*} \quad \text{(S1-1)}$$

where index *v* indicates the valence band (VB), *c* indicates the conduction band (CB) states; V is the volume of the unit cell; $\varepsilon_{c\vec{k}}$ and $\varepsilon_{v\vec{k}}$ are CB and VB single-electron energy at $\vec{k}$; $u_{c\vec{k}}$ is the cell periodic part of the orbitals at the wave vector $\vec{k}$; $w_{\vec{k}}$ is the weight of the k-points, $\hat{e}_i$ and $\hat{e}_j$ are the unit vectors for the three Cartesian directions.

The Kramers-Kronig transformation is used to obtain the real part of the dielectric function $\varepsilon^{'}(\omega)$ from $\varepsilon^{''}(\omega)$:

$$\varepsilon_{ij}^{'}(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\varepsilon_{ij}^{''}(\omega^{'})\omega^{'}}{\omega^{'2} - \omega^2 + i\eta} d\omega^{'} \quad \text{(S1-2)}$$

Where P is the principal value and η is a small complex shift. The absorption coefficient $\alpha(\omega)$ can be expressed in terms of $\varepsilon^{'}(\omega)$ and $\varepsilon^{''}(\omega)$ as:

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c}\left[\sqrt{\varepsilon^{'}(\omega)^2 + \varepsilon^{''}(\omega)^2} - \varepsilon^{'}(\omega)\right]^{1/2} \quad \text{(S1-3)}$$

Section SI2: Thermoelectric properties

The thermoelectric parameters can be computed using the electronic band structure and semi-classical Boltzmann transport theory within the rigid band approach.

The shift in the chemical potential can be used to simulate the carrier concentration (*p*- or *n*-type) in the system. The electrical conductivity (σ_{ij}) can be expressed in terms of chemical potential (μ) and temperature (T) as:

$$\sigma_{ij}(T;\mu) = \frac{1}{V}\int \sigma_{ij}(\epsilon)\left[-\frac{\partial f_{\mu}(T;\mu)}{\partial \epsilon}\right] d\epsilon \quad \text{(S2-1)}$$

where $f_{\mu}(T;\mu)$ is the Fermi function, V is the volume, ϵ is the energy. Further, the σ_{ij} as function of energy (ϵ) can be expressed as:

$$\sigma_{ij}(\epsilon) = \frac{1}{N}\sum_{n,\vec{k}} \sigma_{ij}(n,\vec{k})\ \delta\left(\epsilon - \epsilon_{n,\vec{k}}\right) \tag{S2-2}$$

Where N is the number of $\vec{k}$ points in the Brillouin zone and $\epsilon_{n,\vec{k}}$ are the band energies. $\sigma_{ij}(n,\vec{k})$ can be obtained using relaxation time $\tau_{n,\vec{k}}$ and group velocity $\vec{v}(n,\vec{k})$ as:

$$\sigma_{ij}(n,\vec{k}) = e^2\tau_{n,\vec{k}} v_i(n,\vec{k}) v_j(n,\vec{k}) \tag{S2-3}$$

The Seebeck coefficient tensor (S_{ij}) as a function of temperature (T) and chemical potential (μ) can be expressed as:

$$S_{ij}(T;\mu) = \frac{1}{eTV\sigma_{ij}(T;\mu)} \int \sigma_{ij}(\epsilon)(\epsilon - \mu)\left[-\frac{\partial f_{\mu}(T;\mu)}{\partial \epsilon}\right] d\epsilon \tag{S2-4}$$

The figure of merit (zT) is given as $zT = \frac{S^2\sigma T}{(k_{el} + k_{lat})}$. Here, the k_{el} is the electronic component and k_l is the lattice (phonon) component of thermal conductivity. The k_{el} is related to electrical conductivity (σ) as $k_{el} = L_0\sigma T$ (Wiedemann-Franz relation), where $L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$ is the Lorentz number. The quantities σ and k_{el} are computed with respect to the relaxation time $\tau = \left(T_0 \times n_0^{1/3}\right)/\left(Tn^{1/3}\right) \times 10^{-14} s$ where n_0 is the carrier concentration at $T_0 = 300\ K$.