NEW DIFFRACTION DATA

Crystal structure and X-ray powder diffraction data of barium copper iodate Ba$_2$Cu(IO$_3$)$_6$

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X-ray powder diffraction data, unit-cell parameters, and space group for the barium copper iodate, Ba$_2$Cu(IO$_3$)$_6$, are reported [$a = 7.48540(15)$ Å, $b = 7.51753(19)$ Å, $c = 7.64259(17)$ Å, $\alpha = 98.8823(7)°$, $\beta = 95.0749(7)°$, $\gamma = 97.6297(7)°$, $V = 418.528(9)$ Å^3, $Z = 1$, and space group $P\bar{1}$]. All measured lines are indexed and are consistent with the corresponding space group. The single-crystal diffraction data of Ba$_2$Cu(IO$_3$)$_6$ are also reported [$a = 7.493(3)$ Å, $b = 7.521(6)$ Å, $c = 7.644(5)$ Å, $\alpha = 98.855(18)°$, $\beta = 95.060(16)°$, $\gamma = 97.62(2)°$, $V = 419.3(5)$ Å^3, $Z = 1$, and space group $P\bar{1}$]. The crystal structure of Ba$_2$Cu(IO$_3$)$_6$ features isolated [Cu(IO$_3$)$_6$]$^{4-}$ anionic clusters separated by Ba^{2+} cations. The experimental powder diffraction pattern matches well with the simulated pattern derived from the single crystal data.

I. INTRODUCTION

Metal iodates are an attractive inorganic compound system with a diversity of unusual structures and various physical properties, which mainly arise from the stereochemical active lone pair electrons on the I^{5+} ion and the asymmetric pyramidal coordination geometry of IO$_3$ building units. Over the past two decades, the incorporation of d^0 transition-metal ions (Ti^{4+}, Nb^{5+}, V^{5+}, and Mo^{6+}) into ternary metal iodates afforded abundant new quaternary iodates, many of which exhibit noncentrosymmetric structures and promising nonlinear optical properties (Hu and Mao, 2015; Chen et al., 2021). The quaternary metal iodates containing magnetic transition-metal ions (Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) have also been explored, and their magnetic properties have been studied, such as (LiFe$_{1/3}$)(IO$_3$)$_2$ (Lan et al., 2002a, 2002b). The Cu^{2+} ion possesses a partially filled d-orbital and usually occupies a distorted octahedral CuO$_6$ coordination geometry; hence, the combination of copper cations with iodate groups is expected to form novel structures with various connection fashion of CuO$_6$ units, and may further afford interesting magnetic properties. As far, only seven Cu-containing quaternary iodates, NaCu(IO$_3$)$_3$ (Sen Gupta et al., 1987), AgCu(IO$_3$)$_3$ (Wang et al., 2017), KCu(IO)$_3$ (Mitoudi-Vagourdi et al., 2019), and LnCu(IO$_3$)$_5$ ($Ln =$ La, Ce, Pr, and Nd) (Geng et al., 2022), have been reported. In this study, a new Cu-containing quaternary iodate, namely, Ba$_2$Cu(IO$_3$)$_6$, has been synthesized. The crystal structure and powder X-ray diffraction data of Ba$_2$Cu(IO$_3$)$_6$ are reported.

II. EXPERIMENTAL

A. Sample preparation

Crystal samples of Ba$_2$Cu(IO$_3$)$_6$ were synthesized by hydrothermal reactions of a mixture of BaCO$_3$, CuO, and I$_2$O$_5$ sealed in a 25 ml Teflon-lined stainless-steel autoclave. The loaded compositions were BaCO$_3$ (19.7 mg, 0.1 mmol), CuO (4.0 mg, 0.05 mmol), I$_2$O$_5$ (2670.4 mg, 8.0 mmol), and H$_2$O (2.0 ml). The mixture was heated at 220 °C for 70 h, followed by slow cooling to ambient temperature at a rate of 3.0 °C/h. Colorless Ba$_2$Cu(IO$_3$)$_6$ crystals were obtained as a single phase. The as-grown Ba$_2$Cu(IO$_3$)$_6$ crystals exhibit long granular shapes with sizes ranging from 0.1 to 0.5 mm (Supplementary Figure S1). Elemental analyses were carried out on a field emission scanning electron microscope (FEI, NovaNanoSEM450) equipped with an energy-dispersive X-ray spectroscope (EDS; Oxford, X-MaxN). The Ba:Cu:I:O molar ratio based on the EDS analyses was given to be 2.08:1.00:6.11:18.58 (Supplementary Figure S2). The Ba$_2$Cu (IO$_3$)$_6$ crystals were ground into powder and screened through 50 μm mesh for the X-ray powder diffraction measurement.

