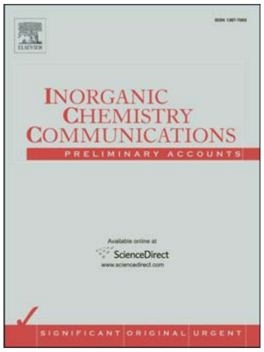

Copper polytellurite-chlorides with A^{2+} cations (A = Cd, Pb) obtained by CVT reactions

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Copper polytellurite-chlorides with A^{2+} cations (A=Cd, Pb) obtained by CVT reactions

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ABSTRACT. Two novel polytellurite-chlorides $Pb_5Cu_2(Te_4O_{11})Cl_8$ (**1**) and $CdCu_2(Te_3O_8)Cl_2$ (**2**) were obtained by a chemical vapour transport (CVT-reactions) reactions. The structure of **1** is based on $[Pb_5Cu_2(Te_4O_{11})]^{8+}$ one-dimensional blocks with full and partially occupied Cl sites around. The structure of **2** can be described as being formed by two types of one-dimensional units formed by Cd,Cu-centered polyhedra and TeO_3, TeO_4 pyramids sharing via common O atoms into electroneutral $[CdCu_2(Te_3O_8)Cl_2]^0$ sheets. Obtaining of novel polytellurite-chlorides demonstrates effectiveness of CVT techniques for preparation of different tellurite-based complex layered materials.

KEYWORDS: copper, tellurium, polytellurites, CVT-reactions, single crystal x-ray diffraction, lone-pair

Crystalline materials with Te(IV) and divalent metal cations have received attention for their fascinating structural chemistry and physical properties [1-5]. One-sided TeO_3, TeO_4 or TeO_5 coordination environments are very typical for Te^{4+} cations due to the presence of $5s^2$ lone electron pair. $Te^{4+}O_n$ polyhedra reveal tendency to form various $Te^{4+}{}_nO_m$ polyanions in contrast to Se^{4+}- and I^{5+}-centered polyhedra. The degree of $Te^{4+}{}_nO_m$ polymerization is affected by the type and number of the other cations within the structure. Tellurite compounds with Cu^{2+} represent particular interest in the sense of copper asymmetric coordination environments attributable to Jahn–Teller distortions. Many of copper tellurite halides reveal interesting magnetic properties [6-8]. Insertion of large Pb^{2+} cations or Cd^{2+} into copper tellurite chlorides may result in formation of unusual structural topologies and possible interesting properties. To date only one Pb-Cu tellurite chloride was reported $PbCu_2(TeO_3)_2Cl_2$ [8] and Cd-Cu tellurite chlorides are unknown. Recently we have employed chemical vapor transport reactions for obtaining of Cu^{2+} selenite chlorides with various cations [9,10]. Thus it was decided to apply the latter method of synthesis for tellurite containing systems. Herein we report on the synthesis and structural studies of $Pb_5Cu_2(Te_4O_{11})Cl_8$(**1**) and $CdCu_2(Te_3O_8)Cl_2$(**2**) obtained in evacuated quartz ampoules in $CuCl_2$-TeO_2-PbO and $CuCl_2$-TeO_2-CdO system, respectively [11-13].

The structure of **1** contains five symmetrically independent Pb^{2+} cations, two Cu^{2+}, and four Te^{4+} sites. The coordination of all Pb sites is asymmetric due to the presence of the stereochemically active lone-pairs. Shorter and stronger Pb-O bonds are located in one coordination hemisphere and longer Pb-Cl in another. Te(1) and Te(2) atoms form TeO_3 trigonal pyramids with three short distances ranging from 1.8614(3) to 1.8908(2) Å for Te(1) and from 1.8365(3) Å to 1.8873(2) Å for Te(2). Te(3) and Te(4) form TeO_4 polyhedra. Te(3) have three short Te-O bonds of 1.8940(2)-1.9231(3) Å and one long Te(3)-O(4) bond of 2.3982(4) Å. Te(4) coordination is similar to Te(3). Thus Te sites demonstrate typical for Te^{4+} coordination environments with formation of Te(1)O_3, Te(2)O_3 and Te(3)O_4, Te(4)O_4 pyramids further interconnected via common corners into $[Te_4O_{11}]^{6+}$ tetrameric units (Fig. 2). Similar $[Te_4O_{11}]^{6+}$ isolated units were previously reported in $Pr_2Te_4O_{11}$ [16], $Er_2Te_4O_{11}$[17], $Sr_3Te_4O_{11}$ [18] and $Ni_{15}Te_{12}O_{34}Cl_{10}$ [19]. The structure of **1** contains also two symmetrically independent Cu atoms forming CuO_4 squares isolated one from each other and further complemented by Cl atoms to CuO_4Cl_2 octahedra with the average <Cu-Cl> bond lengths equal to 2.8921(3)-2.962(5) Å. Taking into account only the strongest *A*-O (*A* = Pb, Te, Cu) bonds one-dimensional $[Pb_5Cu_2(Te_4O_{11})]^{8+}$ block in the structure of **1** can be obtained via the list of subsequent

