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Articles

Synthesis and Structure of Cadmium Chalcogenide Beryllosilicate Sodalites

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Sodalites of the composition $Cd_8[BeSiO_4]_6X_2$, X = S, Se, and Te, have been synthesized by hydrothermal reaction of CdO, BeO, SiO_2, and X at 750 °C and 2 kbar. The materials crystallize with the cubic sodalite unit cell with an ordered Be/Si framework in the space group $P\bar{4}3n$. Their structures have been refined from powder diffraction data in order to delineate the dimensions of the Cd_4X units in the sodalite cage and the intercage separation of these units. Infrared, UV−vis and ^{29}Si MAS NMR spectra of these materials are also reported. Correlations between structural parameters and ^{29}Si chemical shifts have been determined for this series of compounds. UV−vis data demonstrate that the Cd_4X units do not interact electronically.

Introduction

The sodalites are a well-known class of anion containing framework consisting of β cages, formed from (Be, Al, Ga, Si, Ge, Zn, or P)O_4 tetrahedra, directly linked through the six-membered rings and containing a centrally placed anion coordinated tetrahedrally to four cations. The composition of this class of material is very diverse; for example, the anions incorporated into $M_8[AlSiO_4]_6X_n$ ($n = 1, 2$) have included Cl^-, Br^-, I^-, SCN^-, NO_2^-, NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, PO_4^{3-}, VO_4^{3-}, MnO_4^-, MoO_4^{2-}, CrO_4^{2-}, WO_4^{2-}, ClO_4^-, ClO_3^-, S^{2-}, $C_2O_4^{2-}$, CO_3^{2-}, OH^- and $B(OH)_4^-$.[1−3] Of note, as members of this class, are the well-known ultramarines which contain the polysulfide anion radicals S_3^- and S_2^- and the corresponding selenium analogues which are widely used as pigments. The structural diversity of the sodalite framework has been demonstrated by a number of groups worldwide. Of note are the berylloarsenate frameworks,[4] pure silica sodalite[5] and the aluminogermanates;[6] even more unusual is the phosphonitride sodalite framework of $Zn_7[P_{12}N_{14}]Cl_2$ synthesized by Schnick.[7] In addition, a number of small symmetric organic molecules have recently been trapped in the aluminosilicate sodalite framework, e.g. 1,3-dioxolane.[8]

Aluminate sodalites have frameworks consisting solely of AlO_4 tetrahedra, with the general formula, $M_8[AlO_2]_{12}X_2$, containing divalent cations and anions in the cavities.[9,10] These sodalites are unusual in that they clearly disobey Löwenstein's rule of aluminum avoidance but are still readily synthesized at high temperature. Related materials are the borate sodalites $M_8[BO_2]_{12}X_2$ which have smaller cages suitable for coordinating to smaller divalent cations such as zinc and magnesium.[11] Compositionally equivalent to the pure aluminate frameworks are the beryllosilicates, and the naturally occurring mineral genthelvite, $Zn_8[BeSiO_4]_6S_2$, is a member of this family.[12] Mel'nikov *et al*. synthesized a number of materials of this type, but reported no more than lattice constants.[13]

Some of these pure aluminate and beryllosilicate sodalites with more covalent entrapped ions are of interest as they may be considered to contain small blocks of (II,VI) semiconductor separated by the inert framework. Electronic interaction between these units would be of considerable interest as these materials may then be considered to be framework-expanded semiconductors. The electronic properties of a variety of compounds including $Zn_8[BO_2]_{12}X_2$,[14] $Zn_8[BeSiO_4]_6X_2$,[15] X = S, Se, and Te, and $Ga_xZn_{8-x}P_x[BO_2]_{12}Se_{2-x}$[16] have been investigated by Moran *et al*. This work describes the optical absorption bands as having a large blue-shift away from those of the bulk MX materials; rather than describing this as a blue-shifted absorption, the optical spectrum could be described as that expected for discrete M_4X units. The electrostatic isolation effect of the framework was also demonstrated in the ^{77}Se and ^{125}Te MAS NMR spectra which exhibited upfield shifts from the bulk MX materials. This indicated a reduction in the paramagnetic contribution to the chemical shift suggesting greater localization of the electron density in the sodalite compared with that of the bulk. These authors also mention the synthesis of cadmium-containing beryllosilicate and beryllogermanate sodalites,[15] but practically no results are presented on these materials. Our initial work on $Cd_4[AlO2]_6S_2$ initially indicated that the individual M_4X groups in these materials may

