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# A Solid-State Diastereomer, $AgLa_3GeS_7$

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The detailed structural analysis for the noncentrosymmetric $AgLa_3GeS_7$ chalcogenide has revealed evidence of the formation of an interesting solid-state diastereomer. This finding is demonstrated by the lattice matching of two newly recognized parallel chains of staggered $[AgS_3]$ units and interconnected cubane-like $[La_3GeS_4]$ blocks. The title compound belongs to a large family of complex chalcogenides that have a general formulation of $A(RE)_3MQ_7$, where A = Cu, Ag; RE = La-Er, Y; M = Si, Ge, Sn; and Q = S, Se, first synthesized by Guittard *et al.* in 1968.[1] The unit cells of these compounds have been indexed in the hexagonal crystal system with the space group correctly assigned to $P6_3$ (No. 173). The crystal structure of $CuLa_3SiS_7$, determined by Flahaut *et al.* in 1970,[2] has been the structural type adopted to describe the frameworks of analogous compounds.[3] Despite the observed strong piezoelectric effects,[2] which may generate potential interests in materials applications,[4] no further reports concerning structure and property of this class of chalcogenides have ever been published. Our investigations suggest that the $A(RE)_3MQ_7$ family presents a rich structural chemistry, in that parameters to govern the formation of the specific diastereomer may exist, which is of importance to property tuning with respect to the piezo responses and related areas.

This study has been made possible because of the success in single crystal growth of the $AgLa_3GeS_7$ phase using the KBr flux. It is noted that the flux growth method has prompted a number of investigations in refractory oxide[5] and rare-earth-metal-containing chalcogenide[6] systems, where only powder materials could be prepared otherwise. The crystal structure has thus been determined by the X-ray diffraction technique (Table 1).[7]

**Table 1.** Crystallographic Data[a] for $AgLa_3GeS_7$

| | | | |
|---|---|---|---|
| chemical formula | $AgLa_3GeS_7$ | fw | 821.61 |
| $a$, Å | 10.423 (1) | space group | $P6_3$ (No. 173) |
| $c$, Å | 5.840 (2) | $T$, °C | 23 |
| $V$, Å$^3$ | 549.4 (3) | $\lambda$, Å | 0.710 69 |
| $Z$ | 2 | $\varrho_{calcd}$, g cm$^{-3}$ | 4.966 |
| $R$[b] | 0.027 | linear abs coeff, cm$^{-1}$ | 170.98 |
| $R_w$[c] | 0.040 | | |

[a] The cell constants are refined in the hexagonal crystal system using 25 reflections ($9.04° \leq 2\theta \leq 17.79°$). [b] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [c] $R_w = [\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2}$.

In an extension of studying the Ag-based chalcogenide systems, where the formation of non-centrosymmetric solids seems promising,[8] investigations of compounds containing rare-earth (RE) elements have been initiated. RE-containing chalcogenides have attracted attention in materials development due to unique features that result from the intrinsic bonding and electronic characteristics associated with RE cations. Through our recent studies,[6] it has also been realized that the RE-incorporated chalcogenides possess enhanced thermal properties compared to their counter systems. Here we present an interesting result concerning the noncentrosymmetric lattice of a silver lanthanum germanium sulfide composed of rarely seen structural features that account for the origin of what can be claimed a diastereomer.

The extended framework of the title compound can be best described as cross-linked parallel chains of acentric sub-lattices composed of staggered $[AgS_3]$ units and interconnected cubane-like $[La_3GeS_4]$ blocks, as shown in Figure 1. Two parallel chains, centered around the $6_3$ or 3-fold axes, respectively, are connected through S(1). The $[AgS_3]$ unit forms a slightly distorted trigonal coordination geometry in that each silver atom is displaced by 0.26 Å with respect to the triangular sulfur plane. The staggered $[AgS_3]_\infty$ configuration allows a close Ag−Ag distance, 2.92 Å (≡ $c/2$), which is similar to that in elemental silver, 2.89 Å;[10] however, it is longer than the closest contact in $Ag_2S$, 2.76 Å.[11] In any case, this observed distance indicates a weak Ag−Ag interaction, which is consistent with the elongated thermal ellipsoid displayed by the Ag atom.[12] As to the $[La_3GeS_4]$ cubane, it is severely distorted from a cube as evidenced by the four distinctly different bond distances, e.g., 2.22 Å (Ge−S(3)), 2.91, 3.04 Å (La−S(3)), and 3.09 Å (La−S(2)). The $[La_3GeS_4]$ cubanes are oriented along the body-diagonal (3-fold) axis with the germanium corner pointing along the chain direction to facilitate the connectivity with neighboring blocks through the apical Ge−S(2) bond of the tetrahedrally

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(1) (a) Guittard, M.; Julien-Pouzol, M.; Laruelle, P.; Flahaut, J. *C. R. Acad. Sc. Paris* **1968**, *C267*, 767−9. (b) The compound $AgLa_3GeSe_7$, which originally failed to be synthesized by conventional solid-state reactions according to ref 1a, is now able to be prepared via the halide flux method. Synthesis of the tin analogs, $AgLa_3SnQ_7$ (Q = S, Se), was not reported in ref 1a. Bucher, C. K.; Taylor, S. P.; Hwu, S.-J. Unpublished research, Rice University, 1994.

