Electronic supporting information for paper

Crystallographic insights into $(CH_3NH_3)_3(Bi_2I_9)$: A new lead-free hybrid organic-inorganic material for photovoltaics

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1. Single crystal X-ray diffraction study

The diffraction images from the red needle like single crystal of $(CH_3NH_3)_3(Bi_2I_9)$ were collected on a STOE IPDS II single crystal diffractometer. All devices are operated with Mo-K_α-radiation (λ = 0.71073 Å, fine-focus sealed tube, graphite monochromator). The diffraction experiments were carried out at room temperature. Initially, a few hundred incidental reflections were collected and the cell parameters were determined. Complete data collection was performed with an optimized instrumental setup. Collected raw data were integrated with Lorenz- and polarization correction. Due to the presence of Bi atoms in the structure, the analytical absorption correction procedure, implemented in the X-Red32 program and based on the crystal size and orientation on the diffractometer was performed.[1] Finally the dataset was examined for systematic absences and the space group $P6_3/mmc$ was used for the structure solution. An initial structural model was determined by the use of direct methods within the SHELXS program.[2] Missing nitrogen and carbon atoms were located via difference Fourier map. The model was improved by full matrix least squares refinement with ShelXL.[2] Non-hydrogen atoms of the networks were refined with anisotropic temperature parameters. Because of the very small difference between the scattering factors of C and N atoms in the presence of Bi and I atoms with large scattering factors from the one hand and molecular structure of methyl ammonium cation from the another hand, it was impossible exactly identify the carbon and nitrogen atom in this structural fragment. Similarity of the distances between these atoms and I atoms of the $Bi_2I_9^{3-}$ anion as well as large thermal motion of the atoms suggest the presence of the rare case of substitutional disorder in the cation C1-N1. Another independent methyl ammonium cation C2-N2 involves positional disorder of one of the atoms. The hydrogen atoms were positioned geometrically and refined using a riding model. CCDC-1433118 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The experimental data and are given in table S1. The bond lengths and angles are presented in Table S2.

Table S1. Crystal data and structure refinement information for $(CH_3NH_3)_3(Bi_2I_9)$.

compound	$(CH_3NH_3)_3(Bi_2I_9)$
empirical formula	$C_3H_{18}Bi_2I_9N_3$
formula weight	1656.26
temperature	293(2) K
wavelength	0.71073 Å
crystal system	hexagonal
space group	$P6_3/mmc$ (No. 194)
unit cell dimensions	a = 8.5843(12) Å
	c = 21.690(4) Å
volume	1384.2(5) $Å^3$
Z	2
density (calculated)	3.974 $g \cdot cm^{-3}$
absorption coefficient	22.725 mm^{-1}
Absorption (exp) T_{min}, T_{max}	0.253, 0.374
F(000)	1400
crystal size	0.06 x 0.06 x 0.09 mm^3
θ range for data collection	1.878 to 29.191°
index ranges	$-11 \le h \le 5$
	$0 \le k \le 11$
	$0 \le l \le 29$
reflections collected	2357
independent reflections	764 [R_{int} = 0.0985]
completeness to θ	96.5 %
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	764 / 26 / 32
goodness-of-fit on F^2	0.865
final R indices [$I>2\sigma(I)$]	R_1 = 0.0453,
	wR_2 = 0.1080
R indices (all data)	R_1 = 0.0945,
	wR_2 = 0.1250
largest diff. peak and hole	1.86 and -1.51 e A^{-3}

Table S2. Bond lengths and angles for $(CH_3NH_3)_3(Bi_2I_9)$.

Bond lengths, angles	Å, deg
Bi1—I1	3.2288(15)
Bi1—I2	2.9531(17)
I1—Bi1—I2	173.62(5)
I1—Bi1—I1_a	84.02(4)
I1—Bi1—I2_a	91.25(4)
I1—Bi1—I1_b	84.02(3)
I1—Bi1—I2_b	91.25(3)
I1_a—Bi1—I2	91.25(4)
I1_b—Bi1—I2	91.25(3)
I2—Bi1—I2_b	93.13(4)
I1_a—Bi1—I2_a	173.62(5)
I1_a—Bi1—I1_b	84.01(4)
I1_a—Bi1—I2_b	91.26(4)
I1_b—Bi1—I2_a	91.26(4)
I2_a—Bi1—I2_b	93.13(5)
I1_b—Bi1—I2_b	173.62(5)
Bi1—I1—Bi1_c	78.79(4)

Symmetry codes

a =1-y,x-y,z; b =1-x+y,1-x,z; c =1-y,1-x,1/2-z

References:

1. Stoe & Cie (2002). *X-Area and X-red32.* Stoe & Cie, Darmstadt, Germany.
2. G. M. Sheldrick *Acta Cryst.* (2015). **C71**, 3-8