

Crystal Growth of New Germanate framework structures: Impact of the presence of square planar copper species and mixed Ge/Mn sites on the overall structures of $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$

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Abstract

Single crystals of four new germanate framework structures were synthesized via the flux growth method. $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ and $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ crystallize in the triclinic space group $P\bar{1}$ with lattice parameters of $a = 6.23840(10)$ Å, $b = 7.175(2)$ Å, $c = 7.8731(2)$ Å, $\alpha = 82.1540(10)^\circ$, $\beta = 71.6150(10)^\circ$, and $\gamma = 80.7040(10)^\circ$ for the Rb analog; and $a = 6.3626(3)$ Å, $b = 7.2272(3)$ Å, $c = 7.9360(4)$ Å, $\alpha = 82.285(2)^\circ$, $\beta = 70.978(2)^\circ$, and $\gamma = 80.619(2)^\circ$ for the Cs analog. $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ crystallizes in a new structure that adopts the orthorhombic space group $Pmma$ with lattice parameters $a = 20.0462(4)$ Å, $b = 10.9087(2)$ Å, and $c = 7.66080(10)$ Å. The fourth structure, $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$, crystallizes in the cubic space group $F\bar{4}3m$ with lattice parameter of $15.5197(4)$ Å and is structurally related to a Ge_7O_{16} family of zeotypes. The syntheses and structures of the four compounds are reported. The assignment of square planar versus octahedral coordination for the Cu^{2+} coordination sites in this structure type is commented on, as is the impact of subtle synthetic changes on the formation of the specific structures in this phase space.

Introduction

As a close cousin to framework silicates, which are constructed from corner-sharing SiO_4 tetrahedra, germanates create additional structural diversity via their ability to take on, in addition to the expected GeO_4 tetrahedra, the less common GeO_5 trigonal bipyramidal and GeO_6 octahedral coordination environments. A second important distinction between germanates and silicates is that GeO_5 trigonal bipyramids and GeO_6 octahedra, unlike the SiO_4 tetrahedra, are able to share edges, which enables germanates to form in structure motifs that are not accessible to silicates. Capitalizing on these abilities of germanium has led to the synthesis of numerous open framework germanates whose structures are, consequently, often uniquely different from what has been found among silicates. For that reason, germanates have great utility in the discovery of solid-state materials in new structure types. Germanium, as a network former, can readily connect to other elements, such as transition metals, lanthanides, actinides, and even alkali halide salts, and adopt open framework structures that make them promising candidates for applications in the fields of phosphors and potential nuclear waste forms with ion exchange capabilities.^{1–3}

We have been exploring the germanate phase space at relatively high temperatures via flux crystal growth where, in particular, the use of mixed alkali halide fluxes has resulted in the formation of single crystals of numerous germanates, including alkali rare earth germanates,⁴ uranyl germanate salt-inclusion materials,⁵ and new members of the Wadeite and Wadeite related structure types.^{6,7} In addition, we recently obtained several alkali germanate framework salt-inclusion materials with the compositions $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$,⁸ $[(\text{Rb}_6\text{F})(\text{Rb}_4\text{F})][\text{Ge}_{14}\text{O}_{32}]$, and $[(\text{Rb}_6\text{F})(\text{Rb}_{3.1}\text{Co}_{0.9}\text{F}_{0.96})][\text{Co}_{3.8}\text{Ge}_{10.2}\text{O}_{30}\text{F}_2]$.⁹ In our continued exploration of the alkali germanate phase space, we investigated the impact of introducing 3d transition metals to the reaction mixture, resulting in the synthesis of $\text{Rb}_2\text{Co}_{1.85}\text{Ge}_{1.15}\text{O}_6$,¹⁰ $\text{Cs}_2\text{CoGe}_4\text{O}_{10}$,¹¹ and CsFeGeO_4 .¹² In this paper we discuss the discovery of new germanate compositions that crystallize in new structural modifications when we add copper and manganese to the flux synthesis, which resulted in framework structures containing square planar copper species and a mixed Ge/Mn framework salt-inclusion material. The syntheses, structures, and optical properties of $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$ are detailed herein.

