

## Flux Growth of Tungsten Oxychloride $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$

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**Abstract:** Mixed anion compounds can generate the emergence of novel properties that differ from those with mono-type anion due to the difference of electronegativities, ionic radii, polarizabilities, and oxidation states between unlike anions. Abundant research has been conducted on metallic mixed-anion materials with potential application in electronics, detectors of moisture, gas sensors, electrodes for solar batteries, *etc.* The flux method has been widely applied for mixed-anion crystal growth, which based on metathetical reaction with appropriate metal-salts flux under mild conditions. It is meaningful to synthesize the mixed anion compounds by the flux method. Single crystals of tungsten oxychloride  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  were prepared *via*  $\text{CuCl}_2$  flux-growth method by two steps, which using high quality and phase-pure polycrystalline  $\text{Li}_4\text{WO}_5$  as precursor. The crystal structure was determined by single-crystal X-ray diffraction analysis, which indicates that  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  crystallizes in  $\text{P}6_3/\text{mcm}$  space group ( $a=1.02846(3)$  nm,  $c=1.98768(9)$  nm,  $V=1.82076(11)$  nm<sup>3</sup>, and  $Z=2$ ). There are crystallographically independent five Li, two W, one Cu, two Cl, and five O atoms in the unit cell, where W(1) atoms are coordinated with one Cl and five O atoms in a distorted octahedra geometry, while W(2) atoms are connected with four O atoms in a tetrahedral coordination. The Cu atoms are connected with six O atoms forming  $[\text{CuO}_6]$  octahedra. Thus, the crystal structure of the titled compound consists of  $[\text{CuO}_6]$  and  $[\text{W}(1)\text{O}_5\text{Cl}]$  octahedra, and  $[\text{W}(2)\text{O}_4]$  tetrahedra. The successful synthesis of tungsten oxychloride  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  through flux-growth method is meaningful for explore new mixed anion compounds in future.

**Key words:** tungsten oxychloride;  $\text{CuCl}_2$  flux; crystal structure; X-ray diffraction

Mixed anion compounds, especially their unique structures and excellent physical properties, have been extensively studied and have great applications in military and civilization. They have attracted abundant attention since the difference of electronegativities, ionic radii, polarizabilities, and oxidation states between unlike anions can generate the emergence of novel properties that differ from those with mono-type anion<sup>[1-4]</sup>. The active research of metallic mixed-anion materials with potential application in electronics, detectors of moisture, gas sensors, electrodes for solar batteries, *etc.* has been realized in several types of crystalline and thin film materials<sup>[5]</sup>. It is meaningful to search a suitable method to synthesize aforementioned compounds. The main hotspot to research this kind of compounds lies in how to control the arrangement of anions to refine their electronic

structures, such as the two-dimensional quantum anti-ferromagnetism in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  with trans-configuration of Cl ions in the  $\text{CuO}_4\text{Cl}_2$  octahedra<sup>[6]</sup>.

Recently, it has been reported that incorporation of halides into oxides can strikingly change their electronic structures and modify the physical properties<sup>[7-8]</sup>. Several novel transition-metal oxychlorides have been reported to date, such as  $\text{MnSb}_4\text{O}_6\text{Cl}_2$ <sup>[9]</sup>,  $\text{PbCu}_2(\text{SeO}_3)_2\text{Cl}_2$ <sup>[10]</sup>,  $\text{Cu}_3\text{Bi}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ <sup>[11]</sup>,  $\text{FeTe}_2\text{O}_5\text{X}$  ( $\text{X}=\text{Cl}, \text{Br}$ )<sup>[12]</sup>,  $\text{SrCu}_2(\text{SeO}_3)_2\text{Cl}_2$ <sup>[13]</sup>,  $\text{SmSb}_2\text{O}_4\text{Cl}$ <sup>[14]</sup>, and  $\text{MSb}_2\text{O}_3(\text{OH})\text{Cl}$  ( $\text{M}=\text{Co}, \text{Fe}, \text{Mn}$ )<sup>[15]</sup>. Above-mentioned materials show novel structures and special magnetic properties due to their diversity structural which was more helpful to generate the magnetic ordering during low temperature. This was especially manifested in layered transition metal oxyhalide  $\text{FeTe}_2\text{O}_5\text{X}$  ( $\text{X}=\text{Br}, \text{Cl}$ ), where the layers are