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have been electronically coupled;[17] however, further investigation of the luminescent properties of this material showed that the shifted absorption maximum was probably due to small amounts of bulk CdS on the surface of the sodalite.[18] This may be the result of the separation of these units by the framework with a next nearest neighbor Cd−S distance of 5.2 Å. Cd_4S_4 blocks in the β cages of zeolite Y reported by Herron *et al.* are believed to be electronically coupled despite being separated by 6 Å.[19]

The electronic interaction between semiconductor nanounits in framework materials is likely to depend upon the separation of the species unless the framework provides a method of communication. One method of reducing this distance between anions and cations in neighboring cages would be to include larger anions at the cage center; alternatively smaller framework species would also help reduce this intercage separation. With this goal, we have recently synthesized and structurally characterized a series of beryllosilicate sodalites containing cadmium and chalcogenide ions in the sodalite cages. These materials have small framework dimensions due to the small ionic radius of beryllium but are able to incorporate anions as large as telluride, $r(Te^{2-}) = 2.21$ Å.

Results and Discussion

X-ray Refinement. Refinement was carried out in the space group $P\bar{4}3n$ using the starting model of genthelvite[12] with an ordered framework consisting of alternating BeO_4 and SiO_4 tetrahedra. The program DBW-PC9006[20] was used for the refinement which allowed the inclusion of the low level of $CdSiO_3$, typically below 5%, as a second phase. No literature data exist for the structure of $CdSiO_3$ though the material is reported as crystallising with the parawollastonite structure.[21] In order to ensure a good fit to the $CdSiO_3$ impurity in the sodalite phases a Rietveld refinement of a pure sample of $CdSiO_3$ was undertaken as no structural data exists for this phase in the literature. The structural model was taken from ref 21, and a final R_{Bragg} obtained after refinement of the cadmium silicon and oxygen positions was 4.8%. Coordinates obtained from this refinement for cadmium silicate were transferred to the refinement of the sodalite phase, and the scale factor only for this impurity phase was refined.

Initial stages of the refinement of the $Cd_8[BeSiO_4)_6X_2$ phases included all instrument parameters; atomic parameters were slowly introduced and in the later stages all atomic positional parameters were varied. Final stages of the refinement included isotropic temperature factors for all atoms except Be which has only nominal X-ray scattering (i.e. $Z = 4$) and the temperature factor for this atom was therefore set at unity Final atomic parameters are summarized in Tables 1a−c and important bond lengths and angles in Table 2. An example of the profile fit achieved is given in Figure 1.

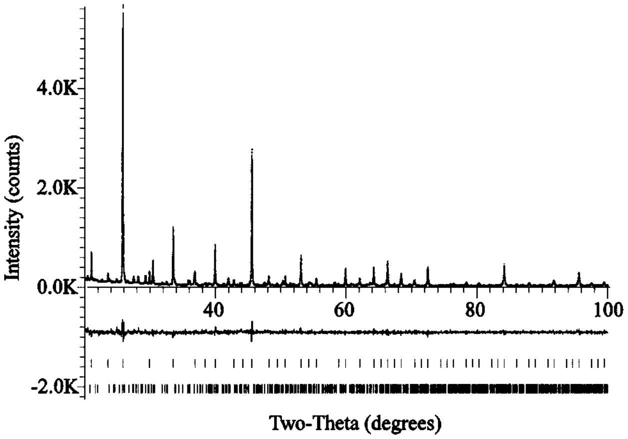

Figure 1. Final fit to the powder X-ray diffraction data from $Cd_8[BeSiO_4]_6S_2$. The upper broken line represents the experimental data and the continuous line the calculated pattern. The lower continuous line shows the fit. Tick marks show reflection positions (upper, $Cd_8[BeSiO_4]_6S_2$; lower, $CdSiO_3$).