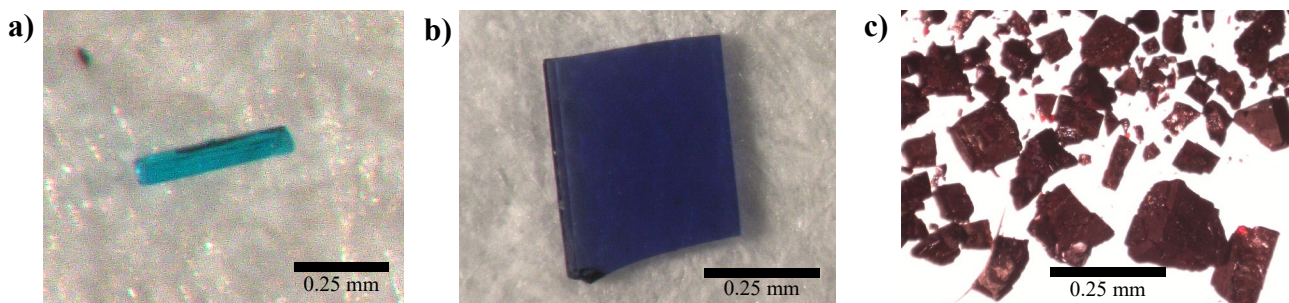


Figure 1. Optical image of (a) $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, (b) $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and (c) $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$ single crystals.

Experimental

Reagents

CuF_2 (Alfa Aesar, 99.5%), GeO_2 (BeanTown Chemical, 99.999%), CsF (Alfa Aesar, 99%), CsCl (VWR, 99%), RbCl (BeanTown Chemical, 99%), and MnF_2 (Alfa Aesar, 99%) were used as received. RbF (Strem, 99.8%) was also used as received but was found to be HRbF_2 following powder X-ray diffraction analysis.

Crystal Growth

All compounds were synthesized via high temperature flux growth using mixed alkali halide fluxes. $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ and $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ were synthesized using 1 mmol CuF_2 and 2 mmol GeO_2 which were covered by eutectic mixtures of 14 mmol RbCl /12.5 mmol RbF and 11 mmol CsCl /9 mmol CsF , respectively. Reagent mixtures were added to a cylindrical silver crucible (1.2 cm D x 5.7 cm H). The loaded crucible was crimped on top, folded over, and crimped again before being heated quickly to 900 °C, dwelled at this temperature for 12 h, slow cooled to 400 °C at a rate of 6 °C/h, and finally cooled to room temperature by shutting off the furnace. The solidified flux was removed by sonication in water and crystals were isolated via vacuum filtration. $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ was obtained as light blue, narrow plates, shown in Figure 1, in nearly quantitative yield. $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ was found to form as a minor phase, with $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ being the major phase, and a suitable crystal was isolated for single-crystal X-ray diffraction.

$\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ was synthesized by loading cylindrical silver crucibles with 0.5 mmol CuF_2 and 2 mmol GeO_2 underneath 11 mmol CsCl and 9 mmol CsF and following the reaction

profile described above. The synthesis resulted in elongated, plate-like crystals, shown in Figure 1, in nearly quantitative yield. Visually, crystals of $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ appear either dark blue or violet depending on their orientation. $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$ was obtained under similar reaction conditions by combining 0.5 mmol MnF_2 , 2 mmol GeO_2 , 9 mmol CsF and 11 mmol CsCl within a cylindrical silver crucible following the temperature profile described above. The reaction mixture was sonicated in water after heating and red/orange blocks were collected via vacuum filtration.

Table 1. Crystallographic data for $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$

Chemical formula	$\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$	$\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$	$\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$	$\text{Cs}_9\text{AgGe}_{12}\text{Mn}_2\text{O}_{32}\text{F}$
Formula weight	948.51	1043.39	2306.94	2835.02
Crystal system	Triclinic	Triclinic	Orthorhombic	Cubic
Space group, Z	$P\bar{1}$, 1	$P\bar{1}$, 1	$Pmma$, 2	$F\bar{4}3m$, 4
a , Å	6.23840(10)	6.3626(3)	20.0462(4)	15.5197(4)
b , Å	7.1751(2)	7.2272(3)	10.9087(2)	15.5197(4)
c , Å ³	7.8731(2)	7.9360(4)	7.66080(10)	15.5197(4)
α , deg	82.1540(10)	82.285(2)	90	90
β , deg	71.6150(10)	70.978(2)	90	90
γ , deg	80.7040(10)	80.619(2)	90	90
Volume, Å ³	328.649(14)	339.10(3)	1675.25(5)	3738.1(3)
ρ_{calcd} , g/cm ³	4.792	5.109	4.573	5.038
Radiation (λ , Å)	$\text{MoK}\alpha$ (0.71073)	$\text{MoK}\alpha$ (0.71073)	$\text{MoK}\alpha$ (0.71073)	$\text{MoK}\alpha$ (0.71073)
μ , mm ⁻¹	23.458	20.895	18.544	19.403
T, K	300(2)	300(2)	302(2)	299(2)
Crystal dim., mm ³	0.12 x 0.07 x 0.07	0.09 x 0.03 x 0.01	0.06 x 0.03 x 0.02	0.04 x 0.03 x 0.03
2θ range, deg.	2.738 – 36.377	2.725 – 36.284	2.659 – 33.141	2.273 – 33.172
Reflections collected	28417	28713	157212	83494
Data/parameters/restraints	3124/113/0	2970/112/0	3064/170/1	752/44/0
R_{int}	0.0441	0.0424	0.0571	0.0359

