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Synthesis and Structure of a New Quinary Sulfide Halide: $LaCa_2GeS_4Cl_3$

Robert L. Gitzendanner[1] **and Francis J. DiSalvo***

Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

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A new quinary rare earth sulfide−halide compound has been synthesized and its structure determined by single-crystal X-ray diffraction. $LaCa_2GeS_4Cl_3$ crystallizes in the noncentrosymmetric hexagonal space group C_{6v}^4-$P6_3mc$ (No. 186) with $Z = 2$, $a = 9.731(1)$ Å, and $c = 6.337(1)$ Å. Lanthanum and calcium are mixed on a pseudo-trigonal prismatic site, coordinated to three sulfur atoms on one triangular face and three chlorine atoms on the other. Isolated, slightly distorted tetrahedra of GeS_4 are oriented with a tetrahedral 3-fold axis aligned along the crystallographic 3-fold rotation axis. Preliminary optical studies indicate that this material has a useful optical window extending approximately from 0.5 to 10 μm. Nonlinear optical activity of $LaCa_2GeS_4Cl_3$ is demonstrated by the generation of green light when pumped with a 1.064 μm Nd:YAG laser.

Introduction

Materials with optically transparent windows that extend into the far-IR (10−14 μm) are increasingly important for many modern optical and opto-electronic applications.[2] Similarly, materials which demonstrate nonlinear optical behavior are also highly sought for many applications and devices.[3] In both instances, the property demands for these applications are quite extensive and rigorous, and in many cases, despite the wealth of known materials which demonstrate desirable properties, these areas remain materials-driven. For these reasons, new materials which demonstrate large optical windows or appreciable nonlinear optic susceptibility are in high demand.

Sulfide materials are well-known to demonstrate large optically transparent windows extending into the far-infrared. Many useful sulfide materials have transmission windows ranging from 0.5 to 14 μm.[2] Sulfides containing rare earth elements show increased thermal stability[4] as well as reasonable mechanical strength and stability.[5] For these reasons, we began investigating the synthesis of novel rare earth metal sulfides. In order to increase the polarizability of such phases and to improve nonlinear optic and ferroelectric properties, we include the electropositive alkaline earth metals as well. However, both rare earth and alkaline earth metals typically adopt centrosymmetric coordination in sulfides. To try to encourage the formation of noncentrosymmetric structures, we also include main group elements, such as Ge, which prefer to adopt noncentrosymmetric tetrahedral coordination in sulfides. While the presence of noncentrosymmetric polyhedra does not guarantee that the overall structure is noncentrosymmetric, mixing coordination environments of different symmetries can encourage the formation of noncentrosymmetric structures. Many known crystalline sulfides are easily grown via flux methods;[6,7] thus our current work focuses on reactions in molten halide salts. One disadvantage of flux growth methods is the occasional inclusion of the flux elements into the isolated phases. (We have already demonstrated one other instance in which such “contamination” has led to the formation of new phases.[8]) Here we present the synthesis and crystal structure of $LaCa_2GeS_4Cl_3$, as well as some preliminary optical and nonlinear optical studies which suggest that the materials in this structural class may be suitable for technological applications.

Experimental Section

Materials. All reagents were stored and handled in an argon-filled glovebox to prevent air and moisture exposure. La and CaS were purified before use by the method previously described.[8] The $CaCl_2$ (Aldrich, 97%) was dried by heating under dynamic vacuum at 150 °C for several hours. All other reagents were used as obtained from the suppliers.