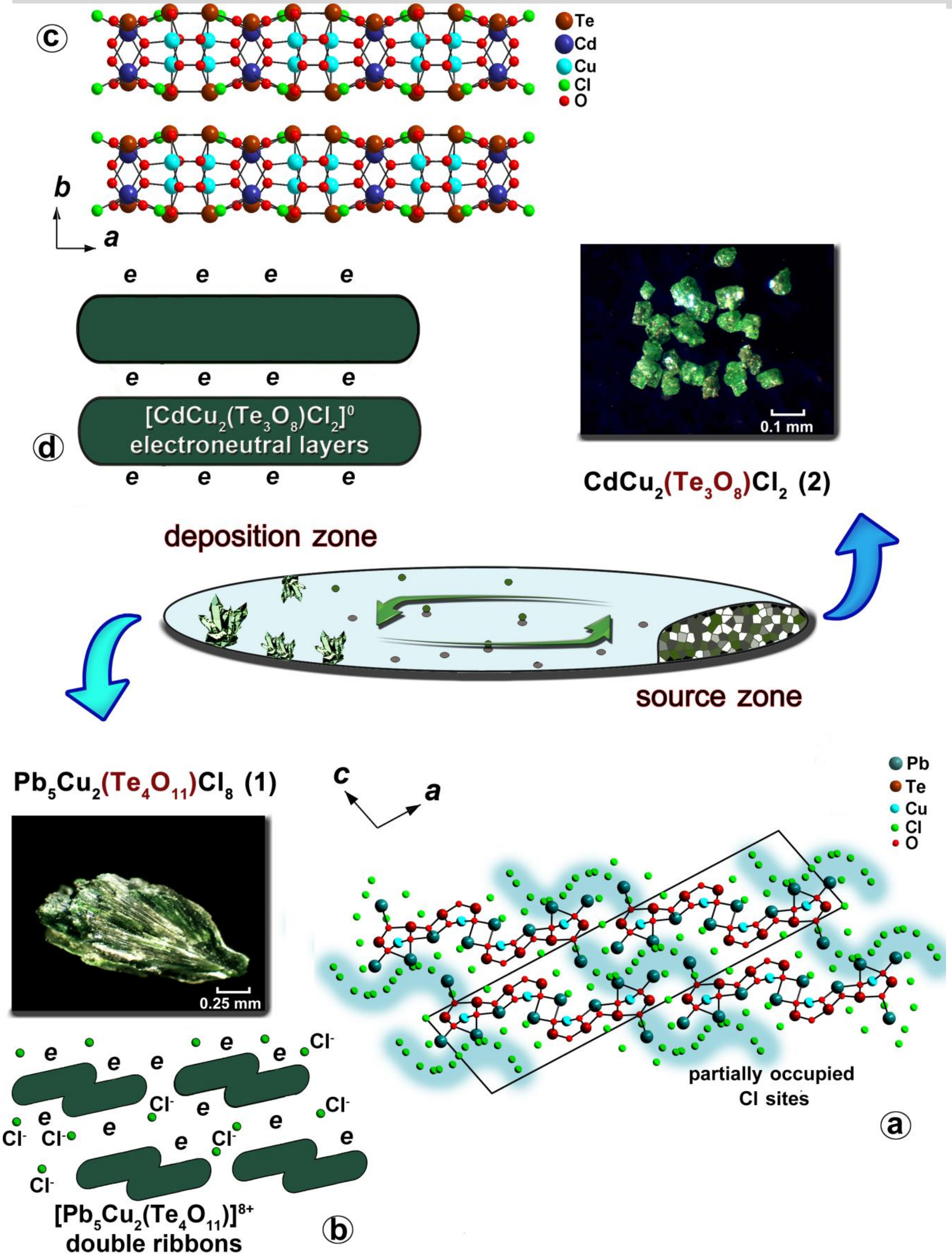

Fig. 1. General projections of the structure of **1** (below) and **2** (above) and their schematic representations (lone pairs on Pb^{2+} and Te^{4+} are symbolized as *e*). The structure of **1** (a) represents type of structural architecture with positively charged $[Pb_5Cu_2(Te_4O_{11})]^{8+}$ one-dimensional units and Cl^- anions (partially occupied Cl sites are highlighted) associating with stereochemically active lone electron pairs in between (b). The structure of **2** (c) consists of neutral $[CdCu_2(Te_3O_8)Cl_2]^0$ layers (d) interconnected via weak *A*-Cl (*A* = metal) bonds only. Crystals of **1** and **2** were obtained by the chemical vapour transport reactions in evacuated quartz ampoules. Crystals of **1** were grown in the deposition part of the tube, whereas crystals of **2** are observed in the source zone.