Goodness of fit	1.163	1.109	1.188	1.159
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0166$ $wR_2 = 0.0376$	$R_1 = 0.0454$ $wR_2 = 0.1347$	$R_1 = 0.0247$ $wR_2 = 0.0524$	$R_1 = 0.0139$ $wR_2 = 0.0354$
<i>R</i> indices (all data)	$R_1 = 0.0170$ $wR_2 = 0.0377$	$R_1 = 0.0500$ $wR_2 = 0.1381$	$R_1 = 0.0312$ $wR_2 = 0.0571$	$R_1 = 0.0147$ $wR_2 = 0.0359$
Largest diff. peak and hole	1.572 and -1.136 e.Å ⁻³	8.578 and -3.290 e.Å ⁻³	2.112 and -1.793 e.Å ⁻³	1.100 and -0.963 e.Å ⁻³

Single-crystal X-ray diffraction

For all compounds, X-ray intensity data from suitable single crystals were collected at 301(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073$ Å). The raw area detector frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.^{13,14} Initial structural models were obtained with SHELXT.¹⁵ Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018 using the ShelXle¹⁶ or Olex2 interface.¹⁷ Crystallographic refinement data for all compounds are listed in Table 1.

Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction data were collected on a Bruker D2 Phaser powder X-ray diffractometer using Cu K α radiation. The step scan covered the angular range 5-65° 2θ in steps of 0.04°. Experimental and calculated PXRD patterns for Rb₂Cu₃Ge₅O₁₄ and Cs₇Cu₂Ge₁₁O₂₇F are provided as Figures S1-S2.

Energy Dispersive Spectroscopy (EDS)

Semiquantitative elemental analysis was carried out using a TESCAN Vega-3 SBU SEM with EDS capabilities. Single crystals of each compound were mounted on carbon tape and analyzed using a 20 kV accelerating voltage and an accumulation time of 90 seconds. As a qualitative measure, EDS confirmed the presence of the appropriate elements in crystals of Cs₇Cu₂Ge₁₁O₂₇F and [(Cs₆F)(Cs₃AgF)][Ge₁₂Mn₂O₃₂] (Figures S3-S4), corroborating the compositions determined by single-crystal X-ray diffraction.

Optical Properties

UV-vis spectra were collected in the diffuse reflectance mode using a PerkinElmer Lambda 35 UV/visible scanning spectrophotometer equipped with an integrating sphere. Diffuse

reflectance spectra were recorded in the 200-900 nm range on polycrystalline samples of ground single crystals. Reflectance data were converted to absorbance via the Kubelka-Munk function.

Results and Discussion

Alkali Halide Flux Growth

The use of mixed alkali halide salts of the fluoride and chloride variety have proven exceptionally successful in the discovery of complex silicates and germanates in single crystal form, and were used in the synthesis of the title compounds $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$. Our flux growth syntheses rely on the relatively low melting points that can be achieved with ratios of alkali halide salts near the eutectic point, allowing for a large liquid range for crystal growth. The title compounds of this study were synthesized as a result of exploring the alkali - germanium phase space in an oxygen/fluorine-rich environment, while introducing transition metals. From the crystal growth description, it is notable how strikingly similar the syntheses for each of the title compounds are, including identical reaction temperatures and heating/cooling rates. Despite these similarities, slight alterations of reagent ratios and introduction of different transition metals resulted in the formation of different complex structure types: three structure types from cesium chloride/fluoride mixtures alone.

Crystal Structure

$\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ and $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ are isostructural and crystallize in the triclinic space group $P\bar{1}$ with lattice parameters of $a = 6.23840(10)$ Å, $b = 7.175(2)$ Å, $c = 7.8731(2)$ Å, $\alpha = 82.1540(10)^\circ$, $\beta = 71.6150(10)^\circ$, and $\gamma = 80.7040(10)^\circ$ for the Rb analog; and $a = 6.3626(3)$ Å, $b = 7.2272(3)$ Å, $c = 7.9360(4)$ Å, $\alpha = 82.285(2)^\circ$, $\beta = 70.978(2)^\circ$, and $\gamma = 80.619(2)^\circ$ for the Cs analog. These two compositions expand upon a previous report on the isostructural $\text{K}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ by Monge et al.,¹⁸ and a comparison of the lattice parameters of each analog is shown in Figure 2. Their asymmetric units consist of one alkali metal site, two Cu sites, three Ge sites, and seven oxygen sites. Their overall structure is shown in Figure 3a. All three structures contain a germanate layer comprised of GeO_4 tetrahedra and GeO_6 octahedra (Figure 3b). The layer is formed from Ge_4O_{12} rings consisting of two independent GeO_4 tetrahedra that are connected through oxygen atoms of GeO_6 octahedra. The most intriguing feature of these structures are the chains of copper polyhedra that connect the germanate layers. For $\text{K}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, the authors report the chains to be made up of edge sharing CuO_5 square pyramids and CuO_6 octahedra. The octahedra are elongated with apical bond lengths of 2.286(5) Å, longer than the equatorial bonds but still within bonding