Synthesis. $LaCa_2GeS_4Cl_3$ was first isolated from the reaction of equimolar amounts of La (0.200 g) and CaS (0.1038 g), 2 equiv of Ge (0.2090 g, Cerac, 99.999%), and 5.5 equiv of S (0.2539 g, Metalspecialties, 99.9995%). The reactants were mixed with an approximately equal mass of dry $CaCl_2$ (0.8698 g) to act as a flux. The mixture was loaded into an open graphite crucible and sealed in an evacuated fused silica tube. It was then heated slowly (40 °C/h) to 600 °C and held there for 24 h to allow for the complete reaction of the sulfur. [*CAUTION: The vapor pressure of S at 600 °C is approximately 10 atm; heating rapidly beyond 600 °C often results in explosions!*] The temperature was then raised to 875 °C and held for 50 h. To encourage crystal growth, the mixture was slowly cooled back to 600 °C (2.5 °C/h), the furnace was then shut off, and the reaction mixture was allowed to cool to room temperature with no external quenching. Excess $CaCl_2$ flux was removed by soaking the crucible in deionized water for several hours. The remaining product was filtered off, washed with more water, and allowed to dry overnight in a desiccator. This flux removal process ensures that the products isolated are water-stable. The title compound has also been found to be air-stable on the time scale of at least months. Approximately 97% (0.7488 g) of the original reactant mass (excluding flux) was recovered as product, with the major phase consisting of deep red transparent crystals. Several of these crystals were selected for electron microprobe analysis (semiquantitative EDAX) on a JEOL 733 Superprobe. This analysis indicated an atomic composition of 6% La, 11% Ca, 20% Ge, 42% S, and 21% Cl with an average statistical scatter of ±3% (i.e., 6 ± 3% La etc. Calculated for $LaCa_2GeS_4Cl_3$: 9.1% La, 18.2% Ca, 9.1% Ge, 36.4% S, 27.3% Cl.) Since appropriate standards were not available for quantitative corrections and since ideal flat polished samples were not prepared, the accuracy of these semiquantitative experimental measurements is only fair, as can be seen by comparing the theoretical and experimental

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(1) Present address: School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland.

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Table 1. Madelung Potentials for $LaCa_2GeS_4Cl_3$

atom	charge	pot. (V)	atom	charge	pot. (V)
Ge	4.00	−35.153	S(1)	−2.00	19.974
La/Ca	2.33	−19.188	S(2)	−2.00	19.236
Cl	−1.00	8.592			

numbers, especially for Ca and Ge. However, it is clear that the material contains all five elements added to the reaction mixture (including the flux elements). It has also been determined that this compound is thermally stable at 600 °C but decomposes, rather than congruently melting, when heated above 1100 °C under vacuum.

Note on synthesis: This phase was also identified by powder X-ray diffraction as a major product of several other reactions involving various La:Ca:Ge ratios whenever a pure $CaCl_2$ flux was used. However, identical reactions, except for the substitution of a eutectic 1:1 molar mixture of NaCl−$CaCl_2$ for the flux, produced predominately a transparent yellow crystalline phase. This phase, which does not seem to contain any Cl by electron microprobe analysis, has not yet been identified.

Crystallographic Studies. Precession photographs of a small needlelike crystal were taken to confirm crystal quality and determine a preliminary unit cell and space group. These photographs indicated hexagonal symmetry and the systematic conditions on $I(000l)$, $l = 2n$, and $I(h, h, \overline{2h}, l)$, $l = 2n$; these are consistent with three possible space groups: C_{6v}^4-$P6_3mc$, D_{3h}^4-$P\bar{6}2c$, and D_{6h}^4-$P6_3/mmc$. The unit cell parameters of $a = 9.731(1)$ Å, and $c = 6.337(1)$ Å (which agree with the precession data), were refined from 39 reflections in the range 9.6° < 2Θ(Mo Kα_1) < 24.9° that had been automatically centered on a Siemens P4 four-circle diffractometer at room temperature. During data collection, three standard reflections were checked every 97 reflections to watch for crystal decomposition or movement out of the beam; no appreciable change in intensity of these peaks was observed. Data were collected in the Θ−2Θ mode from $-1 \le h \le 12$, $-12 \le k \le 1$, $-8 \le l \le 8$; a total of 1966 reflections were collected. An empirical ψ-scan correction was applied to the data using XPREP.[9] Subsequent averaging resulted in an R_{int} of 0.0403. Statistical analysis of the complete data set found $\langle|E^2 - 1|\rangle = 0.700$, which indicates a noncentrosymmetric space group.[10] A preliminary model was found in C_{6v}^4-$P6_3mc$ using the direct methods program XS;[9] no satisfactory model could be found in the centrosymmetric space group D_{6h}^4-$P6_3/mmc$. As S and Cl have almost identical scattering factors, EUTAX-1[11] was utilized to separate the S^{2-} and Cl^- sites on the basis of Madelung potentials. In an ionic model, the potential at a given site is usually proportional to the charge, or oxidation state, of the atom at that site. EUTAX-1 was initially run on a model which assumed that all anions were S^{2-} and all cations were La^{3+}. Since the cationic and anionic charges would not balance in such a model, EUTAX-1 applies a uniform neutralizing charge. Such a model resulted in two anionic sites with potentials consistent with an estimated charge of −2 and one anionic site with a potential consistent with an estimated charge slightly more positive than −1. Changes in the total cation charge did not change the site differentiation. The unique anion site was thus redefined as Cl^-; the resulting potentials (assuming a La:Ca ratio that results in a zero net charge) are listed in Table 1. As the unique site determined by EUTAX-1 agrees well with the structural data, we are confident of our assignment of anion positions. Further EUTAX-1 runs with the two different anions indicated a potential calculated for the La−Ca site consistent with an average charge of +2.33 on this site, implying a La:Ca ratio of 1:2. This La:Ca ratio is also consistent with the semiquantitative EDAX ratios. Thus, in following structural refinements, the La to Ca ratio was fixed at 1:2 to preserve charge balance and their positions were constrained to be identical. These constraints provided reasonable thermal parameters in the refinements. Allowing the La:Ca ratio to vary resulted in unstable refinements, and fully occupying the site with either just La or just Ca resulted in exaggerated thermal parameters and large residuals in the Fourier electron difference map. Final refinements on F_o^2 with XL[9] resulted in an $R_w(F^2)$ of 0.0666 for all data and 26 parameters and an $R(F)$ ($F_o^2 > 4\sigma(F_o^2)$) of 0.0268. A Flack x parameter of −0.037(36) was calculated, indicating a correct absolute structure.[12] The final structure was examined for missing symmetry using the program MISSYM;[13] no symmetry other than what was expected for $P6_3mc$ was detected. The program STRUCTURE TIDY[14] was used to put the positional parameters in a standard setting. The crystallographic details are listed in Table 2, and the atomic positions and thermal parameters are given in Table 3.