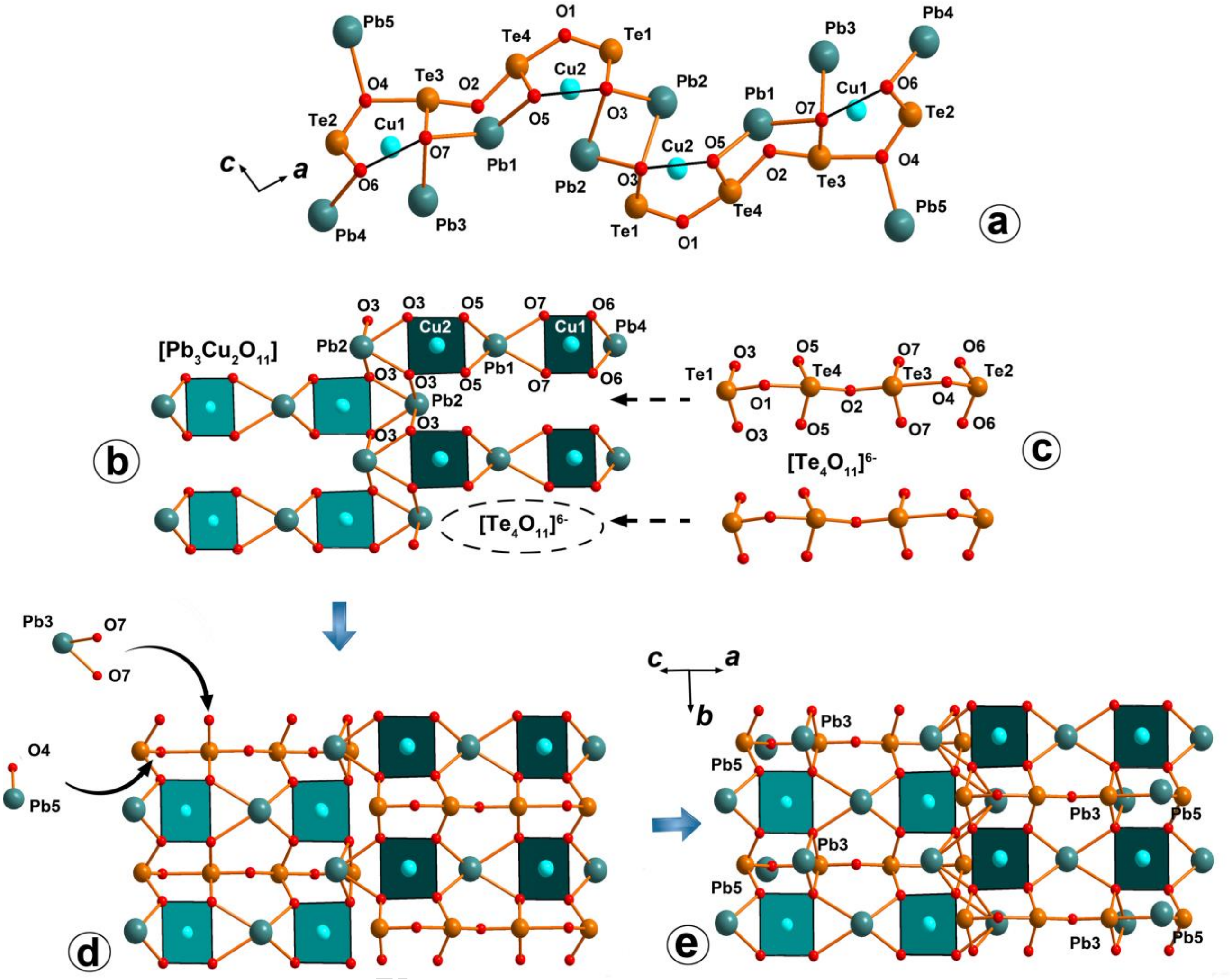

Fig. 2. $[Pb_5Cu_2(Te_4O_{11})]^{8+}$ block (a) in the structure of **1** can be obtained according to the following subsequent transformations: (1) $[Pb_3Cu_2O_{11})]$ units (b) are formed by CuO_4 squares and one-sided PbO_4 and PbO_2 polyhedra which are further stacked via common O(3) atoms and related by inversion center; (2) tellurite tetramers are inserted (c) in between $[Pb_3Cu_2O_{11})]$; (3) additional Pb(3) and Pb(5) atoms are attached under and above $[Pb_3Cu_2(Te_4O_{11})]$ units (d) thus forming $Pb_5Cu_2(Te_4O_{11})]^{8+}$ blocks (e).

transformations listed in Fig. 2. There are a number of Cl sites compensating positive charge of $[Pb_5Cu_2(Te_4O_{11})]^{8+}$ one-dimensional blocks in the structure of **1**. Lone-electron pairs on Te^{4+} and Pb^{2+} demonstrate typical halophilic behavior and locate jointly in the areas with Cl sites. Cl(1)-Cl(6) sites are fully occupied, whereas the rest of Cl sites demonstrate partial occupancies. Partially occupied Cl(7)-Cl(13) sites are segregated into separate regions of the structure of **1** depicted in Fig. 1 and reveal possible pathways for ionic conduction.