range. Interestingly, in $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ and $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, the increase in ionic radii from K to Rb to Cs influences the structure to result in an increase in the interatomic distance between the copper cations and the axial oxygen atoms for both Cu coordination environments. The detailed interatomic distances are tabulated in Table 2.

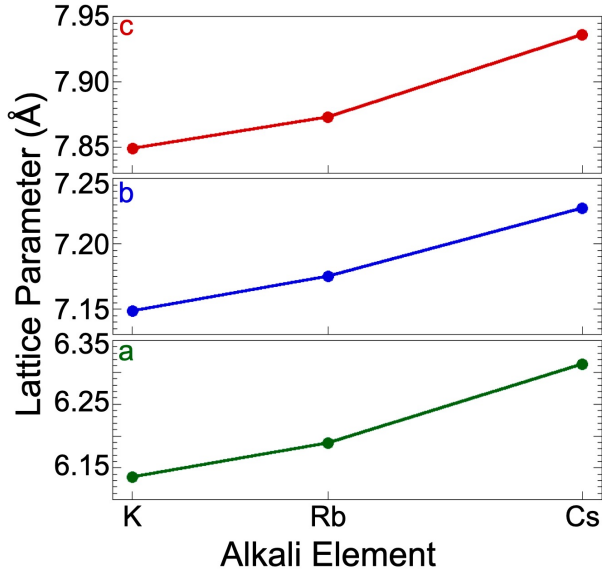


Figure 2. Plot of the lattice constants a , b , and c as a function of alkali metal radius in $\text{A}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$).

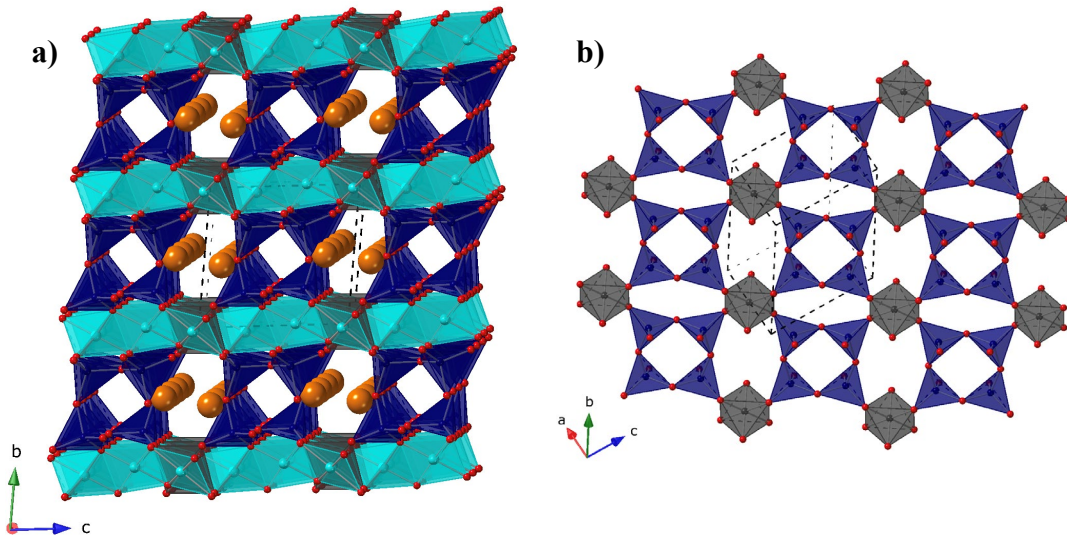


Figure 3. (a) Overall representation of the crystal structure of $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ viewed down the a -axis and (b) the germanate layer consisting of Ge_4O_{12} rings connected by GeO_6 octahedra. Rubidium cations are shown in orange, copper in turquoise, germanium tetrahedra in deep blue, germanium octahedra in grey, and oxygen in red.

