Inorganic Chemistry
Article
pubs.acs.org/IC

Five New Chalcohalides, Ba_3GaS_4X (X = Cl, Br), Ba_3MSe_4Cl (M = Ga, In), and $Ba_7In_2Se_6F_8$: Syntheses, Crystal Structures, and Optical Properties

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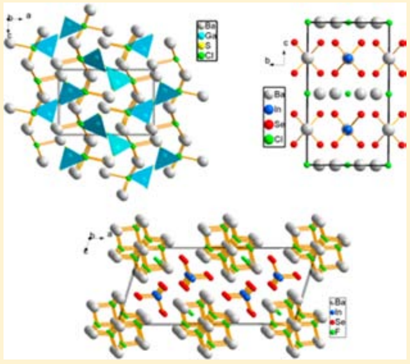
Ⓢ *Supporting Information*

ABSTRACT: Five new chalcohalides, Ba_3GaS_4X (X = Cl, Br), Ba_3MSe_4Cl (M = Ga, In), and $Ba_7In_2Se_6F_8$, have been synthesized by conventional high-temperature solid-state method. These compounds crystallize in three different interesting structure types. Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl) contain zigzag BaX pseudolayers and isolated GaQ_4 tetrahedra, while Ba_3InSe_4Cl possesses one Ba−In−Se pseudolayer and one Ba−Cl pseudolayer, which are stacked alternately along the *c*-direction. $Ba_7In_2Se_6F_8$ is comprised of one-dimensional $^{\infty}_{1}[InSe_3]^{3-}$ chains and unique $[Ba_7F_8]^{6+}$ chains. In all those mixed anion compounds, the halide anions are only connected to alkaline-earth metal through strong ionic bonding, while the M (M = Ga, In) cations are only connected to chalcogenide anions through covalent bonding. UV−vis-NIR spectroscopy measurements indicate that Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl) have band gaps of 2.14, 1.80, and 2.05 eV, respectively.



INTRODUCTION

Mixed anions compounds have received worldwide intensive investigation in recent years due to their unique bonding characteristics and fascinating physical properties.[1−18] For example the LnFeOPn (Ln = rare-earth; Pn = P, As)[6−11,14] oxypnictides are the first Fe-based superconductors with high Tc and tremendous research has been carried out in increasing the Tc or in elucidating the superconducting mechanism. The LaCuOQ[3] oxychalcogenides and the BaCuQF (Q = S, Se, Te)[2] chalcohalides show very promising property as p-type transparent conducting materials that have important industrial applications. The newly discovered supramolecular pnictidehalide compounds, $(Hg_6P_3)(In_2Cl_9)$ and $(Hg_8As_4)(Bi_3Cl_{13})$[16] possess chiral three dimensional (3D) frameworks, large SHG efficiencies, and piezoelectric performance. Ag_5Te_2Cl[15] shows very low thermal conductivity, a desirable property for thermoelectric materials. More recently, the Tl_6SeI_4[17] chalcohalide was found to exhibit very promising property for efficient X-ray and γ-ray detection. It should be noted that the ionic liquid method has been applied as an effective way to synthesize the chalcohalide mixed anion compounds.[19−22]

An interesting structural feature in these mixed anion compounds is that if different kinds of cations are involved, the different anions will exhibit different bond propensity with different cations. Generally, a highly electronegative element (e.g., O, F, Cl) tends to form strong ionic bonding (electrostatic interactions) with a highly electropositive element (e.g., alkali metal, alkaline-earth metal, and rare-earth metals), whereas a less electronegative element (e.g., P, As, S, Se, Te) tends to form a stable covalent bonding with a less electropositive element (e.g., transition metal, or p-block element).[14] For example, the LnFeOPn[6,14] superconductors consist of alternately stacked Ln_2O_2 layers dominated by ionic $Ln^{3+}-O^{2-}$ bonding and Fe_2Pn_2 layers formed by covalent Fe−Pn bonding. The combination and interactions of these secondary building units with different bonding nature and functions bring these materials unique and fascinating properties.

In this paper, we focus on one subset of mixed anions compounds, namely the chalcohalides. We thoroughly investigated the Ba−M−Q−X (M = Ga, In; Q = S, Se; X = F, Cl, Br) system as it is possible to generate new compounds with interesting structures and properties by combining the covalent MQ_4 tetrahedra, which are typical functional units for a number of applications such as NLO property, with the strong ionic Ba−X bonding that are helpful to achieve a large band gap, a desired property for a number of materials such as IR NLO materials and transparent conductors. We first discovered four new compounds with the stoichiometry Ba_3MQ_4X (M = Ga, Q = S, X = Cl, Br; M = Ga, In, Q = Se, X = Cl). Then, efforts to synthesize fluoride analogue led to the isolation of $Ba_7In_2Se_6F_8$, which has a different composition and structure from the Ba_3MQ_4X compounds. These five new chalcohalides possess three different structure types, all belonging to centrosymmetric structure types. In this paper, we report the syntheses, crystal structures, and optical properties of these compounds.

