A Complex Mayenite-Type Strontium Oxy-chloride Exhibiting Three-Component Site Mixing: Sr₁₂Al_{3.44}Fe_{8.16}Ge_{2.38}O₃₂Cl_{4.34}

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Abstract: A new mayenite-type strontium oxy-chloride, $Sr_{12}Al_{3.44}Fe_{8.16}Ge_{2.38}O_{32}Cl_{4.34}$, was grown from a SrCl₂ flux at 1000 °C. The compound crystallizes in the complex threedimensional chloromayenite structure type, a rare calcium aluminum oxide mineral of cubic symmetry, exhibiting nanocages that contain Sr and Cl ions. The lattice framework is composed of corner-sharing, three-component Al/Fe/Ge site-mixed tetrahedra. The compound crystallizes in the cubic space group *I*-43*d* with lattice parameter *a* = 12.6126(3) Å.

Keywords: Oxychloride; molten salt flux synthesis; crystal structure.

Introduction

Chlormayenite, Ca₁₂Al₁₄O₃₂Cl₂, is a rare calcium aluminum oxide mineral. Numerous compositional derivatives are known, in part because the crystal structure, related to the Ca₁₂Al₁₄O₃₃ mayenite, is able to accommodate diverse anions and cations while maintaining the overall framework structure consisting of corner sharing tetrahedra. An intriguing aspect of the mayenite structure is the fact that the framework carries a positive charge, which is compensated by extra-framework oxygens: [Ca₂₄Al₂₈O₆₄]⁴⁺•2O²⁻. The positive charge of the mayenite framework can be increased via the substitution of higher valent cations into the framework, leading to a corresponding increase in the anion occupancy of the small framework cages that can be occupied by an array of cations and anions. [1-4]

Substitution of the Ca site by a larger alkaline earth, such as Sr, has been achieved by solgel and conventional solid-state routes using a Sr hydroxide source. [5-8] However, such Srbased mayenite type materials contain OH⁻ ions in the nanocages and are relatively thermally unstable compared to other mayenite materials prepared via high temperature solid-state methods. [9] For example, Sr₁₂Al₁₃O₃₂(OH)₂ decomposes to SrO and Al₂O₃ at a temperature close to 1000 °C, thus making it difficult to synthesize via high temperature solid state reactions. It is interesting to note that Sr-based mayenite does not form when the Sr source is changed from Sr(OH)₂•xH₂O to a carbonate or an oxide reagent, suggesting that rigorous synthetic conditions must be used when carrying out the solid-state reaction, primarily due to the hygroscopic nature of the strontium hydroxide precursor. [6] It is, therefore, of interest that easier synthetic routes are devised for preparing Sr-based mayenite materials.

Papers reporting new Sr mayenites have shown that the stability of the mayenite structure can be improved by incorporating halides (F^- or CI^-), as in the case of Sr₁₂Al₁₄O₃₂Cl₂ and Sr₁₂Al₁₄O₃₂F₂. [10,11] These structures, in contrast to the hydroxide mayenites, are quite thermally stable and can be formed via high temperature solid state reactions. [12] They are amenable to substitution and doping reactions and Sr₁₂Al₁₄O₃₂Cl₂:Eu²⁺ was recently reported as synthesized via a solid-state reaction that included reducing conditions to create Eu²⁺. This material is a green-emitting phosphor as a result of the presence of Eu²⁺ on the Sr site. [13]

It is of interest to mention a related material 12CaO•7Al₂O₃, an electride in which oxygens are replaced by electrons in the sub-nanometer cages. Whereas the mayenite structure

has extra-framework oxygens, this material lacks framework oxygens and charge balance is provided by electrons that become superconducting at low temperature. [14]

Mayenites are typically prepared via solid state syntheses and, thus, the structural determination requires a careful Rietveld analysis. When single crystals are available, they can be used to determine the structure as well as be used for other physical property measurements that cannot be done on powders. One synthesis technique that allows the preparation of compounds at relatively lower reaction temperatures is molten salt flux crystal growth that we have used for years to obtain single crystals of a variety of oxide, fluoride, and chalcogenide materials. Using a SrCl₂•6H₂O flux we were able to obtain single crystals of a new Sr-based mayenite composition, Sr₁₂Al_{3.44}Fe_{8.16}Ge_{2.38}O₃₂Cl_{4.34}, and determine its structure using single crystal X-ray diffraction.

