



# Synthesis and crystal structure of $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ through alkali halide flux growth

Nicholas R. Spagnuolo, Gregory Morrison, Hans-Conrad zur Loye\*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

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## ABSTRACT

Single crystals of a new germanate,  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ , were obtained via high temperature cesium chloride/cesium fluoride flux growth and characterized by single crystal X-ray diffraction.  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  crystallizes in the  $F-43m$  space group with  $a = 15.5049(4)$  Å. This compound is related to the  $\text{Ge}_7\text{O}_{16}$  family of zeotypes, such as  $\text{Rb}_3\text{HGe}_7\text{O}_{16}$ ,  $\text{Li}_4\text{HGe}_7\text{O}_{16}$ ,  $\text{Na}_4\text{Ge}_7\text{O}_{16}$ , and  $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ .  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  is a salt-inclusion material with two distinct inclusions: tetrahedral  $\text{Cs}_3\text{AgF}$  and octahedral  $\text{Cs}_6\text{F}$ . The material is shown to participate in ion exchange, making  $\text{Rb}_3\text{HGe}_7\text{O}_{16}\cdot 4\text{H}_2\text{O}$  and  $\text{K}_3\text{HGe}_7\text{O}_{16}\cdot 4\text{H}_2\text{O}$ .

## 1. Introduction

Exploratory flux growth has been proven to be an excellent technique for the discovery of new compounds and structure types. A significant advantage of flux growth is the ability to use a wide range of temperatures to achieve crystal formation of both thermodynamically stable and metastable compounds [1]. Many different types of fluxes can be utilized, including chlorides, oxides, hydroxides, and carbonates, where different fluxes work best for different classes of materials [1]. For example, fluxes can be utilized as “reactive fluxes”, such that they take up the role of a reagent to be incorporated into the crystal [1,2]. In particular, when using salt fluxes such as the alkali halides, salt-inclusion materials, SIMs, can be obtained [3,4]. SIMs are an interesting class of materials with covalent frameworks containing channels filled by ionic salt lattices [4–6].

In some cases, SIMs adopt the same framework structures as zeolites, or more generally zeotypes [5,7,8]. Zeolites are compounds with aluminosilicate frameworks containing large pores that are typically filled with cations and water [9]. Zeotypes display similar topologies and properties to zeolites but are composed of non-aluminosilicate frameworks. One extended family of zeotypes are based on a  $\text{Ge}_7\text{O}_{16}$  framework and include compounds such as  $\text{Rb}_3\text{HGe}_7\text{O}_{16}\cdot x\text{H}_2\text{O}$ ,  $\text{Li}_4\text{HGe}_7\text{O}_{16}\cdot x\text{H}_2\text{O}$ , and  $\text{Na}_4\text{Ge}_7\text{O}_{16}\cdot x\text{H}_2\text{O}$ . These compounds crystallize in tetragonal, rhombohedral, and cubic structures and consist of tetrahedral clusters of four  $\text{GeO}_6$  octahedra (formula  $\text{Ge}_4\text{O}_{16}$ ) that are connected into a 3D structure by  $\text{GeO}_4$  tetrahedra [10–13]. The channels created by this framework are occupied by three or four monovalent cations (alkali metal,  $\text{Ag}^+$ , or  $\text{NH}_4^+$ ) and up to six water molecules

depending on the cation identity and extent of dehydration. In the case of three cations in the channel, a proton (hydrogen cation) lies in the center of the  $\text{Ge}_4\text{O}_{16}$  cluster providing charge balance. For example, the structures of  $\text{K}_3\text{HGe}_7\text{O}_{16}\cdot x\text{H}_2\text{O}$  and  $\text{Rb}_3\text{HGe}_7\text{O}_{16}\cdot x\text{H}_2\text{O}$ , solved using synchrotron powder X-ray diffraction data, contain three alkali cations and water in the channels and a proton at the center of each  $\text{Ge}_4\text{O}_{16}$  cluster [11]. This family of zeotypes has been studied for their ion exchange properties and reversible dehydration behavior and has also been shown to exhibit ionic conductivity [10–13]. We have synthesized  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ , a salt-inclusion material containing the same framework as the  $\text{Ge}_7\text{O}_{16}$  zeotypes. The crystal growth conditions and structure determination of  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  are detailed in this paper.

