Journal of Solid State Chemistry 269 (2019) 51–55

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

# Rare earth silicates and germanates crystallizing in the wadeite and related structure types

Gregory Morrison, Branford O. Wilkins, Nicholas R. Spagnuolo, Mark D. Smith, Hans-Conrad zur Loye*

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

ARTICLE INFO

*Keywords:*
Flux growth
X-ray diffraction
Germanates
Silicates

ABSTRACT

Single crystals of six new alkali lanthanide silicates and germanates were synthesized via the flux growth method. $A_2CeSi_3O_9$ (A = Rb, Cs) and $Cs_2CeGe_3O_9$ crystallize in the Wadeite structure with space group $P6_3/m$ and lattice parameters $a = 7.1950(2)$ Å and $c = 10.5109(3)$ Å for the Rb analogue. $K_2CeSi_3O_9$ crystallizes in a previously unobserved monoclinic distortion of the Wadeite structure with space group $P2_1/n$ and lattice parameters $a = 7.0801(2)$ Å, $b = 10.458(2)$ Å, $c = 12.238(2)$ Å and $\beta = 90.07(3)°$. Finally, $Cs_8Dy_2Ge_{16}O_{39}$ and $Cs_8Dy_2Ge_{16}O_{38}F_2$ crystallize in two new structure types that are related to each other and to the Wadeite structure. $Cs_8Dy_2Ge_{16}O_{39}$ crystallizes in the monoclinic space group $P2/c$ with lattice parameters $a = 12.4054(3)$ Å, $b = 7.4310(2)$ Å, $c = 24.5761(6)$ Å, and $\beta = 90.8849(16)°$ and $Cs_8Dy_2Ge_{16}O_{38}F_2$ crystallizes in the orthorhombic space group $Pnn2$ with lattice parameters $a = 12.3489(4)$ Å, $b = 12.4805(5)$ Å, and $c = 7.3802(3)$ Å. The synthesis and structure of the six compounds are reported and the crystallochemical reasons for the formation of each structure are discussed.

## 1. Introduction

Silica and silicates comprise about 95% of the earth's crust and represent an abundant and diverse class of network oxides [1]. These materials are primarily composed of $SiO_4^{4-}$ tetrahedra, with $SiO_5^{6-}$ polyhedra and $SiO_6^{8-}$ octahedra being much less common and only observed at high pressures [2–5]. Silicates can be composed of isolated $SiO_4^{4-}$ tetrahedra or these tetrahedra can share oxygens to form a wide variety of condensed silicate units including 0-D units, such as $Si_2O_7$ dimers and $Si_6O_{18}$ rings, 1-D chains, 2-D sheets and 3-D frameworks [1]. The topologies of these units can be explained by a few principles. The valence of the Si-O bond within a tetrahedron is approximately one, meaning that an oxygen can either be terminal or shared between two Si atoms but cannot be shared by three Si atoms [6]. Furthermore, due to the high charge of the Si(+4) ion and the small size of $SiO_4$ tetrahedra, only corner-sharing silicate units exist, as edge- and face-sharing would bring the high-valent silicon ions too close together. One report of a structure containing chains of edge-sharing $SiO_4$ in a fibrous $SiO_2$ was made in 1954 but no further evidence of this phase has been observed [7,8]. Finally, the Si-O-Si bond angle within condensed silicates can range between ~140 and 180° but is most frequently close to 145° with a shallow energy penalty for larger angles and a steep penalty for shorter ones. This preference results from the interplay between the bonding preference of the shared oxygen and Si-Si repulsion [9].

Germanium, being a metalloid tetragen like silicon, similarly forms germanates, often with analogous topologies or in the same structure types as silicates. While similar, some differences exist between silicates and germanates. Like in the silicates, $GeO_4$ tetrahedra dominate the germanates but, as a result of the larger size of Ge, $GeO_5$ trigonal bipyramids and $GeO_6$ octahedra also exist at ambient pressure [10]. Furthermore, germanate polyhedra can share edges. For example, edge sharing occurs between $GeO_4$ and $GeO_6$ polyhedra in $LiNaGeGe_3O_9$ [11]. Finally, more acute Ge-O-Ge angles are preferred with 125–130° being the most favorable and with a steeper energy penalty for larger angles than in the silicates [9].

