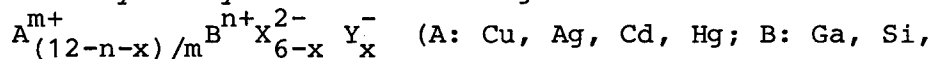# THE ARGYRODITES - A NEW FAMILY OF TETRAHEDRALLY CLOSE-PACKED STRUCTURES

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ABSTRACT

Numerous members of a new, hitherto unrecognized family of tetrahedrally close-packed structures, termed the argyrodites, have been synthesized and characterized by x-ray methods. Their general formula is:
$A^{m+}_{(12-n-x)/m} B^{n+} X^{2-}_{6-x} Y^{-}_{x}$ (A: Cu, Ag, Cd, Hg; B: Ga, Si, Ge, Sn, P, As; X = S, Se, Te; Y = Cl, Br, I; $0 \leq x \leq 1$).
They have a common cubic ($F\bar{4}3m$) HT-structure with a disordered A-cation sublattice. At lower temperatures transitions into various ordered structures occur. Typical structural feature is an anion framework of interpenetrating, centred icosahedra providing ideal and distorted tetrahedral cation sites.
Some argyrodites are efficient ionic conductors, others are of interest as non-linear optical materials

Introduction

Recent investigations (1, 2, 3, 4, 5) have shown that numerous chalcogenides and chalcogenide-halides belong to a hitherto not recognized family of closely related, tetrahedrally close-packed structures. We shall term these materials argyrodites – after a naturally occurring representative, the mineral Ag_8GeS_6.

In addition to their novel, acentric crystal structures and the concomitant physical properties, the argyrodites are of considerable interest because of:
1. The vast range of possible chemical substitutions.
2. Incomplete occupancy of certain cation sites, giving rise to order-disorder phenomena and phase transitions.
3. The occurrence of high ionic conductivies in certain Cu and Ag containing members.

We have attempted to synthesize systematically new, potential argyrodites in order to survey the range of existence of these compounds. The paper first discusses the compositional gamut and the pertinent structural features of the argyrodite family. Then the results are given in form of a table containing the presently known argyrodites, their lattice constants, transition temperatures, literature data etc.

Crystal chemistry and argyrodite structures

The general formula of halogen-free argyrodites is:

$$A^{m+}_{(12-n)/m} B^{n+} X^{2-}_6 ,$$
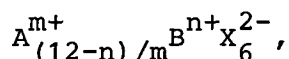
where m and n are the valencies of the A-cations (Cu^+, Ag^+, Cd^{2+}, Hg^{2+}) and the B-cations (Ga^{3+}, Si^{4+}, Ge^{4+}, Sn^{4+}, P^{5+}, As^{5+}) resp. and X (S^{2-}, Se^{2-}, Te^{2-}) is a divalent anion. Many examples for combinations of various elements are found in table 1.

The first structure determinations were undertaken for Cd_4GeS_6(7) and Cd_4SiS_6(8), but at this time these compounds were considered singular cases rather than members of a widerspread structure family. Further structural information was recently published for Ag_8SiS_6(9), Ag_8GeS_6(10), Ag_8GeTe_6(11) and Cu_7PS_6(5). The above formula shows that, depending on chemical composition, the number of A-cations per formula unit can vary considerably. The maximum number of 9 is found in Ag_9GaS_6(6) (m=1, n=3), the smallest number in $Cd_3._5PS_6$(cell contents: $Cd_{14}P_4S_{24}$) (2) (m=2, n=5). It is remarkable to note that both compounds crystallize in closely related structures.

This variety of compositions, which is typical for the argyrodite family, is still further enlarged by the fact that in most of the above compounds a sizable fraction of the divalent chalcogenide anions X can be substituted by monovalent halogenide anions Y (Cl^-, Br^-, I^-). The resulting reduction in total anionic charge is compensated for by a corresponding reduction in the number of A-cations. This leads to the more general argyrodite formula:

$$A^{m+}_{(12-n-x)/m} B^{n+} X^{2-}_{6-x} Y_x \qquad \text{with } 0 \leq X \leq 1.$$
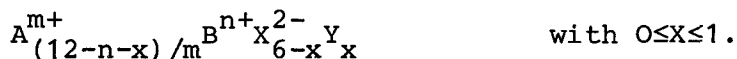
For examples see table 1. The structures of two representatives of such mixed-anion argyrodites have been determined recently: Cu_6PS_5Br(4) and $Cd_3._{25}PS_5._5I._5$(cell contents: $Cd_{13}P_4S_{22}I_2$) (3).