## 2. Experimental

### 2.1. Materials and methods

Single crystals of  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  were grown by heating  $\text{GeO}_2$  (99.9%, BTC) in a CsCl (Ultra Pure, VWR Life Sciences) and CsF (99%, Alfa Aesar) flux. 2 mmol of germanium oxide with 20 mmol of flux, 55% CsCl and 45% CsF, were placed in a silver crucible 1.2 cm in diameter and 5.6 cm tall. The crucible was loosely covered with a silver lid and placed into a programmable furnace. The furnace was heated to 750 °C at a rate of 600 °C/h, where it dwelled for 12 hours before being slowly cooled to 400 °C at a rate of 6 °C/h. When the furnace reached 400 °C it was turned off and allowed to cool to room temperature. The crystals were removed from the flux matrix by dissolving the flux in

\* Corresponding author.

E-mail address: [zurloye@mailbox.sc.edu](mailto:zurloye@mailbox.sc.edu) (H.-C. zur Loye).

water, aided by sonication for 30–45 minutes, and isolated by vacuum filtration.

## 2.2. Ion exchange

Single crystals of  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  were placed in a small vial with 3 mL of water and 6 mmol of either NaCl (ACS Grade, Fisher Chemical), KCl (ACS Grade, Macron Fine Chemicals), or RbCl (99.8%, Alfa Aesar) to make 2 molal solutions. The solutions were heated to 90 °C and held at constant temperature for 45 hours before being removed without cooling. The crystals were isolated through vacuum filtration.

## 2.3. Single crystal X-ray diffraction (SXRD)

X-ray intensity data from a colorless cube of  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  (approximate dimensions  $0.04 \times 0.04 \times 0.04 \text{ mm}^3$ ) was measured at 301(2) K on a Bruker D8 Quest diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). The data collection covered reciprocal space  $2\theta_{\text{max}} = 72.6^\circ$ , and final unit cell parameters were determined from a total of 949 unique reflections. Raw diffraction data were collected and processed through SAINT and corrected for absorption effects using SADABS programs [14]. Initial structures were determined using direct methods via ShelXT and refined using ShelXL in Olex2 [15–17]. After the final refinement cycle, the R indices were  $R_1 = 0.0205$  and  $wR_2 = 0.0505$ . Crystallographic and structure refinement data for  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  can be found in Table 1. Table 2 contains select interatomic distances for the structure.

Single crystal X-ray diffraction (SXRD) data collected using white shards of the RbCl and KCl ion-exchange product and a colorless shard of the NaCl ion-exchange product, were collected at between 299(2) and 303(2) K and treated in a similar fashion to  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ . Merohedral and inversion twinning were observed in the KCl ion-exchange product. The relevant twin law, 0 0 1 0 -1 0 1 0 0, was determined using the TwinRotMat function in Platon [18]. The crystal was then modeled as a four component twin using the TWIN and BASF commands in ShelXL.

## 2.4. Energy dispersive spectroscopy

Elemental analysis was performed using energy dispersive spectroscopy (EDS). Data were collected on single crystals using a TESCAN Vega-3 SBU equipped with an EDS detector. Qualitatively, the data confirmed the presence of Cs, Ag, Ge, O, and F in  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ . Elemental analysis of the ion-exchange products will be discussed in the Results and Discussion section.

**Table 1**

Crystallographic and refinement data for  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ .

Formula	$[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$
Formula weight (g mol <sup>-1</sup> )	2870.09
Temperature (K)	301 (2)
Space group	<i>F-43m</i>
a (Å)	15.5049 (4)
b (Å)	15.5049 (4)
c (Å)	15.5049 (4)
V (Å <sup>3</sup> )	3727.4 (3)
Z	4
Density (g cm <sup>-3</sup> )	5.115
$\mu$ (mm <sup>-1</sup> )	20.394
<i>F</i> (000)	5056
Crystal size (mm x mm x mm)	0.04 × 0.04 × 0.04
$\theta_{\text{max}}$ (deg)	36.294
Unique reflections	949
GoF	11.080
R indices	$R_1 = 0.0205$ $wR_2 = 0.0505$
Largest diff. peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	1.87 and -1.15

**Table 2**

Selected interatomic distances (Å) of  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ .

Bond	Distance (Å)
F(1)–Cs(1) × 3	2.836 (16)
F(1)–Ag(1)	2.04 (3)
F(2)–Cs(2) × 6	3.0155 (7)
Ge(1)–O(1) × 3	1.958 (3)
Ge(1)–O(2) × 3	1.834 (3)
Ge(2)–O(3) × 3	1.968 (3)
Ge(2)–O(4) × 3	1.855 (3)
Ge(3)–O(2) × 2	1.752 (3)
Ge(3)–O(4) × 2	1.738 (3)

## 3. Results and Discussion

Small colorless cubic crystals (approximate dimensions  $0.04 \times 0.04 \times 0.04 \text{ mm}^3$ ) were isolated from a CsCl/CsF flux and used for single crystal X-ray diffraction measurement. An analysis of the single crystal diffraction data confirmed  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  crystallizes in the cubic space group *F-43m* and consists of a germanium framework containing open channels filled by salt inclusions. The framework consists of tetrahedral  $\text{GeO}_4$  and octahedral  $\text{GeO}_6$  polyhedra. While in silicate chemistry,  $\text{SiO}_6$  octahedra are only observed in materials formed at very high pressures, due to the larger size of germanium,  $\text{GeO}_6$  octahedra readily form at atmospheric pressure [19,20]. The stability of the  $\text{GeO}_6$  polyhedra in ambient conditions can be seen in other reactions, such as the synthesis of  $\text{K}_2\text{Ge}_4\text{O}_9 \cdot x\text{Mn}^{4+}$  [21] and  $\text{Na}_2\text{Ge}_4\text{O}_9$  [22].

In the structure of  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ , four germanium octahedra are connected through edges to form a  $\text{Ge}_4\text{O}_{16}$  cluster with a tetrahedral arrangement of Ge polyhedra. Each of these tetrahedral clusters are connected through  $\text{GeO}_4$  tetrahedra that share edges with the  $\text{Ge}_4\text{O}_{16}$  cluster, creating the extended germanate framework, as shown in Fig. 1. The bond distances for Ge–O range between 1.738(3) and 1.958(3) Å. The shorter bond distances correspond to the germanium in tetrahedral coordination environments, while the longer bond distances correspond to germanium in octahedral coordination environments. These values are in good agreement with values reported in previous studies describing the family of  $\text{Ge}_7\text{O}_{16}$  compounds [10–13].

The germanate framework contains a 3D channel filled with two unique salt-inclusions:  $\text{Cs}_3\text{AgF}$  tetrahedra and  $\text{Cs}_6\text{F}$  octahedra, shown in Fig. 2. The  $\text{Cs}_6\text{F}$  unit has bond angles of 90° and 180° for the Cs–F(2)–Cs bonds and all six Cs–F bond distances are 3.0155(7) Å, indicating that the inclusion is a regular octahedron. The  $\text{Cs}_3\text{AgF}$  tetrahedron has bond angles of 128.1° for the Ag–F(1)–Cs and 85.9° for the Cs–F(1)–Cs. The deviation from the expected angle of 109.5° for a regular tetrahedron is caused by the presence of the Ag atom in place of one Cs in the tetrahedron. The bond length of Cs–F is 2.836 Å, which is comparatively much longer than the bond length of Ag–F of 2.020 Å. The  $\text{Cs}_3\text{AgF}$  unit is disordered about a central site with point symmetry  $-43m$  (Wyckoff position 8b). This generates four instances of the tetrahedra, with each instance containing the Ag atom on a different vertex. The two salt inclusions lie in the open spaces between the germanium framework, and the two unique fluorine inclusions alternate between spaces in the *a*, *b*, and *c* directions, as seen in Fig. 2. The salt inclusions are ordered in the pores of the framework structure in a rock salt fashion, which results in a doubling of the unit cell length relative to the primitive cubic  $\text{Ge}_7\text{O}_{16}$  zeotypes.

