

## Supplementary Information

# Efficient Raman scattering response and large piezoelectricity in noncentrosymmetry MnHg(SCN)<sub>4</sub> crystals

*Xitao Liu<sup>ab</sup>, Peiqing Long<sup>a</sup>, Xinqiang Wang<sup>b\*</sup>, Zeliang Gao<sup>b</sup>, Yadong Lü<sup>b</sup> and Zhiguo Yi<sup>a\*</sup>*

*<sup>a</sup>Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P.R. China*

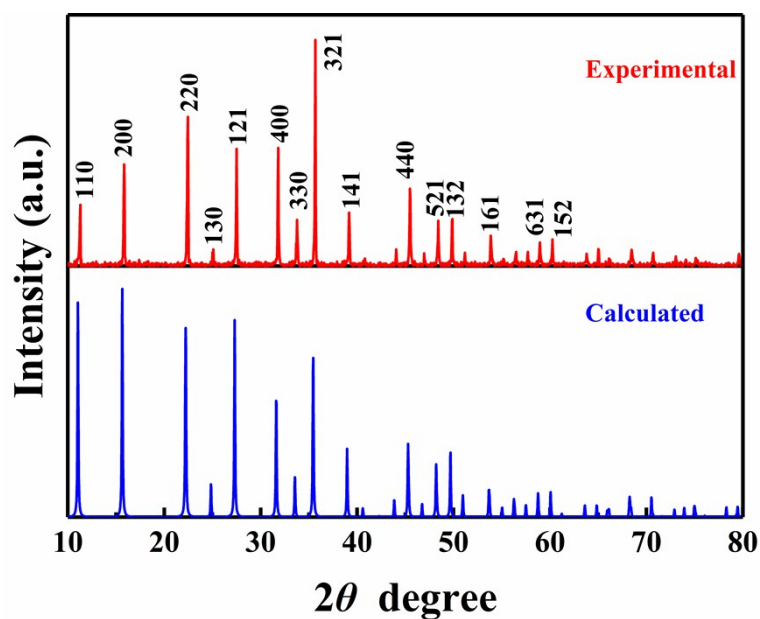
*<sup>b</sup>State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, P.R. China*

**Fig. S1** Experimental and calculated XRD patterns of MMTC crystal.

**Fig. S2** Typical growth morphologies of MMTC grown by temperature lowering method.

**Fig. S3** Temperature dependence of the density of MMTC crystal.

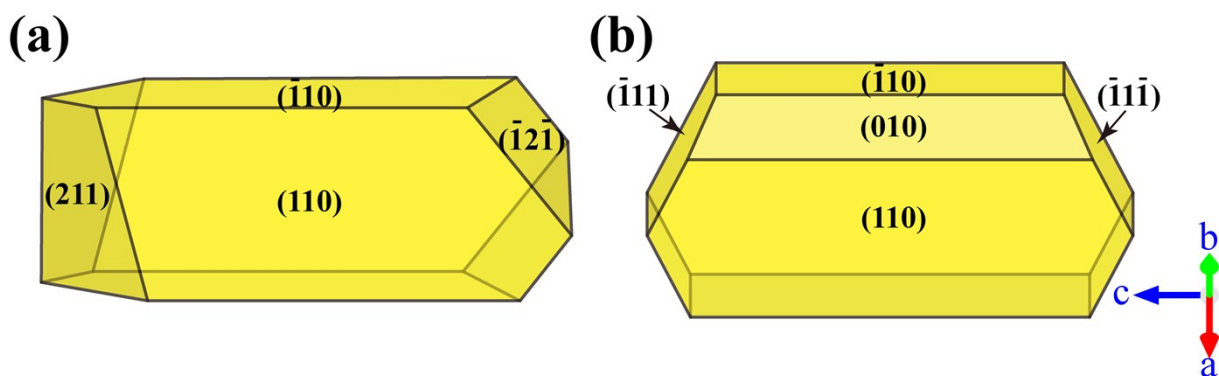
**Fig. S4** Temperature dependence of the specific heat of MMTC crystal.



**Fig. S1** Experimental and calculated XRD patterns of MMTC crystal.

### X-ray diffraction

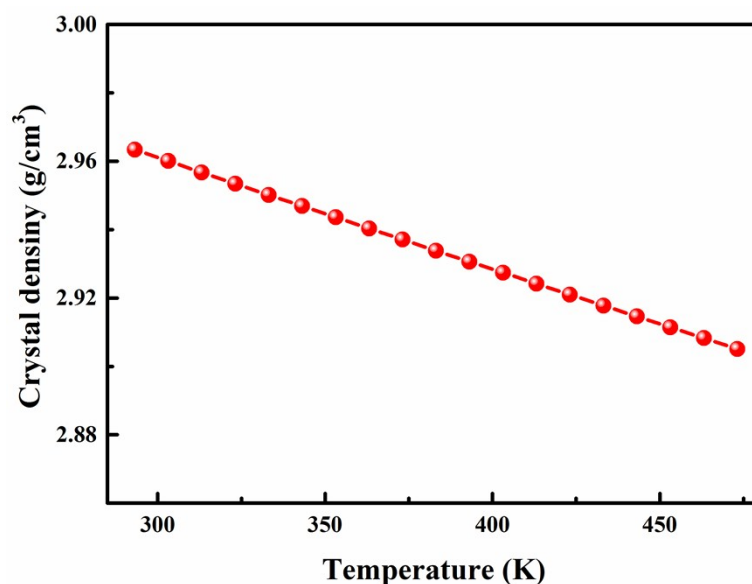
Powder X-ray diffraction (XRD) data of MMTC ground from the grown single crystals were collected in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$  with each scan step of  $0.02^\circ/0.4$  s using MiniFlex 600 equipment (Cu K $\alpha$  radiation; Rigaku Co., Tokyo, Japan) at room temperature. The XRD pattern and diffraction indices of the crystal are shown in Fig. S1, in comparison with the calculated one derived from the single-crystal data by the Mercury program<sup>2</sup>. The XRD experiments showed that the grown crystals contain a single phase of MMTC with NCS tetragonal space group  $I\bar{4}$  and lattice parameters  $a$  and  $c$  equal to 11.332(3) and 4.263(4) Å, respectively, which are in good agreement with the calculated one.



