Coordination Chemistry Reviews 368 (2018) 115–133

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Multinary metal chalcogenides with tetrahedral structures for second-order nonlinear optical, photocatalytic, and photovoltaic applications

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ARTICLE INFO

Article history:
Received 7 February 2018
Accepted 16 April 2018

Keywords:
Tetrahedral chalcogenide
Structural chemistry, second-order nonlinear optics
Photocatalysis
Solar cell

ABSTRACT

There are a large number of metal chalcogenides crystallized in the wurtzite or zinc blende-derived structures, in which all of the anions or cations are fourfold-surrounded by their neighboring counter ions. These compounds can be defined as tetrahedral chalcogenides. According to valence electrons' configuration obeying valence electron rules or not, they can be classified into two types, normal or defect tetrahedral chalcogenides. There is a closely structural relationship between them. As all the atoms have the tetrahedral-coordination styles, structure disorders of occupancies or sites can be easily happened to them. So, there are also many alloys or solid-solutions members belonging to tetrahedral chalcogenides. In view of their special structure features, rich chemical compositions, and tunable optical band gaps, they are ones of the most promising second-order nonlinear optical (NLO), photocatalytic, photovoltaic (PV), and thermoelectric candidate materials. In fact, most of these chalcogenides can be applied in more than one of the aforementioned fields.

To date, there are several review works on part of these chalcogenides, including typical I-III-VI_2, I_2-II-IV-VI_4, and diamond-like chalcogenides. However, hitherto there is not a systematical summary about chalcogenides with tetrahedral structures. Intrigued by their flourishing developments, it is very necessary to summarize them, focusing on their structural chemistry and versatile applications. To compact this review, only several application fields related with utilization of lights are discussed, including second-order NLO, photocatalytic, and PV applications.

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https://doi.org/10.1016/j.ccr.2018.04.014
0010-8545/

1. Introduction

To date, there is a huge number of chalcogenides crystallizing in the wurtzite or zinc blende-derived structures, which can be uniformly named as tetrahedral chalcogenides. In normal tetrahedral structures, each atom on a cation site is tetrahedrally coordinated by four anions, and conversely, every atom on an anion site is tetrahedrally coordinated by four (or less in the case of a defect tetrahedral structure) cations [1] The cubic close packing of the anions in zinc blende and the hexagonal close anion packing in wurtzite are the most common among more than 200 known anion stacking variants in tetrahedral structures [2], where the cations and anions occupy the Zn and S sites, respectively, of the wurtzite or zinc blende structure. Such multinary tetrahedral chalcogenides can be designed by various combinations of elements in the vicinity of the group IV element, covering alkali-earth metal Li, divalent transition metal Mn, Fe, Co, Ni, coin-metal Ag, Cu, group 12 metal Zn, Cd, group 13 metal Al, Ga, In, group 14 element Si, Ge, Sn, group 15 element As, Sb, group 16 element S, Se, Te. They are crystallized in the (defect) chalcopyrite, (defect) stannite, wurtzstannite, enargite, famatinite, kesterite structures, and so on (Fig. 1).

There is an increasing interest in these tetrahedral chalcogenides because of their rich crystal structures, phase transition behavior [3] and potential applications in magnetic [4], second-order nonlinear optical (NLO) [5], thermoelectric and photocatalytic [6] materials, and absorber materials in thin film solar cell [7]. In view of their crystal structures, the majority of quaternary chalcogenides I_2-II-IV-VI_4 (I = Cu, Ag; II = Cd, Hg, Zn, Co, Mn, Fe, Ni; IV = Si, Ge, Sn; VI = S, Se, Te) crystallize in the tetragonal stannite structure (structural type Cu_2FeSnS_4, SG $I\bar{4}2m$) or in the orthorhombic wurtzstannite structure (structural type Cu_2CdGeS_4, SG $Pmn2_1$) derived from the zinc blende or wurtzite cell with an ordering of the metals on the cation sites, respectively. The tetragonal stannite structure is derived from the zinc blende by doubling the lattice parameters in the c direction, and the orthorhombic wurtzstannite cell is a superstructure of the wurtzite cell. In both structures, there are two formula units per cell, each anion VI is surrounded by two I, one II and one IV cations, and every cation is tetrahedrally coordinated by VI atoms [8]. Besides, Ag_2CdSnS_4, Cu_2NiSnS_4 and another crystal phase of Cu_2FeSnS_4 crystallize in the space group $Cmc2_1$, $F\bar{4}3m$, and $P\bar{4}$, respectively. Ternary Cu_3-V-S_4 (V = P, As, Sb) compounds crystallize either in $I\bar{4}2m$ for V = Sb or in $Pmn2_1$ for V = P and As. Almost all ternary chalcopyrite-type chalcogenides I-III-VI_2 (I = Li, Ag, Cu; III = Al, Ga, In; VI = S, Se, Te) can crystallize in the tetragonal space group $I\bar{4}2d$ except for $LiGaS_2$ and $LiGaSe_2$ ($Pna2_1$). Furthermore, $AgInSe_2$, $LiInSe_2$, $AgGaTe_2$, and $AgInTe_2$ can be transferred to cubic structures (SG $Fm\bar{3}m$) under pressure [9].