Due to the aversion to Si-O-Si angles below 140°, cyclic $Si_3O_9$ triangular rings are uncommon in silicate topologies. Despite this, multiple structures are known which contain cyclic $Si_3O_9$ units, including several minerals. Notably, the Wadeite structure type, named after $K_2ZrSi_3O_9$, [12] is a rather extensive group of compounds with the general formula $A_2BT_3O_9$, where A is an alkali metal, B is a tetravalent element, and T is either Ge or Si [13]. This structure consists of cyclic $T_3O_9$ units which corner share with octahedral $BO_6$ units to form the overall framework which is charge balanced by A cations.

The B site within the Wadeite structure type has been reported as

---

* Corresponding author.
*E-mail address:* zurLoye@mailbox.sc.edu (H.-C. zur Loye).

https://doi.org/10.1016/j.jssc.2018.09.011
Received 6 July 2018; Received in revised form 5 September 2018; Accepted 8 September 2018

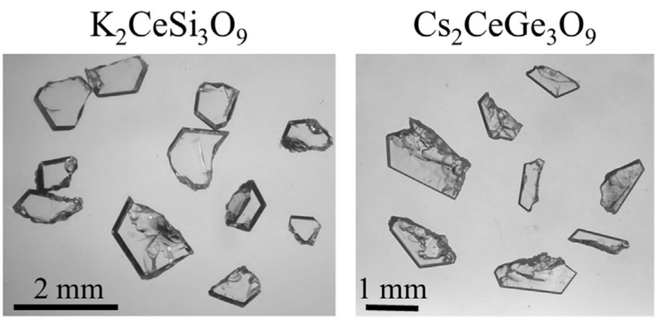

**Fig. 1.** Representative crystals of $K_2CeSi_3O_9$ and $Cs_2CeGe_3O_9$.

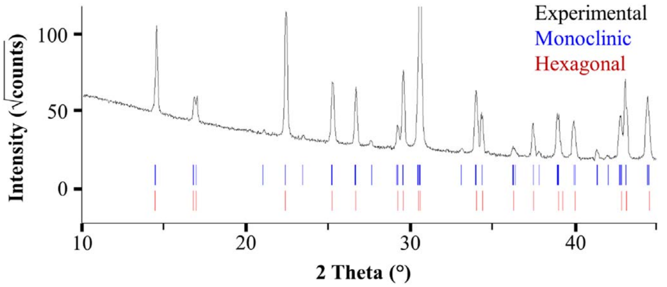

**Fig. 2.** Powder pattern of $K_2CeSi_3O_9$ and the calculated peak locations for the hexagonal Wadeite structure and the monoclinic distortion.

main group elements, Si, Sn, and Ge, transition metals, Ti, and Zr, and as an actinide, Th [12–19]. To date, a lanthanide on the B site has not been observed. As the B site atom is tetravalent, only Ce and Tb can accommodate the necessary charge. Using flux growth conditions, where Ce readily adopts the 4+ oxidation state, we have achieved the synthesis of Wadeite-type compounds with Ce on the B site. The use of another lanthanide, $Dy^{3+}$, under similar conditions resulted in crystals of two new structure types related to Wadeite. Herein, we report the synthesis and structure of three new compounds crystallizing in the Wadeite structure type, $A_2CeSi_3O_9$ (A = Rb, Cs) and $Cs_2CeGe_3O_9$, along with $K_2CeSi_3O_9$, which crystallizes in a previously unobserved monoclinic distortion of the Wadeite structure, and two new Dy germanates, $Cs_8Dy_2Ge_{16}O_{39}$ and $Cs_8Dy_2Ge_{16}O_{38}F_2$.

## 2. Experimental section

### 2.1. Synthesis

All compounds were synthesized from mixed alkali halide fluxes [20]. $A_2CeT_3O_9$ were grown by layering a mixture of ½ mmol $CeF_3$ and 1 mmol $GeO_2$ (Ge analogues), 1.5 mmol $SiO_2$ ($Cs_2CeSi_3O_9$), or 2 mmol $SiO_2$ (remaining analogues) under a eutectic or near eutectic mixture of 20 mmol KF and 20 mmol KCl, 9 mmol RbF and 11 mmol RbCl, or 9 mmol CsF and 11 mmol CsCl in a silver crucible 1.2 cm diameter and 5.7 cm tall. The tube was loosely covered with a silver lid and heated in 1.5 h to 800 °C (Si analogues) or 900 °C ($Cs_2CeGe_3O_9$). The reactions were dwelled at this temperature for 12 h and then slow cooled at 6 °C/h to below the freezing point of the flux, at which point the furnace was shut off. The resulting crystals were separated from the frozen flux by dissolving the flux in water, aided by sonication, and then recovered via vacuum filtration. The $K_2CeSi_3O_9$ and $Cs_2CeGe_3O_9$ reactions yielded large polyhedral crystals of $A_2CeT_3O_9$, Fig. 1, along with a large amount of AgCl, which results from the fluoride containing flux attacking the silver crucible. The $Rb_2CeSi_3O_9$ and $Cs_2CeSi_3O_9$ reactions each yielded small plate crystals of $A_2CeSi_3O_9$ along with AgCl.