(2) Flahaut, J.; Laruelle, P. In *Chemistry of Extended Defects of Non-Metallic Solids; Proceedings of the Institute of Advanced Study 1969*; Eyring, L., Okeeffe, M., Eds.; North-Holland Publishing Co.: Amsterdam, 1970; pp 109−23.

(3) (a) Guittard, M.; Julien-Pouzol, M. *Bull. Soc. chim. Fr.* **1970**, *7*, 2467−9. (b) The noncentrosymmetric framework of $CuLa_3SiS_7$ was descibed as a complex framework of $LaS_7$, $SiS_4$, and $CuS_6$. The copper atom is in a dissymmetric site of the sulfur octahedron, $CuS_6$, where three of the Cu−S distances related by a 3-fold symmetry were measured much longer (3.39 Å) than the other three (2.29 Å).

(4) (a) *Materials for Nonlinear Optics*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1991. (b) Chu, D. K. T.; Bierlein, J. D.; Hunsperger, R. G. *IEEE Trans. Ultrason., Ferroelectrics Frequency Control* **1992**, *39*, 683−7.

(5) (a) Wang, S.; Hwu, S.-J. *J. Am. Chem. Soc.* **1991**, *114*, 6920−2. (b) Serra, D. L.; Hwu, S.-J. *J. Solid State Chem.* **1992**, *101*, 32−40. (c) Wang, S.; Hwu, S.-J. *Inorg. Chem.* **1995**, *34*, 166.

(6) (a) Carpenter, J. D.; Hwu, S.-J. *Chem. Mater.* **1992**, *4*, 1368−72. (b) Carpenter, J. D.; Hwu, S.-J. *Acta Crystallogr.* **1992**, *C48*, 1164−8. (c) Carpenter, J. D.; Hwu, S.-J. *J. Solid State Chem.* **1992**, *97*, 332−9. (d) Carpenter, J. D. Ph. D. Dissertation, Rice University (**1993**). (e) Bucher, C. K.; Hwu, S.-J. *Inorg. Chem.* **1994**, *33*, 5831−5.

(7) Redundant data were collected so that Friedel pair analysis could be performed to determine the correct enantiomorph.

(8) (a) A total of 242 (56%) out of 430 Ag-based compounds found in Pearson's handbook are noncentrosymmetric. The high percentage of noncentrosymmetric phases observed may have some structurally related reasons concerning the coordination geometry of Ag(I) with respect to the chalcogenide anions. (b) *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd ed.; Villars, P., Calvert, L. D., Eds.; ASM International: Metal Park, OH, 1991.

(9) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(10) *Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990.

(11) Sodanaga, R.; Sveno, S. *Mineral. J., Jpn.* **1967**, *5*, 124−43.

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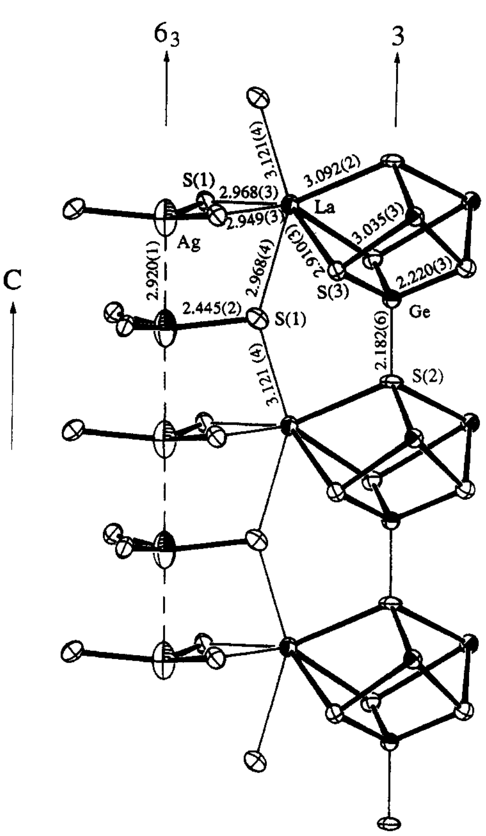

**Figure 1.** ORETP[9] drawing of the partial structure of $AgLa_3GeS_7$ showing the connectivity of the parallel chains of the staggered $[AgS_3]$ unit and interconnected $[La_3GeS_4]$ cubane-like blocks. Only the four terminal sulfur atoms shared between two chains are shown for clarity. The bond distances are given in ångstroms. The anisotropic atoms are presented at 90% probability.