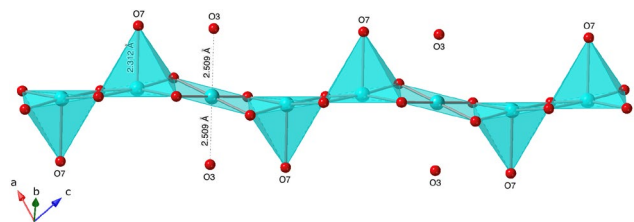


Figure 4. A single copper chain present in $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ emphasizing the 2:1 arrangement of CuO_5 square pyramids and CuO_4 square planar units. The interatomic distances between Cu and O atoms for the elongated apical oxygens are provided.

To help assign an appropriate coordination environment for Cu1 in $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ and $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, interatomic distances between copper and oxygen atoms were used to calculate bond valence sums. For the rubidium analog, BVS calculations resulted in values of 1.93 and 2.14 for Cu1 when evaluated as square planar and octahedral, respectively. For the cesium analog, BVS calculations resulted in values of 1.97 and 2.12 for square planar and octahedral geometry, respectively. Square planar Cu1 coordination environments produced BVS values moderately closer to 2 in the Rb analog and significantly closer for the Cs analog, supporting the assignment of square planar Cu^{2+} in the chains of the Rb and Cs compositions. For the previously reported K analog, BVS calculations resulted in values of 1.90 and 2.15 for square planar and octahedral geometries, respectively. These values are more ambiguous than those for the Rb and Cs analogs, which led to their assignment as octahedra in the $\text{K}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$. With these considerations in mind, we model the copper chains in $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ and $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ as square pyramids and square planar in a 2:1 ratio, shown in Figure 4. The connection between germanium rings and copper chains creates multiple channels occupied by either Rb or Cs cations in 7-fold coordination with oxygen.

Table 2. Select interatomic distances for $A_2Cu_3Ge_5O_{14}$ ($A = Rb, Cs$) and equivalent distances for $K_2Cu_3Ge_5O_{14}$ from Monge et al.

Interaction	$K_2Cu_3Ge_5O_{14}$	$Rb_2Cu_3Ge_5O_{14}$	$Cs_2Cu_3Ge_5O_{14}$
	Distance Å	Distance Å	Distance Å
Cu1 – O1 x2	1.9257(50)	1.9232(14)	1.9210(45)
Cu1 – O2 x2	1.9848(53)	1.9764(15)	1.9613(50)
Cu1 – O3 x2	2.448(5)	2.5093(16)	2.6504(63)
Cu2 – O1	1.9217(47)	1.9183(13)	1.9118(49)
Cu2 – O2	1.9303(53)	1.9155(14)	1.9226(49)
Cu2 – O2	1.9642(52)	1.9714(17)	1.9928(53)
Cu2 – O6	1.9613(52)	1.9558(16)	1.9709(48)
Cu2 – O7	2.286(5)	2.3121(15)	2.3676(57)

$Cs_7Cu_2Ge_{11}O_{27}F$ crystallizes in the orthorhombic space group *Pmma* with lattice parameters $a = 20.0462(4)$ Å, $b = 10.9087(2)$ Å, and $c = 7.66080(10)$ Å in a new structure type. The asymmetric unit consists of three Cs sites, one Cu site, five Ge sites, ten oxygen sites, and one F site. The structural model contains disorder affecting the locations of the Cs atoms, the F atom, the copper atom, one Ge atom, and two oxygen atoms. For clarity, this structure description will discuss the idealized structure of $Cs_7Cu_2Ge_{11}O_{27}F$; the disorder is described in detail within the supporting information section. The most interesting structural feature of $Cs_7Cu_2Ge_{11}O_{27}F$ is the observance of isolated $[Cu_2O_6]^{8-}$ dimeric units, joining a limited group of existing square planar copper germanates.^{19–21} The individual CuO_4 units can be connected in various ways, for example via corners, as in Sr_2CuO_3 ²² or via edges, as in $Cs_7Cu_2Ge_{11}O_{27}F$ and Li_2CuO_2 ²³ creating dimers, trimers, and infinite chains. The $[Cu_2O_6]^{8-}$ unit in $Cs_7Cu_2Ge_{11}O_{27}F$ consists of two edge-sharing distorted CuO_4 square planar units. The Cu–O bond lengths in the idealized model are 1.843(3), 1.933(3), 1.993(4), and 1.956(4) Å, which are in good agreement with the bond lengths reported for the trimeric $[Cu_3O_8]^{10-}$ units of $K_2Cu_3Ge_4O_{12}$ ²⁴ and for the chains of CuO_4 squares in $CaCuGeO_4 \cdot H_2O$.²⁵ Each oxygen of the $[Cu_2O_6]^{8-}$ dimers is shared with a GeO_4 tetrahedron for a total of six GeO_4 tetrahedra connected to the dimers. The dimers are linked through two corner-sharing tetrahedra, creating a zigzag chain oriented along the *c*-axis (Figure 5). The other four tetrahedra corner share to GeO_6 octahedra that are part of Ge_4O_{16} tetramers. The tetramers are further connected by GeO_4 tetrahedra along the *c*-axis (Figure 6b), in the same fashion as is observed in the cubic germanate framework structure of $[(Cs_6F)(Cs_3AgF)][Ge_{14}O_{32}]$ and