The structure of **2** contains one Cd^{2+} cation, one Cu^{2+}, and two Te^{4+} sites (Fig. 3). Cd atoms are coordinated by four O with the Cd-O bond lengths in the range of 2.313(1) - 2.414(1) Å and two Cl atoms at distances of 2.540(2) Å thus forming irregular CdO_4Cl_2 polyhedra. Te atoms form two types of polyhedra: TeO_3 and TeO_4. Te(1) atoms form three short Te(1)-O bonds in the range of 1.883(1)-1.911(1) Å, whereas Te(2) form four short Te(2)-O bonds each in the range of 1.868(1)-2.165(1) Å. The crystal structure of **2** contains one symmetrically independent Cu site coordinated by four O atoms thus forming CuO_4 squares (Fig. 3). CuO_4 squares share common edges thus forming Cu_2O_8 dimers (Fig. 3). CdO_4Cl_2 polyhedra and Cu_2O_8 dimers via common corners produce one-dimensional chains in the structure of **2** (Fig. 3a,c). TeO_3 and TeO_4 pyramids form $[Te_3O_8]^{4-}$ polyanions. The structure of **2** can be described as being formed by two intertwisting one dimensional units formed by Cd,Cu-centered polyhedra and tellurite pyramids thus forming electroneutral $[CdCu_2(Te_3O_8)Cl_2]^0$ sheets parallel to the (001) plane (Fig. 2). The interlayer space is occupied by lone-pairs on Te^{4+} cations. Compounds with electroneutral layers formed by lone-pair and transition elements were recently described as promising materials in different fields [20-22]. However crystal structure of **2** is the first example of such kind of structural architecture with Cd^{2+} cations.