Table 2. Crystallographic Data for $LaCa_2GeS_4Cl_3$

empirical formula $LaCa_2GeS_4Cl_3$	fw 526.25
$a = 9.7311(14)$ Å	space group $P6_3mc$ (No. 186)
$b = 9.7311(14)$ Å	$T = 20$ °C
$c = 6.3366(13)$ Å	$\lambda = 0.710\,73$ Å
$\alpha = 90°$	$\rho_{calcd} = 3.363$ g/cm^3
$\beta = 90°$	$\mu = 94.38$ cm^{-1}
$\gamma = 120°$	$R^a = 0.0282$
$V = 519.7(2)$ Å^3	$R_w{}^b = 0.0666$
$Z = 2$	

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [(\sum w|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $LaCa_2GeS_4Cl_3$

atom	Wycoff site	x	y	z	U(eq)[a]
La/Ca	6(c)	0.8118(1)	0.1882	0.0720(1)	25(1)
Ge	2(b)	$^1/_3$	$^2/_3$	0.0000(2)	20(1)
Cl	6(c)	0.1222(1)	0.8778	0.1670(4)	24(1)
S(1)	2(b)	$^1/_3$	$^2/_3$	0.3501(5)	18(1)
S(2)	6(c)	0.5459(1)	0.4541	0.3608(3)	24(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

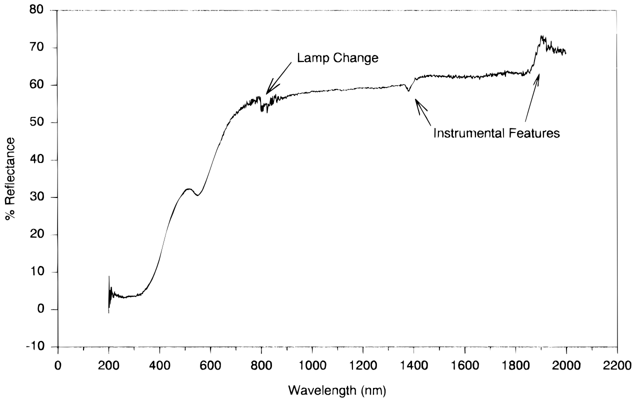

Figure 1. Diffuse-reflectance spectrum of $LaCa_2GeS_4Cl_3$ taken on a Shimadzu UV-3101 PC uv−vis−near-IR scanning spectrophotometer. The small peak seen around 1400 nm and the noise obtained above 1900 nm are repeatable features caused by the instrument.

