Supporting information for

Phase transition, optical and dielectric properties regulated by anion-substitution in a homologous series of 2D hybrid organic-inorganic perovskites

Wen-Juan Wei,[†] Chao Li,[†] Lin-Sui Li,[†] Yun-Zhi Tang,*[†] Xing-Xing Jiang,*[‡] Zhe-Shuai Lin*[‡]

[†]*Engineering Research Institute, Jiangxi University of Science and Technology, Ganzhou 341000, China*
[‡]*Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

Methods

Synthesis

All chemicals and solvents were of reagent grade and used as received. Single crystals of [(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbX$_4$ (X= Cl$^-$, Br$^-$, I$^-$) are synthesized as follow:

[(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbCl$_4$. PbCl$_2$ (0.278g, 1mmol) was dissolved in 4 mL concentrated hydrochloric acid HCl solution in a beaker. Then add 2 mmol thienylmethylamine to 2 mL H$_2$O in another beaker. Whereafter, the latter was slowly dripped into the former along the wall. Several days later, colorless transparent plate crystals were precipitated.

[(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbBr$_4$. Similar to the above synthesis procedure, only replace PbCl$_2$ and HCl with PbBr$_2$ and HBr, respectively. Several days later, colorless transparent plate crystals were precipitated.

[(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbI$_4$. Likewise, PbI$_2$ (0.461 mg, 1mmol) was dissolved in 4 mL hydroiodic acid HI solution in a beaker. However, add 2 mmol thienylmethylamine to 2 mL HI in another beaker, which is different from the previous step. After mixing the above two solutions, yellow precipitate appeared. Then it is stirred in water bath at 90 ℃ for 30 min, the precipitate dissolved. Finally, the solution is filtered and cooled to room temperature, yellow plate crystals precipitated, which is similar to the reported synthetic crystals.[1]