subsequent analogs reported by our group.^{8,9} The $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ framework contains two types of channels occupied by Cs cations. The large channels created by the space between Ge_4O_{16} tetramers along the b -axis contain disordered Cs_6F octahedral salt inclusion units (Figure 6a), matching one of the inclusions found in $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$. The overall framework structure with Cs_6F inclusions filling the large channels is shown in Figure 6. The second, significantly smaller channel is created by the presence of the $[\text{Cu}_2\text{O}_6]^{8-}$ units and contains isolated Cs atoms, also shown in Figure 6.

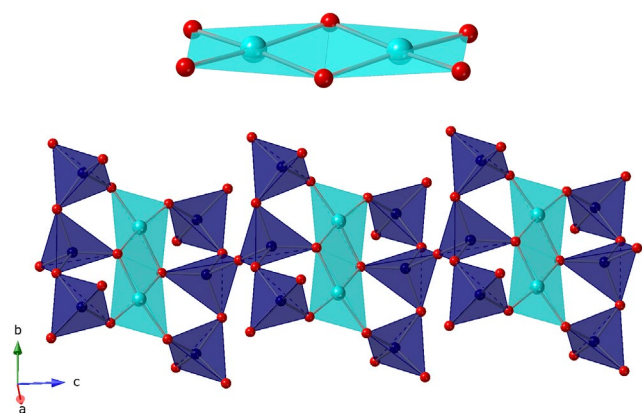


Figure 5. (top) $[\text{Cu}_2\text{O}_6]^{8-}$ dimers in $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ and (bottom) their connectivity through GeO_4 tetrahedra to form a zigzag chain along the c -axis. Copper and germanium atoms are shown in turquoise and deep blue, respectively.

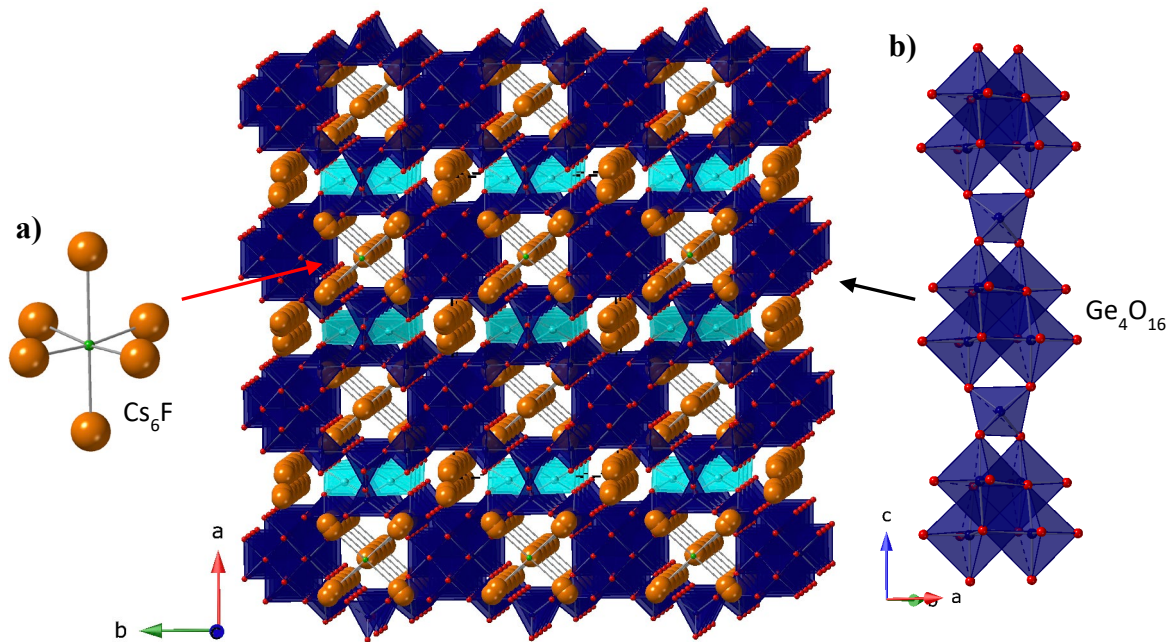


Figure 6. Overall structural representation of $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ viewed highlighting (a) the Cs_6F salt inclusion in the large channels and (b) the Ge_4O_{16} tetramers and their connectivity through GeO_4 tetrahedra along the c -axis. The smaller channel filled with isolated cesium cations is also shown. Cesium cations are shown in orange, copper in turquoise, germanium in deep blue, fluorine in green, and oxygen in red.