Received: July 15, 2013
Published: September 11, 2013

Table 1. Crystal Data and Structure Refinements for Ba_3GaS_4X (X = Cl, Br), Ba_3MSe_4Cl (M = Ga, In), and $Ba_7In_2Se_6F_8$

	Ba_3GaS_4Cl	Ba_3GaS_4Br	Ba_3GaSe_4Cl	Ba_3InSe_4Cl	$Ba_7In_2Se_6F_8$
fw	645.43	689.90	833.03	878.13	1816.78
a (Å)	12.264(3)	12.311(1)	12.691(3)	8.536(1)	24.007(5)
b (Å)	9.557(2)	9.493(2)	9.870(2)	8.536(1)	4.3816(9)
c (Å)	8.427(2)	8.491(1)	8.716(2)	15.015(3)	10.902(2)
β (°)	90	90	90	90	107.19(3)
space group	*Pnma*	*Pnma*	*Pnma*	*I*4/*mcm*	*C*2/*m*
V ($Å^3$)	987.7(3)	992.3(1)	1091.7(4)	1093.9(3)	1095.5(4)
Z	4	4	4	4	2
T (K)	153(2)	153(2)	153(2)	153(2)	153(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_c (g/cm^3)	4.340	4.618	5.068	4.452	5.507
μ (mm^{-1})	15.533	19.220	26.625	26.217	24.441
$R(F)^a$	0.0215	0.0411	0.0331	0.0234	0.0312
$R_W(F_o^2)^b$	0.0395	0.1130	0.0734	0.0612	0.0626

$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. $^b R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (zP)^2$, z = 0.0155, 0.03, 0.03, and 0.0212 for Ba_3GaS_4Cl, Ba_3GaSe_4Cl, Ba_3InSe_4Cl and $Ba_7In_2Se_6F_8$, respectively, and $w^{-1} = \sigma^2(F_o^2) + (zP)^2 + 20.000P$, z = 0.05 for Ba_3GaS_4Br, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

■ EXPERIMENTAL SECTION

Single-Crystal Growth. All the following reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as obtained: Ba (99.9%), Ga (99.99%), In (99.99%), S (99.999%), Se (99.999%), BaF_2 (99%), $BaCl_2$ (99%), $BaBr_2$ (99%). BaSe, BaS, Ga_2S_3, Ga_2Se_3, In_2S_3, and In_2Se_3 were synthesized by high-temperature reaction of elements in sealed silica tubes evacuated to 10^{-3} Pa.

A mixture of BaQ, M_2Q_3, and BaX_2 in the molar ratio of 2:1:2 was ground and loaded into fused silica tubes under an Ar atmosphere in a glovebox, which was sealed under 10^{-3} Pa atmosphere, and then placed in a computer-controlled furnace. The sample were heated to 1123 K in 20 h and kept at that temperature for 48 h, then cooled at a slow rate of 4 K/h to 673 K, and finally cooled to room temperature. The produced crystals were manually selected for structure characterization. All the yields based on BaQ are about 20%. Analyses of the crystals with an EDX-equipped Hitachi S-4800 SEM showed the presence of Ba−Ga/In−S/Se−Cl/Br in the approximate molar ratio of 31:10:47:12 and Ba−In−Se−F in the approximate molar ratio of 30:9:25:36. The color of Ba_3GaS_4Cl, Ba_3GaS_4Br, and Ba_3GaSe_4Cl are orange, dark red, and red, respectively.

Solid-State Synthesis. Polycrystalline samples of the three compounds, Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl) were synthesized by solid-state reaction technique. A mixture of BaQ, M_2Q_3, and BaX_2 according to the stoichiometric ratio were ground and loaded into fused silica tubes under an Ar atmosphere in a glovebox, which was sealed under 10^{-3} Pa atmosphere and then placed in a computer-controlled furnace. The sample was heated to 1173 K in 20 h, kept at that temperature for 48 h, and then the furnace was turned off.

X-ray powder diffraction analyses of the powder samples were performed at room temperature in the angular range of 2θ = 10−70° with a scan step width of 0.05° and a fixed counting time of 0.2 s/step using an automated Bruker D8 X-ray diffractometer equipped with a diffracted monochromator set for Cu K_α (λ = 1.5418 Å) radiation.

Supporting Information Figure S1 shows XRD patterns of the polycrystalline samples of Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl) along with the calculated ones on the basis of the single crystal graphic data. The patterns of the samples are in good agreement with the calculated ones. Efforts to synthesize the powder of Ba_3InSe_4Cl and $Ba_7In_2Se_6F_8$ were unsuccessful, which indicates that they may be kinetically stable compounds available only by the flux method.

Structure Determination. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo K_α (λ = 0.71073 Å) at 153 K on a Rigaku AFC10 diffractometer equipped with a Saturn CCD detector. The collection of the intensity data, cell refinement, and data reduction were carried out with the use of the program Crystalclear.[23] Face-indexed absorption corrections were performed numerically with the use of the program XPREP.[24]

The structures were solved with the direct methods program SHELXS and refined with the least-squares program SHELXL of the SHELXTL.PC suite of programs.[24] In the situation that elements next to each other in the periodic table are involved, the assignments of atoms are based on the bonding characteristics and bond valence sums[25] calculations. Considering the bonding characteristics in mixed anion/mixed cation compounds, in Ba_3GaS_4Cl, all anions connected to the Ga atoms are assigned as S atoms and the one connected to Ba only is assigned as Cl atoms. The calculated bond valence sums[25] is 0.97 for the Cl atom in Ba_3GaS_4Cl, which further proves the validity of the atoms assignments. The final refinement included anisotropic displacement parameters and a secondary extinction correction. Additional experimental details are given in Table 1 and selected metrical data are given in Tables 2, 3, and 4. Further information may be found in Supporting Information.