An investigation into exchange of the salt inclusion of the parent compound,  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ , was performed using aqueous solutions of NaCl, KCl, and RbCl. The compound exhibits the ability to exchange with K and Rb ions forming the known compounds  $\text{K}_3\text{HGe}_7\text{O}_{16} \cdot x\text{H}_2\text{O}$  and  $\text{Rb}_3\text{HGe}_7\text{O}_{16} \cdot x\text{H}_2\text{O}$  ( $x \approx 4$ ), respectively, which exhibit the identical germanium framework as  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  [11]. As shown in Fig. 3, the ion exchange led to a change in

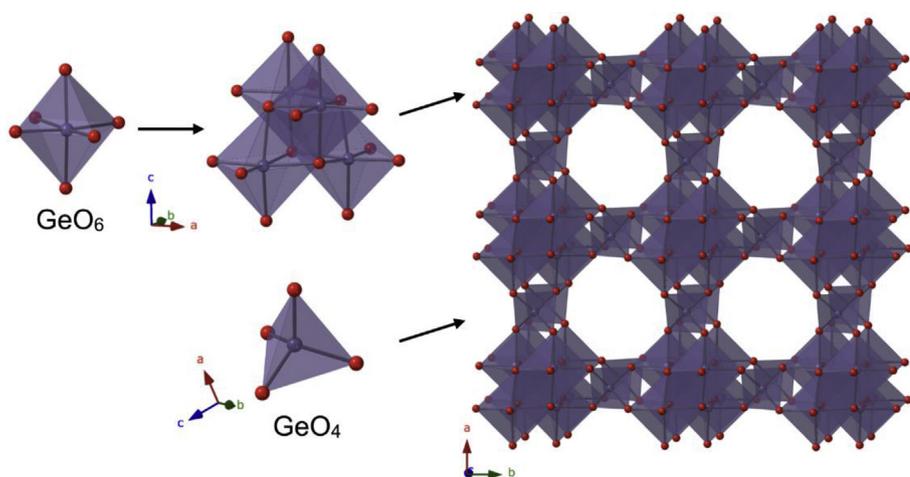


Fig. 1. Structural representation of the  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  germanium framework illustrating how the  $\text{GeO}_6$  octahedra edge share with each other and the  $\text{GeO}_4$  tetrahedra. O is shown in red and Ge is shown in dark gray. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

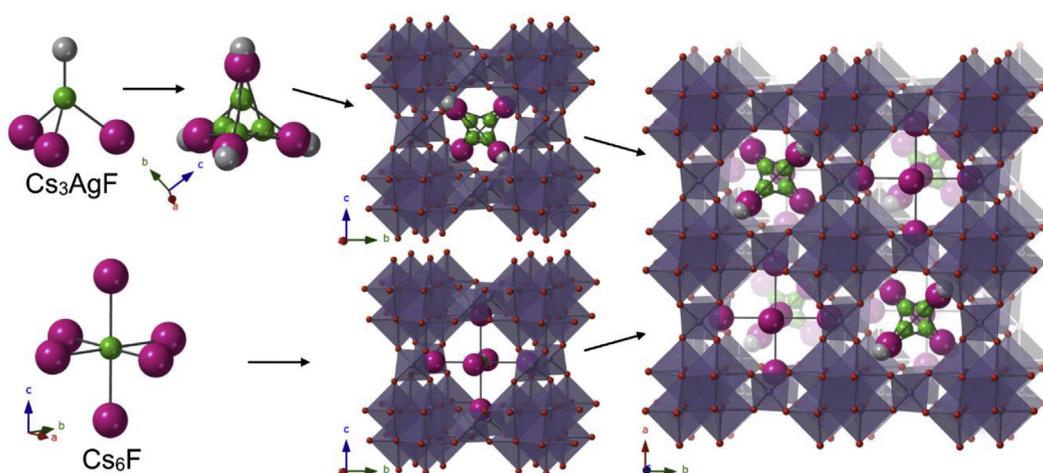


Fig. 2. Structural representation of  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  salt inclusions, illustrating how the  $\text{Cs}_3\text{AgF}$  and  $\text{Cs}_6\text{F}$  are connected and fill the framework. Cs is shown in pink, F is shown in green, Ag is shown in light gray, Ge is shown in dark gray, and O is shown in red. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

