26卷10期 结 构 化 学 (JIEGOU HUAXUE) Vol. 26, No. 10
2007. 10 Chinese J. Struct. Chem. 1159~1164

Synthesis, Crystal Structure and Luminescent Properties of $TbCu(TeO_3)_2Cl$①

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ABSTRACT $TbCu(TeO_3)_2Cl$ was obtained in high yield from high temperature solid-state reaction of Tb_4O_7, CuO, $CuCl_2$ and TeO_2 in a 1:2:2:8 molar ratio at 710 ℃ in an evacuated quartz tube. Its structure was established by single-crystal X-ray diffraction. The title compound crystallizes in monoclinic, space group $P2_1/c$, with $a = 5.409(2)$, $b = 14.994(6)$, $c = 9.183(4)$ Å, $\beta = 98.884(5)°$, $V = 735.8(5)$ Å^3 and $Z = 4$. $TbCu(TeO_3)_2Cl$ is isostructural with $LnCu(TeO_3)_2X$ (Ln = Dy, X= Cl; Ln = Er, X = Cl, Br). Its structure features a three-dimensional (3D) network built from Tb(III) and Cu(II) ions interconnected by tellurite and chloride anions; the chloride anion and the lone-pair electrons of the tellurium(IV) ions are oriented toward the cavities of the tunnels in the network. Solid-state luminescent spectrum of $TbCu(TeO_3)_2Cl$ shows a strong emission band at 545 nm with a luminescent life time of 291 μs.

Keywords: terbium(III) tellurium(IV) oxychloride, solid-state reaction, crystal structure, luminescence

1 INTRODUCTION

Metal selenites and tellurites can form a variety of unusual structures due to the presence of stereochemically active lone pair[1]. The asymmetric coordination polyhedron adopted by Se(IV) or Te(IV) atom may also result in noncentrosymmetric structures with consequent interesting physical properties, such as nonlinear optical second harmonic generation (SHG)[2~4]. Different from selenium(IV), tellurium(IV) can form various polymeric tellu- rium(IV) oxide anions polymerized into a variety of polymeric tellurium(IV) oxide anions with extended structures[5], hence lanthanide transition metal tellurium(IV) oxyhalide system may afford compounds with new structural types as well as novel optical and magnetic properties. So far only six lanthanide transition metal tellurite halides, namely $LnCuTe_2O_6X$ (Ln = Dy, X = Cl; Ln = Er, X = Cl, Br), $Sm_2Mn(Te_5O_{13})Cl_2$, $Dy_2Cu(Te_5O_{13})Br_2$ and $Nd_4Cu(TeO_3)_5Cl_3$ have been structurally characterized[6]. Terbium compounds are especially rarely reported in lanthanon(III) tellurites, and to the best of our knowledge, only $Tb_2Te_4O_{11}$ has been isolated of all lanthanon(III) tellurites[7]. To further our knowledge on the lanthanide transition metal tellurium(IV) oxyhalides and terbium tellurites, we have prepared $TbCu(TeO_3)_2Cl$. Herein we describe its synthesis and structure as well as its IR and luminescent properties.

2 EXPERIMENTAL

Received 27 December 2006; accepted 7 February 2007 (CSD 418617)
① Supported by the National Natural Science Foundation of China (No. 20573113)
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2.1 Synthesis of the compound

The title compound was initially obtained by the high temperature solid-state reaction of Tb_4O_7 (93.5 mg, 0.125 mmol), CuO (19.9 mg, 0.25 mmol), $CuCl_2$ (33.6 mg, 0.25mmol) and TeO_2 (239.4 mg, 1.5 mmol) in our attempt to synthesize a new phase of terbium copper tellurium(IV) oxychloride. The reaction mixture was thoroughly ground and pressed into a pellet, put into a silica tube, evacuated and sealed. This tube was heated to 700 ℃ for 7 days and then cooled to 250 ℃ at 4.5 ℃/h before switching off the furnace. Sky blue prism-shaped crystals of $TbCu(TeO_3)_2Cl$ were obtained. The measured molar ratio of Tb:Cu:Te:Cl by microprobe elemental analysis resulted in 1.0:1.1:2.3:1.3, which is in good agreement with that determined from single-crystal X-ray structure analysis. After proper structural analysis, a pure powder sample of $TbCu(TeO_3)_2Cl$ was prepared quantitatively by reacting a mixture of Tb_4O_7:CuO:$CuCl_2$:TeO_2 in a molar ratio of 1:2:2:8 at 710 ℃ for 7 days in a sealed silica tube. The measured XRD powder pattern matches well with that simulated from single-crystal structure data (Fig. S1). Thus, the powder sample is a single phase and used for subsequent IR and luminescent studies.