Optical and Nonlinear Optical Studies. The diffuse-reflectance spectrum of selected, powdered crystals of $LaCa_2GeS_4Cl_3$ was taken on a Shimadzu UV-3101 PC UV−vis−near-IR scanning spectrophotometer from 2000 to 200 nm (see Figure 1). This showed a continuous absorption band beginning around 700 nm and extending down to 400 nm. There is a small peak in the reflectance at 550 nm, at which point the total reflectance has dropped to approximately half of its long-wavelength value. An optically transparent window of KBr and approximately 1.5 wt % of the title compound were pressed in a Wilks

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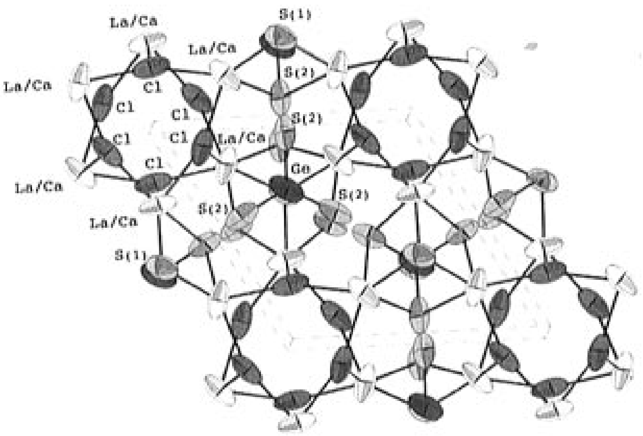

Figure 2. Structure of $LaCa_2GeS_4Cl_3$ as viewed approximately down the *c* axis. Atoms are represented by thermal ellipsoids of 90% probability. Figures in this paper were generated with the help of ATOMS v.3.1 from Shape Software.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $LaCa_2GeS_4Cl_3$[a]

La(1)−Cl(1)#1	2.797(2)	La(1)−Cl(1)#3	2.8518(10)
La(1)−S(1)#1	2.822(2)	La(1)−S(2)#4	2.915(2)
La(1)−Cl(1)#2	2.8518(10)	La(1)−S(2)#5	2.915(2)
Ge(1)−S(1)	2.219(3)	Ge(1)−S(2)#7	2.219(2)
Ge(1)−S(2)#6	2.219(2)	Ge(1)−S(2)#1	2.219(2)
Cl(1)#1−La(1)−S(1)#1	83.53(8)	Cl(1)#2−La(1)−S(2)#4	81.78(6)
Cl(1)#1−La(1)−Cl(1)#2	83.98(5)	Cl(1)#3−La(1)−S(2)#4	127.88(6)
S(1)#1−La(1)−Cl(1)#2	139.14(5)	Cl(1)#1−La(1)−S(2)#5	140.42(4)
Cl(1)#1−La(1)−Cl(1)#3	83.98(5)	S(1)#1−La(1)−S(2)#5	83.57(6)
S(1)#1−La(1)−Cl(1)#3	139.14(5)	Cl(1)#2−La(1)−S(2)#5	127.88(6)
Cl(1)#2−La(1)−Cl(1)#3	77.45(8)	Cl(1)#3−La(1)−S(2)#5	81.78(6)
Cl(1)#1−La(1)−S(2)#4	140.42(4)	S(2)#4−La(1)−S(2)#5	74.45(8)
S(1)#1−La(1)−S(2)#4	83.57(6)		
S(1)−Ge(1)−S(2)#6	113.43(6)	S(1)−Ge(1)−S(2)#1	113.43(6)
S(1)−Ge(1)−S(2)#7	113.43(6)	S(2)#6−Ge(1)−S(2)#1	105.24(7)
S(2)#6−Ge(1)−S(2)#7	105.24(7)	S(2)#7−Ge(1)−S(2)#1	105.24(7)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x+1, -y+1, z-{}^1/_2$; (#2) $-y+2, x-y+1, z$; (#3) $-x+y, -x, z$; (#4) $-x+y+1, -x+1, z$; (#5) $-y+1, x-y, z$; (#6) $x-y, x, z-{}^1/_2$; (#7) $y, -x+y+1, z-{}^1/_2$.

Mini-Press using 30 ft lb of torque; and the transmission in the range 2.5−25 μm was studied using a Matteson Instruments FTIR spectrometer. This indicated a transmission window out to at least 10 μm in the IR range. Larger single crystals, or specially prepared windows, will be required to obtain more quantitative results.

Powdered, hand-selected crystals of the title compound were placed in the beam of a Nd:YAG (Quanta-Ray GCR series) laser, operating at 10 Hz, with a 1.064 μm fundamental. An intense green light from the sample was clearly visible, even with full room lighting. This green light is attributed to the nonlinear optic second-harmonic generation at 532 nm.