Except for these normal tetrahedral chalcogenides, several types of defect tetrahedral ones can be obtained by cations and vacancy substitutions based on zinc blende and wurtzite structures. Take II-III_2-VI_4 chalcogenides for examples, $CdGa_2S_4$ is isotypical to kesterite (Cu_2ZnSnS_4), in which half of Ga atoms occupy the position of Sn as in kesterite and the other half and the Cd atoms occupy the position of Cu. It can be constructed from the chalcopyrite structure of $CuGaS_2$ by doubling the formula unit and replacing Cu by Cd and a vacancy to maintain the valence.

Lots of mixed tetrahedral chalcogenides, especially ones containing Cu^+ cation, have been investigated, such as $Cu_2ZnGeS_{4-y}Se$ [10], $Cu_2Cd_{1-x}Mn_xSnSe$ [8], $Cu_2Zn_{1-x}Mn_xGeS_4$ [4], $Cu_2MnGe_xSn_{1-x}S_4$ [2], $Cu_3CdAs_{1-x}Sb_xS_4$ [11], and so on. To predict the structure types of normal tetrahedral chalcogenides, A. Pfitzner and coworkers systematically investigated tetrahedral chalcogenides and originally employed analyzing the volumes of the tetrahedra around the cations to elucidate the stability range of the wurtzite and the zinc blende superstructure types [2,11,12].

Pressure- or temperature-induced phase transitions have been observed in tetrahedral chalcogenides arising from their rich structural types. For example, $ZnGa_2Se_4$ with the defect tetragonal stannite-type structure ($I\bar{4}2m$) and $CdGa_2S_4$ with the defect tetragonal chalcopyrite-type structure ($I\bar{4}$) can be transferred to defect-cubic NaCl-type structures ($Fm\bar{3}m$) under high-pressures [13]. Phase transitions from the α phase with chalcopyrite structure to the β phase with zinc blende structure were obtained in $CuInQ_2$ (Q = S, Se, Te) and $CuGaTe_2$ [9].

I_2-II-IV-VI_4 compounds may show interesting magnetic properties since they contain transition metal ions with magnetic moments, such as Fe^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} ions. For example, exciton splittings as large as ~170 and ~230 meV are observed in $Cu_2Zn_{1-x}Mn_xGeS_4$ for light polarization vector $E||a$ and $E||c$, respectively [4]. G. Nénert discovered that all the reported members of Cu_2-II-IV-S_4 having the $Pnm2_1$ symmetry exhibit a large spontaneous polarization, which suggests that several such compounds are likely to be multiferroics since they order magnetically at low temperatures. Cu_2MnSnS_4 can be considered as a new magnetically induced ferroelectric, and Cu_2MnIVS_4 (IV = Ge and Sn) are good magnetoelectric candidates [14]. $Cu_2FeGeSe_4$ is antiferromagnetic with a Néel temperature of 20 K, while $Cu_2FeGeTe_4$ is ferrimagnetic with T_N 160.1 K [15]. $Cu_2FeSnSe_4$ is antiferromagnetic showing ideal Curie-Weiss behavior with a Néel temperature of about 19 K, and $Cu_2MnSnSe_4$ shows spin-glass behavior with a freezing temperature of about 22 K [16]. Though magnetic properties of tetrahedral chalcogenides have been largely studied, ones containing Ag^+ cation have been relatively rare discussed until now.

Not just magnetic properties, it is very interesting to find out that the crystal structures of tetrahedral chalcogenides with the space groups $I\bar{4}2m$, $Pmn2_1$, $Cmc2_1$, $F\bar{4}3m$, $P\bar{4}$, $I\bar{4}2d$, or $Pna2_1$ are all noncentrosymmetric, therefore, some interesting properties, such as second-order NLO, piezoelectric, pyroelectric, and ferroelectric properties, can be well investigated in view of their acentric structures. The most interesting one among them is their second-order NLO properties. Their major application is to generate second harmonics, and the crystalline materials have to be crystallized in the noncentrosymmetric (NCS) space group.