Table 1. Refined Atomic Parameters (Esd's Given in Parentheses)

a. $Cd_8[BeSiO_4]_6S_2$

atom	site	*x*	*y*	*z*	B_{iso}
Be	6c	$^1/_4$	$^1/_2$	0	1.00
Si	6b	$^1/_4$	0	$^1/_2$	0.61(23)
O1	24i	0.3607(11)	0.3564(12)	−0.0686(10)	0.19(25)
Cd	8e	0.1700(2)	0.1700(2)	0.1700(2)	1.14(5)
S	2a	0	0	0	0.28(27)

space group: $P\bar{4}3n$ $\chi^2 = 1.38$
$a = 8.4474(1)$ Å $R_{Bragg} = 5.96$

b. $Cd_8[BeSiO_4]_6Se_2$

atom	site	*x*	*y*	*z*	B_{iso}
Be	6c	$^1/_4$	$^1/_2$	0	1.00
Si	6b	$^1/_4$	0	$^1/_2$	0.90(22)
O1	24i	0.3582(11)	0.3530(12)	−0.0681(10)	0.24(28)
Cd	8e	0.1761(2)	0.1761(2)	0.1761(2)	1.39(5)
Se	2a	0	0	0	0.86(13)

space group: $P\bar{4}3n$ $\chi^2 = 1.48$
$a = 8.4925(1)$ Å $R_{Bragg} = 3.62$

c. $Cd_8[BeSiO_4]_6Te_2$

atom	site	*x*	*y*	*z*	B_{iso}
Be	6c	$^1/_4$	$^1/_2$	0	1.00
Si	6b	$^1/_4$	0	$^1/_2$	1.36(49)
O1	24i	0.3545(21)	0.3597(21)	−0.0585(21)	0.09(48)
Cd	8e	0.1856(3)	0.1856(3)	0.1856(3)	1.12(9)
Te	2a	0	0	0	2.50(24)

space group: $P\bar{4}3n$ $\chi^2 = 1.48$
$a = 8.5637(1)$ Å $R_{Bragg} = 5.21$

The vibrational spectra of sodalites are characteristic of the framework geometry and have been investigated by a number of groups.[22−24] The framework modes occur below 1200 cm^{-1}, and Table 3 summarizes the positions and assignments of the various absorption bands.

^{29}Si MAS NMR spectra from all three materials showed a single resonance indicative of an ordered framework with alternating BeO_4 and SiO_4 tetrahedra. Of note are the frequencies of the ^{29}Si shifts which are amongst the lowest observed for silicon based framework materials, i.e. for silicon bound through oxygen to other cations.

Structure. All beryllosilicate structures were successfully refined in the space group $P\bar{4}3n$ demonstrating an ordering of

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Table 2. Selected Bond Angles (deg) and Distances (Å) for $Cd_8[BeSiO_4]_6X_2$, with Esd's Given in Parentheses

atom−atom	S	Se	Te
Be−O1	1.638(1) × 4	1.655(1) × 4	1.642(1) × 4
Si−O1	1.591(1) × 4	1.596(1) × 4	1.590(1) × 4
Cd−O1	3.023(16) × 3	2.992(11) × 3	2.947(19) × 3
Cd−O1	2.233(5) × 3	2.2069(7) × 3	2.252(13) × 3
Cd−X	2.487(1) × 1	2.594(1) × 1	2.745(1) × 1
Be−O−Si	2.987(1)	3.003(1)	3.028(1)
Be−O−Si angle	135.2(7)	137.8(6)	139.6(10)

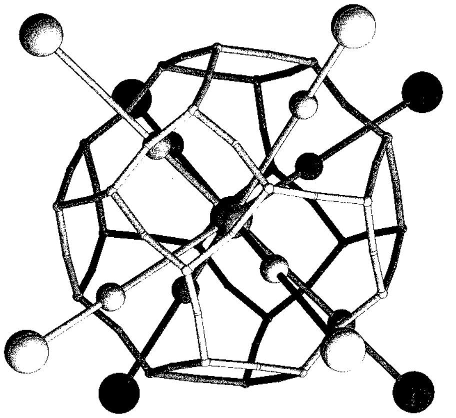

Figure 2. Part of the $Cd_8[BeSiO_4]_6X_2$ structure showing a single β cage, its contents and the intercage interactions between cadmium (small spheres) and the chalcogenide ion (large spheres) in the neighboring unit cell.