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built by  $[\text{FeO}_6]$  octahedra, and then forming the  $[\text{Fe}_4\text{O}_{16}]^{20-}$  units which were linked *via*  $[\text{Te}_4\text{O}_{10}\text{X}_2]^{6-}$  anionic groups. The magnetic properties are reported within a cluster approach of antiferromagnetically coupled tetramers including spin frustration and a ferromagnetic inter-tetramer interaction<sup>[12]</sup>.

The flux method widely applied for mixed-anion crystal growth is based on metathetical reaction with appropriate metal-salts flux under mild conditions. Experimentally, zone melting and hydrothermal synthesis methods are all comparatively complex and expensive for growing single crystals, and the flux method is at present one of the most economic and convenient methods for mixed anions compounds<sup>[16]</sup>. In this study, we report the single crystal growth of tungsten oxychloride  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  in copper chloride ( $\text{CuCl}_2$ , melting point of 498 °C) flux, and analyze its crystal in details.

## 1 Experimental

### 1.1 Materials and methods

Reagents were used as received:  $\text{Li}_2\text{CO}_3$  (Macklin, 99.99%),  $\text{WO}_3$  (Aladdin, 99.99%), and  $\text{CuCl}_2$  (Macklin, 98%).

The tungsten oxychloride  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  was synthesized through flux method in open-end quartz tubes. And the synthesis of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  adopt a two-step process. Firstly, precursor polycrystalline  $\text{Li}_4\text{WO}_5$  were synthesized by reacting high-purity reagents in solid-state method.  $\text{Li}_2\text{CO}_3$  and  $\text{WO}_3$  were mixed with the mole ratio of 2:1. Then these raw materials were placed in a covered alumina crucible and calcinated at 890 °C for 12 h as described in reference<sup>[17]</sup>. Then, single crystal of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  was grown from  $\text{CuCl}_2$  flux and precursor  $\text{Li}_4\text{WO}_5$ .  $\text{Li}_4\text{WO}_5$  polycrystalline samples and ten times excess  $\text{CuCl}_2$  was loaded into an open-end quartz tube, and put into a vertical pit furnace. The raw mixture was heated at 873 K for 2 d, and then cooling down to 573 K with a cooling rate of 5 K/h before shutting down the furnace.

Finally, the reaction products were washed by hot demineralized water to eliminate the fluxing agents. After subsequent drying at 353 K, yellow, block shaped single crystals of the desired products were grown and suitable for subsequent single-crystal X-ray diffraction measurements.

### 1.2 Single-crystal structure determination

Block-shaped single crystal of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  was selected for single-crystal diffraction measurements. The R-Axis Spider CCD diffractometer were used to collect data equipped with the graphite monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071073$  nm) at 293 K.

The structure of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  was determined

through direct method and refined by full-matrix least-squared methods on  $F^2$  with SHELXL package<sup>[18]</sup>. ADDSYM/PLATON was performed to studied with the final structure for additional symmetry, and no other missed or higher symmetry was found<sup>[19]</sup>. Crystallographic data (including structure factors) for the structures in this study have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1952905.

## 2 Results and discussion

The tungsten oxychloride  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  synthesized from  $\text{CuCl}_2$  flux in a vertical pit furnace crystallizes hexagonally in space group of  $P6_3/\text{mcm}$  with the unit cell parameters of  $a=1.02846(3)$  nm,  $c=1.98768(9)$  nm, and  $Z=2$ . There are crystallographically independent five Li, two W, one Cu, two Cl, and five O atoms in the unit cell, respectively, where W(1) atoms are coordinated with one Cl and five O atoms in a distorted octahedra geometry, while W(2) atoms are connected with four O atoms in a tetrahedral coordination. The Cu atoms are connected with six O atoms forming  $[\text{CuO}_6]$  octahedra.