2.2 Materials and physical measurements

All of the chemicals were analytically pure from commercial sources and used without further purification. TeO_2 (99+%) was purchased from ACROS ORGANICS. Terbium oxide, copper oxide and chloride were purchased from the Shanghai Reagent Factory. Microprobe elemental analysis was performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA). X-ray powder diffraction (XRD) patterns (Cu*Kα*) were collected on a XPERT-MPD ω-2θ diffractometer. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer with KBr pellets in the 4000～400 cm^{-1} range. Photoluminescence analyses were carried out on an Edinburgh FLS920 fluorescence spectrometer with a microsecond flash lamp (μF900, Edinburgh) as the excitation source.

2.3 X-ray crystallography

A sky blue prism crystal of $TbCu(TeO_3)_2Cl$ with dimensions of 0.10mm × 0.08mm × 0.05mm was put on a Rigaku Mercury CCD (Mo*Kα* radiation, λ = 0.71073 Å, graphite monochromator) at 293(2) K. The data were corrected for Lorentz-polarization factors, air absorption, and absorption due to variations in the path length through detector face-plate. Absorption correction based on a multi-scan technique was also applied[8]. A total of 5557 reflections were collected in the θ range from 2.62 to 27.48°, of which 1669 were independent with $R_{int} = 0.0272$ and 1584 were observed with $I > 2\sigma(I)$. The space group was determined to be $P2_1/c$ based on systematic absences, *E*-value statistics, and subsequent successful refinements of the crystal structure. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares techniques with atomic coordinates and anisotropic thermal displacement parameters[8]. The crystallographic data collection and refinement parameters are summarized in Table 1, and the selected bond lengths and bond angles are listed in Table 2.

Table 1. Crystallographic Data

Empirical formula	$ClCuO_6TbTe_2$
Formula weight	609.11
Temp, K	293(2)
Crystal dimensions(mm)	0.1000×0.0800×0.0500
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	5.409(2)
b (Å)	14.994(6)
c (Å)	9.183(4)
β (°)	98.884(5)
V (Å^3)	967.6(2)

Z	4
Density, calculated (g/cm^3)	5.499
Absorption correction	Empirical
Absorption coefficient (mm^{-1})	20.535
F(000)	1052
θ range (deg)	2.62~27.48
Limiting indices	$-7 \leqslant h \leqslant 7$, $-19 \leqslant k \leqslant 19$, $-11 \leqslant l \leqslant 9$
Reflections collected	5557
Independent reflections	1669
Observed reflections	1584
Weighting scheme	calcd. $w = 1/[\sigma^2(F_o^2) + (0.0152P)^2 + 0.6648P]$
$(\Delta/\sigma)_{max}$	0.000
R_{int}	0.0272
S	1.104
Final R indices ($I > 2\sigma(I)$)	$R = 0.0182$, $wR = 0.0398^{b}$
R indices (all data)	$R = 0.0202$, $wR = 0.0406$
Residual extremes/e/Å^3	0.974 and –1.151

Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.
Tb(1)–O(5)i	2.324(3)	Tb(1)–O(3)ii	2.328(3)
Tb(1)–O(6)	2.337(3)	Tb(1)–O(2)iii	2.351(3)
Tb(1)–O(5)	2.376(3)	Tb(1)–O(2)iv	2.425(3)
Tb(1)–O(1)ii	2.468(3)	Tb(1)–O(4)	2.564(3)
Cu(1)–O(1)	1.913(3)	Cu(1)–O(4)	1.923(3)
Cu(1)–O(3)	1.992(3)	Cu(1)–O(6)	2.009(3)
Cu(1)–Cl(1)	2.653(2)		
Te(1)–O(3)	1.881(3)	Te(1)–O(2)	1.884(3)
Te(1)–O(1)v	1.888(3)	Te(2)–O(5)	1.871(3)
Te(2)–O(6)v	1.874(3)	Te(2)–O(4)	1.895(3)
Angle	(°)	Angle	(°)
O(3)–Te(1)–O(2)	98.42(13)	O(3)–Te(1)–O(1)v	96.72(14)
O(2)–Te(1)–O(1)v	88.32(13)	O(5)–Te(2)–O(6)v	98.56(14)
O(5)–Te(2)–O(4)	87.61(14)	O(6)v–Te(2)–O(4)	96.07(14)

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x, -y+1/2, z-1/2$; (iii) $-x+1, y-1/2, -z+1/2$; (iv) #4 $x-1, -y+1/2, z-1/2$; (v) $x+1, y, z$

