



Porous layered and open-framework mixed-valence copper tellurites



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ABSTRACT

$\text{ICu}^+\text{Cl}_3[\text{Cu}_2^{2+}(\text{TeO}_3)]$ (**1**), $\text{ICu}_{1.7}\text{Cl}_{3.8}[\text{Cu}_4^{2+}\text{O}(\text{TeO}_3)_2]$ (**2**) and $\text{TI}_2^+[\text{Cu}_2^{2+}\text{Te}^{6+}\text{Te}_6^{4+}\text{O}_{18}]$ (**3**) were obtained by CVT and hydrothermal methods in $\text{CuCl-CuCl}_2\text{-TeO}_2$ and $\text{TI}_2\text{CO}_3\text{-CuO-TeO}_2$ systems. **1** demonstrates layered topology with pores (1×0.65 nm), whereas **2** has open-framework structural architecture with two-dimensional system of channels (1.16×0.74 nm). Channels in open-framework of **3** are occupied by TI^+ cations. 'Host-guest' structural organization of **1** and **2** with host Cu^{2+} -tellurite units of different dimensionality formed by oxocentered OCu_4 tetrahedra and OCu_2Te triangles and guest Cu^+ -chloride species is the result of formation from gases in CVT reactions. Oxocentered units determine basic topologies of the structures of **1** and **2** and influence their stability and properties. $[\text{Te}^{6+}\text{Te}_6^{4+}\text{O}_{18}]^{6-}$ polytellurite-tellurate framework in **3** can be represented as consisting of Kagome-like layers.

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1. Introduction

Porous inorganic oxide based crystalline materials are well known for a variety of different applications [1]. Mixed-valence compounds have very broad applications in the fields from biology to high-temperature superconducting materials [2]. Transition metal oxyhalide compounds containing lone-pair cations $M\text{-L-O-X}$, and transition metal oxides with mixed lone-pair cations $M\text{-L-L-O}$ (M =transition metal cation, L =lone pair cations, $X=\text{Cl}^-$, Br^-) usually crystallize in low-dimensional structural architectures due to the 'chemical scissors' [3] role of stereochemically active lone electron pairs. Such compounds are manifested with the abundance of interesting physical properties such as magnetic frustration [4], catalytic properties, superconductivity etc [5]. d^{10} - d^9 electronic configurations transformation of Cu^+ to Cu^{2+} is usually characterized by the appearance of uncommon magnetic properties [6]. sp^3d^2 to sp^3d hybridization of Te^{4+} to Te^{6+} is traced with coordination polyhedron transformation from see-saw to regular octahedral coordination, which provokes a strong augmentation of non-linear optical properties [7]. Nine mixed-valence $\text{Cu}^+/\text{Cu}^{2+}$ oxochlorides [8–14] and one mixed-valence $\text{Te}^{4+}/\text{Te}^{6+}$ copper oxide [15] are known to date. $\text{Ba}_2\text{Cu}_4(\text{Te}_4\text{O}_{11})\text{Cl}_4$ [11] and $\text{Cu}_3\text{Yb}_3(\text{TeO}_3)_4\text{Cl}_6$ [14] are the only known mixed-valence $\text{Cu}^+/\text{Cu}^{2+}$ tellurites. Published to date one 'pure' (i.e. without

additional metals) mixed-valence ($\text{Cu}^+/\text{Cu}^{2+}$) oxoselenite [16] suggests that similar Te/Se analogs may exist. Tellurites in the $\text{TI}^-\text{Cu-Te-O}$ system are unknown but three tellurates were reported: $\text{TI}_4\text{CuTeO}_6$ and $\text{TI}_6\text{CuTe}_2\text{O}_{10}$ [17], $\text{NaTI}_3\text{Cu}_4(\text{TeO}_6)_2$ [18]. All of them are represented by low-dimensional structural architectures, which is unusual for structures with octahedrally coordinated Te^{6+} . Recently we have successfully employed CVT (chemical vapor transport) reactions for obtaining of a number of copper selenite compounds [19]. Thus it was decided to apply similar method of synthesis for tellurite containing systems with copper.