Table 3. Characteristic IR Bands (cm^{-1}) for $Cd_8[BeSiO_4]_6X_2$

X	ν_s	ν_{as}	ν_{as}	ν_{as}	bend
S	942	762	735	701	521
Se	947	759	732	698	517
Te	955	754	723	693	514

the beryllium and silicon atoms in the framework. Part of the structure is shown in Figure 2. Framework bond lengths [Be−O 1.64 Å, Si-O 1.59 Å] were consistent with literature values for tetrahedral beryllium and silicon. The Be−O−Si bond angles are somewhat lower than the corresponding Al−O−Al angle in the cadmium chalcogenide aluminate sodalites reflecting the shorter T−O distances and need for greater collapse of the sodalite cage in order to coordinate well to the cadmium ions. The cadmium ion is approximately tetrahedrally coordinated to three framework oxides and the cage anion though there are longer interactions between cadmium and three further cage oxides and, still further away, the anion in the neighboring cage. The tetrahedral coordination around the chalcogenide anion reflects closely that in the pure cadmium chalcogenide, with distances Cd−X of CdS [beryllosilicate 2.488 Å, bulk CdS 2.519 Å] CdSe [beryllosilicate 2.594 Å, bulk CdSe 2.631 Å] and CdTe [beryllosilicate 2.745 Å, bulk CdTe 2.806 Å].

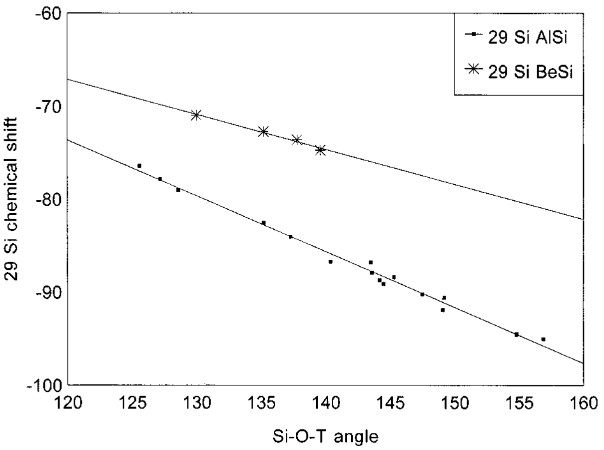

Figure 3. Variation of the ^{29}Si MAS NMR chemical shift as a function of T−O−T bond angle in aluminate and beryllosilicate sodalites.

^{29}Si MAS NMR. ^{29}Si spectra showed a single peak in all three materials consistent with the structure refinement with the single $Si(OBe)_4$ environment. The ^{29}Si chemical shift in aluminosilicate frameworks containing SiO_4 tetrahedra of various geometries and a range of environments has been studied in some detail.[25] The chemical shift has been found to depend on the Si−O−Al bond angle, and a good linear correlation exists between these two parameters.[26] Altering the nature of the other tetrahedral species in the framework modifies the absolute chemical shift; however, a similar correlation between chemical shift and Si−O−Be bond angle would be expected. Data for the three compounds studied and genthelvite are plotted in Figure 3 together with data from aluminosilicate sodalites with the same bond angle range. The data for the beryllosilicates shows a similar trend to that which is well documented for aluminosilicates with decreasing (less negative) ^{29}Si chemical shift with decreasing bond angle; this variation reflects changes in the Si−O orbital interaction as a function of bond angle. The rate of change is similar for the beryllosilicates and the aluminosilicates and the lower absolute values for the beryllosilicates probably reflect greater shielding of the Si nucleus associated with the smaller electropositive charge on the Be.