Single crystal X-ray diffraction

Single crystal X-ray diffractions were carried out with graphite monochromated Mo radiation (λ = 0.71073 Å) on an Oxford Diffraction Gemini E Ultra diffractometer. Data sets were collected by using *CrysAlis^{Pro}* software. The program Olex2-1.2 was employed as an interface to invoke program SHELXS97 and SHELXL97 executables. The crystal structures were solved by direct methods with SHELXS97 and refined by full-matrix least squares on F^2 with anisotropic atomic displacement parameters for all non-hydrogen atoms using SHELXL97. All H atoms were located from molecular geometric calculations and refined with isotropic temperature parameters. The crystallographic information of [(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbX$_4$ (X= Cl$^-$, Br$^-$, I$^-$) crystal structures determined at temperatures far from their respective phase transition have been deposited in the CIF format in the Cambridge Crystallographic Database Centre as supplementary material, CCDC 1935993-1935997.
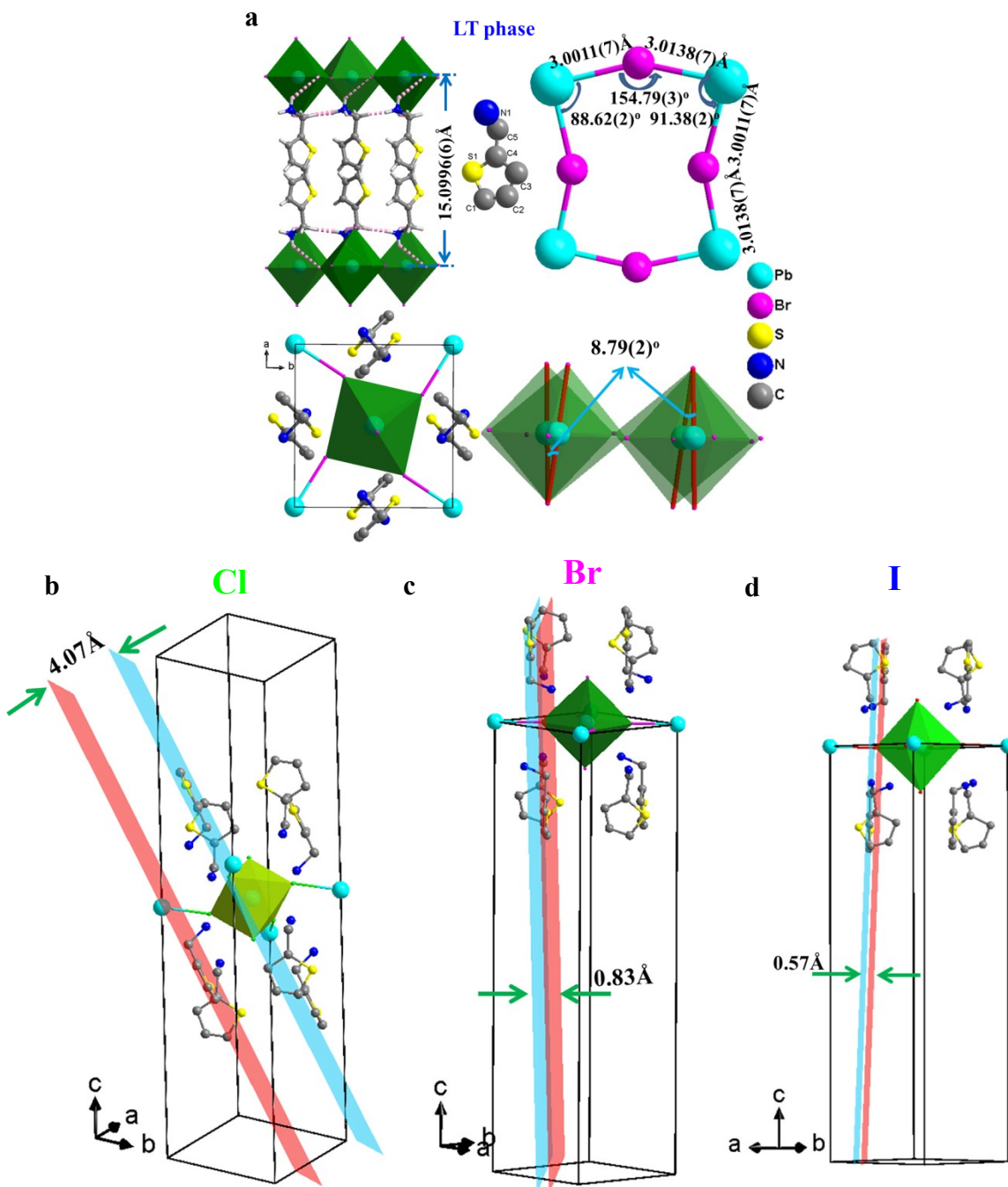
Figure S1. (a) The LT phase crystal structure of $[(C_4H_3S)CH_2NH_3]_2PbBr_4$. (b-d) The planes formed by the five-membered rings on the front and rear $[(C_4H_3S)CH_2NH_3]^+$ cations in $[(C_4H_3S)CH_2NH_3]_2PbX_4$ (X= Cl⁻, Br⁻, I⁻), respectively.

Table S1. Crystal data and structure refinement details for [(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbX$_4$ (X= Cl⁻, Br⁻, I⁻).