Herein we report on the studies of the $\text{CuCl-CuCl}_2\text{-TeO}_2$ and $\text{TI}_2\text{CO}_3\text{-CuO-TeO}_2$ systems, where novel mixed-valence $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Te}^{4+}/\text{Te}^{6+}$ porous tellurite based compounds were obtained by CVT (**1**, **2**) and hydrothermal methods (**3**). $\text{ICu}^+\text{Cl}_3[\text{Cu}_2^{2+}(\text{TeO}_3)]$ (**1**) demonstrates layered topology with pores (1×0.65 nm), whereas $\text{ICu}_{1.7}\text{Cl}_{3.8}[\text{Cu}_4^{2+}\text{O}(\text{TeO}_3)_2]$ (**2**) has open-framework structural architecture with two-dimensional system of channels. Channels in open-framework of $\text{TI}_2^+[\text{Cu}_2^{2+}\text{Te}^{6+}\text{Te}_6^{4+}\text{O}_{18}]$ (**3**) are occupied by TI^+ cations.

2. Experimental section

2.1. Syntheses

All the reagents were analytically pure obtained from Sigma-Aldrich and used without further purification. The synthesis of **1**

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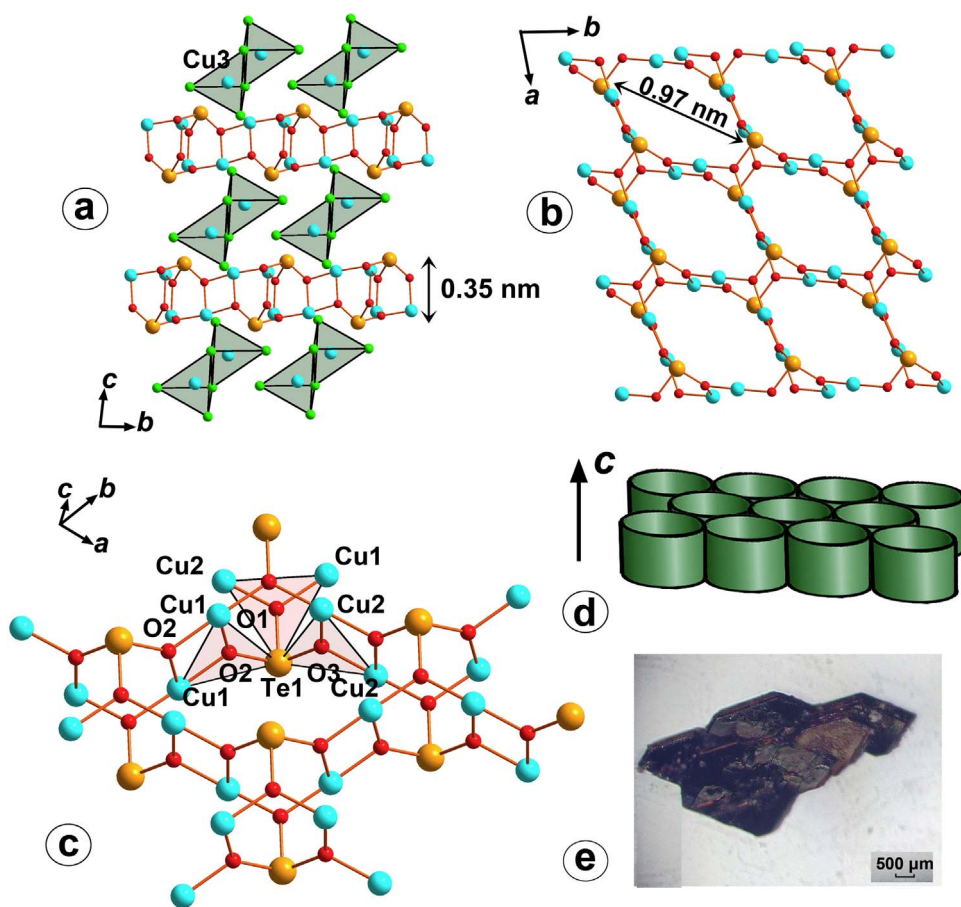