B. Powder diffraction data collection

X-ray powder diffraction data were collected at room temperature on a Bruker D8 ADVANCE X-ray diffractometer with a LynxEye detector and graphite-filtered Cu $K\alpha$ radiation ($K\alpha_1$: 1.54059 Å, $K\alpha_2$: 1.54439 Å, $K\alpha_2/K\alpha_1$ ratio: 0.5). The X-ray generator operated with voltage and electric current set at 40 kV and 40 mA. The measurement was performed over the 2θ range from 5° to 95° with a scanning step width of 0.02° and a counting time of 1.5 s per step. The profile fitting and refinement of the experimental X-ray powder diffraction pattern were performed using the software package

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GSAS-II (Toby and Von Dreele, 2013). The Rietveld method (Rietveld, 2014) was adopted for the refinement. In addition, the software package MDI Jade 7.5 (MDI, 2002) was used to fit the background, strip off the Cu $K\alpha_2$ component, and perform the assignment of Miller indices (h, k, l) to the observed peaks in the experimental X-ray powder diffraction pattern. The values of $2\theta_{obs}$, d_{obs}, $(I/I_o)_{obs}$, h, k, l, $2\theta_{cal}$, d_{cal}, $(I/I_o)_{cal}$, and $\Delta 2\theta$ were obtained (Supplementary Table SI). The Cu $K\alpha_1$ wavelength ($\lambda = 1.5405981$ Å) was used in converting observed line positions to d-spacing.

C. Single-crystal diffraction data collection

X-ray single-crystal diffraction data were collected on a Rigaku SCXMini CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K. Data reduction was performed with the software *CrystalClear*, and absorption correction based on multi-scan method (Blessing, 1995) was applied. The structure was solved by the direct method and refined by the full-matrix least-squares fitting on F^2 using the structure solution program package *SHELX* (Sheldrick, 2015).

III. RESULTS AND DISCUSSION

Through the Rietveld refinements based on the experimental X-ray powder diffraction patterns using the software package GSAS-II, the profile fitting has been performed, and the unit cell and atomic coordinates have been refined. $Ba_2Cu(IO_3)_6$ is identified to crystallize in the triclinic space group $P\bar{1}$ with unit-cell parameters of $a = 7.48540(15)$ Å, $b = 7.51753(19)$ Å, $c = 7.64259(17)$ Å, $\alpha = 98.8823(7)°$, $\beta = 95.0749(7)°$, $\gamma = 97.6297(7)°$, $V = 418.528(9)$ Å^3, Z = 1, $\rho = 5.5055$ g/cm^3. The calculated XRD pattern of the Rietveld refinement fits well with the observed pattern (Figure 1), and the final reliability factors wR and GOF are 0.0529 and 2.52, respectively. All observed diffraction peaks of the experimental pattern are well indexed, and no detectable impurities were observed. Using the software package MDI Jade 7.5, the
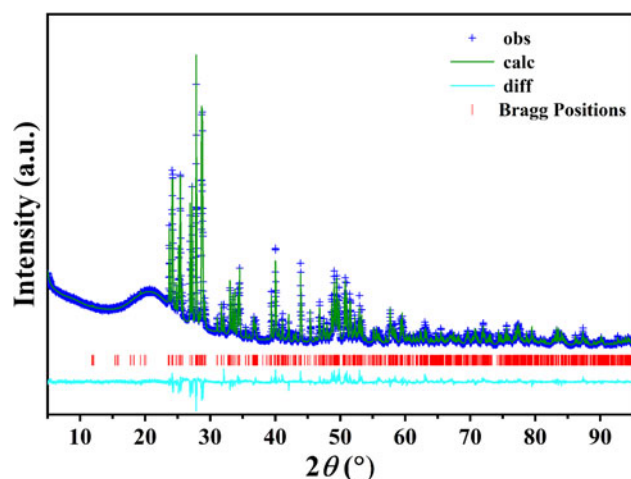