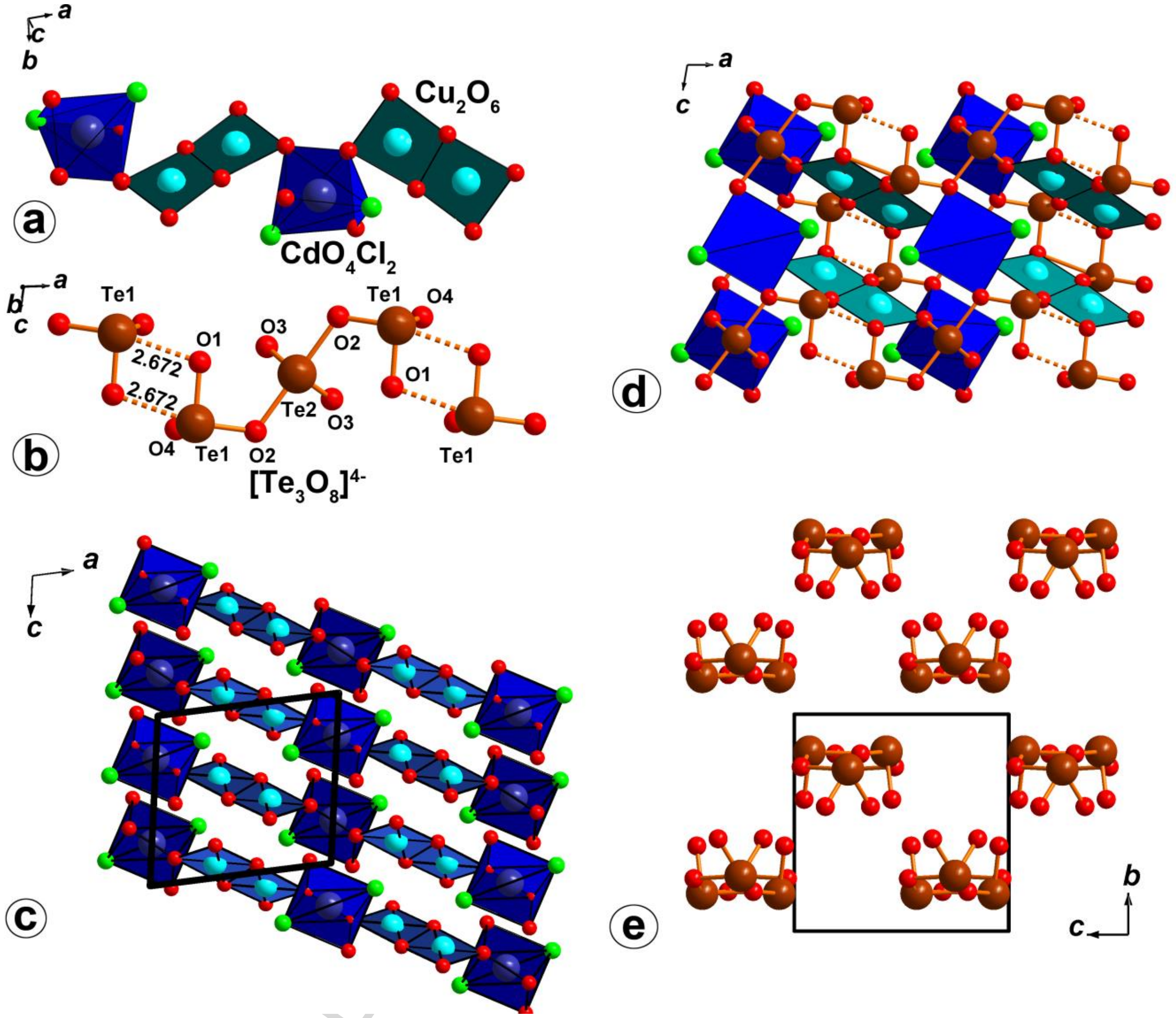

Fig. 3. Cations coordination environments in the structure of **2** (a, b). Cu_2O_6 dimers and CdO_4Cl_2 share via common corners into one-dimensional units (a), whereas TeO_4 and TeO_3 pyramids form $[Te_3O_8]^{4-}$ trimers (b). General projection of $[CdCu_2(Te_3O_8)Cl_2]^0$ units along the *b* axis (c). Orientation of Cd-Cu oxochloride (d) and $[Te_3O_8]^{4-}$ units (e) in the structure of **2**.

In conclusion, our exploration of copper-tellurite systems with Pb^{2+} and Cd^{2+} produced two novel polytellurite-chlorides with complex structural topologies and demonstrates effectiveness of CVT techniques for preparation of different Te-based complex layered materials. Tellurites and metal halides play the role of transport agents. This method hasn't been used before for obtaining of Cd and Pb containing tellurites. However, difficulties of this method to obtain pure phases should be taken into account. Formation of Cu_2O_8 dimers in the structure of **2** could be of interest from the viewpoint of interesting magnetic properties. We are in the process of exploring new tellurite based compounds with copper by this method and their properties.

Acknowledgments

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Appendix A. Supplementary data

CSD entries 431271 and 431270 contain structural data for **1** and **2**, respectively. Supplementary data for this paper can be found online at http://dx.doi.org/XX.XXXX/*.

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[11] Synthesis of **1** and **2**: Single crystals of **1** and **2** were prepared by the chemical vapour transport reactions method from the mixture of $CuCl_2$, TeO_2 and PbO in the ratio of 3:1:1 for **1** and $CuCl_2$, TeO_2 and CdO in the ratio of 1:2:1 for **2**. The reaction mixtures were grounded and put in a silica tube, which was evacuated and sealed. One end of silica tube with loaded mixture of reagents was heated to 450°C and another end to 430°C for 24 h and then slowly cooled to room temperature for 3 days for **1** and 10 days for **2**. Green crystals of **1** (Fig. 1) were observed in deposition zone of the tube in association with crystals of $PbCl_2$ and $CuTeO_3$. Phase **2** appeared in the source zone together with $Cu_2Te_2O_5Cl_2$ [14] Qualitative electron microprobe analysis (Hitachi TM3000) revealed no other elements, except Pb, Cu, Cl and Te in **1** and Cd, Cu, Cl and Te in **2** with the atomic number greater than 11 (Na).

[12] Single crystal data collections (Bruker Apex II DUO diffractometer with a micro-focus X-ray tube at 100K) were performed on crystals of **1** and **2** mounted on glass fibers. Structure solution and refinement has been carried out using SHELX-2014 program [15]. **1**: crystal 0.12 × 0.10 × 0.05 mm^3, monoclinic, $C2/m$, a = 42.881(8), b = 5.4475(10), c = 10.741(2) Å, β = 103.340(3), V = 2441.4(8) $Å^3$, ρ = 5.803 g cm^{-3}, $\mu(MoK\alpha)$ = 41.661 mm^{-1}, 9522 measured reflections, 2048 unique (R_{int} = 0.056), R_1 = 0.049, wR_2 = 0.100, $\rho_{max,min}$ = +3.42 (1.17 Å from Pb(2))/-1.72 e.$Å^{-3}$ (0.77 Å from Pb(5). **2:** crystal 0.10 × 0.06 × 0.04 mm^3, monoclinic, $P2/c$, a = 8.5433(3), b = 7.9599(3), c = 7.9857(3) Å, β = 99.864(2)°, V = 535.03(3) $Å^3$, ρ = 5.097 g cm^{-3}, μ(MoKα) = 14.443 mm^{-1}, 17184 measured reflections, 5544 unique (R_{int} = 0.036), R_1 = 0.024, wR_2 = 0.050, $\rho_{max,min}$ = +2.19 (0.50 Å from Te(1))/-2.12 e.$Å^{-3}$ (0.52 Å from Te(2).

[13] Thermal behavior of **1** (Fig. 1S) was studied in air by means of a Rigaku Ultima X-ray diffractometer with Cu-Kα radiation using a high-temperature camera Rigaku HTA 1600. The sample was prepared from heptane's suspension on a Pt-Rh plate. The temperature step was 10 °C in the range of 25-500 °C. Compound **1** reveals no phase transitions and starts to decompose at 340°C. Products of decomposition are: CuO, $Pb_3O_2Cl_2$ and $Pb_3TeO_4Cl_2$.