Vibrational Spectra. The vibrational spectra of sodalites have recently been fully analyzed and discussed in detail by Creighton et al.[24] For materials of the sodalite structure crystallizing in the space group $P\bar{4}3n$ 14 modes are infrared active in aluminosilicate derivatives, with ordered Si and Al; intensity calculations show that nine of these vibrations with frequencies up to 1200 cm^{-1} are of reasonable intensity. However, typically only five or six absorptions are readily resolved in the infrared spectrum, which can be assigned to a combination of asymmetric stretches near 950 cm^{-1}, three symmetric bands in the region 700−1000 cm^{-1} and one or two bends at lower frequency, typically 400−550 cm^{-1}.

The frequencies of the symmetric stretches and the bend have been shown to be correlated with the sodalite *a* lattice parameter and T−O−T bond angle in a number of sodalite systems and show a shift to lower frequencies as the size of the cage increases. The vibrational assignments for the beryllosilicates are given in Table 3 and show that replacement of aluminum in the framework by beryllium with maintenance of the $P\bar{4}3n$ framework symmetry produces analogous spectra in terms of the numbers of absorptions. The absolute positions and intensities are changed with the lower charged and smaller beryllium; for example the symmetric stretches are in the range 690−765 cm^{-1} for the beryllosilicates compared with 630−725 cm^{-1} for typical aluminosilicates. Inspection of the data in Table 3 shows the expected frequency variations with the asymmetric stretches and bends moving to lower frequencies as the cage size increases while the symmetric stretch moves to higher values.

UV−Vis Spectra. The UV−vis spectra, Figure 4, in the 1000−200 nm range of the three cadmium chalcogenide sodalites show reasonable strong absorptions between 250 and 300 nm. In addition each material exhibits a very weak absorption edge at much lower energies (CdS (500 nm), CdSe (720 nm), CdTe (830 nm)). These absorption edges follow those expected for the pure bulk cadmium chalcogenide

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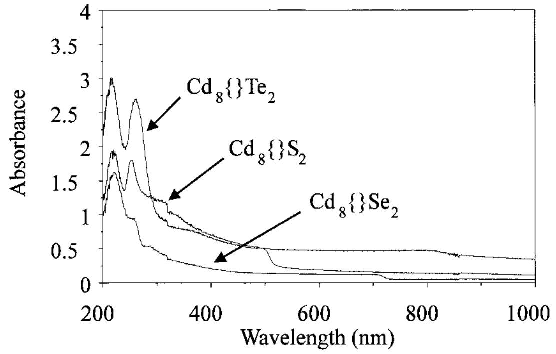

Figure 4. UV−vis spectra from the $Cd_8[BeSiO_4]_6X_2$ in the range 200−1000 nm.

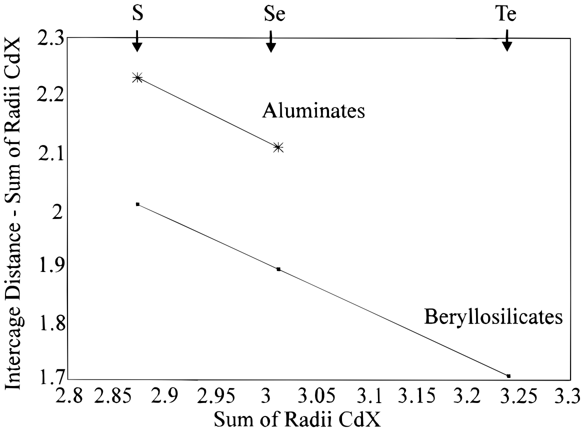

Figure 5. Intercage Cd−X distance as a function of bulk Cd−X distance in aluminate and beryllosilicate sodalites.

materials and probably reflect very low levels of CdS, CdSe, and CdTe remaining in the material. Despite washing with bromine water, small amounts of these simple phases remain, probably encased in the sodalite. Similar behavior was seen with the cadmium chalcogenide aluminate sodalites. The absorptions in the 250−300 nm region in borate and aluminate sodalites containing M_4X groups ($M = Zn, Cd$; $X = O, S, Se, Te$) have been assigned to a charge transfer located within the cluster[18] though consideration of absorption in materials such as $Zn_4O(acetate)_6$ indicate that interaction of the framework oxygens is likely. Comparisons of the position of the absorption maxima in the 200−300 nm region for $X = S$, Se, and Te in the beryllosilicates and aluminate show no obvious trend.