Typical for the architecture of all argyrodites is a framework of interpenetrating, centered, distorted anion icosahedra, forming a tetrahedrally close-packed sublattice. Therefore they have been also referred to as "icosahedral structures" (1, 2). The same icosahedral framework is formed by the metal atoms in the Laves phase $MgCu_2$. Crystallographically the two cations differ considerably.

The B-cations, by virtue of their size and chemical nature are coordinated nearly tetrahedrally by four anions. Their number per cell is always four, i.e. 1/6 of the number of anions.

The A-cations may occur in various coordinations. Thus in Cu_7PS_6 three types of Cu ions are discernible with distorted tetrahedral, trigonal planar and linear coordination by 4, 3 and 2 anions resp. The number of A-cations per cell is - for reasons of charge neutrality - determined by the total number of negative charges of the X and Y anions minus the charge of the B-cations. Thus a host of additional argyrodite compositions with differing stoichiometries can be synthesized by employing various ratios of chalcogenide/halogenide anions and combining these with A- and B-cations of various valencies. Halogen incorporation into the chalcogenide-anion sublattice reduces the number of A-cations. (Compare e.g. $Cd_{3.5}PS_6$ (x = 0) with $Cd_{3.25}PS_{5.5}I_{.5}$ (x =.5)). There even exist argyrodites in which two different metal ions share the permissible (stoichiometry-limited) A-sites, e.g. $(Cu_{1.5}.In_{1.5})$ PS_5I. This argyrodite contains only 3 A-cations per formula unit, the lowest number found so far.

The numerous, although closely related structures of the argyrodite family can be considered to derive from one common, high-temperature parent phase of (overall) cubic symmetry $F\bar{4}3m$. The structure of this phase (the "aristo-type" according to Megaw (12)) has been determined for the compound $Cu_6PS_5Br(4)$. The unit cell of this phase contains four formula units. The A-cations are distributed randomly among 48 equivalent, tetrahedral sites within the framework of the anion icosahedra. Depending on composition, the parent phase undergoes a transition into one of several, typical low-temperature phases ("hetto-types"). Due to distortions of the cell, the 48 tetrahedral sites are now split into several, non-equivalent sets which, depending on the nature and number of A-cations, can accommodate these in various ordered fashions. So far we have observed (at least)7 different low-temperature argyrodite phases to occur (see end of table 1 for notation) in which various patterns of order of the A-cations are realized. The transition temperatures vary over a wide range; e.g T_C = 663 K for $Cd_{3.5}PS_6$ and T_C = 113 K for Cu_6PS_5I. It is important to note, that the seemingly high symmetry $F\bar{4}3m$ of the disordered parent phase is actually produced by the averaging effect of the diffraction methods. The (random) arrangement of the A-cations in each individual cell is highly asymmetric. In the low-temperature phases the cell symmetry is raised and the arrangement of the A-cations in all cells of the crystal becomes identical. Nevertheless, their overall symmetries appear to be lowered as compared to the disordered, cubic parent phase.

Experimental Results

The compounds were prepared by reacting stoichiometric amounts of high-purity elements (total charge about 8 g) in evacuated, sealed quartz ampoules for about 6 days at temperatures of 600 to 700°C. In many cases, small crystals, suitable for x-ray and analytical work were obtained. The growth of larger crystals of selected argyrodites by chemical vapour transport has been described elsewhere (1, 2). The reaction products were characterized by Guinier powder photographs, using As_2O_3

as a standard. Compounds, crystallizing in the high-temperature parent phase were identified by their typical, F-centered, cubic lattice. The low-temperature phases of reduced symmetry could also be readily recognized by their similar patterns showing line splitting and occurrence of additional lines.

In table 1 newly synthesized materials and (for the sake of completeness) such compounds are listed which on the basis of lattice parameters, symmetries or structure determinations appear to belong to the argyrodite family.

