Journal of Molecular Structure 1049 (2013) 288–292

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Hydrothermal synthesis, growth, and properties of a new chloride iodate

Wenwu Zhao [a], Shilie Pan [b,c,*], Lingyun Dong [b,c], Zhihua Yang [b,c], Xiaoyu Dong [b,c], Zhaohui Chen [b,c], Min Zhang [b,c], Fangfang Zhang [b,c]

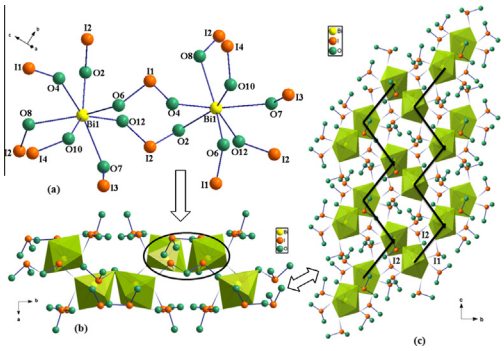
[a] Environmental and Chemical Engineering Department, Tangshan College, Hebei 063000, China
[b] Xinjiang Technical Institute of Physics & Chemistry, Key Laboratory of Functional Materials and Devices under Special Environments, CAS, China
[c] Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China

HIGHLIGHTS

- A new compound, $K_2Bi(IO_3)_4Cl$, is obtained from the KIO_3–$BiCl_3$ system.
- It crystallizes in the monoclinic system, space group $P2_1/c$.
- Its structure consists of iodide-linked infinite $_\infty[Bi(IO_3)_4]$ layer.
- Thermal analysis indicated four weight losses occurred between 398 °C and 805 °C.

GRAPHICAL ABSTRACT

In $K_2Bi(IO_3)_4Cl$ structure, the BiO_7 polyhedra are connected by the I(1) atoms and I(2) atoms to form infinite $_\infty[Bi(IO_3)_5]$ W-type chain structure extended along the *c*-axis. And the W-type chains are connected by I(2) atom to form the infinite $_\infty[Bi(IO_3)_4]$ layer along the (100) plane.



ARTICLE INFO

Article history:
Received 4 May 2012
Received in revised form 23 June 2013
Accepted 23 June 2013
Available online 29 June 2013

Keywords:
$K_2Bi(IO_3)_4Cl$
Hydrothermal method
Crystal structure
Thermal analysis

ABSTRACT

A new chloride iodate, $K_2Bi(IO_3)_4Cl$, has been synthesized using hydrothermal method from the KIO_3–$BiCl_3$ system. It crystallizes in the monoclinic system, space group $P2_1/c$ with unit-cell parameters $a = 11.216(3)$ Å, $b = 12.260(3)$ Å, $c = 10.444(2)$ Å, $Z = 4$, $V = 1352.2(5)$ Å^3. The material exhibits a three-dimensional structure consisting of interlocking iodide-linked infinite $_\infty[Bi(IO_3)_4]$ layer with interlayer potassium cations and chloride ions for charge balance. The powder X-ray diffraction pattern of the $K_2Bi(IO_3)_4Cl$ has been measured. Functional groups presented in the sample were identified by Fourier transform infrared spectrum. Thermal analysis and elemental analysis were also performed on the reported material.

1. Introduction

Design and synthesis of new materials with large macroscopic nonlinearities have received more and more attention due to their strong applications in developing optoelectronic devices and modern communication technology [1–11]. Several crystals with good nonlinear optical properties have been well known, such as β-BaB_2O_4 [3], LiB_3O_5 [4], CsB_3O_5 [5] and α-$LiIO_3$ [7], and part of which have been commercially manufactured and used worldwide.

In previous work [12–16], metal iodates, such as α-HIO_3, KIO_3, $A_2Ti(IO_3)_6$ (A = Li, Na) and $Al(IO_3)_3$, have attracted extensively studied for their important properties including ferroelectricity, piezoelectricity, pyroelectricity and second-order non-linear optical

* Corresponding author at: Xinjiang Technical Institute of Physics & Chemistry, Key Laboratory of Functional Materials and Devices under Special Environments, CAS, China. Tel.: +86 991 3674558; fax: +86 991 3838957.
E-mail address: slpan@ms.xjb.ac.cn (S. Pan).

0022-2860/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molstruc.2013.06.058

behavior. We have focused on bismuth iodate, because bismuth(III) is a heavy metal cation containing a lone electron pair which may induce the asymmetry in the structure, such as in $Bi_2(IO_4)(IO_3)_3$, $BiO(IO_3)$, $Bi_2ZnB_2O_7$, BiB_3O_6 and $Cd_4BiO(BO_3)_3$ [17–20].

In the present work, the KIO_3–$BiCl_3$ system was studied, attempting to synthesize novel metal chloride iodate crystals. Finally, a new metal chloride iodate compound with composition of $K_2Bi(IO_3)_4Cl$ was obtained. Single crystal X-ray diffraction reveals that it crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14), with $a = 11.216(3)$ Å, $b = 12.260(3)$ Å, $c = 10.444(2)$ Å, $Z = 4$, $V = 1352.2(5)$ Å^3. Herein its synthesis, growth and crystal structure are reported. IR spectrum, elemental and thermal analysis of $K_2Bi(IO_3)_4Cl$ are also presented.

2. Experimental sections

2.1. Crystal synthesis

All reagents used in the synthesis were of analytical grade. A mixture of KIO_3 (0.214 g), $BiCl_3$ (0.158 g), and 1.5 mL of the secondary deionized water was placed in a 23 mL Teflon-lined stainless steel vessel that was subsequently sealed. The autoclave was then heated to $T = 473$ K gradually, held for 2 days, then cooled down to room temperature for 3 days. The crystals were obtained in the autoclave. The colorless and transparent crystals were separated from the white precipitate by filtration and washing with deionized water and finally dried at room temperature to constant mass. The photograph of the $K_2Bi(IO_3)_4Cl$ crystal is shown in Fig. 1.