Conclusions

In terms of achieving interaction between the semiconductor nanounits in neighboring cages such electronic coupling will depend on the separation of these units. A measure of this separation and potential for interaction can be taken as the distance between the cadmium ion and the anion in the next β cage as compared with the typical Cd−X distance found in the bulk CdX materials or indeed the intracage Cd−X distance. For the three compounds studied in this work plus aluminate sodalites containing CdX, this information is plotted in Figure 5.

As the size of the anion increases the distance between the cage centers increases reflecting the larger lattice parameter; however, the cadmium ions are pushed away from the center of the cages toward the six-rings and the chalcogenide ion in the neighboring unit. Therefore in absolute terms, i.e. by consideration of the intercage Cd-X separation with respect to the bulk Cd-X distance, the Cd_4X units are relatively closer together and electronic interaction through orbital overlap increases.

Even though this interaction is likely to be largest in the cadmium telluride derivative, no evidence is seen in the optical spectrum of intercage electronic interaction. Therefore the interaction within the M_4X unit and between this unit and the framework, as can characterized by the optical absorption spectrum,[18] remain dominant and these materials are best described as having discrete M_4X units.

One possible method of increasing the interaction between units in neighboring cages would be to use larger cations than cadmium which may be sited nearer to the center of the six-membered rings which separate sodalite cages. To this end, we are investigating the synthesis of mercury containing beryllosilicate sodalites.

Experimental Section

The method described by Mel'nikov *et al.* was followed[13] for the synthesis of the beryllosilicates. Homogeneously ground mixtures of BeO, SiO_2, CdO, and X ($X = S, Se, Te$) were placed in gold capsules, previously welded at one end. Then 0.1 mL of a 1% (w/v) NaOH solution was then added using a microsyringe and the other end of the tube was then sealed. The weighed capsule was heated in a conventional cold-seal hydrothermal bomb at 2 kbar pressure and 750 °C for 48 h. The bombs were then slow-cooled to room temperature. The capsules were then removed from the bomb and reweighed to ensure that the sample integrity had been maintained. The product material was removed from the capsule and washed initially with water. In order to remove residual metal chalcogenide, the products were washed further with bromine water, adjusted to pH 6 using sodium hypochlorite solution [14% w/v]. After washing all products were white in coloration.

Powder X-ray diffraction data were collected from the products using a Siemens D5000 diffractometer operating with $CuK\alpha_1$ radiation. The diffraction patterns revealed a majority phase of cubic $Cd_8[BeSiO_4]_6X_2$, ($X = S, Se, Te$) with a small amount, <5%, of $CdSiO_3$ impurity. The sodalite reflections were fully indexed in the space group $P\bar{4}3n$, and no unindexed peak remained in the pattern after allowance for the $CdSiO_3$ impurity. Refined cell parameters were, for $Cd_8[BeSiO_4]_6X_2$, as follows: $X = S$, 8.4474(1) Å; $X = Se$, 8.4925(1) Å; $X = Te$, 8.5637(1) Å. For structure refinement powder X-ray diffraction data were collected over a 2θ range of 20−100° over a period of 15 h using a 0.02° step.

IR spectra were recorded from 4000 to 500 cm^{-1} using Perkin Elmer FT-IR 1710 equipped with a PE 3600 data station using pressed KBr disks. MAS NMR data were collected on a Bruker AM300, and ^{29}Si data were referenced to TMS; a sample spinning rate of 4KHz was used.

Diffuse reflectance optical absorption spectra were measured on undiluted samples using a Perkin-Elmer Lambda19 UV−vis spectrometer.

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