The formula units given designate one fourth of the contents of the unit cell of the high-temperature phase. The sequence in the table corresponds to the main groups of argyrodites known so far, namely those containing as A-cation Cu (or Ag), Cd (or Hg) and the combination (Cu + In). Within these groups, the compounds are arranged in the order of increasing valency and atomic numbers of the A- and B-cations resp. In compounds in which partial substitution of the chalcogenide anions by halogenide ions has been found to be possible, the mole fraction of the latter is indicated by x. Such compounds were all synthesized with component mixtures corresponding to x = 1. However, in many cases inhomogeneous reaction products indicated and subsequent analyses confirmed, that under the conditions of the experiment only a fraction of the halogen resided in the lattice. The x-values in the table thus represent analyzed data of - rather arbitrary - experiments. They cannot by any means be considered as true solubility limits. Samples not analyzed for their x-values are marked by (?). The results show that in each individual system there exists a certain miscibility range between the pure chalcogenide argyrodites (x = 0) and "ideal" stoichiometric chalcogenide-halides, containing an integer number of halogens per cell, as end-members. In certain argyrodites, with Cu, Ag or (Cu + In) as A-cations, a maximal value of x = 1 (four halogens per cell) was found, e.g. in Cu_6PS_5Hal; Ag_6PS_6Br, $Cu_{1.5}In_{1.5}PS_5Br$. In other cases, e.g. for the analogous Si or Ge compounds, only smaller x-values were obtained - at least under the p-T conditions prevailing during synthesis.

The maximal x-value for argyrodites containing Cd (Hg) as A-cations is only 0.5 (two halogens per cell), e.g. in $Cd_{3.25}PS_{5.5}I_{.5}$. This can be made plausible by structural considerations and is confirmed by preliminary work on halogen incorporation into many Cd (Hg) argyrodites (31), although such compositions are not included in table 1. The individual lattice types encountered have been numbered 1-8 and are described at the end of table 1. Lattice constants taken from the literature are marked by*.

Phase transitions have been investigated by DTA methods and by observing suitable crystals on the heating stage of a polarizing microscope.

