Supporting Information for:

Crystallographic Investigations into Properties of Acentric Hybrid Perovskite Single Crystals NH(CH$_3$)$_3$SnX$_3$ (X= Cl, Br)

Yangyang Dang,[†] Cheng Zhong,[‡] Guodong Zhang,[†] Dianxing Ju,[†] Lei Wang,[†] Shengqing Xia,[†] Haibing Xia[†] and Xutang Tao*[†]

[†]State Key Laboratory of Crystal Materials, Shandong University, No. 27 Shanda South Road, Jinan, 250100, P. R. China.

[‡]Solar and Photovoltaic Engineering Research Center (SPERC), King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia.

*E-mail: txt@sdu.edu.cn.

Experimental Section

Figure S1. Schematic illustrations for the growth equipment of bulk NH(CH$_3$)$_3$SnX$_3$ (X= Cl, Br) single crystals.

Figure S2. The photos of opaque NH(CH$_3$)$_3$SnX$_3$ (X=Cl, Br) single crystals.

Figure S3. (a) The powder SHG signal of NH(CH$_3$)$_3$SnX$_3$ (X= Cl, Br) compared with KH$_2$PO$_4$ (KDP) (particle size: 75-100 μ m). (b) Particle size dependence of SHG intensity for NH(CH$_3$)$_3$SnX$_3$ (X= Cl, Br).

Figure S4. Temperature dependence of the SHG intensity of NH(CH$_3$)$_3$SnX$_3$ (X=Cl, Br) measured on crystalline powder samples, compared with the KDP crystalline powder samples.

Figure S5. Powder and calculated X-ray diffraction patterns of NH(CH$_3$)$_3$SnX$_3$ (X= Cl, Br) at different temperature.

Figure S6. Powder and calculated X-ray diffraction patterns of NH(CH$_3$)$_3$SnX$_3$ (X= Cl, Br) when exposure to air for one month.

Experimental Section

Single-Crystal X-ray Diffraction and Powder X-ray diffraction. Single-crystal X-ray diffraction measurements were executed on a _Bruker SMART APEX-II_ diffractometer equipped with a CCD detector (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å) at different temperature. Data integration and refinements were carried out with _APEX2_ software.[1] All the crystal structures were determined by direct methods and refined by full-matrix least-squares on F^2 using the _SHELXTL_ program package.[2] All the atom displacements in the crystal structure were fixed with anisotropic thermal parameters, and the refinements converged for $Fo^2 > 2\sigma$ (Fo^2). Symmetry analysis on the model using _PLATON_ functions [3] of the _WinGX_ platform [4] showed that no evident space group alternation was required. _ISOTROPY_ software[5] was used to calculate the group-subgroup relationships and to find the correct space group. X-Ray powder diffraction (XRD) of polycrystalline material taken from the reaction solution was also collected using a _Bruker-AXS D8 ADVANCE_ X-Ray diffractometer with Cu-Kα$_1$ radiation (λ = 1.54186 Å) in the range of 10°-90° (2θ) with a time setting of 0.1 second per step and a step length of 0.002°.

UV-vis diffuse reflectance spectra measurements. UV−vis diffuse reflectance spectroscopy was carried out using a Shimadzu UV-3101PC spectrophotometer equipped with an integrating sphere over the spectral range 200-800 nm. A $BaSO_4$ plate was used as the standard (100% reflectance). The absorption spectrum was calculated from the reflectance spectrum using the Kubelka-Munk function: $F(R) = \alpha/S = (1-R)^2/(2R)$,[6] where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.