2.2. Powder X-ray diffraction

X-ray diffraction investigations on polycrystalline $K_2Bi(IO_3)_4Cl$ were carried out with a Bruker D2 advanced diffractometer equipped with a diffracted-beamed monochromator set for Cu Kα ($\lambda = 1.5418$ Å) radiation. The data were collected using a Ni-filtered Cu-target tube at room temperature in the 2θ range from 10° to 70°, with a scan step width of 0.01°, and a fixed counting time of 0.2 s/step. Fig. 2 shows the experimentally observed powder X-ray pattern and that simulated from the single-crystal structural data which are similar to each other.

2.3. Single-crystal X-ray crystallography

The crystal structure of $K_2Bi(IO_3)_4Cl$ was determined by standard crystallographic methods: a clear light crystal sized with $0.295 \times 0.287 \times 0.134$ mm^3 was mounted on a thin glass fiber with silicone oil. It was investigated by SMART APEX II Single-Crystal diffractometer using monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K and integrated with the *SAINT-Plus* program [21]. All refinements were completed with programs from the *SHELXTL* crystallographic software package [22]. The structure was solved by direct methods. The crystal structure of $K_2Bi(IO_3)_4Cl$ was solved in space group $P2_1/c$ (No. 14) which was recommended by the *SHELXTL* crystallographic software package with initial heavy-atom positions, iodine and barium, located by direct methods. The other atoms were located by subsequent cycles of refinements and Fourier difference maps. Then, we obtained the formula of the compound. The final full-matrix least-squares refinement was on F_o^2 with data having $F_o^2 \geqslant 2\sigma(F_o^2)$ and all atoms were refined with anisotropic thermal parameters. The final refinement was converged with $R_1 = 0.0321$ and $wR_2 = 0.0732$. The final difference Fourier synthesis may have shown maximum and minimum peaks at 2.079 and −2.036 e/Å^3, respectively. Then the structure was checked for missing symmetry elements with *PLATON* [23].

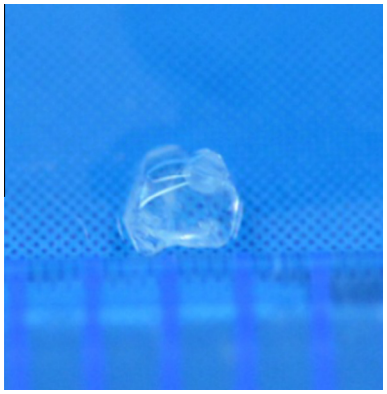


Fig. 1. The photograph of the $K_2Bi(IO_3)_4Cl$ crystal.

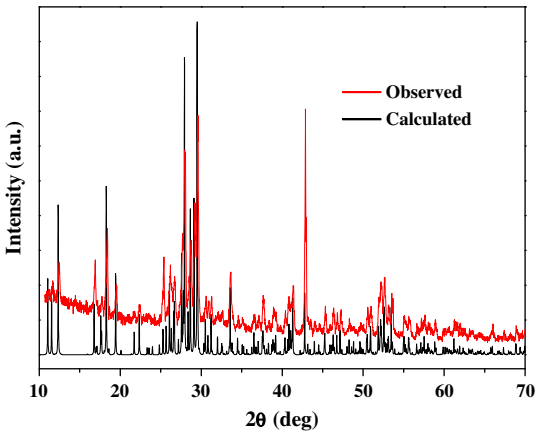


Fig. 2. The calculated and observed X-ray diffraction patterns of $K_2Bi(IO_3)_4Cl$.

The crystallographic data, the details of X-ray data collections, and refinement parameters for the structure determination are presented in Table 1. The final atomic coordinates, equivalent isotropic displacements and bond valence analysis for $K_2Bi(IO_3)_4Cl$ are given in Table S1 in Supporting information. Selected bond distances (Å) and angles (°) for $K_2Bi(IO_3)_4Cl$ are given in Table S2 in Supporting information.

Table 1
Crystal data and structure refinement for $K_2Bi(IO_3)_4Cl$.

Empirical formula	$K_2Bi(IO_3)_4Cl$
Formula weight	1022.23
Temperature	296(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 11.216(3)$ Å $\alpha = 90°$ $b = 12.260(3)$ Å $\beta = 109.685(2)°$ $c = 10.444(2)$ Å $\gamma = 90°$
Z, volume	4, 1352.2(5) Å^3
Density (calculated)	5.021 g/cm^3
Absorption coefficient	23.040/mm
$F(000)$	1784
Crystal size	$0.295 \times 0.287 \times 0.134$ mm^3
Theta range for data collection	2.55–27.47°
Index ranges	$-14 \leqslant h \leqslant 14$, $-15 \leqslant k \leqslant 15$, $-13 \leqslant l \leqslant 8$
Reflections collected	8154
Independent reflections	3092[R(int) = 0.0752]
Completeness to theta = 27.47	99.7%
Max. and min. transmission	0.6178 and 0.3141
Data/restraints/parameters	3092/0/182
Goodness-of-fit on F^2	1.107
Final R indices [$F_o^2 > 2\sigma(F_o^2)$]	$R_1 = 0.0321$, $wR_2 = 0.0732$
R indices (all data)	$R_1 = 0.0355$, $wR_2 = 0.0744$
Absolute correction	Numerical
Extinction coefficient	0.00415(15)
Largest diff. peak and hole	2.079 and −2.036 e/Å^3