TABLE 1

Chemical Formula	x	Latt. Type	a (Å)	b (Å)	c (Å)	β (Å)	Trans. T (K)	References
Cu_8SiS_6	–	3	6.992(2)	6.901(2)	9.768(2)		336	(17,18,19)
$Cu_{8-x}SiS_{6-x}Cl_x$	0.10	3	6.994(3)	6.904(3)	9.773(4)		333	
$Cu_{8-x}SiS_{6-x}Br_x$	0.60	1	9.876(3)					
$Cu_{8-x}SiS_{6-x}I_x$	0.90	1	9.930(2)					
Cu_8SiSe_6	–	3	7.278(3)	7.212(3)	10.223(4)		323	(17)
$Cu_{8-x}SiSe_{6-x}I_x$	0.83	1	10.346(2)					
Cu_8GeS_6	–	7	9.935(3)	9.935(3)	9.935(3)		328*	(17,20,21)
$Cu_{8-x}GeS_{6-x}Cl_x$	0.07	3	7.039(3)	6.968(4)	9.868(4)		309	
$Cu_{8-x}GeS_{6-x}Br_x$	0.70	1	9.953(3)					
$Cu_{8-x}GeS_{6-x}I_x$	0.78	1	10.012(4)					
$Cu_{8-x}GeSe_{6-x}I_x$	0.54	1	10.376(3)					
Cu_7PS_6	–	2	9.669(2)				508	(5,22)
$Cu_{7-x}PS_{6-x}Cl_x$	1.00	1	9.687(2)				247	(1)
$Cu_{7-x}PS_{6-x}Br_x$	1.00	1	9.723(2)				268	(1,4)
$Cu_{7-x}PS_{6-x}I_x$	1.00	1	9.787(2)				113	(1)
Cu_7PSe_6	–	2	10.111(2)				325	(22)
$Cu_{7-x}PSe_{6-x}Br_x$	?	1	10.111(2)					
$Cu_{7-x}PSe_{6-x}I_x$	0.96	1	10.178(3)					
$Cu_{7-x}AsS_{6-x}Br_x$	0.36	1	9.843(3)					
$Cu_{7-x}AsS_{6-x}I_x$	0.95	1	9.892(3)					
Ag_8GaS_6	–	6	10.777(2)*	7.706(1)*	7.605(2)*		308*	(6)
$Ag_{8-x}GaS_{6-x}Cl_x$	?	1	10.759(4)					
$Ag_{8-x}GaS_{6-x}Br_x$	?	1	10.799(3)					
$Ag_{8-x}GaS_{6-x}I_x$	?	1	10.829(3)					
Ag_8GaSe_6	–	1	11.099(5)				281*	(23,24)
$Ag_{8-x}GaSe_{6-x}Br_x$	?	1	11.088(5)					
$Ag_{8-x}GaSe_{6-x}I_x$	?	1	11.139(3)					
Ag_8SiS_6	–	4	15.043(6)	7.452(4)	10.565(5)		507*	(9,19,25,26)
$Ag_{8-x}SiS_{6-x}Cl_x$	?	4	15.047(5)	7.434(3)	10.538(4)		491	
$Ag_{8-x}SiS_{6-x}Br_x$	?	1	10.479(4)					
$Ag_{8-x}SiS_{6-x}I_x$	?	1	10.596(4)					
Ag_8SiSe_6	–	8	unknown				313*	(25,26,27)
$Ag_{8-x}SiSe_{6-x}Br_x$	?	8	unknown					
$Ag_{8-x}SiSe_{6-x}I_x$	?	8	unknown					
Ag_8SiTe_6	–	1	11.515*					(25)
Ag_8GeS_6	–	4	15.149(1)*	7.476(2)*	10.589(1)*		498	(10,25.26)
$Ag_{8-x}GeS_{6-x}Cl_x$	?	4	15.109(9)	7.479(4)	10.599(7)		423	
$Ag_{8-x}GeS_{6-x}Br_x$	?	1	10.650(3)					
$Ag_{8-x}GeS_{6-x}I_x$	?	1	10.713(5)					
Ag_8GeSe_6	–	8	unknown				321*	(25,26,27)
$Ag_{8-x}GeSe_{6-x}Br_x$	?	1	10.955(3)					
$Ag_{8-x}GeSe_{6-x}I_x$	?	1	11.016(3)					
Ag_8GeTe_6	–	1	11.566(2)*				244*	(11,25,26)
$Ag_{8-x}GeTe_{6-x}I_x$	?	1	11.561(3)					
Ag_8SnS_6	–	8	unknown				445*	(17,26)
$Ag_{8-x}SnS_{6-x}Cl_x$	?	8	unknown					
$Ag_{8-x}SnS_{6-x}Br_x$	?	1	10.776(2)					
$Ag_{8-x}SnS_{6-x}I_x$	?	1	10.852(4)					
Ag_8SnSe_6	–	8	unknown				356*	(17,26,27,28, 29)
$Ag_{8-x}SnSe_{6-x}Br_x$	?	8	unknown					
$Ag_{8-x}SnSe_{6-x}I_x$	?	1	11.137(4)					
Ag_7PS_6	–	2	10.402(2)				495	
$Ag_{7-x}PS_{6-x}Cl_x$	?	1	10.345(3)					
$Ag_{7-x}PS_{6-x}Br_x$	1.00	1	10.397(3)					
$Ag_{7-x}PS_{6-x}I_x$	?	1	10.474(3)					
Ag_7PSe_6	–	1	10.768(2)				430	
$Ag_{7-x}PSe_{6-x}Br_x$	?	2	10.731(2)					
$Ag_{7-x}PSe_{6-x}I_x$	?	2	10.797(3)					
Ag_7AsS_6	–	2	10.470(2)				526	
$Ag_{7-x}AsS_{6-x}Cl_x$	?	8	unknown					
$Ag_{7-x}AsS_{6-x}Br_x$	?	8	unknown					
$Ag_{7-x}AsS_{6-x}I_x$	?	1	10.575(2)					
Ag_7AsSe_6	–	2	10.834(3)					
$Ag_{7-x}AsSe_{6-x}I_x$	?	2	10.872(5)					
Cd_4SiS_6	–	5	12.34 (1)*	7.089(6)*	12.35 (1)*	110.73 (1)*		(8,15,16)
Cd_4SiSe_6	–	5	12.816(6)*	7.355(4)*	12.811(6)*	110.06 (5)*		(8)
Cd_4GeS_6	–	5	12.36 (1)*	7.107(6)*	12.38 (1)*	110.13 (1)*		(7,14,16)
Cd_4GeSe_6	–	5	12.81 (2)*	7.38 (1)*	12.79 (5)*	109.57 (5)*		(30)
Hg_4SiS_6	–	5	12.29 (1)*	7.096(6)*	12.30 (1)*	109.47 (1)*		(16)
Hg_4GeS_6	–	5	12.34 (1)*	7.127(6)*	12.36 (1)*	109.45 (1)*		(16)
$Cd_{3.5}PS_6$	–	5	12.16 (1)*	6.98 (1)*	12.26 (1)*	110.55 (3)*	663*	(2)
$Cd_{3.5-x/2}PS_{6-x}I_x$	0.50	5	12.236(5)*	7.016(4)*	12.289(6)*	110.33 (5)*	653*	(2,3)
$(Cu,In)_{3.5-x/2}PS_{6-x}Br_x$	1.00	1	9.620(4)					
$(Cu,In)_{3.5-x/2}PS_{6-x}I_x$	1.00	1	9.662(4)					

Notation of Lattice Types:

1 $F\bar{4}3m$	3 $Pmn2_1$	5 Cc	7 pseudo cubic
2 $P2_13$	4 $Pna2_1$	6 o'rhb.I	8 not yet determined

*Values from literature

†Values from least-squares analysis of Guinier data using As_2O_3 (a=11.075 Å) as internal standard.