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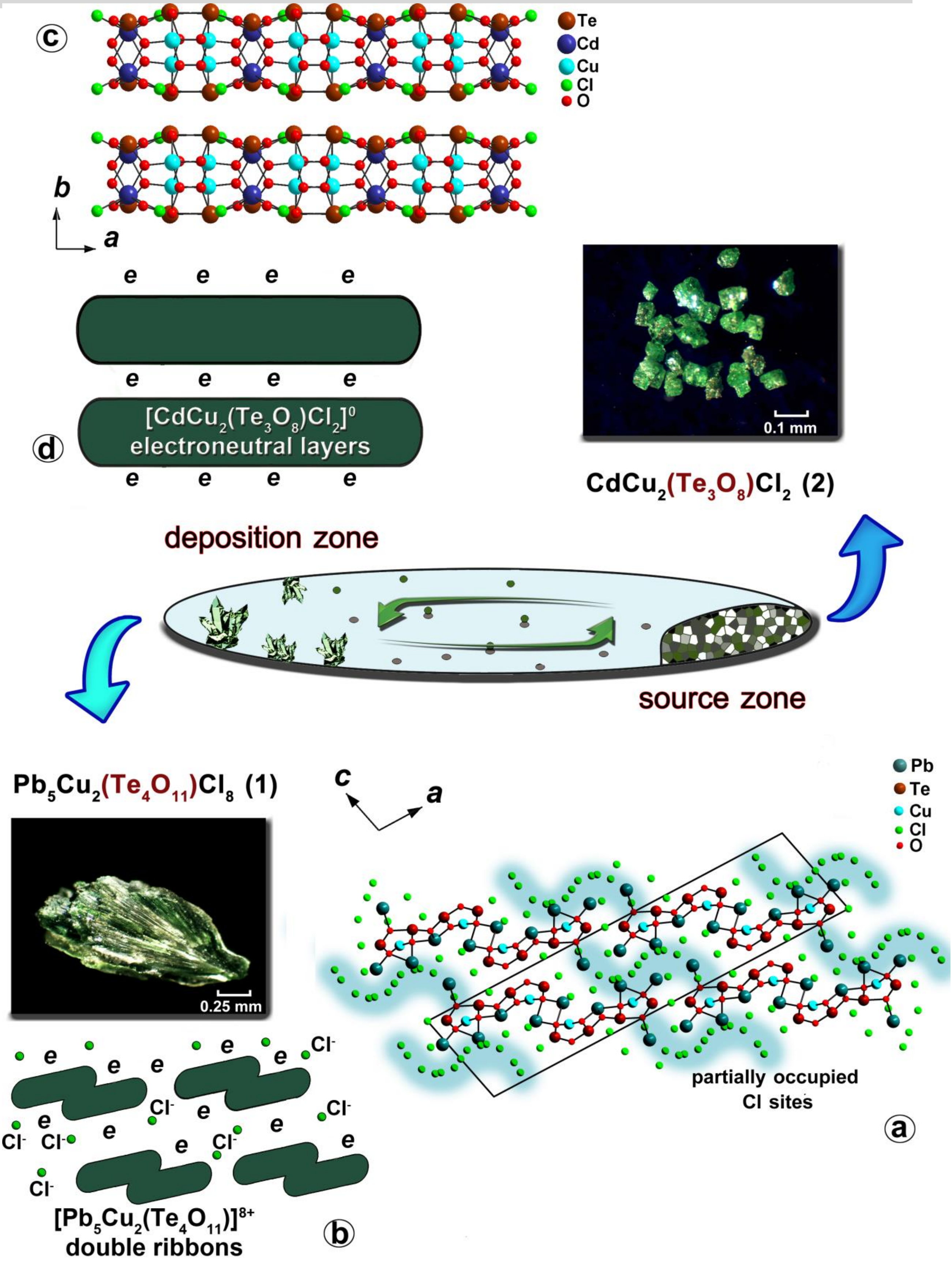
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Figure 1