	[(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbCl$_4$		[(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbBr$_4$	[(C$_4$H$_3$S)CH$_2$NH$_3$]$_2$PbI$_4$	
Temperature (K)	293	415	293	212	293
Formula weight	577.39	577.39	755.19	943.19	943.19
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pbca*	*Cmca*	*Pbca*	*Cmca*	*Pbca*
a (Å)	7.6733(4)	32.397(7)	8.4013(3)	29.051(2)	8.810(2)
b (Å)	7.6733(4)	7.7997(13)	8.2000(3)	8.6982(6)	8.6780(19)
c (Å)	32.330(3)	7.7943(14)	29.0071(12)	8.7096(6)	28.972(6)
Volume (Å^3)	1903.6(2)	1969.5 (6)	1998.32(13)	2200.8 (3)	2215.0(8)
Z	4	4	4	2	4
Density (g/cm^3)	2.022	0.254	2.510	2.924	2.812
Mu (mm^{-1})	9.633	2.190	16.640	13.309	13.306
F(000)	1096.0	129.0	1376.0	1684.0	1670.0
Theta range (°)	5.04 ~ 50	7.5 ~ 55.18	5.604 ~ 63.218	5.61 ~ 55.014	5.412 ~ 55.228
Index ranges	-9≤h≤9, -9≤k≤8, -38≤l≤38	-40≤*h*≤42, -10≤*k*≤9, -9≤*l*≤10	-10≤h≤10, -10≤k≤11, -42≤l≤40	-37≤*h*≤35, -10≤*k*≤11, -11≤*l*≤11	-11≤h≤11, -11≤k≤11, -36≤l≤37
Data / restraints / parameters	1678 / 0 / 89	1160 / 12 / 49	2868 / 0 / 89	1281 / 80 / 64	2566 /129 / 92
Goodness-of-fit on *F*^{2}	1.258	1.029	1.126	1.175	1.246
Final *R* indices [*I* > 2sigma(I)]	*R*1 = 0.0337 *wR*2 = 0.0709	*R*1 = 0.0294 *wR*2 = 0.0725	*R*1 = 0.0432 *wR*2 = 0.0886	*R*1 = 0.0428 *wR*2 = 0.0934	*R*1 = 0.0620 *wR*2 = 0.1313
R indices (all data)	*R*1 = 0.0374 *wR*2 = 0.0721	*R*1 = 0.0487 *wR*2 = 0.0826	*R*1 = 0.0655 *wR*2 = 0.0959	*R*1 = 0.0477 *wR*2 = 0.0955	*R*1 = 0.0888 *wR*2 = 0.1402

Table S2. The Pb-X bonds lengths in $[(C_4H_3S)CH_2NH_3]_2PbX_4$ (X= Cl⁻, Br⁻, I⁻) at LT and HT phases, respectively.

	Temperature (K)	
	295	415
Pb-Cl	2.8770(16)	2.8402(33)
	2.8603(15)	2.8589(18)
	2.8399(15)	2.8600(22)
	295	
Pb-Br	3.0054(19)	
	3.0011(7)	
	3.0138(7)	
	295	212
Pb-I	3.2067(13)	3.1889(12)
	3.1801(11)	3.1800(9)
	3.1715(12)	3.1791(10)