Diffuse Reflectance Spectroscopy. A Cary 5000 UV−vis−NIR spectrophotometer with a diffuse reflectance accessory was used to measure the spectrum of Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl) in the range of 200 nm (6.2 eV) to 1500 nm (0.83 eV).

Table 2. Selected Interatomic Distances (Å) for Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl)

	Ba_3GaS_4Cl	Ba_3GaS_4Br	Ba_3GaSe_4Cl
Ba1−Q2	3.029(1)	3.030(4)	3.158(1)
Ba1−Q1 × 2	3.042(1)	3.019(3)	3.148(1)
Ba1−X	3.134(1)	3.177(2)	3.107(2)
Ba1−Q3	3.185(1)	3.222(4)	3.277(1)
Ba1−Q1 × 2	3.209(1)	3.172(3)	3.296(1)
Ba2−Q3	3.235(1)	3.233(3)	3.355(1)
Ba2−Q2	3.266(1)	3.267(3)	3.398(1)
Ba2−Q3	3.275(1)	3.283(2)	3.389(1)
Ba2−X	3.303(1)	3.337(2)	3.349(2)
Ba2−Q1	3.306(1)	3.722(2)	3.379(1)
Ba2−X	3.406(1)	3.372(1)	3.570(2)
Ba2−Q2	3.503(1)	3.488(3)	3.614(1)
Ba2−Q1	3.537(1)	3.352(3)	3.668(1)
Ba2−Q1	3.612(1)	3.512(3)	3.734(1)
Ga−Q1 × 2	2.232(1)	2.231(3)	2.352(1)
Ga−Q3	2.266(1)	2.258(4)	2.377(2)
Ga−Q2	2.268(1)	2.276(4)	2.384(1)

Table 3. Selected Interatomic Distances (Å) for Ba_3InSe_4Cl

Ba1−Se × 2	3.100(1)
Ba1−Cl × 2	3.236(1)
Ba1−Se × 4	3.435(1)
Ba2−Se × 8	3.585(1)
In−Se × 4	2.525(1)

Table 4. Selected Interatomic Distances (Å) for $Ba_7In_2Se_6F_8$

Ba1−F4 × 4	2.709(2)	Ba3−Se3	3.437(2)
Ba1−F3 × 2	2.753(4)	Ba3−Se3 × 2	3.469(1)
Ba1−F2 × 2	2.833(5)	Ba3−Se2 × 2	3.612(1)
Ba2−F1 × 2	2.584(3)	Ba4−F2 × 2	2.538(2)
Ba2−F3	2.616(5)	Ba4−F4	2.579(5)
Ba2−F2	2.669(4)	Ba4−Se1	3.421(1)
Ba2−Se3 × 2	3.399(1)	Ba4−Se2 × 2	3.471(1)
Ba2−Se1 × 2	3.513(1)	Ba4−Se2 × 2	3.618(1)
Ba2−Se1	3.649(2)	In−Se3	2.512(1)
Ba3−F3 × 2	2.557(2)	In−Se2	2.533(1)
Ba3−F4	2.623(4)	In−Se1 × 2	2.658(1)

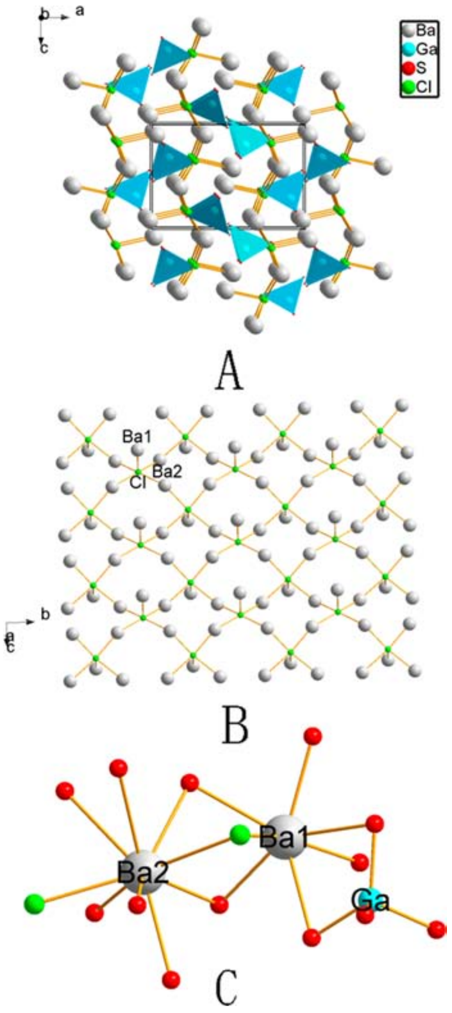


Figure 1. Crystal structure of Ba_3GaS_4Cl viewed down [010] direction (A), the Ba−Cl pseudolayer viewed down [$10\bar{1}$] direction (B), and coordination environments of all cations (C).

■ RESULTS AND DISCUSSION

Crystal Structure of Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl). The three compounds containing Ga are isostructural and crystallize in the centrosymmetric space group *Pnma* of the orthorhombic system. Only the structure of Ba_3GaS_4Cl will be discussed here. The asymmetric unit contains two crystallographically independent Ba atoms, one independent Ga atom, three independent S atoms, and one independent Cl atom. Ba2 and S1 atoms are at general positions 8d, while others are all at Wyckoff sites 4c with *m* symmetry. Considering no metal−metal bond and S−S bond, the oxidation state of 2+, 3+, 2− and 1− can be attributed to Ba, Ga, S and Cl, respectively. In addition, the structure is isotypic to that of Ba_3FeS_5[26] with Ga^{3+} taking the Fe^{2+} and Cl^- taking one S^{2-} in Ba_3FeS_5 simultaneously to maintain charge balance.