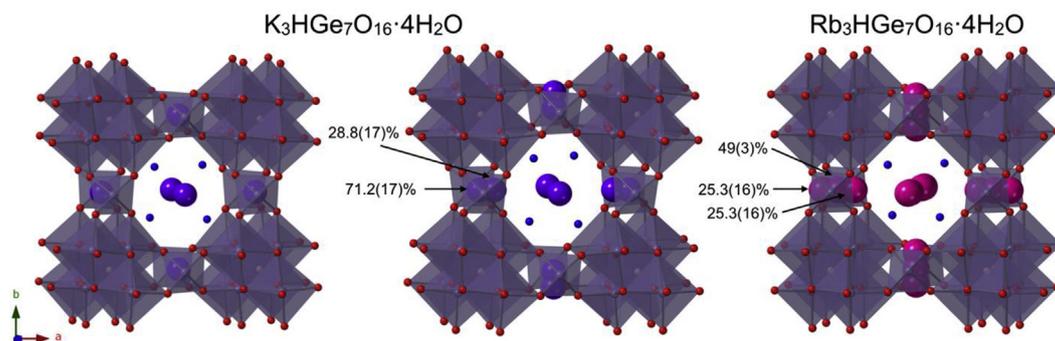


Fig. 3. Structures of the ion exchange products. Framework O are in red, O that are part of water molecules are shown in blue, Rb are shown in pink, K are shown in purple, and Ge are shown in dark gray. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

salt inclusions while the framework was sustained. The two unique salt inclusions of  $\text{Cs}_3\text{AgF}$  and  $\text{Cs}_6\text{F}$  were replaced by three alkali metal ions and water molecules, i.e. the material was transformed from a SIM to a zeotype. Charge balance is maintained by the introduction of a  $\text{H}^+$  ion into the center of the  $\text{Ge}_4\text{O}_{16}$  cluster, whose presence is in agreement with the previously reported structures [11]. EDS confirmed the complete removal of the Cs, Ag, and F ions and the addition of K and Rb ions. Interestingly, the crystals became opaque white during the exchange process, typically associated with the sample becoming polycrystalline, but X-ray diffraction data indicated the samples remained

high quality single crystals. The single crystal X-ray diffraction data, which confirms the structures by Fitch, is included.

Interestingly, when the ion-exchange was attempted with  $\text{NaCl}_{(\text{aq})}$  using the same conditions as for the K and Rb exchange, EDS data indicated only a partial exchange (Cs:Na atomic ratio = 3:2) of the salt. Furthermore, refining the SXRD data as  $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$  resulted in an  $R_1$  value of 2.40% with the largest residual electron density peak and hole being 2.073 and  $-2.559 \text{ e}^- \text{ \AA}^{-3}$ , respectively. This suggests that while in the case of the K and Rb ion exchange the salt inclusion was completely removed, in the case of sodium ion

exchange, the exchange occurs only superficially. It is likely that under more extreme hydrothermal conditions the exchange of the salt inclusion for sodium will take place.

#### 4. Conclusion

$[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$ , a new germanate was grown as single crystals in a high temperature cesium chloride/cesium fluoride flux. The compound crystallizes in the space group  $F-43m$  and is a complex three-dimensional structure. The salt inclusion in the framework can be completely ion exchanged with Rb and K, forming  $\text{Rb}_3\text{HGe}_7\text{O}_{16}\cdot 4\text{H}_2\text{O}$  and  $\text{K}_3\text{HGe}_7\text{O}_{16}\cdot 4\text{H}_2\text{O}$ , respectively.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solidstatesciences.2019.105973>.

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