DSC and TGA

At ambient pressure thermal properties of $[(C_4H_3S)CH_2NH_3]_2PbX_4$ (X= Cl⁻, Br⁻, I⁻) were studied by differential scanning calorimetry (DSC) using a TA Q2000 DSC instrument. The DSC runs were recorded on cooling and on heating the powdered sample at the rate of temperature changes of 10 K/min. Indium standard was used for the temperature and enthalpy calibration. Thermogravimetric analysis (TGA) measurement was performed on a TA-Instruments STD2960 system from room temperature to 1050 K in nitrogen atmosphere at a rate of 10 K/min (Figure S3).
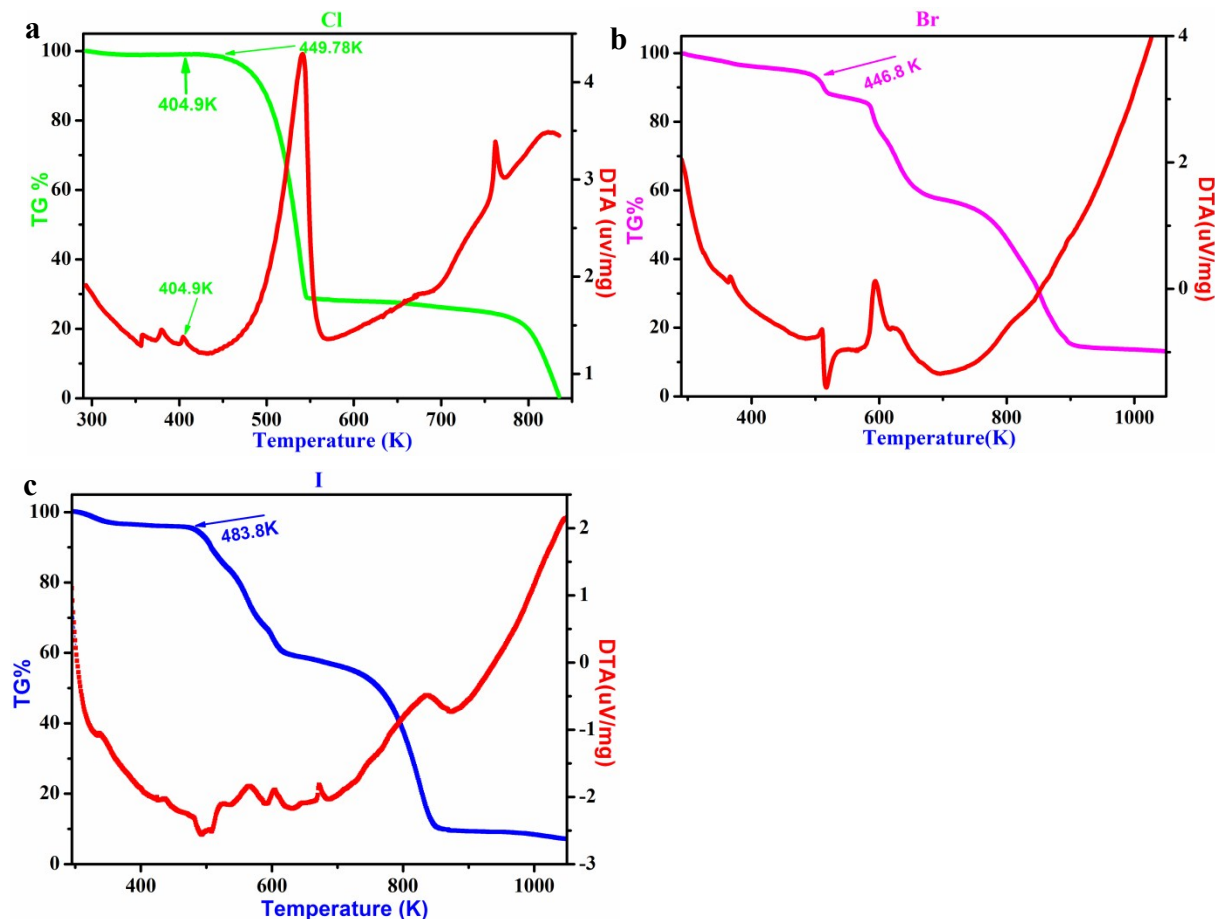

Figure S2. The thermogravimetric analysis of $[(C_4H_3S)CH_2NH_3]_2PbX_4$ (X= Cl⁻, Br⁻, I⁻) in the range of 300-1050 K.

Powder X-ray diffraction

Room temperature powder X-ray diffraction (PXRD) experiments of $[(C_4H_3S)CH_2NH_3]_2PbX_4$ (X= Cl$^-$, Br$^-$, I$^-$) were performed on a Rigaku D/MAX 2000 PC X-ray diffraction instrument with Cu radiation ($K_{\alpha1}$=1.54060 Å, $K_{\alpha2}$=1.54443 Å).