In these chalcohalides with mixed cations, the more electronegative halide anions are only connected to the highly electropositive alkaline-earth element through strong ionic bonding. In Ba_3GaS_4Cl, the Cl atom is surrounded by five Ba atoms to form square pyramid with Ba1 atom as apex and four Ba2 atoms as corners of square. Ba1 atom is linked with only one Cl atom while Ba2 atom is linked by two Cl atoms. These quadrangular pyramids are linked via sharing corner Ba2 atoms to form a zigzag BaCl pseudolayer, which spread along *bc* plane and stacked along *a*-direction with Ba1 atoms locating on two sides (Figure 1A). In the meantime, the group IIIA element (less electropositive element) is only connected to the chalcogen element (less electronegative element) through stable covalent bonding. The Ga atoms in Ba_3GaS_4Cl are coordinated to four S atoms to form tetrahedra, which are isolated from each other and located between the zigzag BaCl pseudolayers (Figure 1B).

Figure 1C illustrates the complete coordination environment of cations. Ga atoms are tetrahedrally coordinated to four S atoms with Ga−S distances from 2.232(1) to 2.268(1) Å, (Table 2), which is usual in $BaGa_4S_7$ (2.228(1) to 2.338(1) Å),[27] $BaGa_2SiS_6$ (2.212(1) to 2.239(1) Å),[28] and Ba_2NdGaS_5 (2.239(2) Å).[29] The 7-fold Ba1 atom is connected with six S atoms and one Cl atom to generate monocapped trigonal prism, while 9-fold Ba2 atom is joined to seven S atoms and two Cl atoms in distorted tricapped trigonal prisms geometry with three S atoms as caps. Ba−S interatomic distances range from 3.029(1) to 3.612(1) Å, a little longer than those of Ba_2AgInS_4 (3.128(2) to 3.314(2) Å),[30] Ba_3PrInS_6 (3.171(1) to 3.335(1) Å),[29] and Ba−Cl distances change from 3.134(1) to 3.406(1) Å, a little longer than those of $BaCl_2$ (3.159(1) to 3.197(1) Å).[31]

Crystal Structure of Ba_3InSe_4Cl. Although Ba_3InSe_4Cl possesses the same stoichiometry as Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl), it has a different structure type in the centrosymmetric tetragonal space group *I*4/*mcm*. There are two crystallographically independent Ba atoms, one independent In atom, one independent Se atom, and one independent Cl atom in the asymmetric unit. Ba1, Ba2, In, Se, and Cl atoms are at Wyckoff sites 8*h*, 4*a*, 4*b*, 16*l*, and 4*c* with symmetries of $m2m$, 422, $\bar{4}2m$, m and $4/m$, respectively. Considering no metal−metal bond and Se−Se bond, the oxidation state of 2+, 3+, 2− and 1− can be attributed to Ba, In, Se and Cl, respectively. Moreover, the structure may be seen as the Cs_3CoCl_5[32] structure type with Ba^{2+} taking all the Cs^+ positions, In^{3+} taking the Co^{2+}, and four S^{2-} replacing four Cl^- in Cs_3CoCl_5 simultaneously to achieve the balance of charge.

Again, the Cl atom is connected to Ba atom only in the Ba_3InSe_4Cl compound and the group IIIA element In is only connected to Se element. As shown in Figure 2A, the structure of Ba_3InSe_4Cl can be depicted as containing two kinds of pseudolayers. The first pseudolayer contains only Ba1 and Cl atoms. Each Cl is linked by four Ba1 atoms in a rectangular geometry, which are joined through edge-sharing to form a pseudolayer parallel to the *ab* plane (Figure 2B). On the other hand, the Ba2 and In atoms are alternately connected via Se atoms, forming chains along the *a*-direction. These chains then extend along the *b*-direction, generating another kind of pseudolayer. These two kinds of pseudolayers are stacked along *c*-axis alternately to build up the structure.

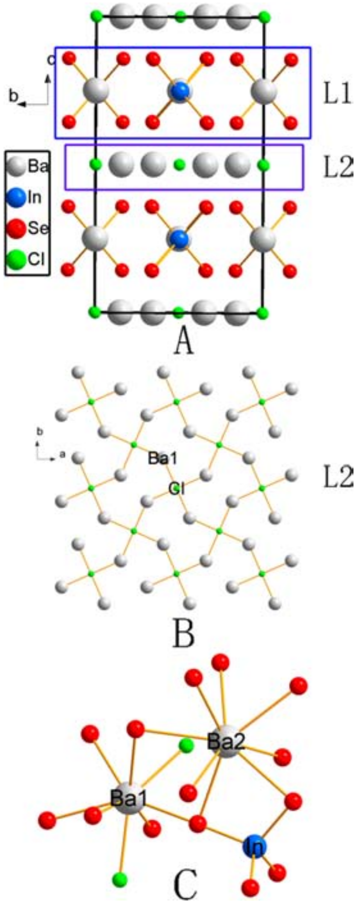


Figure 2. Crystal structure of Ba_3InSe_4Cl viewed down [100] direction (A), the Ba1Cl pseudolayer viewed down [001] direction (B), and coordination environments of all cations (C).