coordinated $GeS_4$. The $[AgS_3]$ and $[La_3GeS_4]$ units are physically matched in the unit cell as $[AgS_3]_{8/4}[La_3GeS_4]_{2/1}$ to give rise to the empirical formula $AgLa_3GeS_7$. The La−S(1) distances at the interface (2.95−3.12 Å, as shown by the four La−S bonds in the $LaS_8$ polyhedron[13]) are diverse, indicating size mismatching of the two structural units, which may be in part the reason for the distortion of the $[AgS_3]$ unit. All observed bond distances are comparable with what have been reported in the sum of Shannon crystal radii[14] and/or other chalcogenide phases.[6] On the basis of the displacement direction of the silver atom and the orientation of the cubane block, the polar axis is thus defined along the *c* axis of the unit cell.

An important aspect of the communication is the first recognition of a solid-state diastereomer attributed to the configurational reorientation of the above stated structural units. The $AgLa_3GeS_7$ structure differs from the originally assigned $CuLa_3SiS_7$ type in the strict sense that the relative spatial orientations of the two structural units are in an opposite order. In the $AgLa_3GeS_7$ structure (**I**), the directions of the two acentric chains are parallel, a relative configuration shown in the schematic diagram below designated as (− −). The $CuLa_3SiS_7$ structure[15] (**II**) consists of two isostructural chains, but the displacement direction for the copper atom in the chain of staggered $[CuS_3]$ units is in an opposite direction to that of the Si-S bond pointing along the chain of interconnected cubane-like $[La_3SiS_4]$ blocks. That is to say these two parallel chains are oriented in an anti-parallel fashion, to which the configuration is designated as (− +).

From the stereo point of view, **I** and **II** can be considered as diastereomers, commonly seen in organic molecules, but less common in extended solids. This case is the first to be recognized, to our knowledge. It should be noted that, from our preliminary examinations, two diastereomers coexist in compounds from systems where the Shannon crystal radii ratios for M/Q are small and only type **I** is found in the systems where the M/Q ratios are reasonably large.[16] In drawing a correlation between diastereomer type and the M/Q ratio, it seems that the size of post-transition-metal (M) cations is a possible parameter that governs the diastereomer formation and can be used for selective synthesis. Also, single crystal analysis of a mixed-ion sulfide, $AgSm_3(Ge/Si)S_7$, shows an extended distortion with respect to the $[AgS_3]$ unit, with a Ag-displacement of ca. 0.57 Å. This suggests that the cubane distortion is dictated by the distinct differences between La−S and (Ge/Si)−S bonds and is used to fine tune the overall characteristics of the material's property induced by the Ag-displacement of the $[AgS_3]$ unit. While only limited properties have been examined,[17] it is evident from the above discussions that a rich structural chemistry is present in the $A(RE)_3MQ_7$ family to be further explored.

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**Supplementary Material Available:** Text giving experimental procedures and tables of detailed crystallographic data, atomic positional and thermal parameters, and selected bond distances and angles and a figure showing $CuLa_3SiS_7$, featuring the same chains as the title structure (8 pages). Ordering information is given on any current masthead page.

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(12) The orbital overlap between the neighboring silver atoms may correspond to the $p_z-p_z$ interaction, while the bonding orbitals for the trigonal geometry is likely hybridized $sp^2$. The former orbital interaction may be attributed to the elongation of the thermal ellipsoid for the silver atom.

(13) The $LaS_8$ polyhedron can be viewed as a bicapped trigonal prism (btp) with one $S_3$ triangular plane embedded in the cubane and the opposite $S_3$ associated with the $[AgS_3]_\infty$ chain. The two capping La−S distances are 2.868 (3) and 3.084 (3) Å with respect to the S(1) and S(3) atoms. The latter is not shown in Figure 1.

(14) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−67.

(15) The copper cation is displaced by 0.38 Å with respect to the $S_3$ triangular plane, by our calculations.

(16) The single-crystal compounds $A(RE)_3MQ_7$ examined with their structural types and M/Q ratios of Shannon crystal radii given in parentheses: $AgLa_3SnS_7$ (**I**, 0.41), $AgLa_3SnSe_7$ (**I**, 0.38), $AgLa_3GeSe_7$ (**I/II**, 0.29), $AgSm_3(Ge/Si)S_7$ (**I/II**, 0.27), $CuLa_3SiS_7$ (**II**, 0.24). Assignment of types **I** vs **II** is independent of the orientation of the polar axis (c) of the absolute configuration, and thus incorrect assignment of type results in divergent structural refinements.

(17) The DTA (differential thermal analysis) indicates that the $AgLa_3GeS_7$ phase melts congruently at ~1196 °C, and the UV−vis reflectance spectroscopy gives rise to an optical bandgap of 2.50 eV. Further studies of mechanical, thermal, and optical properties of $AgLa_3GeS_7$ await the results of growth studies aimed at producing larger crystals.