Fig. 1. General projection of the crystal structure of **1** along the *a* axis (Cu3) sites belong to Cu^+ cations (a). Guest $\text{Cu}_2^+ \text{Cl}_6$ dimers are located between porous host cationic $[\text{Cu}_2^+(\text{TeO}_3)]^{2+}$ layers. Ball-and-stick (b) and schematical (d) representation showing arrangement of pores in $[\text{Cu}_2^+(\text{TeO}_3)]^{2+}$ layer along the *c* axis. Detailed structure of $[\text{Cu}_2^+(\text{TeO}_3)]^{2+}$ layer, where each of O atoms is central in OCu_2^+Te triangles (c). Brown crystals of **1** under optical microscope (e). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and **2** were made by CVT reactions in sealed evacuated silica tubes. $\text{TeO}_2:\text{CuCl}:\text{CuCl}_2$ were mixed in a mortar in the molar ratios 3:0.5:0.5, 2:0.5:0.5, 1:0.5:0.5, 1:1:1, 1:1.5:1.5, put into silica tubes (~13 cm long) and further evacuated to 10^{-2} mbar, sealed and placed horizontally into a furnace, heated at 450 °C for 50 h and slowly cooled to room temperature with a cooling rate of 3 °C/h. The temperature gradient between the source (hot) and deposition (cold) zones of the tube in the furnace was 50 °C. Brown crystals of **1** (Fig. 1e) were observed in cold zone of the tube with molar ratio $\text{TeO}_2:\text{CuCl}:\text{CuCl}_2$ of 1:1.5:1.5. Yellow-brown prismatic crystals of **2** (Fig. 2f) were grown also in cold zone of the tube with molar ratio $\text{TeO}_2:\text{CuCl}:\text{CuCl}_2$ of 2:0.5:0.5. Both novel phases were in association with already known Cu_3TeO_6 and CuTe_2O_5 , except for the tube with $\text{TeO}_2:\text{CuCl}:\text{CuCl}_2$ of 3:0.5:0.5 where light-green crystals of $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ formed in cold zone. The same CVT method with identical conditions was used to explore the quaternary system of $\text{TlCl}:\text{TeO}_2:\text{CuCl}:\text{CuCl}_2$ with molar ratios of 3:1:0.5:0.5, 2:1:0.5:0.5, 1:1:0.5:0.5, 1:1:1:1, 1:1:1.5:1.5 and no novel phases were obtained. Dark-brown tints of crystals of **1** and **2** suggested presence of Cu^+ in composition. Aquamarine blue single crystals of **3** (Fig. 3g) were synthesized using hydrothermal technique. $\text{Tl}_2(\text{CO}_3)_3$, CuO and TeO_2 were mixed in a mortar in a molar ratio 1.5:3:1 respectively, and combined with 8 mL of KOH (1 M). The solution was placed in a 23 mL Teflon-lined autoclave. The closed autoclave was heated at 220 °C during 48 h and then cooled to room temperature with a cooling rate of 7 °C/h. Single crystals of **1** in association with already known $\text{Tl}_2\text{Te}_2\text{O}_5$ were filtered and

washed with hexane. The electron-microprobe analyses (HITACHI-TM 3000) were performed for **1**, **2** and **3**. Qualitative electron microprobe analysis (Hitachi TM-3000) revealed no other elements, except Cu, Cl and Te with the atomic number greater than 11 (Na) in **1** and **2** and Tl, Cu and Te in **3**.

2.2. X-ray crystallography

Single crystals of **1**, **2** and **3** were mounted on a thin glass fibers for the X-ray diffraction analysis using Bruker APEX II DUO X-ray diffractometer with a micro-focus X-ray tube operated with $\text{MoK}\alpha$ radiation at 50 kV and 40 mA. The data were integrated and corrected for absorption using a multi scan type model using the Bruker programs APEX and SADABS. More than a hemisphere of X-ray diffraction data were collected. Crystallographic information is summarized in Table 1 and selected interatomic distances in Table 2.

For powder x-ray diffraction of **1**, **2** and **3** ten crystals of each phase were preliminary checked by single-crystal x-ray and later crushed and glued with epoxy into balls. X-ray powder diffraction data were collected with a Rigaku R-Axis Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using Debye-Scherrer geometry (with $d=127.4$ mm). Experimental and calculated X-ray powder diffraction data ($\text{CoK}\alpha$) are in good agreement and given in Fig. 1S, 2S, 3S.

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