Physical Properties

Presently the argyrodites appear to be of interest in the following fields:

a) As non-linear optical materials. It has been observed (14) that in certain high-bandgap argyrodites second harmonic radiation is produced with high efficiency (for $Cd_{3.25}PS_{5.5}I_{0.5}$ the effect is comparable with that of $LiNbO_3$),

b) As efficient ionic conductors. All argyrodites containing Cu^+ and Ag^+, meet the structural requirements for this effect: partial occupancy of a sublattice by ions of high mobility in the structurally disordered high-temperature phase. In particular, many chalcogenide-halides are structurally disordered already at room-temperature.

Ionic conductivity was established in the compounds Cu_6PS_5Hal (Hal = Cl, Br, I). The total (electronic + ionic) conductivity σ_{tot} was determined by a two-probe technique measuring the impedances with an automatic ac-bridge (Hewlett Packard 4270A), at 2 frequencies (100 KHZ, 1 MHZ). Sandwiched pellets were pressed from Cu_6PS_5Hal and CuS as electrodes. Fig. 1 shows the Arrhenius plots (log σ_{tot} versus 1/T) for these compounds. Cu_6PS_5Cl shows the highest conductivity:

$$\sigma_{tot} = 4.7 \times 10^{-4} (\Omega \ cm)^{-1} \text{ at RT}$$

and $1.0 \times 10^{-2} (\Omega \ cm)^{-1}$ at $200^{\circ}C$.

The activation energy is equal for both Cu_6PS_5Br and Cu_6PS_5I (0.35 eV), while Cu_6PS_5Cl shows a lower value (0.22 eV). Transference measurements for determining the electronic part σ_{el} of the total conductivity could not be carried out with copper electrodes, because the compounds Cu_6PS_5Hal are thermodynamically not stable in contact with metallic copper. Therefore σ_{el} was measured potentiostatically, using a symmetrical arrangement of ion-blocking graphite electrodes. In interpreting these measurements it was assumed that the degree of disorder of the Cu^+ ions was so high that the electronic conductivity was not affected by the undefined copper activity. The results indicate that at room temperature σ_{el} is less than 1 % of σ_{tot}, i.e. the conduction is nearly purely ionic and at least two orders of magnitude higher than in the binary copper halides.
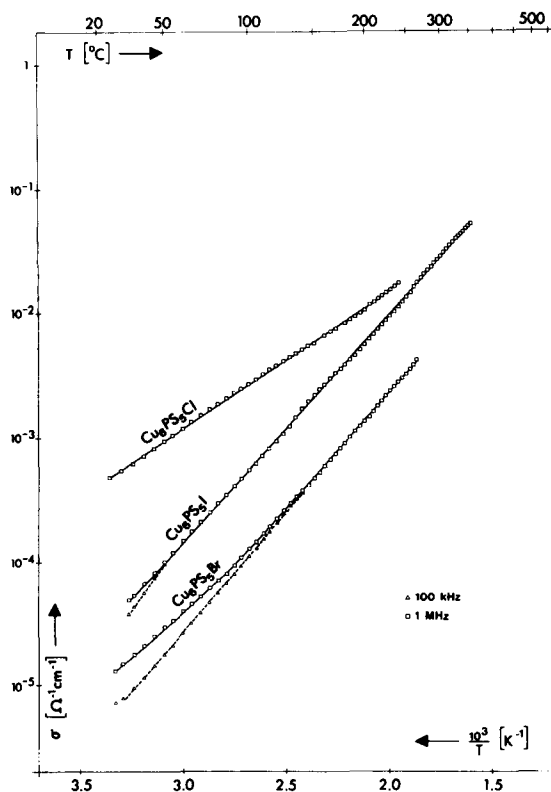

FIG. 1

Total conductivities of Cu_6PS_5Hal

At higher temperatures σ_{el} increases and becomes equal to σ_{ion} at 150°C in Cu_6PS_5I, 250°C in Cu_6PS_5Br and 300°C in Cu_6PS_5Cl. Therefore these compounds become mixed ionic-electronic conductors at higher temperatures. Further electrochemical and structural investigations of various other argyrodites are in progress.

Acknowledgement

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