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Layered tellurite-chlorides obtained by CVT: simple way for complex structures

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Crystalline materials with Te(IV) and divalent metal cations have received attention for their fascinating structural chemistry [1] and physical properties. One-sided TeO3, TeO4 or TeO5 coordination environments are very typical for Te(IV) cations due to the presence of 5s2 lone electron pair. Te4+On polyhedra reveal tendency to form various Te4+nOm polyanions in contrast to Se(IV)–and I(V) -centered polyhedra. Five new layered compounds were obtained in evacuated quartz ampoules: CsCu4(TeO3)2Cl5(1), Pb5Cu2(Te4O11)Cl8(2), CdCu2(Te3O8)Cl2(3), Cu(I)4Cu(II)Pb(II)11(TeO3)8Cl12(4) and Pb(II)8Cu(I)10[Te(VI)Cu(II)12O8](Te(IV)O3)8Cl24(5). (TeO3)2- anions are isolated in 1, whereas [Te4O11]6- and [Te3O8]4- polyanions are formed in 2 and 3. The degree of Te4+nOm polymerization is affected by the type and number of the other cations within the structure. The structure of 2 is based on [Pb5Cu2(Te4O11)]8+ one-dimensional blocks with full and partially occupied Cl in between. The structure of 3 can be described as being formed by two types of one-dimensional units formed by Cd,Cu-centered polyhedra and TeO3, TeO4 pyramids sharing via common O atoms into electroneutral [CdCu2(Te3O8)Cl2]0 sheets. Structures of 4 and 5 contain complex [O8Pb9Te4]18+ and [O8Cu12Te]12+ oxocentered clusters [2] formed by OA3Te (A = Pb, Cu) heterometallic oxocentered tetrahedra. Our exploration of copper-tellurite systems with Pb2+, Cd2+ and Cs+ produced five novel tellurite-chlorides with complex structural topologies and demonstrates effectiveness of CVT techniques for preparation of different Te-based layered materials. Compound 4 is noncentrosymmetric and non-linear optical properties will be discussed.

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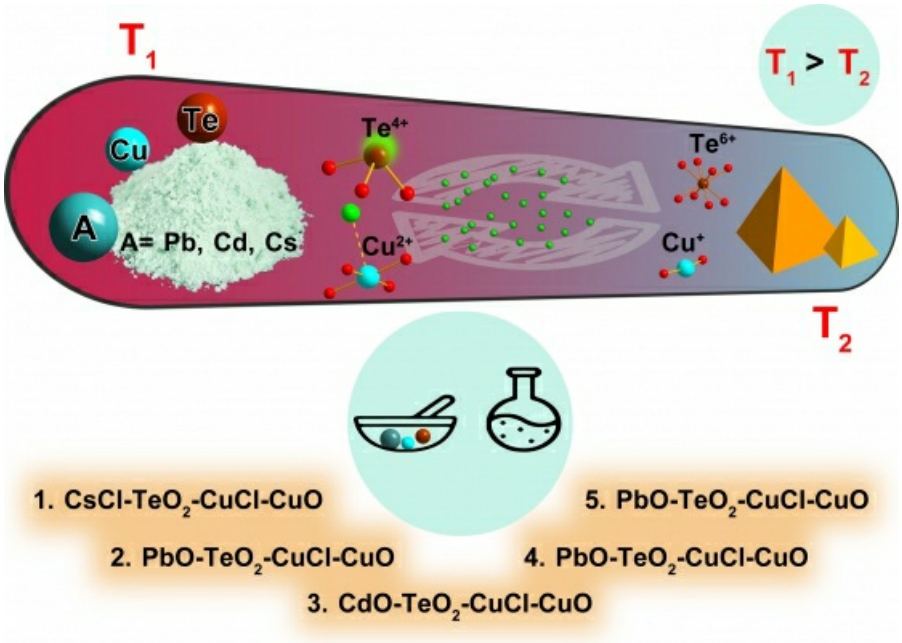
Figure 1. General scheme of CVT syntheses of layered Cu tellurite-chloride layered materials with various additional cations.



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