Every two W(2) $\text{O}_4$  tetrahedra are in reverse symmetry along the  $c$  direction (Fig. 1 and 3). Three  $[\text{W}(1)\text{O}_5\text{Cl}]$  octahedra are connected with each other *via* sharing one Cl atom, and three O atoms with  $[\text{CuO}_6]$  octahedra to form the  $[\text{W}(1)_6\text{CuO}_{24}\text{Cl}_2]$  unit (Fig. 2). The three-dimensional (3D) structure of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  is assembled by the  $[\text{W}(1)_6\text{CuO}_{24}\text{Cl}_2]$  units sharing O and Cl atoms with Li. The Li atoms in  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  present four kinds of environments (Fig. 4): Li(1) atoms are connected with two Cl atoms and four O atoms and Li(2) with one Cl atom and five O atoms, while Li(3) and Li(4) atoms are coordinated with six O atoms, and Li(5) atoms are surrounded by three Cl and four O atoms.

In  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$ , the W–O distances ranging from 0.1778(9) to 0.2154(5) and the bond lengths of W–Cl are 0.2141(5) nm, which are comparable to those in  $\text{Ba}_3\text{WO}_5\text{Cl}_2$ <sup>[20]</sup>,  $\text{K}_2\text{W}_3\text{O}_{10}$ <sup>[21]</sup>,  $\text{WCl}_6$ <sup>[22]</sup>, and  $\text{WOCl}_4$ <sup>[23]</sup>, the Cu–O distances are 0.1992(8) nm in good agreement with  $\text{Ba}_3\text{Cu}_2\text{O}_4\text{Cl}_2$ <sup>[23]</sup>, and  $\text{BaCuSi}_2\text{O}_6$ <sup>[24]</sup>, from bond valence sums (BVS, Table 3) calculations in  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$ , Cu displays +2 formal oxidation states according to charge balance.

The Li–O and Li–Cl distances range from 0.2012(6) to 0.249(3) nm and 0.248(3) to 0.295(4) nm, which are closed to those in  $\text{Li}_2\text{MnCl}_4$ <sup>[25]</sup>,  $\text{Li}_2\text{ZnCl}_4$ <sup>[26]</sup>,  $\text{LiWCl}_6$ <sup>[27]</sup>,  $\text{Li}_2\text{CaTa}_2\text{O}_7$ <sup>[28]</sup>. The crystallographic data and structural refinements for  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  are summarized in Table 1.

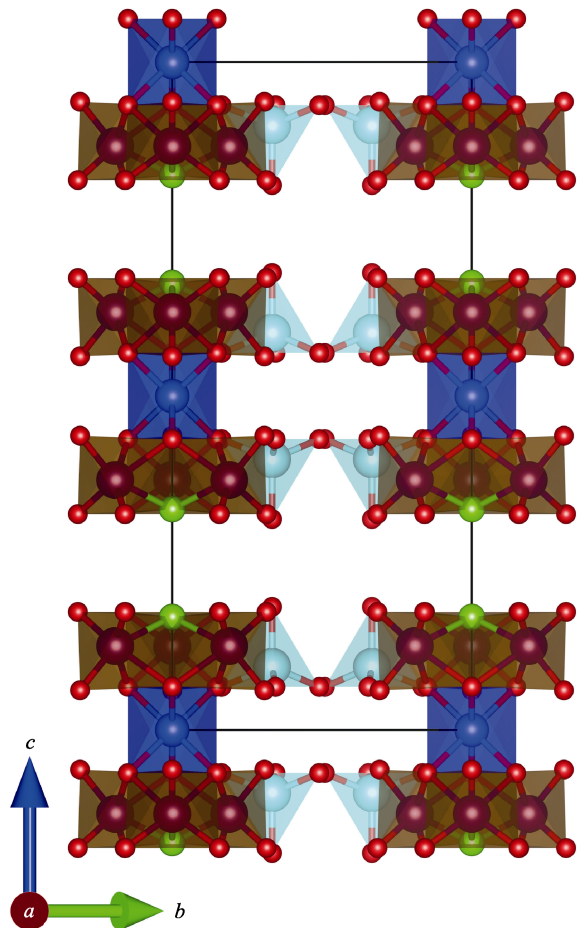


Fig. 1 View of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  along  $a$  direction, the Li atoms are omitted for clarity  
Cu: blue; W(1): brown; W(2): cyan; Cl: Green; O: red