The complete coordination environments of cations are shown in Figure 2C. The In atom is connected with four Se atoms in perfect tetrahedra geometry with In−Se interatomic distance of 2.525(1) Å, (Table 3) a little shorter than those in $Ba_4AgInSe_6$ (2.612(1) to 2.660(1) Å)[33] and Ba_2InYSe_5 (2.505(1) to 2.684(1) Å).[34] The 8-fold Ba1 atom is enjoined with six Se atoms and two Cl atoms to form bicapped trigonal prisms with two Cl atoms as caps. However, 8-fold Ba2 atom is connected with eight Se atoms in distorted square antiprism with torsion angle about 40° and identical Ba−Se interatomic distances. The Ba−Se distances range from 3.100(1) to 3.585(1) Å, shorter than those in $BaGa_4Se_7$ (3.611(2) to 3.861(2) Å)[35] and $BaGa_2GeSe_6$ (3.487(1) to 3.638(1) Å).[28] The Ba−Cl interatomic distances is 3.236(1) Å, resembling that of $BaCl_2$ (3.159(1) to 3.197(1) Å).[31]

Crystal Structure of $Ba_7In_2Se_6F_8$. $Ba_7In_2Se_6F_8$ crystallizes in a new structure type in the centrosymmetric monoclinic space group *C*2/*m*. There are four crystallographically unique Ba atoms, one unique In atom, three unique Se atoms, and four F atoms in the asymmetric unit. Ba1 atom is at Wyckoff sites 2*a* with 2/*m* symmetry, while others are all at Wyckoff sites 4*i* with *m* symmetry. Considering no metal−metal bond and Se−Se bond, the oxidation state of 2+, 3+, 2−, and 1− can be attributed to Ba, In, Se and F, respectively.

As shown in Figure 3A, each crystallographically unique atom can be viewed as stacking along a chain parallel to the *b*-axis. As in the three chalcohalides discussed above, the halide anion, F^- in this case, is connected to Ba^{2+} cations only and the In atom is only tetrahedrally connected to Se atoms. But unlike the GaQ_4 tetrahedra in Ba_3MS_4X (M = Ga, X = Cl, Br; M = Ga, In, X = Cl), which are isolated from each other, the $InSe_4$ tetrahedra in $Ba_7In_2Se_6F_8$ are joined together via corner-sharing forming one-dimensional chains $_{1}^{\infty}[InSe_3]^{3-}$ along *b*-direction. For the Ba−F sublattice, they form another set of complex $[Ba_7F_8]^{6+}$ chains along *b* in which the F2, F3, and F4 atoms are all tetrahedrally coordinated to four Ba atoms, while the F1 atoms bridge two Ba atoms (Figure 3B).

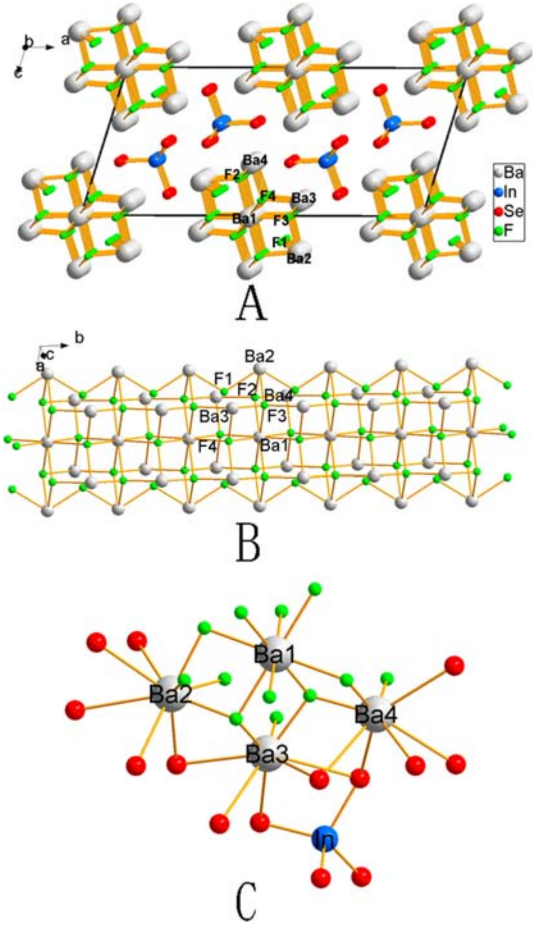


Figure 3. Crystal structure of $Ba_7In_2Se_6F_8$ viewed down [010] direction (A), the $[Ba_7F_8]^{6+}$ chains viewed down [10$\bar{1}$] (B), and coordination environments of all cations (C).