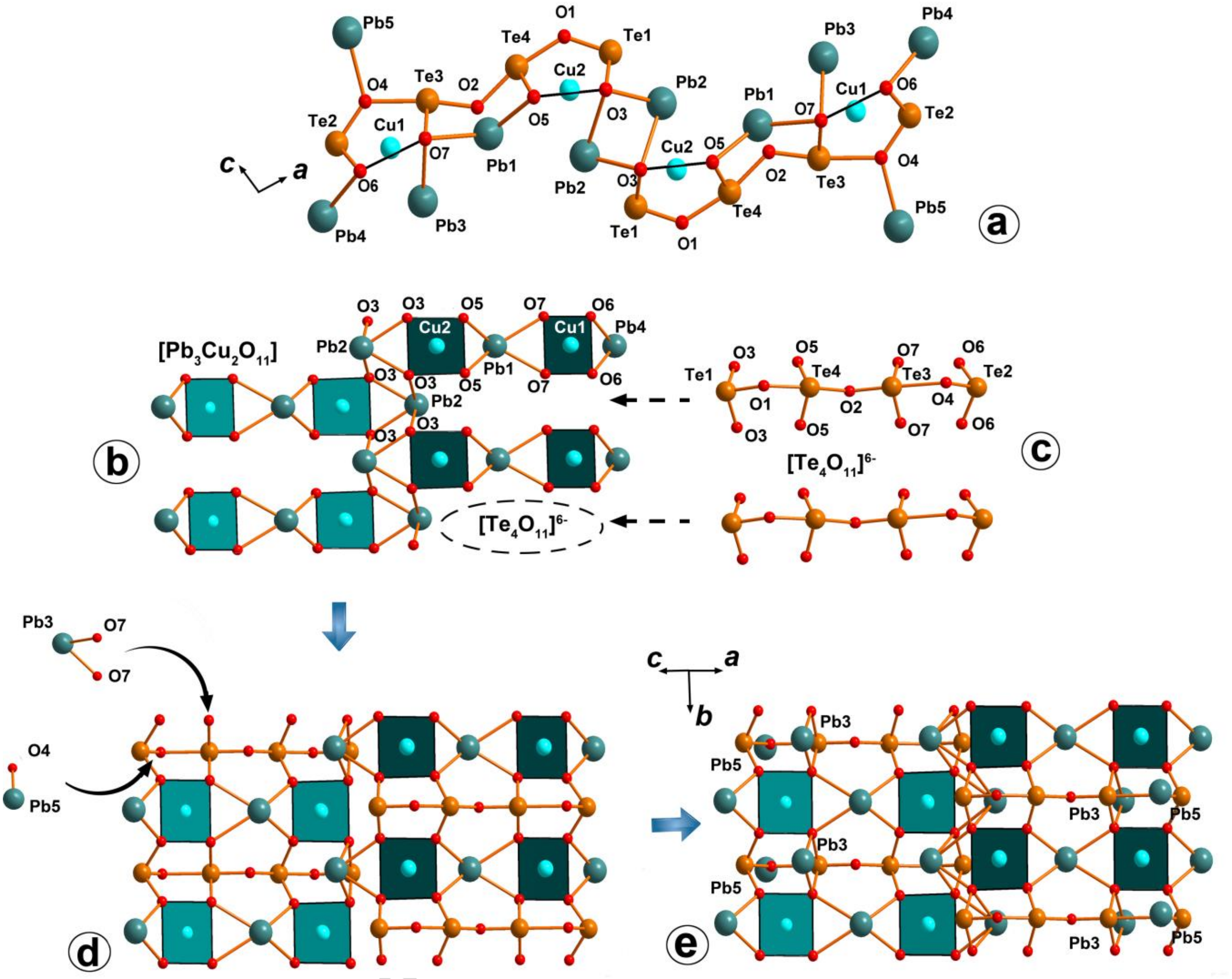
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Figure 2