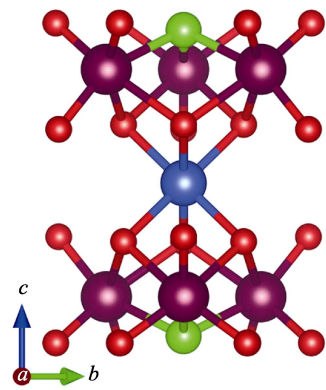


Fig. 2  $[\text{W}(1)_6\text{CuO}_{24}\text{Cl}_2]$  unit in  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$   
Cu: blue; W(1): brown; Cl: Green; O: red

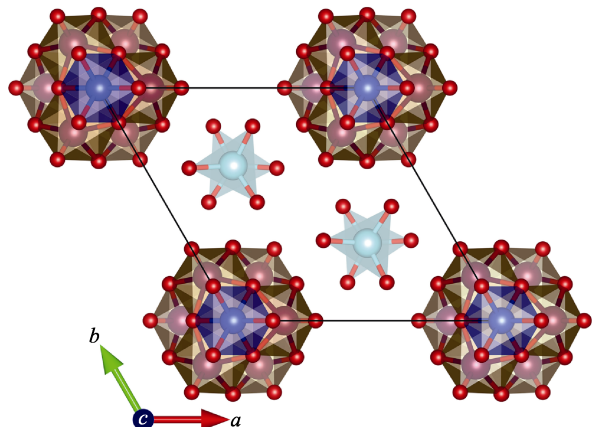


Fig. 3 View of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  along  $c$  axis, the Li atoms are omitted for clarity  
Cu: blue; W(1): brown; W(2): cyan; Cl: Green; O: red

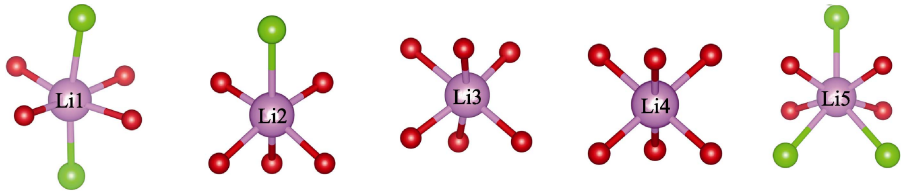


Fig. 4 Coordination geometry Li atoms in  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$   
Cl: Green ball; O: red ball; Li: pink ball

Table 1 Summary of crystallographic data and structure refinement parameters for  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$

Chemical formula	$\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$	Chemical formula	$\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$
Formula weight	2878.91	$\mu/\text{mm}^{-1}$	32.505
Crystal size/ $\text{mm}^3$	$0.162 \times 0.115 \times 0.090$	$\theta_{\text{range}}/(^{\circ})$	3.07–25.49
Crystal system	Hexagonal	GOF on $F^2$	1.171
Space group	$P6_3/\text{mcm}$	$R_1^a [I > 2\sigma(I)]$	0.0229
$a/\text{nm}$	1.02846(3)	$wR_2^b [I > 2\sigma(I)]$	0.0637
$c/\text{nm}$	1.98768(9)	$R_1^a (\text{all data})$	0.0232
$V/\text{nm}^3$	1.82076(11)	$wR_2^b (\text{all data})$	0.0640
$Z$	2	Extinction coefficient	0.00171(14)
$D_{\text{calcd}}/(\text{g} \cdot \text{cm}^{-3})$	5.251		