Results and Discussion

The structure of $LaCa_2GeS_4Cl_3$ can be simply described in terms of the metal sulfide halide polyhedra (see Figure 2). Individual GeS_4 tetrahedra are aligned along the 3-fold axis of the unit cell. All four Ge−S bond distances are nearly identical, 2.219(3) Å, and closely correspond to the Ge−S distance of 2.21Å found in GeS_2.[15] However the S−Ge−S bond angles are slightly distorted from ideal, ranging from 105.2 to 113.4°. The La−Ca sites are in 6-fold, slightly distorted, trigonal prismatic coordination, with three S atoms making up one face at M−S distances of 2.822(2)−2.915(1) Å and three Cl atoms making up the other face at M−Cl distances of 2.797(2)−2.852(1) Å. In this way, a typically centrosymmetric coordination becomes noncentrosymmetric and polar, as allowed in the C_{6v}^4 point group of this structure. It is also important to notice that not only are the trigonal prisms themselves polar but they are arranged in such a way that the entire structure should have a net polar moment. The 3-fold axis of each trigonal prism is identically tilted out of the *a*−*b* plane, producing a dipole moment component along the crystallographic *c* axis (see Figure 3). It is noteworthy that the single crystal selected for the structural determination appeared to be a single domain, suggesting that the size of pyroelectric domains in this material would be fairly large. The trigonal prisms share edges on the S face and share vertices on the Cl face. The Cl atoms form a chain of face-shared, empty octahedra running up the 6_3 axis, the center of these octahedra lies 2.55 Å from the surrounding Cl atoms, yet there is no indication of any element filling this position. The largest peak in the Fourier electron difference map, which is somewhat displaced from this central position, is only 1.43 e/Å^3. There is no metal−metal bonding or any S−S bonding, the shortest S−S distance being greater than 3.5 Å.

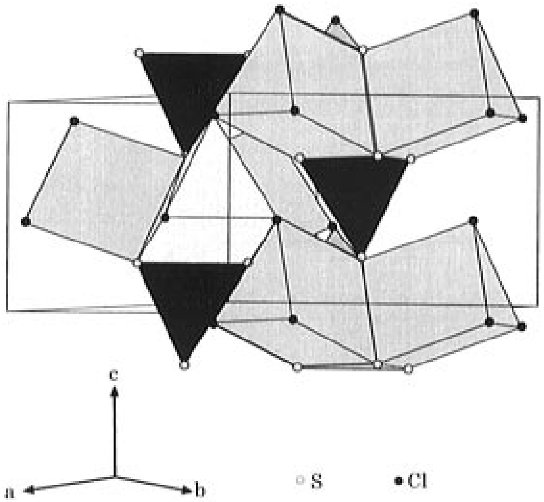

Figure 3. Polyhedral representation of the structure of $LaCa_2GeS_4Cl_3$. The GeS_4 tetrahedra are black. The $(La{-}Ca)S_{3/2}Cl_{3/3}$ trigonal prisms are shown in light gray fill.

Related structural motifs have been reported for numerous oxychlorides,[16,17] oxychloride sulfides,[18] and sulfides.[19] Comparison of $LaCa_2GeS_4Cl_3$ with the typical Ba_4OCl_6 structure shows partial anti-site rearrangement of the anion and cation positions. In the second compound, the Ba occupies the La−Ca 6(c) positions but also occupies the S 2(b) site of the first structure. The O sits in the Ge 2(b) position and thus centers a Ba tetrahedron. The chlorine atoms remain on the same 6(c) site, as well as occupying the S 6(c) position. To the best of our knowledge, there is no true iso-type, or anti-type, structure in which all the cations and anions occupy the same, or opposite, positions as in $LaCa_2GeS_4Cl_3$. However, these similar structures lead us to believe that true iso-type structures could be formed with fewer than five different element types. Possible compositions of such structures might include $La_3ZnS_4Cl_3$, or, if all the anions were a single type, a ternary composition such as La_3PS_7 could result. Future studies will address such possibilities.

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The optical transparency and nonlinear optical susceptibility of this material clearly indicate it is a good candidate for further studies. We are currently attempting to quantify the conversion efficiency and phase-matching conditions for the material. The demonstrated stabilities with respect to air and water, as well as reasonable thermal stability, indicate $LaCa_2GeS_4Cl_3$ could become a useful material for many optical and nonlinear optical applications.

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Supporting Information Available: Complete tables of experimental crystallographic details, anisotropic displacement parameters, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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