**Fig. S2** Typical growth morphologies of MMTC grown by temperature lowering method.

### Crystal Growth Morphology

The morphology of a crystal is a reflection of its structure which was mainly determined by the relative growth rates of various facets. The growth morphology of MMTC crystal was also indexed on the diffractometer combined with measuring the interfacial angles in the habit (Fig. S2). The  $\{110\}$ ,  $\{100\}$ ,  $\{111\}$  and  $\{211\}$  facets were formed during the crystal growth. The theoretical morphology of MMTC crystal was also predicted by the Bravais-Friedel-Donnay-Harker (BFDH)<sup>1</sup> model using the Mercury program,<sup>2</sup> which is presented in Fig. S2 (b). It is worth noting that the two morphologies (Figs. S2a and b) are largely the same but with a little difference which may be attributable to growth conditions such as seed orientation, solvent supersaturation, pH value, temperature, impurities, hydrodynamics and cooling rate.



**Fig. S3** Temperature dependence of the density of MMTC crystal.

### Crystal density

The density of MMTC is  $2.95(1) \text{ g}\cdot\text{cm}^{-3}$  at room temperature, which was measured by the buoyancy method using the formula below:

$$\rho_{\text{exp}} = m\rho_l(m - m') \quad (14)$$

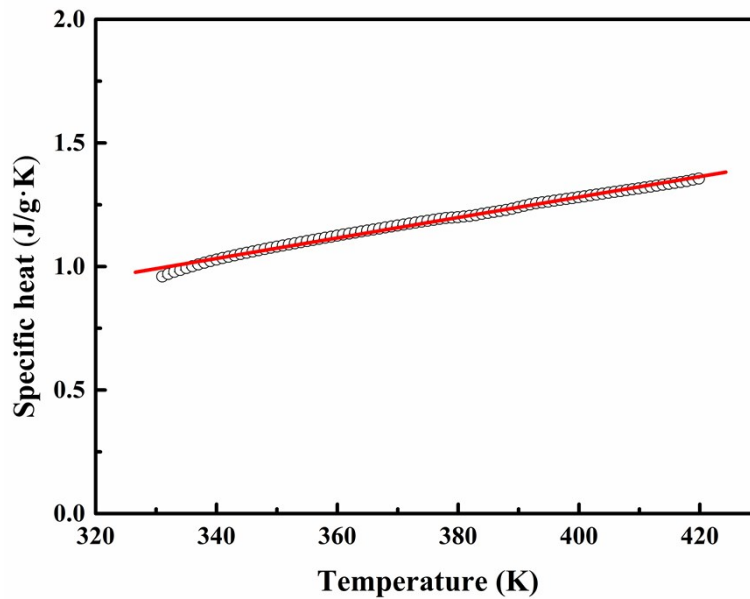
where  $m$  is the sample weight in air condition,  $(m - m')$  is the float force of the liquid (monochlorobenzene), and  $\rho_l(1.10630 \text{ g}\cdot\text{cm}^{-3})$  is density of monochlorobenzene.

The density of material can also be calculated by the formula:

$$\rho_{\text{cal}} = \frac{MZ}{NV} \quad (15)$$

where  $M$ ,  $Z$ ,  $N$  and  $V$  are the molecular weight, number of molecules per unit cell, Avogadro's number and the volume of the unit cell, respectively.

The measured density of MMTC crystal at room temperature agrees well with the calculated one of  $2.959 \text{ g}\cdot\text{cm}^{-3}$ . Fig. S2 shows the calculated density values at different temperatures through the thermal expansion coefficients. From Fig. S3, one can see that the density of MMTC crystal decreases with the rise of temperature.



**Fig. S4** Temperature dependence of the specific heat of MMTC crystal.

### Specific heat

Fig. S4 presents the temperature dependence of the specific heat for MMTC ranging from 293 to 347 K. As one can see, the specific heat increases linearly with the temperature with a value from 1.339 to 1.614 J/g·K, which means the MMTC crystal can tolerate more energy with a smaller temperature gradient when irradiated by a pulsed laser beam.

1. (a) Bravais, A., *Etudes Crystallographiques*. Academie des Sciences, Paris, 1913; (b) Donnay, J. D. H.; Harker, D. *Am. Mineral* **1937**, 22 (5), 446.
2. (a) Taylor, R.; Macrae, C. F. *Acta Crystallogr. Sect. B: Struct. Sci.* **2001**, 57 (6), 815; (b) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr. Sect. B: Struct. Sci.* **2002**, 58 (3-1), 389.