3 RESULTS AND DISCUSSION

3.1 Description of the structure

$TbCu(TeO_3)_2Cl$ is isostructural with $LnCuTe_2O_6X$ (Ln = Dy, X = Cl; Ln = Er, X = Cl, Br)[6]. Its structure features a porous 3D network with tunnels along the *a* axis, and the halide anion and lone-pair electrons of the tellurium(IV) ions are oriented toward the cavities of the tunnels (Fig. 1). There are one terbium atom, one copper atom, one chloride and two tellurite anions present in the asymmetric unit of $TbCu(TeO_3)_2Cl$. Tb(1) is eight-coordinated by oxygen atoms with a distorted square antiprismatic geometry. The Tb–O distances are in the range of 2.324(3)～2.564(3) Å, slightly longer than those in isomorphous Dy and Er compounds[6] and comparable to those in other terbium tellurites[7]. The copper(II) ion is in a distorted square pyramidal coordination environment composed of four oxygen atoms from four tellurite groups and a chloride anion. The four oxygen atoms form an approximate square, and the chloride anion is located at the pyramidal position. The Cu–Cl distance of 2.653(2) Å is significantly longer than those of Cu–O bonds (ranging from 1.913(3) to 2.009(3) Å), as shown in Table 2. Hence the square pyramid is also severely distorted, comparable to that in LnCuTe$_2$O$_6$X (Ln = Dy, X = Cl; Ln = Er, X = Cl, Br)[6]. Both the tellurium(IV) atoms are in a Ψ-TeO$_3$ tetrahedral coordination geometry with the fourth coordination site occupied by the lone-pair electrons of Te(IV) ion. The Te–O distances fall in the 1.871(3) ~ 1.895(3) Å range. The assignment of copper and tellurium atoms to have oxidation states of +2 and +4 is supported by the bond valence calculations. The calculated total bond valences are 2.002, 3.854 and 3.901 respectively for Cu(1), Te(1) and Te(2)[9].

The TbO$_8$ polyhedra are interconnected *via* edge sharing (O(5)···O(5)) into a 1D terbium (III) oxide chain along the *a* axis (Fig. 2). Each pair of CuO$_4$Cl polyhedra are bridged by a pair of tellurite groups (Te(1)O$_3$ and Te(2)O$_3$) to form a 1D chain along the *a* axis (Fig. 3). These two types of chains are interconnected alternately through Tb-O-Te bridges into a 3D network structure with large apertures along the *a* axis (Fig. 1). Likewise, the same coordination mode was adopted by both Te(1)O$_3$ and Te(2)O$_3$ groups, each of which chelates bidentately with a Tb(III) ion and bridges with two Tb(III) and two Cu(II) ions. Hence, the structure of TbCu(TeO$_3$)$_2$Cl can be also seen as Tb^{3+} and Cu^{2+} ions bridged by TeO$_3^{2-}$ groups (Fig. 1). The large apertures in the network are formed by tenmembered rings composed of four terbium, four copper atoms, and two tellurite anions. The chloride anions and lone pairs of the tellurium(IV) atoms are orientated toward the above apertures (Fig. 1).

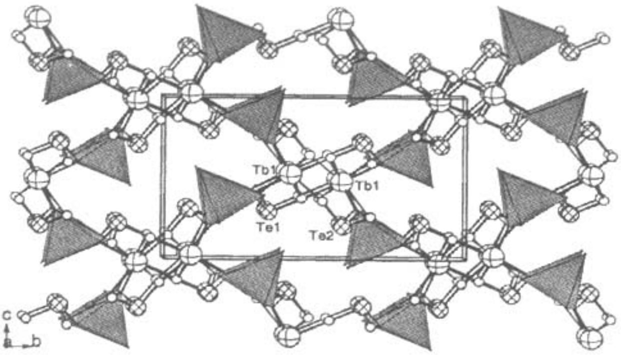

Fig. 1. **View of the structure of TbCu(TeO$_3$)$_2$Cl down the *a* axis. The CuO$_4$Cl square pyramids are shaded in middle gray. Tb, Te, and O atoms are drawn as crossed, hatched, and open (small) circles, respectively**

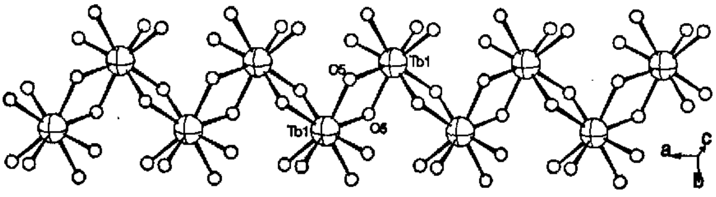

Fig. 2. **A 1D terbium (III) oxide chain along the *a* axis in TbCu(TeO$_3$)$_2$Cl**