Figure 3C depicts the complete coordination environment of the cations. The In atom is coordinated by four Se atoms to form tetrahedra with In−Se interatomic distances from 2.512(1) to 2.658(1) Å, (Table 4) comparable to those in

$Ba_4AgInSe_6$ (2.612(1) to 2.660(1) Å)[33] and Ba_2InYSe_5 (2.505(1) to 2.684(1) Å).[34] The 8-fold Ba1 atom is connected by eight F atoms in quadrangular prism geometry, 9-fold Ba2 atom is surrounded by five Se atoms and four F atoms to generate tricapped trigonal prisms with two F atom and one Se atom as caps, while Ba3 and Ba4 atoms are enjoined by five Se atoms and three F atoms to generate bicapped trigonal prisms with one F atom and one Se atom as caps. The Ba−F band length is from 2.557(2) to 2.833(5) Å, much more dispersive than those of $Ba_2SnSe_3F_2$ (2.663(1) to 2.696(1) Å).[5] The Ba−Se distances vary from 3.399(1) to 3.649(2) Å, resembling those in $BaGa_2GeSe_6$ (3.487(1) to 3.638(1) Å)[28] and shorter than those in $BaGa_4Se_7$ (3.611(2) to 3.861(2) Å).[35]

Structural Comparison. In all these five compounds, the halide X^- anions are only enjoined to Ba^{2+} cations, while the chalcogenide Q^{2-} anions are connected to Ba^{2+} and M^{3+} cations simultaneously. As for the group IIIA M (M = Ga, In) atoms, they are only connected to the chalcogenide anions through covalent bonding to generate MQ_4 tetrahedra, while most of the Ba^{2+} cations are surrounded by X^- and Q^{2-} anions simultaneously. Such bonding characteristics may be explained empirically in view of the difference in the electronegativity, or alternatively by the qualitative HASB (hard and soft acids and bases) principle,[36−38] which states that hard acids prefer to binding to hard bases and soft acids prefer to binding to soft bases. Here, Ba^{2+} is a harder Lewis acid than Ga^{3+}/In^{3+}; S^{2-}/Se^{2-} are softer Lewis bases than $F^-/Cl^-/Br^-$, and hence in theses structure, Ga^{3+}/In^{3+} are only connected by S^{2-}/Se^{2-} and $F^-/Cl^-/Br^-$ are only linked to Ba^{2+}. On the other hand, the relative size of the cations/anions have obvious influence of the local coordination environments of the cations and anions and the long-range packing of the coordination polyhedra, leading to the formation of three different types of structures in this system of compounds.[39,40] For example, the larger halide anion, Cl^- and Br^-, are coordinated to a square pyramid of five Ba cations in Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl) or to a square of four Ba cations in Ba_3InSe_4Cl. However, such "loose" coordination environment is unstable for the smallest halide anion, F^-, which prefers more compact environment of Ba cations, such as tetrahedral environment.[4,5] Hence the F analogue of Ba_3GaQ_4X could not be synthesized and a new composition $Ba_7In_2Se_6F_8$ was isolated in which the F anions were coordinated to a tetrahedron of four Ba cations or nearly linearly coordinated to two Ba cations, leading to a completely different structures. Among compounds containing the group VIIA anions, the fluorides often exhibit different structures and bonding characteristics from the chlorides, bromides, and iodides due to the much larger electronegativity and small radius of the F atom.[39,40] A similar situation exists in the compounds containing the group VIA anions, as the oxides often show distinct structures compare with sulfides, selenides, or tellurides.[41−44]

Experimental Band Gap. Figure 4 shows the optical absorption spectra of Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl). To determine the band gap being direct or indirect, the plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus $h\nu$ were performed.[45,46] The band gaps obtained from the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ are much more consistent with the color of the compounds. So these semiconductors should be with indirect band structure and possess band gaps of 2.14, 1.80, and 2.05 eV for Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl), respectively. According to the concept of "dimensional reduction",[47−51] lower dimensionality may bring larger band gap. The structure of the Ba_3GaS_4X (X = Cl, Br) and Ba_3InSe_4Cl may be considered as incorporating equal molar BaX_2 into the $Ba_5Ga_2Q_8$ (Q = S, Se)[52,53] structure types. $Ba_5Ga_2S_8$ and $Ba_5Ga_2Se_8$ contain completely isolated GaQ_4 tetrahedra, while in the three new compounds, Ba_3GaS_4X (X = Cl, Br) and Ba_3InSe_4Cl, the introduction of BaX_2 makes the structure change from zero-dimensional to pseudo two-dimensional layered structure. As a result, the band gaps are reduced compared with those of about 2.5 eV for $Ba_5Ga_2Q_8$ (Q = S, Se).[52,53]

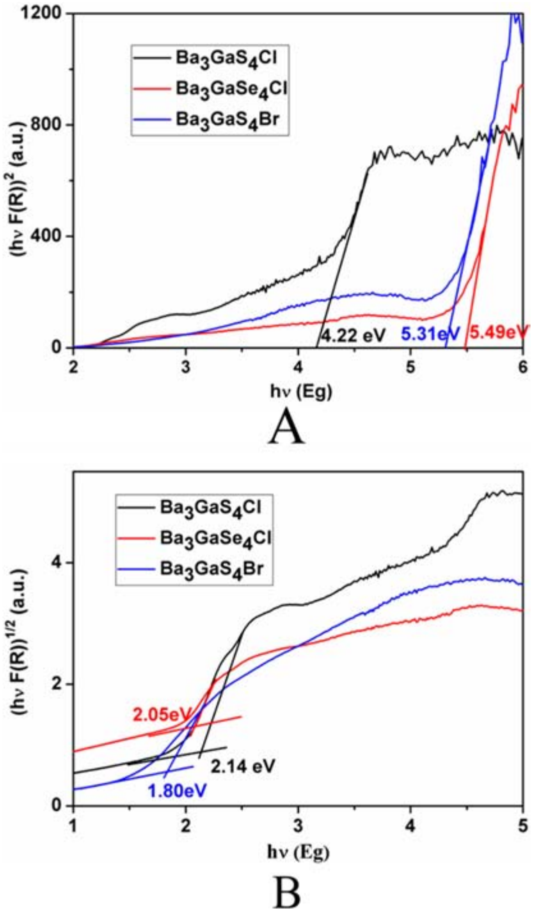


Figure 4. Optical absorption spectra of Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl): (A) the plot of $(\alpha h\nu)^2$ versus $h\nu$; (B) the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$.