Experimental Section

Materials and Methods

Fe₂O₃ (99.5%, Alfa Aesar), GeO₂ (99.999%, Alfa Aesar) and SrCl₂•6H₂O (99%, Alfa Aesar) were used as received for the synthesis of Sr₁₂Al_{3.44}Fe_{8.16}Ge_{2.38}O₃₂Cl_{4.34}. Sr₁₂Al_{3.44}Fe_{8.16}Ge_{2.38}O₃₂Cl_{4.34} was prepared by layering a mixture of 0.5 mmol of Fe₂O₃ and 1 mmol of GeO₂ beneath 3 g of SrCl₂•6H₂O in an alumina crucible that was thoroughly cleaned in aqua regia and then dried in a drying oven prior to use. The crucible containing the charge was placed into a programmable furnace and was heated at 10 °C/min to 1000 °C, maintained at this temperature for 12 h, slow cooled at 0.1 °C/min to 850 °C, and then rapidly cooled to room temperature by shutting the furnace off. Once cooled to ambient temperature, the solidified flux was dissolved in hot distilled water, aided by sonication, and the resulting products were isolated via vacuum filtration. Yellow polyhedral crystals rods of Sr₁₂Al_{3.44}Fe_{8.16}Ge_{2.38}O₃₂Cl_{4.34} (approximate dimensions 0.060 x 0.050 x 0.050 mm³) were obtained in about 10-15 % yield. *Single Crystal X-ray Diffraction*

X-ray diffraction data from a yellow polyhedral crystal 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).[15] The data collection covered 100% of reciprocal space to $2\theta_{\text{max}} = 70.2^{\circ}$, with an average reflection redundancy of 25.0 and R_{int} = 0.039 after absorption correction. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs. [15,16] Final unit cell parameters were determined by least-squares refinement of 6141 reflections taken from the data set. An initial structural model was obtained with SHELXT. [17] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018 using the ShelXle interface. [18]

Energy Dispersive Spectroscopy (EDS)

Semi-quantitative elemental analysis was performed on a yellow polyhedral crystal using a TESCAN VEGA-3 SBU scanning electron microscope (SEM) with a Thermo EDS attachment operated in an ultralow vacuum mode. The crystal was mounted on a SEM stub with carbon tape and analyzed using a 20 kV accelerating voltage and an accumulation time of 20 s. EDS corroborated the presence of the elements in the composition obtained from the single crystal Xray diffraction data.

Results and Discussion

Synthesis and Structure of Sr12Al3.44Fe8.16Ge2.38O32Cl4.34

Recently, Dong et al. reported on Sr mayenite, $Sr_{12}Al_{14}O_{32}Cl_2$, containing Cl⁻ ions up to the theoretical maximum occupancy, and established that the presence of Cl⁻ in the cage sites accounts for the phase stability. [19] As supported by previous reports, co-doping of the Al site with more positively charged ions, such as Si⁴⁺, leads to a concomitant increase of halides in the framework cage sites and has also been reported to enhance thermal stability. We were interested in synthesizing the Fe analogue of the Sr/Al mayenite, as well as co-doping the Fe-site with a more positively charged species, Ge^{4+} , to achieve a high Cl⁻ incorporation. We have had success in the past synthesizing structures containing mixed *M*/Ge (*M* = Fe, Co) tetrahedral sites [20,21] and decided to use a similar approach to create new mayenite compositions.

 $SrCl_2$ (melting point = 874 °C) is empirically known to be an effective flux for crystallizing complex Sr- and Fe-containing systems [22]; therefore, it was the preferred choice of flux for preparing the desired Sr/Fe mayenite with the added advantage of simultaneously functioning as a Cl source in the reaction mixture. One advantage of using a chloride melt is the ease with which the flux can be removed upon completion of the experiment by simple sonication-assisted water workup. This reaction was carried out at 1000 °C, resulting in significant flux evaporation which likely affected the crystal growth positively by supersaturating the melt. An alumina crucible was used as the reaction vessel due to the relatively high melting point of the SrCl₂ flux, which led to the adventitious incorporation of Al into the resulting crystals. It is possible that this further stabilized the formation of the Cl-rich mayenite phase as these reaction conditions proved successful and afforded single crystals of $Sr_{12}Al_{3.44}Fe_{8.16}Ge_{2.38}O_{32}Cl_{4.34}$, which contains more than twice as much Cl⁻ than the previously reported polycrystalline Ca₁₂Al₁₄O₃₂Cl₂. [19]

Structure Determination:

The Mayenite Sr₁₂Al_{3.44}Fe_{8.16}Ge_{2.38}O₃₂Cl_{4.34} crystallizes in the cubic system. The space group I-43d (No. 220) was uniquely determined by the pattern of systematic absences in the intensity data and was confirmed by structure solution. The asymmetric unit consists of six atomic positions. One strontium site (Sr1, Wyckoff position 24d, site symmetry 2..) and two oxygen sites (O1, 48e, 1 and O2, 16c, .3.) refine normally and are unambiguously established. Another anion site was modeled as chloride ion Cl1 from its coordination environment at the center of a large cage and bonded only to two Sr ions at d(Sr-Cl) = 2.93 Å. The Cl site is a general position (48e) but is disordered about a four-fold rotoinversion axis (site 12b, -4..), resulting in a maximum site occupation factor (sof) of 0.25. Refinement of the Cl sof showed a significant reduction from the maximum possible occupancy to 0.181(2) or 72% occupancy. Refinement of the sof values of Sr1 and the two oxygen atoms showed no significant decrease from full occupancy. The main problematic issue is the identity of two remaining tetrahedral sites: T1 (16c, .3.) with bond distances of T1-O = 1.775 Å and 1.849 Å (x3), and T2 (12a, -4..) with bond distances of T2-O = 1.822 Å (x4). Both appear to be mixed sites composed of three elements, Al, Fe, and Ge. Several models were refined, including single atom/ vacancy models Fe+3/[] or Ge+4/[], and two-atom mixed site models, Al/Fe, Al/Ge and Fe/Ge. All were unsuccessful, resulting either in an unstable refinement or in a non-charge-balanced composition. For example, Al/Ge mixed-site models gave an excess positive charge of +2.7 e⁻ per formula unit, while Fe/Ge models gave an excess negative charge of -1.2 e⁻ per formula unit. An electroneutral composition was achieved by modeling both tetrahedral sites as fully occupied by a three-atom mixture of Al³⁺, Fe³⁺ and Ge⁴⁺. SHELX SUMP instructions were applied to each site to maintain 100% total occupancy. Charge balance was achieved by using a second SUMP instruction on each site to constrain the total site charge to +3.17. This value was determined by the Sr/O/Cl composition. The three-atom mixed site model is also in accordance with semi-quantitative elemental analysis (EA) results on a crystal, which found that the crystal contained Fe, Ge, and Al in addition to Sr, Cl, and O. The model described

above was stable toward refinement, met EA and charge balance requirements and yielded the lowest *R*-values. The composition of each site refined to: Al1/Fe1/Ge1 = 0.132(5)/0.696(7)/0.171(4) and Al2/Fe2/Ge2 = 0.398(7)/0.433(8)/0.169(4). All atoms were refined with anisotropic displacement parameters. The largest residual electron density peak and hole in the final difference map are +0.28 and -0.44 e⁻/Å³, located 0.55 Å from Cl1 and 0.62 Å from Sr1, respectively. A minor correction for inversion twinning (Flack parameter = 0.027(8)) was included in the final refinement cycles. Crystallographic and refinement data are listed in Table 1. Select interatomic distances and atomic coordinates are given in Tables 2 and 3, respectively.

Structure Summary:

The asymmetric unit contains two three-component Al/Fe/Ge/ T sites. The T(1) site is connected to three O(1) atoms and one O(2) atom with bond distances 1.8486(19) Å for O(1) and 1.775(3) Å for O(2). The T(2) site is connected to four O(1) atoms via four equal bonds of length 1.8216(18) Å. In Sr₁₂Al_{3.44}Fe_{8.16}Ge_{2.38}O₃₂Cl_{4.34} the T(1) and T(2) tetrahedra exclusively cornershare via O(1) to produce a complex three-dimensional framework. The connectivity between the two types of mixed occupancy tetrahedral sites, T(1) and T(2), is shown in Figures 1-2, where T(1) is turquoise and T(2) is red. Each T(2) tetrahedra is corner shared to four T(1) tetrahedra via O(1), however, the T(1) tetrahedra only connects to 3 T(2) tetrahedra via O(1), leaving the O(2) oxygen as a terminal site on each T(1) tetrahedra. The presence of the terminal oxygen opens the structure and creates cages in the framework with an approximate width of ~7.5 Å that are occupied by the strontium and chloride ions for charge balance. Figure 3.

Conclusion

We synthesized a new complex mayenite-type strontium oxy-chloride exhibiting three-component site mixing of composition Sr₁₂Al_{3.44}Fe_{8.16}Ge_{2.38}O₃₂Cl_{4.34}. This material has the highest chloride content reported to date for a mayenite type oxy-chloride and contains both cations and anions in the cages of this structure.