$[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$, shown in Figure 7, crystallizes in the cubic space group $F\bar{4}3m$ with lattice parameter of $15.5197(4)$ Å and is a new analog of the family of cubic germanate framework compounds that include $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$, $[(\text{Rb}_6\text{F})(\text{Rb}_4\text{F})][\text{Ge}_{14}\text{O}_{32}]$, and $[(\text{Rb}_6\text{F})(\text{Rb}_{3.1}\text{Co}_{0.9}\text{F}_{0.96})][\text{Co}_{3.8}\text{Ge}_{10.2}\text{O}_{30}\text{F}_2]$.^{8,9} The asymmetric unit consists of one Cs site, one Cs/Ag site, one Ge site, two Ge/Mn sites, four O sites, and 2 F sites. The structure consists of clusters of $(\text{Ge/Mn})\text{O}_6$ octahedra that connect to form $(\text{Ge/Mn})_4\text{O}_{16}$ tetramers, similar to the all germanium Ge_4O_{16} tetramers found in $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$. The incorporation of Mn into the Ge octahedral sites of the framework was determined to be in a 3:1 Ge:Mn ratio. The site mixing between Ge and Mn is favored by their identical ionic radii of 0.53 Å in six coordinate environments as tetravalent cations. The M – O bond lengths for the $(\text{Ge/Mn})\text{O}_6$ octahedra range from $1.839(3) - 1.966(2)$ Å consistent with the GeO_6 and $(\text{Ge/Co})\text{O}_6$ octahedra in previous reports. The mixed Ge/Mn tetramers are connected in all directions via corner-sharing GeO_4 tetrahedra to form the overall 3D framework. The Ge – O bond lengths in the GeO_4 tetrahedra range from $1.742(3) - 1.750(3)$ Å consistent with previous reports. The interconnected tetramers and tetrahedra create large channels down the a -, b -, and c -axis that contain both Cs_3AgF and Cs_6F salt

inclusions, matching those found in the pure Ge framework of the Cs analog $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{14}\text{O}_{32}]$.

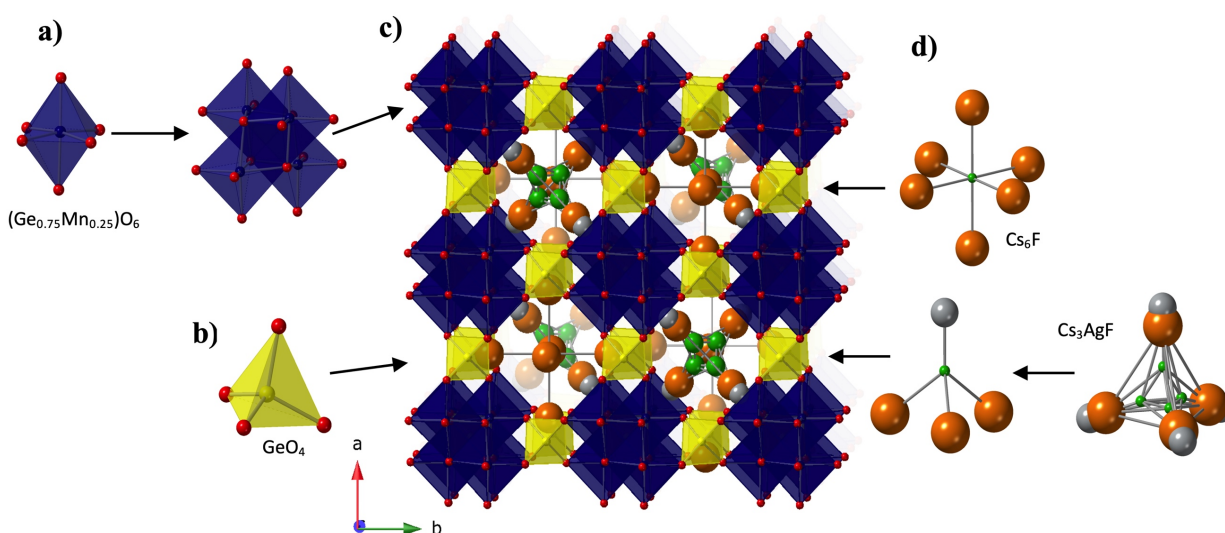


Figure 7. Structure of $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$ showing (a) the tetramers built up of mixed Ge/Mn octahedra, their connectivity through (b) GeO_4 tetrahedra to make (c) the overall framework structure down the c -axis, and (d) the octahedral Cs_6F and tetrahedral Cs_3AgF inclusions occupying the channels. Cesium cations are shown in orange, mixed Ge/Mn in deep blue, pure germanium tetrahedra in yellow, silver in grey, fluorine in green, and oxygen in red.