■ CONCLUSION

A new series of chalcohalides, Ba_3GaS_4X (X = Cl, Br), Ba_3MSe_4Cl (M = Ga, In), and $Ba_7In_2Se_6F_8$ have been obtained. Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl) crystallize in the space group *Pnma* containing zigzag Ba−X pseudolayers and isolated GaQ_4 tetrahedra, while the same stoichiometric Ba_3InSe_4Cl crystallizes in space group *I*4/*mcm* with two kinds of pseudolayers: Ba−In−Se and Ba−Cl pseudolayers. $Ba_7In_2Se_6F_8$ possesses one-dimensional structure containing $^{\infty}_{1}[InSe_3]^{3-}$ and unique $[Ba_7F_8]^{6+}$ chains. As seen, the electronegativity and size of the anions have great influence on the bonding characteristics and structures of the compounds, the detailed analysis of which may supply valuable guidance for further structure design. The Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl) are all semiconductors with indirect band gap of 2.14, 1.80, and 2.05 eV, respectively.

■ ASSOCIATED CONTENT

Supporting Information

Experimental (red) and simulated (black) X-ray powder diffraction data of Ba_3GaQ_4X (Q = S, X = Cl, Br; Q = Se, X = Cl), and crystallographic file in CIF format for $BaGaS_4X$ (X = Cl, Br), Ba_3MSe_4Cl (M = Ga, In), and $Ba_7In_2Se_6F_8$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Basic Research Project of China (No. 2010CB630701) and National Natural Science Foundation of China (No. 91122034, No. 51132008, No. 21271178).

We thank Lei Kang (Center for Crystal Research and Development, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences) for help on discussions during the course of this work.

■ REFERENCES

(1) Park, C. H.; Keszler, D. A.; Yanagi, H.; Tate, J. *Thin Solid Films* **2003**, *445*, 288−293.

(2) Yanagi, H.; Tate, J.; Park, S.; Park, C. H.; Keszler, D. A. *Appl. Phys. Lett.* **2003**, *82*, 2814−2816.

(3) Hiramatsu, H.; Kamioka, H.; Ueda, K.; Ohta, H.; Kamiya, T.; Hirano, M.; Hosono, H. *Phys. Status Solidi A* **2006**, *203*, 2800−2811.

(4) Kabbour, H.; Cario, L. *Inorg. Chem.* **2006**, *45*, 2713−2717.

(5) Kabbour, H.; Cario, L.; Danot, M.; Meerschaut, A. *Inorg. Chem.* **2006**, *45*, 917−922.

(6) Kamihara, Y.; Hiramatsu, H.; Hirano, M.; Kawamura, R.; Yanagi, H.; Kamiya, T.; Hosono, H. *J. Am. Chem. Soc.* **2006**, *128*, 10012−10013.

(7) Chen, X. H.; Wu, T.; Wu, G.; Liu, R. H.; Chen, H.; Fang, D. F. *Nature* **2008**, *453*, 761−762.

(8) de la Cruz, C.; Huang, Q.; Lynn, J. W.; Li, J.; Ratcliff, W., II; Zarestky, J. L.; Mook, H. A.; Chen, G. F.; Luo, J. L.; Wang, N. L.; Dai, P. *Nature* **2008**, *453*, 899−902.

(9) Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. *J. Am. Chem. Soc.* **2008**, *130*, 3296.

(10) Kuroki, K.; Onari, S.; Arita, R.; Usui, H.; Tanaka, Y.; Kontani, H.; Aoki, H. *Phys. Rev. Lett.* **2008**, *101*, 087004.

(11) Mazin, I. I.; Singh, D. J.; Johannes, M. D.; Du, M. H. *Phys. Rev. Lett.* **2008**, *101*, 057003.

(12) Yanagi, H.; Kawamura, R.; Kamiya, T.; Kamihara, Y.; Hirano, M.; Nakamura, T.; Osawa, H.; Hosono, H. *Phys. Rev. B* **2008**, *77*, 224431.

(13) Jiang, S.; Xing, H.; Xuan, G.; Wang, C.; Ren, Z.; Feng, C.; Dai, J.; Xu, Z. a.; Cao, G. *J. Phys.: Condens. Matter* **2009**, *21*, 382203.

(14) Fang, A.-H.; Huang, F.-Q.; Xie, X.-M.; Jiang, M.-H. *J. Am. Chem. Soc.* **2010**, *132*, 3260.

(15) Nilges, T.; Osters, O.; Bawohl, M.; Bobet, J.-L.; Chevalier, B.; Decourt, R.; Weihrich, R. *Chem. Mater.* **2010**, *22*, 2946−2954.

(16) Jiang, X.-M.; Zhang, M.-J.; Zeng, H.-Y.; Guo, G.-C.; Huang, J.-S. *J. Am. Chem. Soc.* **2011**, *133*, 3410−3418.

(17) Johnsen, S.; Liu, Z.; Peters, J. A.; Song, J.-H.; Sandy, N.; Malliakas, C. D.; Jin, H.; Freeman, A. J.; Wessels, B. W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2011**, *133*, 10030−10033.