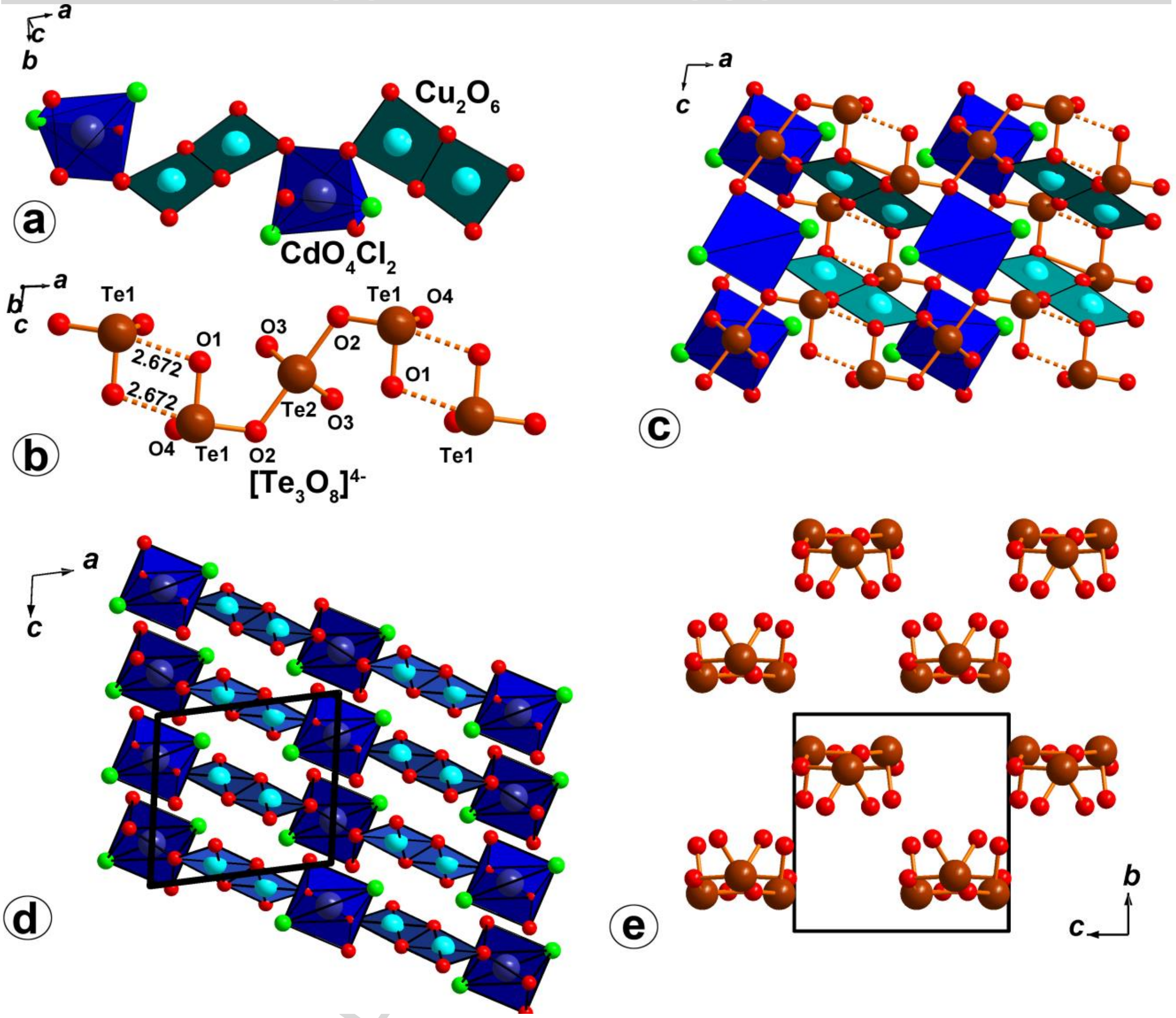
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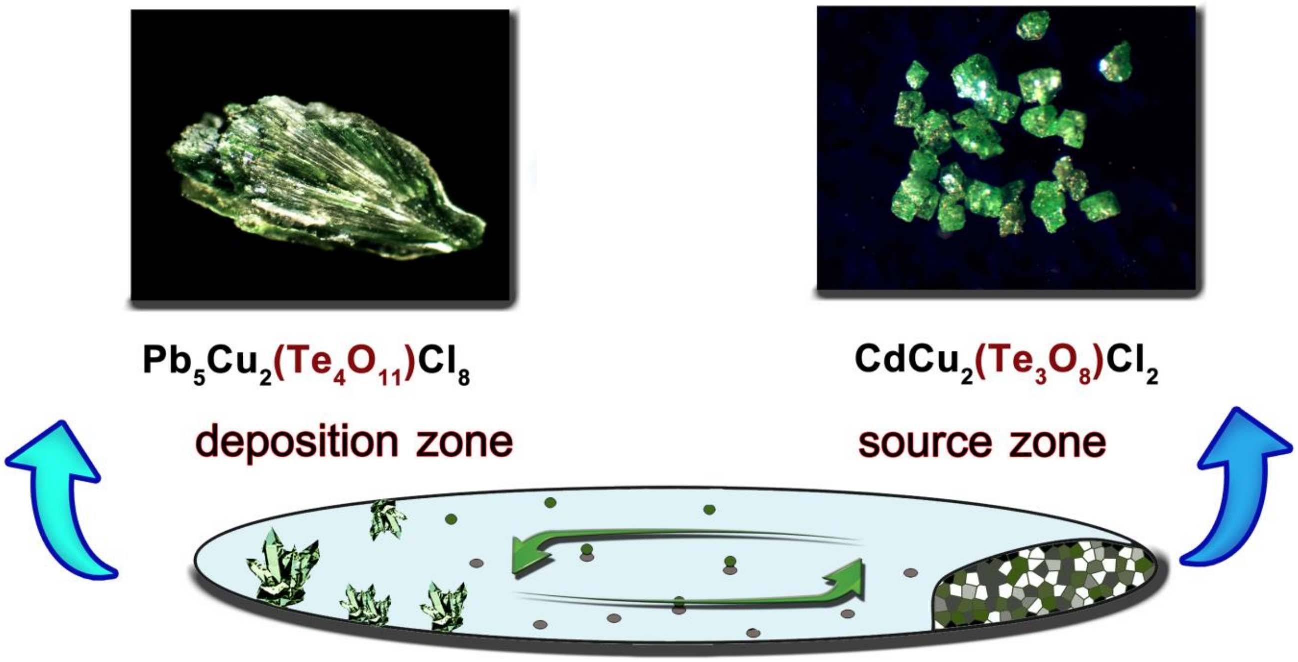
Figure 3



Graphical abstract

Graphical abstract legend

Single crystals of new copper polytellurite chlorides with Cd and Pb were prepared by chemical vapor transport reactions → Both of compounds demonstrate novel structure types → The structure of **1** represents type of structural architecture with positively charged $[Pb_5Cu_2(Te_4O_{11})]^{8+}$ one-dimensional units and Cl^- anions associating with stereochemically active lone electron pairs in between → The structure of **2** consists of neutral $[CdCu_2(Te_3O_8)Cl_2]^0$ layers interconnected via weak *A*-Cl (*A* = metal) bonds only with lone electron pairs on Te^{4+} in between