Second-Harmonic Generation (SHG) measurements. The SHG effect of the $NH(CH_3)_3SnX_3$ (X= Cl, Br) powder samples was investigated using a Kurtz-Perry powder technique.[7] A pulsed Q-switched Nd: YAG laser was utilized to generate fundamental 1064 nm light with a pulse width of pulse width of 10 ns, pulse duration of 1 Hz and pulse energy of 10 mJ. Polycrystalline samples of $NH(CH_3)_3SnX_3$ (X= Cl, Br) and KH_2PO_4 (KDP) were grinded and sieved to obtain distinct grain sizes ranges (40-60, 60-80, 125-175, 225-275, 275-325 μ m) in Figure S3. Microcrystalline KDP was served as the references. Besides, the temperature-dependent-SHG measurements were described elsewhere.[17, 18]

Thermogravimetric analysis and Differential scanning calorimetry (DSC) measurements. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a TGA/DSC1/1600HT analyzer (*METTLER TOLEDO* Instruments). The $NH(CH_3)_3SnX_3$ (X= Cl, Br) powder samples were placed in a platinum crucible, and heated at a rate of 10 °C min^{-1} from room temperature to 800 °C under flowing N_2 gas, respectively. Differential Scan calorimetry (DSC) measurements were performed on Polyma Instruments (*DSC-200-F3 Maia*). The $NH(CH_3)_3SnX_3$ (X= Cl, Br) powder samples were placed in a platinum crucible, and heated at a rate of 10 °C min^{-1} from room temperature to 150 ^{o}C, and then cooled to -70 ^{o}C in liquid N_2 atmosphere and shifted back to room temperature under flowing N_2 gas.

X-ray photoelectron spectroscopy (XPS) measurements. XPS measurements of the $NH(CH_3)_3SnX_3$ (X= Cl, Br) on four samples with 3 × 3 × 1 mm^3 (newly synthesized and exposure to air one month) were performed on *ESCALAB* 250 (*ThermoFisher SCIENTIFIC*) instrument under vacuum atmosphere ($1.7×10^{-10}$ mbar).