UV-vis Diffuse Reflectance Spectroscopy

UV-vis diffuse reflectance spectroscopy data were collected on ground crystals of $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$. The normalized UV-vis spectra for these compounds are shown in Figure 8. They display absorption bands due to $d-d$ electronic transitions of Cu^{2+} , Cu^{2+} , and Mn^{4+} , respectively. The copper containing compounds $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ and $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ exhibit a broad absorption above approximately 500 nm, which is consistent with the typical blue copper coloring observed in the crystals. $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$ also exhibits a broad absorption band centered at approximately 475 nm, consistent with the red/orange color of the crystals. The optical band gaps for $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$ were calculated from Tauc plots (Figure S5) and roughly determined to be 2.4 eV, 2.7 eV, and 1.9 eV, respectively.

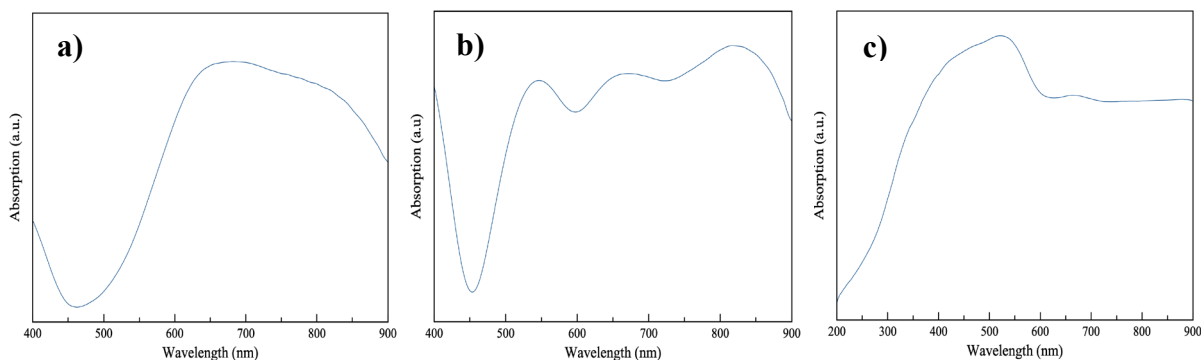


Figure 8. UV-vis optical absorption spectra of (a) $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ (b) $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ and (c) $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$.

Conclusions

Four new germanates were grown as single crystals via the high temperature flux growth method at 900 °C. $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ and $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ contain chains of edge-sharing square pyramidal CuO_5 and square planar CuO_4 polyhedra. Modification of reagent ratios between copper and germanium led to the formation of single crystals of a new complex germanate $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, containing $[\text{Cu}_2\text{O}_6]^{8-}$ dimers among a framework consisting of linked Ge_4O_{16} tetramers. Replacing copper with manganese resulted in single crystals of $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$ which transitioned the structure away from having a unique transition metal site to the 3D arrangement of tetramers containing Ge/Mn site mixing throughout the framework. These compounds further demonstrate the efficacy of high temperature flux growth for the discovery of new complex germanate structures.

Associated Content

Supporting Information

The Supporting Information is available free of charge at

Powder diffraction data for $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ and $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$ overlaid with the calculated pattern based on the SXRD model, EDS data and select interatomic distances for $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$ and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$, and Tauc plots for $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$.

Accession Codes

CCDC 2142179 – 2142181 and 2142213 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by

emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgments

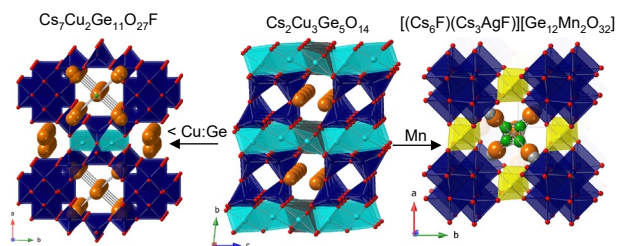
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New Germanate framework structures: Impact of the presence of square planar copper species and mixed Ge/Mn sites on the overall structures of $\text{Rb}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_2\text{Cu}_3\text{Ge}_5\text{O}_{14}$, $\text{Cs}_7\text{Cu}_2\text{Ge}_{11}\text{O}_{27}\text{F}$, and $[(\text{Cs}_6\text{F})(\text{Cs}_3\text{AgF})][\text{Ge}_{12}\text{Mn}_2\text{O}_{32}]$