Acknowledgements

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Accession Codes

CCDC 2163922 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>, or by emailing <u>data_request@ccdc.cam.ac.uk</u>, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Empirical formula	$Al_{1.72}Cl_{2.17}Fe_{4.08}Ge_{1.19}O_{16}Sr_{6}$
Crystal color and habit	Yellow polyhedra
Formula weight	1219.70
Temperature (K)	301(2)
Wavelength (Å)	0.71073
Crystal System	Cubic
Space group	I-43d
Lattice parameters (Å)	a = 12.6126 (3)
Volume (Å ³)	2006.38 (14)
Ζ	4
Density (calculated)	4.038 Mg/m ³
Crystal size (mm)	0.060 x 0.060 x 0.040
Flack parameter	0.027(8)
Final R indices [I>2sigma(I)]	$R_1 = 0.0143, \mathrm{wR_2} = 0.0293$
R indices (all data)	$R_1 = 0.0154, wR_2 = 0.0296$
Largest diff. peak and hole (e. Å $^{-3}$)	0.284 and -0.439

 Table 1. Select Crystallographic and Refinement Data for Sr12Al3.44Fe8.16Ge2.38O32Cl4.34.

Sr(1) - O(1) x(2)	2.5740(19)
Sr(1) - O(1) x(2)	2.6350(19)
Sr(1) - O(2) x(2)	2.5204(14)
M(1) - O(1) x(3)	1.8486(19)
M(1) - O(2)	1.775(3)
M(2) - O(1) x(4)	1.8215(18)

Table 2. Select Interatomic Distances (Å); M = mixed Al/Fe/Ge site.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters for $Sr_{12}Al_{3.44}Fe_{8.16}Ge_{2.38}O_{32}Cl_{4.34}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	Occupancy	X	у	Z	U(eq)
Sr(1)		0.10694(2)	0	0.2500	0.01208(9)
Fe(1)	0.696(7)	0.23459(2)	0.23459(2)	0.23459(2)	0.00714(15)
Al(1)	0.132(5)	0.23459(2)	0.23459(2)	0.23459(2)	0.00714(15)
Ge(1)	0.171(4)	0.23459(2)	0.23459(2)	0.23459(2)	0.00714(15)
Fe(2)	0.433(8)	0.3750	0	0.2500	0.0071(2)
Al(2)	0.398(7)	0.3750	0	0.2500	0.0071(2)
Ge(2)	0.169(4)	0.3750	0	0.2500	0.0071(2)
O(1)		0.28348(14)	0.10051(15)	0.20122(15)	0.0136(3)
O(2)		0.06586(14)	0.06586(14)	0.06586(14)	0.0152(6)
Cl(1)	0.181(2)	-0.1253(6)	-0.0056(12)	0.2317(4)	0.0119(7)



Figure 1. Illustration of the assembly of $T(1)O_4$ (turquois) and $T(2)O_4$ (red) tetrahedra into the $(T_7O_{16})^{11-}$ framework containing channels approximately 7.5 Å across. O sites are shown in red.



Figure 2. Representation of the occupation of the framework cages by Sr and Cl ions, which are shown as green and yellow spheres, respectively.



Figure 3. Polyhedral representation of the $Sr_{12}Al_{3.44}Fe_{8.16}Ge_{2.38}O_{32}Cl_{4.34}$ crystal structure viewed down the *a*- (left), *b*- (middle), and *c*-axis (right). T1 and T2 shown in light and dark brown, respectively. O(1) shown in red and O(2) shown in blue.