(18) Yu, P.; Zhou, L.-J.; Chen, L. *J. Am. Chem. Soc.* **2012**, *134*, 2227−2235.

(19) Dhingra, S.; Kanatzidis, M. G. *Science* **1992**, *258*, 1769−1772.

(20) Jiang, Y.; Zhu, Y. J. *J. Phys. Chem. B* **2005**, *109*, 4361−4364.

(21) Biswas, K.; Rao, C. N. R. *Chem.—Eur. J.* **2007**, *13*, 6123−6129.

(22) Zhang, Q.; Chung, I.; Jang, J. I.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2009**, *131*, 9896.

(23) *CrystalClear*; Rigaku Corporation: Tokyo, Japan, 2008.

(24) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.

(25) Brown, I. D.; Altermatt, D. *Acta Crystallogr.,, Sect. B* **1985**, *41*, 244−247.

(26) Lemley, J. T.; Jenks, J. M.; Hoggins, J. T.; Eliezer, Z.; Steinfink, H. *J. Solid State Chem.* **1976**, *16*, 117−128.

(27) Lin, X.; Zhang, G.; Ye, N. *Cryst. Growth Des.* **2008**, *9*, 1186−1189.

(28) Yin, W.; Feng, K.; He, R.; Mei, D.; Lin, Z.; Yao, J.; Wu, Y. *Dalton Trans.* **2012**, *41*, 5653−5661.

(29) Feng, K.; Shi, Y.; Yin, W.; Wang, W.; Yao, J.; Wu, Y. *Inorg. Chem.* **2012**, *51*, 11144−11149.

(30) Yin, W.; Feng, K.; Mei, D.; Yao, J.; Fu, P.; Wu, Y. *Dalton Trans.* **2012**, *41*, 2272−2276.

(31) Haase, A.; Brauer, G. *Z. Anorg. Allg. Chem.* **1978**, *441*, 181−195.

(32) Powell, H. M.; Wells, A. F. *J. Chem. Soc.* **1935**, 359−362.

(33) Yin, W.; Feng, K.; Hao, W.; Yao, J.; Wu, Y. *J. Solid State Chem.* **2012**, *192*, 168−171.

(34) Feng, K.; Yin, W.; Wang, W.; Kang, L.; Hao, W.; Yao, J.; Shi, Y.; Lin, Z.; Wu, Y. *Z. Anorg. Allg. Chem.* **2013**, *639*, 1021−1025.

(35) Yao, J.; Mei, D.; Bai, L.; Lin, Z.; Yin, W.; Fu, P.; Wu, Y. *Inorg. Chem.* **2010**, *49*, 9212−9216.

(36) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581.

(37) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643.

(38) Chattaraj, P. K.; Lee, H.; Parr, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1855−1856.

(39) Chackraburtty, D. M. *Acta Crystallogr.* **1957**, *10*, 199−200.

(40) Reckeweg, O.; Schulz, A.; DiSalvo, F. J. *Z. Naturforsch., B: Chem. Sci.* **2011**, *66*, 359−365.

(41) Klee, W.; Schaefer, H. *Rev. Chim. Miner.* **1979**, *16*, 465−472.

(42) Eisenmann, B.; Jakowski, M.; Schafer, H. *Rev. Chim. Miner.* **1982**, *19*, 263−273.

(43) Eisenmann, B.; Jakowski, M.; Klee, W.; Schafer, H. *Rev. Chim. Miner.* **1983**, *20*, 255−263.

(44) Lalla, A.; Mullerbuschbaum, H. *J. Less-Common Met.* **1989**, *154*, 233−241.

(45) Bang, T. H.; Choe, S. H.; Park, B. N.; Jin, M. S.; Kim, W. T. *Semicond. Sci. Technol.* **1996**, *11*, 1159−1162.

(46) Mitchell, K.; Huang, F. Q.; McFarland, A. D.; Haynes, C. L.; Somers, R. C.; Van Duyne, R. P.; Ibers, J. A. *Inorg. Chem.* **2003**, *42*, 4109−4116.

(47) Axtell, E. A.; Liao, J. H.; Pikramenou, Z.; Kanatzidis, M. G. *Chem.—Eur. J.* **1996**, *2*, 656−666.

(48) Axtell, E. A.; Park, Y.; Chondroudis, K.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1998**, *120*, 124−136.

(49) Wang, L.; Hwu, S.-J. *Chem. Mater.* **2007**, *19*, 6212−6221.

(50) Androulakis, J.; Peter, S. C.; Li, H.; Malliakas, C. D.; Peters, J. A.; Liu, Z.; Wessels, B. W.; Song, J.-H.; Jin, H.; Freeman, A. J.; Kanatzidis, M. G. *Adv. Mater.* **2011**, *23*, 4163.

(51) Johnsen, S.; Peter, S. C.; Nguyen, S. L.; Song, J.-H.; Jin, H.; Freeman, A. J.; Kanatzidis, M. G. *Chem. Mater.* **2011**, *23*, 4375−4383.

(52) Eisenmann, B.; Jakowski, M.; Schafer, H. *Z. Naturforsch., B: Chem. Sci.* **1984**, *39*, 27−30.

(53) Mei, D.; Yin, W.; Lin, Z.; He, R.; Yao, J.; Fu, P.; Wu, Y. *J. Alloys Compd.* **2011**, *509*, 2981−2985.