$a$ ,  $c$ : unit cell dimensions;  $V$ : volume;  $Z$ : number of formula units per unit cell;  $D_{\text{calcd}}$ : calculated density;  $\mu/\text{mm}^{-1}$ : diffraction wavelength;  $\theta_{\text{range}}$ : theta range for data collection; GOF on  $F^2$ : Goodness of fit on  $F^2$  ( $F$ : structure factors);  $R_1^a [I > 2\sigma(I)]$ : the residual factor for the observable diffraction point;  $wR_2^b [I > 2\sigma(I)]$ : the weighted residual factor for the observable diffraction point;  $R_1^a (\text{all data})$ : the residual factor for all diffraction points;  $wR_2^b (\text{all data})$ : the weighted residual factor for all diffraction points;  $R_1^a = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ ,  $wR_2^b = \Sigma[(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$

**Table 2** Atomic coordinates and equivalent isotropic displacement parameters of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$ 

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq.}}/\text{nm}^2$
W(1)	12 <i>k</i>	0.1904(1)	0	0.6257(1)	0.6(1)
W(2)	8 <i>h</i>	2/3	1/3	0.5947(1)	0.6(1)
Cu(1)	2 <i>b</i>	0	0	1/2	2.0(1)
Cl(1)	6 <i>g</i>	0.4831(4)	0.4831(4)	3/4	1.6(1)
Cl(2)	4 <i>e</i>	0	0	0.6693(6)	7.9(3)
O(1)	12 <i>k</i>	0	0.8520(8)	0.5647(4)	1.3(2)
O(2)	12 <i>k</i>	0.3077(8)	0	0.5594(4)	1.1(2)
O(3)	24 <i>l</i>	0.3150(6)	0.1562(6)	0.6766(3)	1.1(1)
O(4)	24 <i>l</i>	0.5092(7)	0.3447(6)	0.5644(3)	1.2(1)
O(5)	8 <i>h</i>	2/3	1/3	0.6842(5)	1.2(2)
Li(1)	12 <i>j</i>	0.2060(40)	0.2060(40)	3/4	1.4(2)
Li(2)	12 <i>k</i>	1/2	1/2	1/2	2.2(6)
Li(3)	12 <i>i</i>	0.3510(20)	0.1755(12)	1/2	2.3(5)
Li(4)	6 <i>f</i>	0.3520(30)	0.3520(30)	0.6319(1)	4.2(7)
Li(5)	6 <i>g</i>	0.4800(30)	0.2210(30)	3/4	2.8(5)

**Table 3** Selected bond lengths and atomic BVS for  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$ 

Bond	Bond length/nm	Bond	Bond length/nm	Bond	Bond length/nm
W(1)–O(3)	0.1786(6)	Li(1)–O(3)	0.2075(2)	Li(4)–O(4)	0.2086(5)
W(1)–O(3)	0.1786(6)	Li(1)–O(3)	0.2075(2)	Li(4)–O(4)	0.2086(5)
W(1)–O(2)	0.1787(7)	Li(1)–O(5)	0.213(2)	Li(4)–O(4)	0.2086(5)
W(1)–Cl(2)	0.2141(5)	Li(1)–O(5)	0.213(2)	Li(4)–O(4)	0.2086(5)
W(1)–O(1)	0.2154(5)	Li(1)–Cl(1)	0.248(3)	Li(4)–O(2)	0.2303(8)
W(1)–O(1)	0.2154(5)	Li(1)–Cl(1)	0.268(3)	Li(4)–O(2)	0.2303(8)
W(2)–O(5)	0.1778(9)	Li(2)–O(3)	0.2056(2)	(Li(4)–O)	0.2158(3)
W(2)–O(4)	0.1785(6)	Li(2)–O(3)	0.2056(2)	BVS	0.096
W(2)–O(4)	0.1785(6)	Li(2)–O(1)	0.2490(3)	Li(5)–O(3)	0.2054(8)
W(2)–O(4)	0.1785(6)	Li(2)–Cl(1)	0.2710(3)	Li(5)–O(3)	0.2054(8)
(W(2)–O)	0.1784(2)	Li(2)–O(4)	0.213(2)	Li(5)–O(3)	0.2054(8)
BVS	0.574	Li(2)–O(4)	0.213(2)	Li(5)–O(3)	0.2054(8)
Cu(1)–O(1)	0.1992(8)	Li(3)–O(2)	0.2012(6)	Li(5)–Cl(2)	0.266(3)
Cu(1)–O(1)	0.1992(8)	Li(3)–O(2)	0.2012(6)	Li(5)–Cl(2)	0.266(3)
Cu(1)–O(1)	0.1992(8)	Li(3)–O(1)	0.2346(2)	Li(5)–Cl(1)	0.285(4)
Cu(1)–O(1)	0.1992(8)	Li(3)–O(1)	0.2346(2)		
Cu(1)–O(1)	0.1992(8)	Li(3)–O(4)	0.2117(2)		
Cu(1)–O(1)	0.1992(8)	Li(3)–O(4)	0.2117(2)		
(Cu(1)–O)	0.1992(8)	(Li(3)–O)	0.2158(3)		
BVS	0.250	BVS	0.099		

Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Selected bond distances and atomic BVS are displayed in Table 3.

### 3 Conclusion

In summary, new single crystals  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$ (1) have been successfully grown by flux growth method in open-end silica tubes. The crystal structure of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  has been characterized by single crystal diffraction method. The 3D framework is built by  $[\text{CuO}_6]$  octahedra,  $[\text{W}(1)\text{O}_5\text{Cl}]$  octahedra and  $[\text{W}(2)\text{O}_4]$  tetrahedra. The adjacent  $[\text{W}(1)\text{O}_5\text{Cl}]$  octahedra are connected with each other *via* sharing one Cl atom, and further sharing three O atoms with  $[\text{CuO}_6]$  octahedra to form the  $[\text{W}(1)_6\text{CuO}_{24}\text{Cl}_2]$  unit. The successful synthesis of  $\text{Li}_{23}\text{CuW}_{10}\text{O}_{40}\text{Cl}_5$  through flux-growth method is meaningful for explore new mixed

anion compounds in the future work.

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## 助熔剂法合成钨氧氯化化合物 $Li_{23}CuW_{10}O_{40}Cl_5$

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**摘 要:** 由于不同阴离子之间的电负性、离子半径、极化率和氧化态之间的差异, 混合阴离子化合物可以产生不同于单一类型阴离子的新特性。混合阴离子金属材料在电子、湿度探测器、气体传感器、太阳能电池电极等领域有着广泛的应用前景。助熔剂方法是一种广泛应用于混合离子晶体生长的方法, 它以适当的金属盐作为助熔剂, 在较温和的条件下进行复分解反应。助熔剂法在混合阴离子化合物的合成中具有重要意义。钨氧氯化化合物  $Li_{23}CuW_{10}O_{40}Cl_5$  单晶以高质量的  $Li_4WO_5$  为前驱体, 以  $CuCl_2$  为助熔剂通过两步法合成。通过 X 射线单晶衍射确定其晶体结构。结果表明,  $Li_{23}CuW_{10}O_{40}Cl_5$  结晶属于  $P6_3/mcm$  空间群, 晶胞参数分别为  $a=1.02846(3)$  nm,  $c=1.98768(9)$  nm,  $V=1.82076(11)$  nm<sup>3</sup>,  $Z=2$ 。单胞中分别包含五个晶体学独立的 Li 原子, 两个 W 原子, 一个 Cu 原子, 两个 Cl 原子以及五个 O 原子。结构中, W(1)原子和一个 Cl 原子及五个 O 原子相连接, 形成畸变八面体, 而 W(2)原子与四个 O 原子相连接形成四面体, Cu 原子与六个 O 原子相连形成八面体。因此,  $Li_{23}CuW_{10}O_{40}Cl_5$  的晶体结构主要由  $[CuO_6]$  和  $[W(1)O_5Cl]$  八面体以及  $[W(2)O_4]$  四面体构成。助熔剂法合成钨氧氯化化合物  $Li_{23}CuW_{10}O_{40}Cl_5$  对今后探索新型的混合阴离子化合物具有重要意义。

**关 键 词:** 钨氧氯化化合物;  $CuCl_2$  助熔剂; 晶体结构; X 射线衍射

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