References

- K. Hayashi, M. Hirano, H. Hosono, Functionalities of a Nanoporous Crystal 12CaO₇Al₂O₃ Originating from the Incorporation of Active Anions, Bull. Chem. Soc. Jpn., 80 (2007) 872–84.
- 2. J. T. S. Irvine, A. R. West, Ca₁₂Al₁₄O₃₃ Solid Electrolytes Doped with Zinc and Phosphorus, Solid State Ionics, 40–41 (1990) 896–9.
- K. Hayashi, H. Muramatsu, S. Matsuishi, T. Kamiya, and H. Hosono, Humidity-Sensitive Electrical Conductivity in Ca₁₂Al_{14-x}Si_xO₃₂Cl_{2+x} (0 ≤ x ≤ 3.4) Ceramics, Electrochem.Solid-State Lett., 12 [2] (2009) J11–3.
- 4. L. Palacios, S. Bruque, and M. A. G. Aranda, Structure of Gallium- Doped Mayenite and Its Reduction Behaviour, Phys. Stat. Sol. B, 245 (2008) 666–72.
- 5. O. Yamaguchi, A. Narai, and K. Shimizu, New Compound in the System SrO-Al₂O₃, J. Am. Ceram. Soc., 69 (1986) C36–7.
- K. Hayashi, N. Ueda, S. Matsuishi, M. Hirano, T. Kamiya, and H. Hoso- no, Solid State Syntheses of 12SrO₇Al₂O₃ and Formation of High-Density Oxygen Radical Anions, O⁻ and O₂⁻, Chem. Mater., 20 (2008) 5987–96.
- C. Li, M. Wang, F. Dai, and K. Suzuki, New Nickel-Based Material (Sr₁₂Al₁₄O₃₃) for Biomass Tar Steam Reforming for Syngas Production, J. Rene. Sust. Energy, 5 (2013) 043106 11 pp.
- 8. K. Hayashi, P. V. Sushko, Y. Hashimoto, A. L. Shluger, and H. Hosono, Hydride Ions in Oxide Hosts Hidden by Hydroxide Ions, Nat. Commun., 5 (2014) 3515 8 pp.
- X. Ye, W. Zhuang, J. Wang, W. Yuan, Z. Qiao, Thermodynamic Description of SrO-Al₂O₃ System and Comparison with Similar Systems, J. Phase Equilib. Diff., 28 (2007) 362–8.
- 10. J. Jeevaratnam, F. P. Glasser, L. S. D. Glasser, Anion Substitution and Structure of 12CaO₇Al₂O₃, J. Am. Ceram. Soc., 47 (1964) 105–6.
- 11. P. P. Williams, Refinement of the Structure of 11CaO₇Al₂O₃CaF₂, Acta Crystallogr. B, 29 (1973) 1550–1.
- 12. A. K. Chatterjee G. I. Zhmoidin, The Phase Equilibrium Diagram of the System CaO-Al₂O₃-CaF₂, J. Mater. Sci., 7 (1972) 93–7.
- Z. Jiang, Z. Sun, X. Su, L. Duan, X. Yu, Crystal Structure and Luminescence Properties of Eu²⁺ Activated Sr₁₂Al₁₄O₃₂Cl₂: A Potential Green-Emitting Phosphor for Near UV Light-Emitting Diodes, J. Alloy. Compd., 577 (2013) 683–6.
- M. Miyakawa, S. W. Kim, M. Hirano, YU. Kohama, H. Kawaji, T. Atake, H. Ikegami, K. Kono, H. Hosono, Superconductivity in an Inorganic Electride 12CaO·7Al₂O₃:e⁻, J. Am. Chem. Soc., 129 (2007) 7270-7271.
- 15. APEX3 Version 2016.5-0 and SAINT+ Version 8.37A. Bruker AXS, Inc., Madison, Wisconsin, USA, 2016.
- 16. **SADABS**-2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. and Stalke D. *J. Appl. Cryst.* **2015**, *48*, 3-10.
- 17. (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst.* **2015**, *A71*, 3-8. (b) **SHELXL**: Sheldrick, G.M. *Acta Cryst.* **2015**, *C71*, 3-8.
- 18. *ShelXle*: a Qt graphical user interface for *SHELXL*. <u>Hübschle</u>, C. B., Sheldrick, G. M., Bittrich, B. *J. Appl. Cryst.* **2011**, *44*, 1281-1284.

- Y. Dong, K. Hayashi, H. Nozoe, Y. Shinoda, H. Hosono, Chlorine-Ion-Stabilized Strontium Mayenite: Expansion of Versatile Material Family, J. Am. Ceram. Soc., 97 [12] (2014) 4037-4044.
- M. Usman, V. Kocevski, M.D. Smith, G. Morrison, W. Zhang, T. Besmann, P.S. Halasyamani, H.-C. zur Loye, Polymorphism and Molten Nitrate Salt-Assisted Single Crystal to Single Crystal Ion Exchange in the Cesium Ferrogermanate Zeotype: CsFeGeO₄, Inorg. Chem., 59 (14) (2020) 9699-9709.
- 21. M. Usman, M.D. Smith, V. Kocevski, T. Besmann, H.-C. zur Loye, Complex cobalt silicates and germanates crystallizing in a porous three-dimensional framework structure, CrystEngComm, 22 (2020) 1112-1119.
- 22. R. Niewa, L. Shlyk, B. Schüpp-Niewa, L. E. De Long, Z. Anorg. Allg. Chem., 636 (2010) 331-336.