Figure 1. The Rietveld refinement plot of the powder XRD patterns for $Ba_2Cu(IO_3)_6$: experimental data (blue crosses), calculated data (green line), calculated Bragg positions (red tick marks), and difference curves (cyan line). The experimental XRD pattern was measured using the graphite-filtered Cu $K\alpha$ radiation ($K\alpha_1$: 1.54059 Å, $K\alpha_2$: 1.54439 Å, $K\alpha_2/K\alpha_1$ ratio: 0.5).

TABLE I. Single-crystal crystallographic data for $Ba_2Cu(IO_3)_6$.

Empirical formula	$Ba_2Cu(IO_3)_6$
Formula weight	1387.61
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.493(3)
b (Å)	7.521(6)
c (Å)	7.644(5)
α (°)	98.855(18)
β (°)	95.060(16)
γ (°)	97.62(2)
V (Å^3)	419.3(5)
Z	1
ρ_{calc} (g/cm^3)	5.495
μ (mm^{-1})	17.040
F (000)	603
Index ranges	$-8 \leq h \leq 8$
	$-8 \leq k \leq 7$
	$-9 \leq l \leq 9$
Reflections collected	3143
Independent reflections	1435
R_{int}	0.0288
Data/restraints/parameters	1435/0/124
Goodness of fit on F^2	1.068
Final R indexes [I ≥ 2σ]	$R_1 = 0.0346$, $wR_2 = 0.0835$
Final R indexes (all data)	$R_1 = 0.0388$, $wR_2 = 0.0867$

peak positions and intensities have been obtained. The Cu $K\alpha_1$ radiation ($\lambda = 1.5405981$ Å) has been used for the d-values calculation. The values of $2\theta_{obs}$, d_{obs}, $(I/I_o)_{obs}$, h, k, l, $2\theta_{cal}$, d_{cal}, $(I/I_o)_{cal}$, and $\Delta 2\theta$ are listed in Supplementary Table SI. The figure of merit is $F_{30} = 16.1$ (0.0026, 647) (Smith and Snyder, 1979).

The crystal structure of $Ba_2Cu(IO_3)_6$ has also been determined using the X-ray single-crystal diffraction data, which gives the unit cell as $a = 7.493(3)$ Å, $b = 7.521(6)$ Å, $c = 7.644(5)$ Å, $\alpha = 98.855(18)°$, $\beta = 95.060(16)°$, $\gamma = 97.62(2)°$, $V = 419.3(5)$ Å^3, Z = 1, $\rho = 5.495$ g/cm^3, and space group $P\bar{1}$. The detailed crystallographic information is summarized in Table I. As shown in Figure 2, the crystal structure of $Ba_2Cu(IO_3)_6$, features isolated $[Cu(IO_3)_6]^{4-}$ anionic clusters separated by Ba^{2+} cations. The asymmetric unit contains one Ba, one Cu, three I, and nine O atoms [Figure 2(a)]. I(1), I(2), and I(3) atoms are all three-coordinated in IO_3 trigonal-pyramidal geometry. The Cu(1) atom is located in a CuO_6 distorted octahedral geometry. Each CuO_6 unit is corner-sharing with six IO_3 groups [two I(1)O_3, two I(2)O_3, and two I(3)O_3] all in a monodentate fashion, leading to the formation of $[Cu(IO_3)_6]^{4-}$ clusters [Figure 2(b)]. Such $[Cu(IO_3)_6]^{4-}$ anions are discrete from each other and further connected by the Ba^{2+} counter cations [Figure 2(c)].