Variable temperature PXRD experiments of $[(C_4H_3S)CH_2NH_3]_2PbBr_4$ were carried out on a Brucker D8 Discovery diffractometer with Cu radiation ($K_{\alpha1}$=1.54060 Å, $K_{\alpha2}$=1.54443 Å). The data were collected in the temperature range 294–395 K for θ range from 5 to 40°, and then it goes back to the initial temperature 294 K.
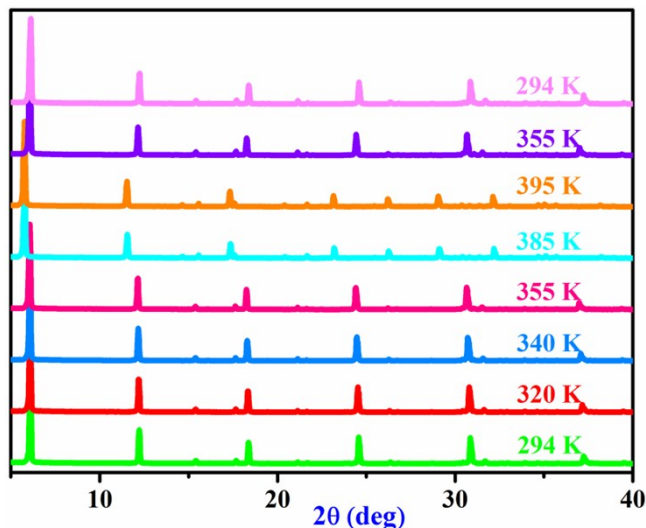

Figure S3. The variable temperature powder X-ray diffractions of $[(C_4H_3S)CH_2NH_3]_2PbBr_4$ in the range of 294-395 K.

Dielectric

Dielectric measurements were implemented with powder samples in the form of tablet which used as electrodes by pasting silver conduction on its both surfaces compactly. The dielectric constants of the compounds were confirmed with an Agilent or a Model TH2828A impedance analyzer over the frequency range from 500 Hz to 1 MHz in the process of heating and then cooling.

UV-vis absorption spectra

UV-vis absorption spectra were obtained using a Shimadzu (Tokyo, Japan) UV-2550 spectrophotometer in a range of 300-700 nm. The powder crystals of three compositions were used for the measurement. The optical band gap was determined by a variant of the *Tauc* equation:[2]

$$[h\nu \cdot F(R_\infty)]^{1/n} = A(h\nu - E_g)$$

where h is the Planck's constant, v represents the frequency of vibration, A is the proportional constant, E_g is the bandgap and $F(R_\infty)$ is Kubelka-Munk equation:[3] $F(R_\infty) = (1-R_\infty)^2/2R_\infty$. In addition, $n=1/2$ stands for direct band gap, while $n=2$ is indirect band gap.

Photoluminescence (PL) spectroscopy

Photoluminescence (PL) and decay curves were measured on a spectrophotometer (FLS980) equipped with both a xenon lamp (450 W) and a pulse xenon lamp (450 W) as well as a pulse tunable laser (OPOTEK) as the lighting source.