Band structure calculations. The initial single crystal structures for $NH(CH_3)_3SnX_3$ (X= Cl, Br) were obtained from single-crystal X-ray crystallographic data. All the calculations were performed using VASP 5.3.3 software [9-12] and then the atomic positions were optimized at PBE [13-14]/PAW [15-16] level with k points set as 2*2*2. Based on the optimized structure, the band structure were calculated along the path G (0.0, 0.0, 0.0)-F (0.0, 0.5, 0.0)-Q (0.0, 0.5, 0.5)-Z (0.0, 0.0, 0.5)-G at the same the level of theory.
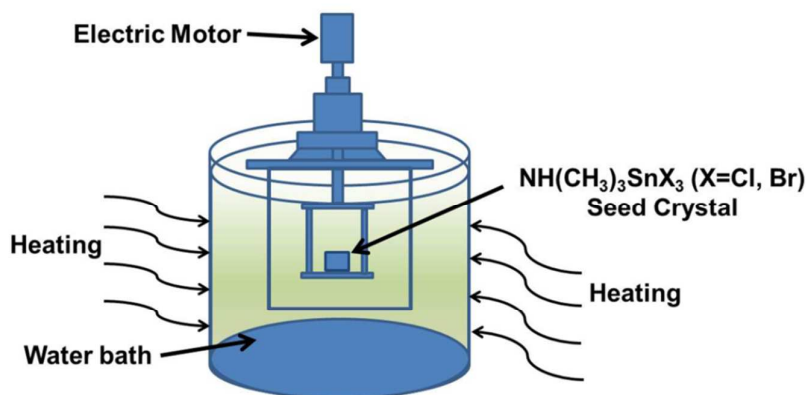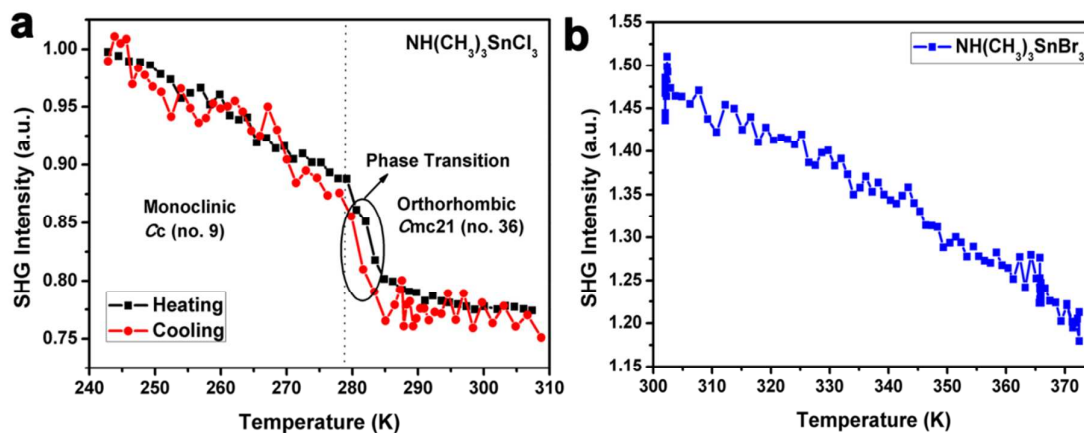
Figure S1. Schematic illustrations for the growth equipment of bulk $NH(CH_3)_3SnX_3$ (X= Cl, Br) single crystals.
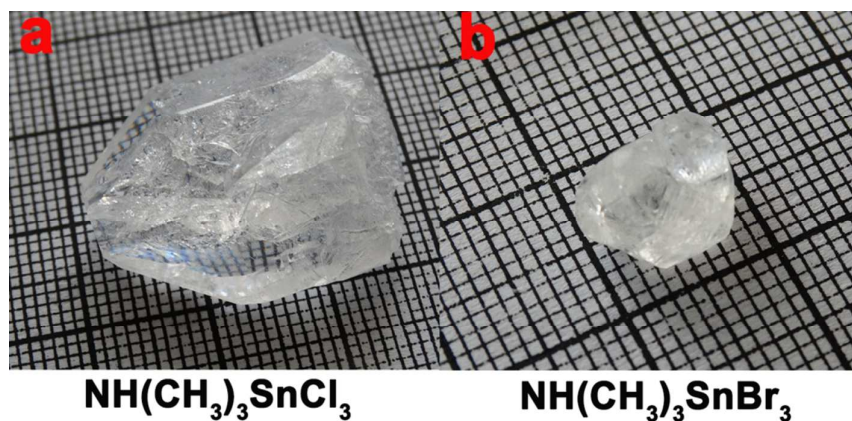

Figure S2. The photos of opaque $NH(CH_3)_3SnX_3$ (X=Cl, Br) single crystals.
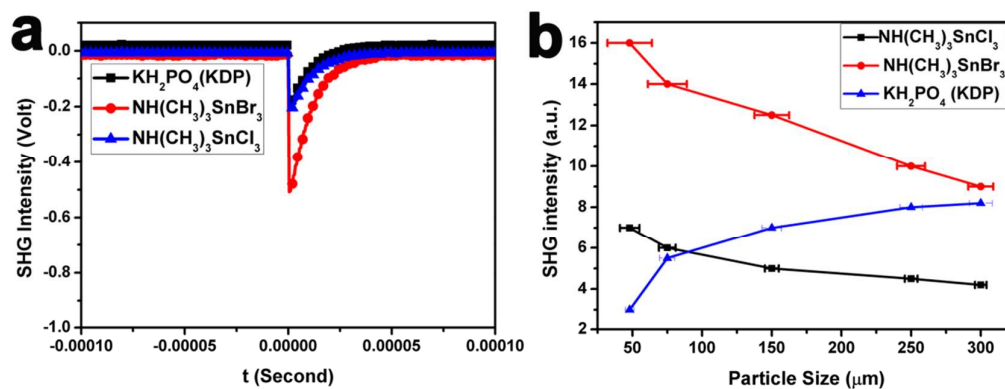