The lattice parameters obtained by the Rietveld refinement of experimental X-ray powder diffraction data are very close to these determined by the X-ray single-crystal diffraction data, and the deviations of the lengths of unit-cell axis a, b, c, and unit-cell volume are as minor as 0.10, 0.05, 0.02, and 0.18%, respectively. In addition, the experimental powder diffraction pattern and the simulated pattern derived from single-crystal data show excellent matching (Supplementary Figure S3). These results confirm the accuracy of the reported crystal structure and the X-ray powder diffraction of $Ba_2Cu(IO_3)_6$.
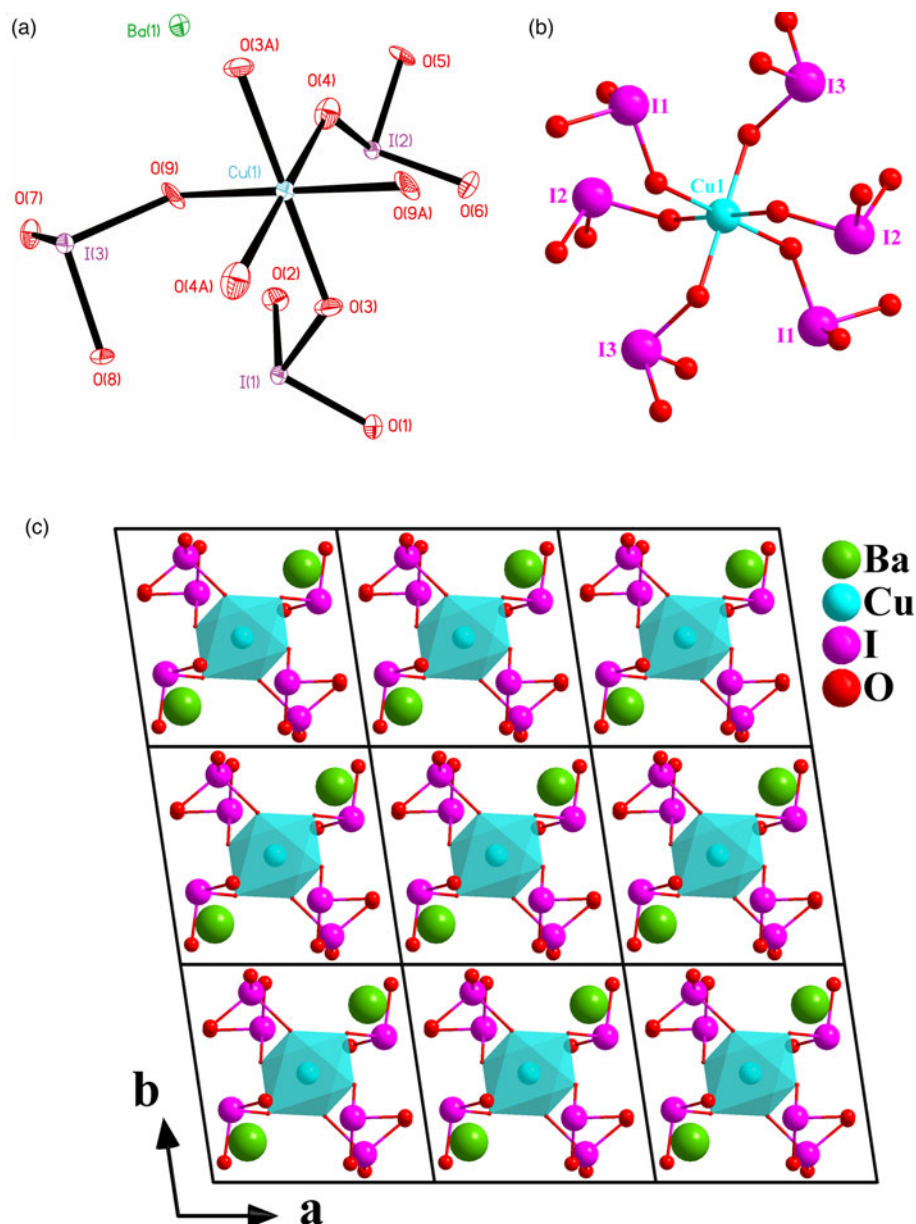
Figure 2. (a) ORTEP representations of the asymmetric unit shown in thermal ellipsoid with 30% probability (Symmetry codes for the generated equivalent atoms: (a) = 1–*x*, 1–*y*, 1–*z*); (b) view of the $[Cu(IO_3)_6]^{4-}$; (c) view of the 3D structure along [001] direction.