Density functional theory (DFT) calculations

The first-principles calculations were performed using the CASTEP code,[4] a total energy package based on pseudopotentail density functional theory (DFT).[5,6] The correlation and exchange terms in the Hamiltonian were described by the functionals developped by Perdew, Burke and Ernzerhof (PBE)[7] in the generalized gradient approximation (GGA)[8] form. The optimized fine pseudopotential was adopted to model the effective interactions between the valence electrons and atomic cores, which allow us to choose a relative small plane-wave basis set without compromising the computational accuracy. Kinetic energy cutoff 240 eV and dense Monkhorst-Pack[9] with medium k-point meshes interval in the Brillouin zones were chosen.
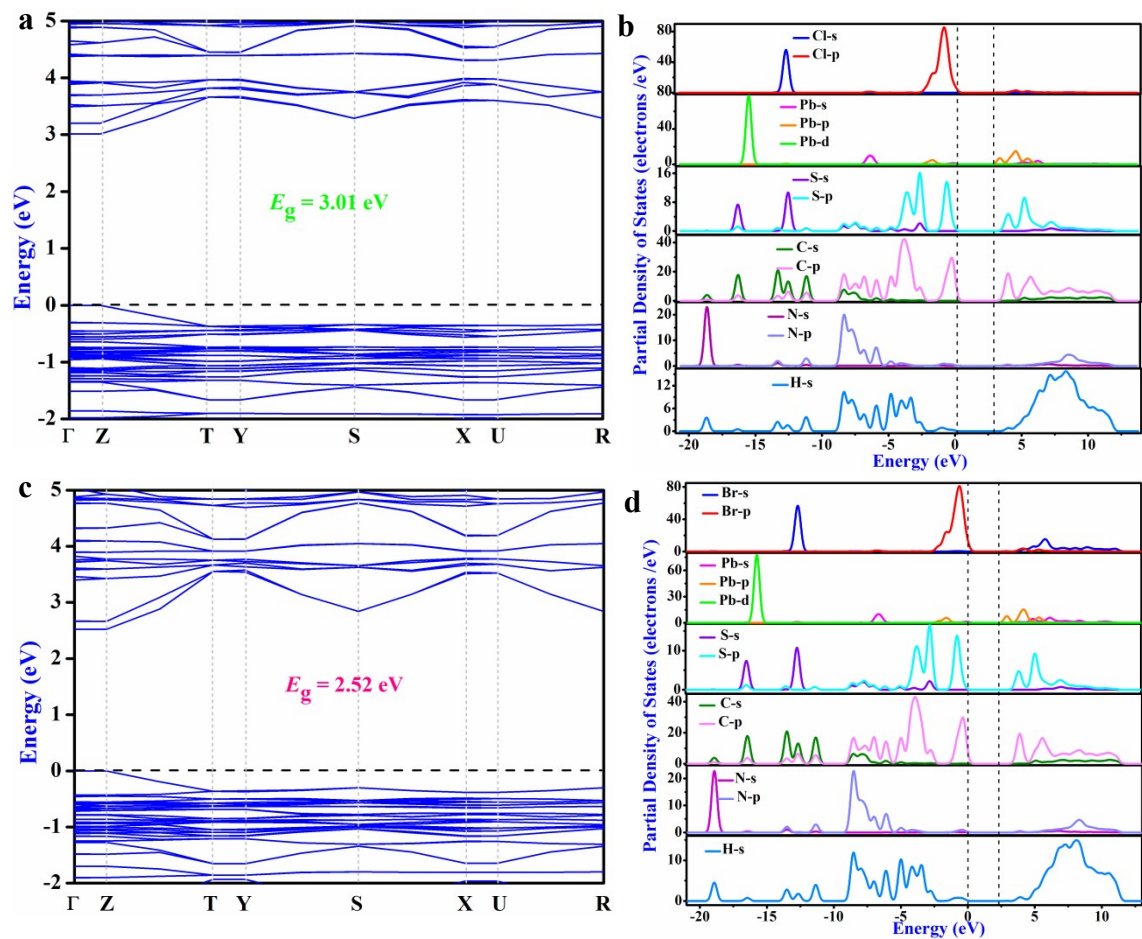
Figure S4. The calculated energy band structures of [(C₄H₃S)CH₂NH₃]₂PbCl₄ (a) and [(C₄H₃S)CH₂NH₃]₂PbBr₄ (c). Partial density of states (PDOS) for [(C₄H₃S)CH₂NH₃]₂PbCl₄ (b) and [(C₄H₃S)CH₂NH₃]₂PbBr₄ (d).

The calculations of entropy changes (ΔS) and corresponding N for the phase transitions of three compositions in cooling and heating processes, respectively.

Cl:

In the cooling cycle mode

$$\Delta S_1 = \int_{T1}^{T2} \frac{\frac{Q}{T}}{T} \, dT$$

$$\approx \frac{\Delta H}{TC}$$

$$= \frac{5.693 \, J{\cdot}g^{-1} \times 579.38 \, g{\cdot}mol^{-1}}{405.15K}$$

$$= 8.141 \, J{\cdot}mol^{-1}{\cdot}K^{-1}$$

$$\Delta S_1 = R \ln N_1$$

$$N_1 = \exp\left(\frac{\Delta S1}{R}\right) = \exp\left(\frac{8.141 J{\cdot}mol^{-1}{\cdot}K^{-1}}{8.314 \, J{\cdot}mol^{-1}{\cdot}K^{-1}}\right)$$