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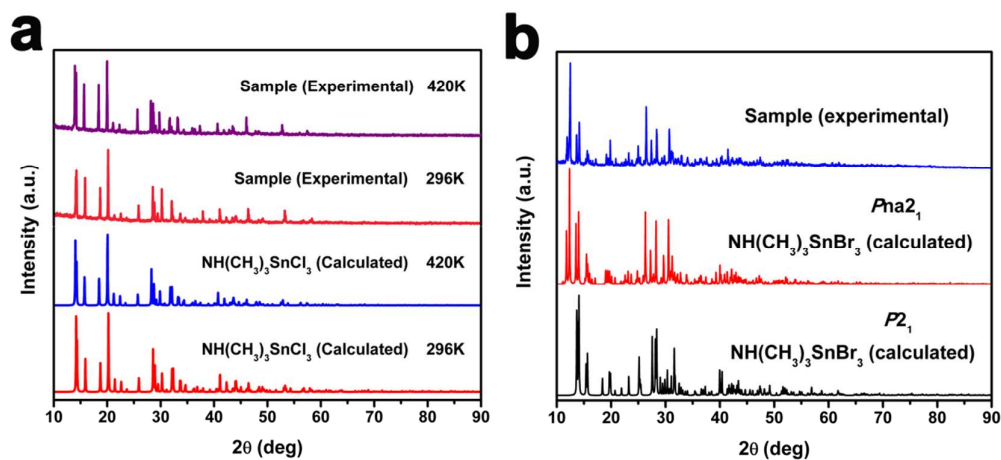
Figure S5. Powder and calculated X-ray diffraction patterns of $NH(CH_3)_3SnX_3$ (X= Cl, Br).

(a) Powder and calculated X-ray diffraction patterns of $NH(CH_3)_3SnCl_3$ at different

temperature; (b) Powder and calculated X-ray diffraction patterns with space group $Pna2_1$

by $NH(CH_3)_3SnBr_3$ single crystal measurements, and calculated X-ray diffraction pattern

with space group $P2_1$ reported by Thiele, et al.[8]
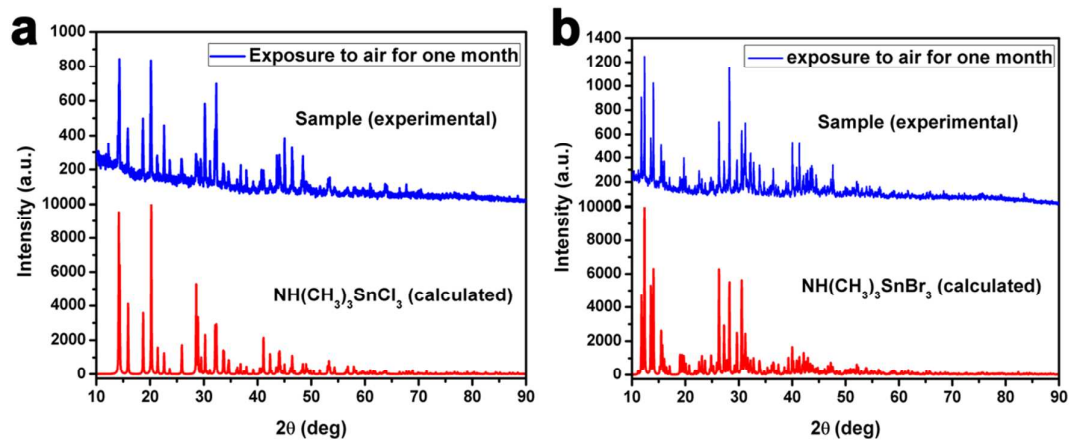
Figure S6. Powder and calculated X-ray diffraction patterns of $NH(CH_3)_3SnX_3$ (X= Cl, Br) when exposure to air for one month.

References

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