IV. DEPOSITED DATA

The Crystallographic Information Framework (CIF) file and powder X-ray diffraction data were deposited with the ICDD. You may request this data from ICDD at pdj@icdd.com.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715623000258.

CONFLICTS OF INTEREST

The authors have no conflict of interest to declare.

REFERENCES

Blessing, R. H. 1995. "An Empirical Correction for Absorption Anisotropy." *Acta Crystallographica Section A: Foundations and Advances* 51: 33–38.

Chen, J., C.-L. Hu, F. Kong, and J.-G. Mao. 2021. "High-Performance Second-Harmonic-Generation (SHG) Materials: New Developments and New Strategies." *Accounts of Chemical Research* 54: 2775–83.

Geng, L., C. Meng, and Q. Yan. 2022. "Polar Lanthanide Copper Iodates LnCu(IO$_3$)$_5$ (Ln=La, Ce, Pr, and Nd): Synthesis, Crystal Structure and Characterization." *Journal of Solid State Chemistry* 308: 122934.

Hu, C.-L., and J.-G. Mao. 2015. "Recent Advances on Second-Order NLO Materials Based on Metal Iodates." *Coordination Chemistry Reviews* 288: 1–17.

Lan, Y. C., X. L. Chen, Z. Tao, A. Y. Xie, P. Z. Jiang, T. Xu, and Y. P. Xu. 2002a. "X-ray Powder Diffraction Data and Rietveld Refinement for a New Iodate: (LiFe$_{1/3}$)(IO$_3$)$_2$." *Powder Diffraction* 17: 132–34.

Lan, Y. C., X. L. Chen, A. Y. Xie, P. Z. Jiang, and C. L. Lin. 2002b. "Synthesis, Thermal and Magnetic Properties of New Metal Iodate: (LiFe$_{1/3}$)(IO$_3$)$_2$." *Journal of Crystal Growth* 240: 526–30.

MDI. 2002. *JADE 7.5 (Computer Software)*. Materials Data, Livermore, CA, USA.

Mitoudi-Vagourdi, E., J. Rienmüller, P. Lemmens, V. Gnezdilov, R. K. Kremer, and M. Johnsson. 2019. "Synthesis and Magnetic Properties

of the KCu(IO$_3$)$_3$ Compound with [CuO$_5$]$_\infty$ Chains." *ACS Omega* 4: 15168–74.

Rietveld, H. M. 2014. "The Rietveld Method." *Physica Scripta* 89: 098002.

Sen Gupta, P. K., S. Ghose, and E. O. Schlemper. 1987. "The Crystal Structure and Predicted Magnetic Behavior of NaCu(IO$_3$)$_3$ – A Quasi-One-Dimensional Magnetic System." *Zeitschrift für Kristallographie* 181: 167–77.

Sheldrick, G. M. 2015. "Crystal Structure Refinement with *SHELXL*." *Acta Crystallographica Section C: Structural Chemistry* 71: 3–8.

Smith, G. S., and R. L. Snyder. 1979. "F_N: A Criterion for Rating Powder Diffraction Patterns and Evaluating the Reliability of Powder-Pattern Indexing." *Journal of Applied Crystallography* 12: 60–65.

Toby, B. H., and R. B. Von Dreele. 2013. "GSAS-II: The Genesis of a Modern Open-Source All Purpose Crystallography Software Package." *Journal of Applied Crystallography* 46: 544–49.

Wang, W.-W., T.-T. Ruan, X. Xu, and J.-G. Mao. 2017. "Agcu(IO$_3$)$_3$: Synthesis, Crystal Structure and Magnetic Property." *Chinese Journal of Structural Chemistry* 36: 1456–64.

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