$$= 2.662$$

In the heating cycle mode

$$\Delta S_2 = \int_{T1}^{T2} \frac{\frac{Q}{T}}{T} \, dT$$

$$\approx \frac{\Delta H}{TC}$$

$$= \frac{5.170 \, J{\cdot}g^{-1} \times 579.38 \, g{\cdot}mol^{-1}}{410.64 \, K}$$

$$= 7.294 \, J{\cdot}mol^{-1}{\cdot}K^{-1}$$

$$\Delta S_2 = R \ln N_2$$

$$N2 = \exp\left(\frac{\Delta S2}{R}\right) = \exp\left(\frac{7.294 \, J{\cdot}mol^{-1}{\cdot}K^{-1}}{8.314 \, J{\cdot}mol^{-1}{\cdot}K^{-1}}\right)$$

$$= 2.384$$

Br:

In the cooling cycle mode

$$\Delta S_1 = \int_{T1}^{T2} \frac{\frac{Q}{T}}{T} \, dT$$

$$\approx \frac{\frac{\Delta H}{TC}}$$

$$= \frac{4.301 \ J \cdot g \ {}^{-1} \times 755.17 \ g \cdot mol \ {}^{-1}}{363.9K}$$

$$= 8.925 \ J \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta S_1 = R \ln N_1$$

$$N_1 = \exp\left(\frac{\frac{\Delta S1}{R}}\right) = \exp\left(\frac{8.925 J \cdot mol \ {}^{-1} \cdot K \ {}^{-1}}{8.314 \ J \cdot mol \ {}^{-1} \cdot K \ {}^{-1}}\right)$$

$$= 2.927$$

In the heating cycle mode

$$\Delta S_2 = \int_{T1}^{T2} \frac{\frac{Q}{T}}{T} \, dT$$

$$\approx \frac{\frac{\Delta H}{TC}}$$

$$= \frac{5.182 \ J \cdot g \ {}^{-1} \times 755.17 \ g \cdot mol \ {}^{-1}}{376.08 \ K}$$

$$= 10.405 \ J \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta S_2 = R \ln N_2$$

$$N2 = \exp\left(\frac{\frac{\Delta S2}{R}}\right) = \exp\left(\frac{10.405 \ J \cdot mol \ {}^{-1} \cdot K \ {}^{-1}}{8.314 \ J \cdot mol \ {}^{-1} \cdot K \ {}^{-1}}\right)$$

$$= 3.403$$

I:

In the cooling cycle mode

$$\Delta S_1 = \int_{T1}^{T2} \frac{\frac{Q}{T}}{T} \, dT$$

$$\approx \frac{\Delta H}{TC}$$

$$= \frac{1.193\ J{\cdot}g^{-1} \times 937.52\ g{\cdot}mol^{-1}}{222.14\ K}$$

$$= 5.035\ J{\cdot}mol^{-1}{\cdot}K^{-1}$$

$$\Delta S_1 = R \ln N_1$$

$$N_1 = \exp\left(\frac{\Delta S1}{R}\right) = \exp\left(\frac{5.035\ J{\cdot}mol^{-1}{\cdot}K^{-1}}{8.314\ J{\cdot}mol^{-1}{\cdot}K^{-1}}\right)$$

$$= 1.647$$

In the heating cycle mode

$$\Delta S_2 = \int_{T1}^{T2} \frac{\frac{Q}{T}}{T}\ dT$$

$$\approx \frac{\Delta H}{TC}$$

$$= \frac{1.428\ J{\cdot}g^{-1} \times 937.52\ g{\cdot}mol^{-1}}{226.84\ K}$$

$$= 5.902\ J{\cdot}mol^{-1}{\cdot}K^{-1}$$

$$\Delta S_2 = R \ln N_2$$

$$N2 = \exp\left(\frac{\Delta S2}{R}\right) = \exp\left(\frac{5.902\ J{\cdot}mol^{-1}{\cdot}K^{-1}}{8.314\ J{\cdot}mol^{-1}{\cdot}K^{-1}}\right)$$

$$= 1.930$$

References

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