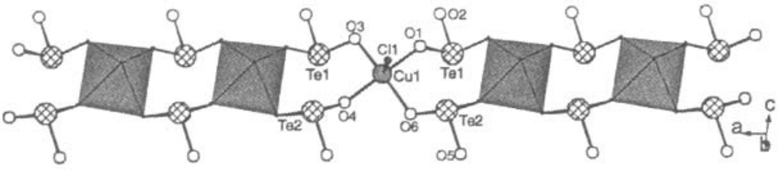

Fig. 3. **A 1D copper(II) tellurium(IV) oxychloride chain in TbCu(TeO$_3$)$_2$Cl**

3.2 UV-vis spectroscopy

IR spectrum of $TbCu(TeO_3)_2Cl$ indicates that it is transparent in the wavelength range of 4000~1000 cm^{-1}. The absorption bands at 778, 724, 695, 657, 500, 473, 451 and 410 cm^{-1} are originated from the tellurium(IV) oxide groups.

3.3 Luminescent property

The solid-state luminescent property of $TbCu(TeO_3)_2Cl$ was investigated at room tempe- rature. Under excitation at 378 nm, $TbCu(TeO_3)_2Cl$ displays the four sets of characteristic emission bands for the Tb(III) ion in the visible region: an emission band at 486 nm ($^5D_4 \rightarrow {}^7F_6$), a strong emission band at 545 nm ($^5D_4 \rightarrow {}^7F_5$), two weak bands at 582 nm ($^5D_4 \rightarrow {}^7F_4$) and 620 nm ($^5D_4 \rightarrow {}^7F_3$), respectively[10] (Fig. 4). Each emission band is further split into several sub-bands due to the crystal field effect and the low symmetry (C_1) of Tb(III) site (Fig. 4). The luminescent life time of ($^5D_4$) for the 379 nm excitation and 545 nm emission is measured to be about 291 μs.

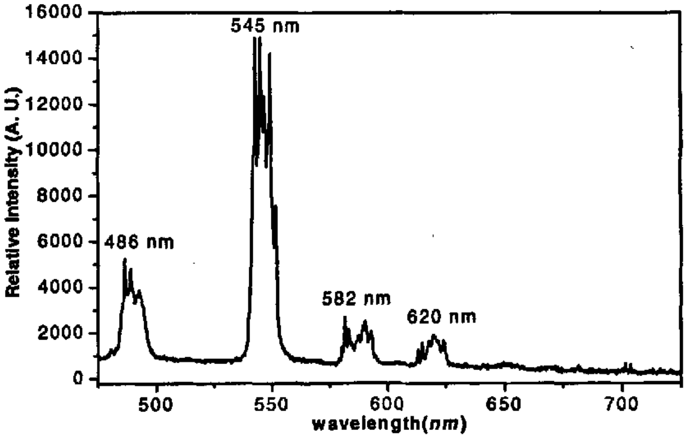

Fig. 4. Solid-state emission spectra of $TbCu(TeO_3)_2Cl$ at room temperature

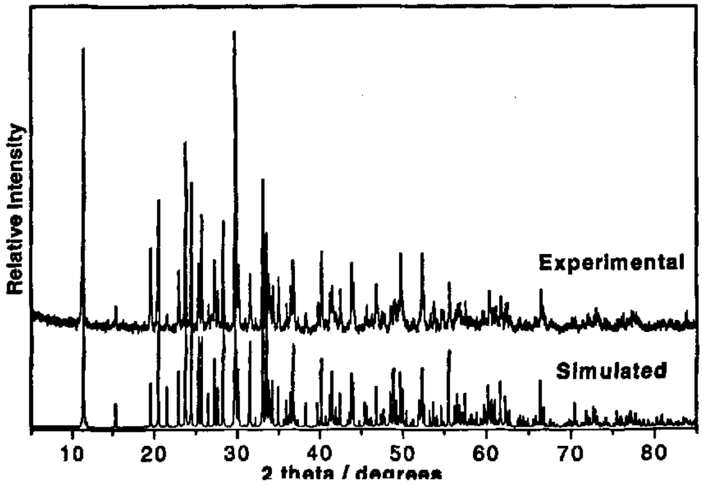

Fig. S1. Simulated and experimental X-ray powder diffraction patterns for $TbCu(TeO_3)_2Cl$

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刊名：	结构化学 ISTIC SCI
英文刊名：	CHINESE JOURNAL OF STRUCTURAL CHEMISTRY
年，卷(期)：	2007,26(10)

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