$Cs_8Dy_2Ge_{16}O_{39}$ was synthesized by layering a mixture of ½ mmol $DyCl_3{\cdot}6H_2O$ and 2 mmol $GeO_2$ under a mixture of 9 mmol CsF and 11 mmol CsCl in the above silver crucible. The covered reaction was heated using the same scheme as for the $A_2CeGe_3O_9$ compounds above and the resulting crystals were isolated via dissolution of the flux in water followed by vacuum filtration. $Cs_8Dy_2Ge_{16}O_{39}$ was synthesized in the same manner except that 2.5 mmol of $MoO_3$ was added to the CsCl/CsF mixed flux. The reaction without $MoO_3$ yielded small, often poorly formed, colorless plates of $Cs_8Dy_2Ge_{16}O_{39}$ and a large amount of AgCl. The reaction with $MoO_3$ yielded small, well formed, colorless plates of $Cs_8Dy_2Ge_{16}O_{38}F_2$ and a large amount of AgCl. From PXRD data, no $Cs_8Dy_2Ge_{16}O_{39}$ forms when $MoO_3$ is added to the reaction. PXRD data of the reaction without $MoO_3$ is less conclusive due to the fact that most of the diffraction peaks of $Cs_8Dy_2Ge_{16}O_{38}F_2$ overlap with diffraction peaks of the $Cs_8Dy_2Ge_{16}O_{39}$. However, ~10 single crystals were examined via SXRD and all were $Cs_8Dy_2Ge_{16}O_{39}$.

## 3. Structure

Structure determination for each compound was performed using single crystal X-ray diffraction data. Data for all compounds except $K_2CeSi_3O_9$ were collected on a Bruker D8 Quest diffractometer equipped with a Mo Kα microfocus source (λ = 0.71073 Å). Data for $K_2CeSi_3O_9$ were collected using a Bruker SMART APEX CCD diffractometer with a Mo Kα source (λ = 0.71073 Å). In each case, the raw data were integrated using SAINT+ and corrected for absorption effects using SADABS [21,22]. Intrinsic phasing using ShelXT [23] or direct methods using ShelXS was carried out to obtain an initial structure solution which was then refined using ShelXL [24] in the Olex2 interface [25]. A summary of the crystallographic data for each compound is provided in Table 1.

$A_2CeSi_3O_9$ (A = Rb, Cs) and $Cs_2CeGe_3O_9$ crystallize in the hexagonal crystal system with space group $P6_3/m$ whereas $K_2CeSi_3O_9$ monoclinically distorts and crystallizes in the space group $P21/n$. Crystals of $K_2CeSi_3O_9$ almost always form as pseudo-merohedral twins that mimic the higher symmetry hexagonal unit cell. The true monoclinic symmetry is apparent in powder X-ray diffraction data, shown in Fig. 2, collected on a Rigaku Ultima IV diffractometer with a Cu Kα source (λ = 1.54056 Å) and a D/teX detector. Ultimately, an un-twinned single crystal was found for data collection and structure solution. Non-merohedral twinning was found to occur in $Cs_8Dy_2Ge_{16}O_{39}$. While attempts to find an untwinned crystal were not successful, a crystal was found with negligible twinning. Finally, inversion twinning was observed in $Cs_8Dy_2Ge_{16}O_{38}F_2$. The collected data was refined as a 2-component inversion twin consisting of 93(3)% of one component and 7(3)% of the other.

## 4. Results and discussion

### 4.1. Structure

$A_2CeSi_3O_9$ (A = Rb, Cs) and $Cs_2CeGe_3O_9$ crystallize in the Wadeite structure type with hexagonal space group $P6_3/m$ and lattice parameters $a = 7.3636(3)$ Å and $c = 10.5831(4)$ Å for the Cs analogue. This structure, shown in Fig. 3a and b, consists of regular triangular $Si_3O_9$ units that corner share to six $CeO_6$ octahedra to form a 3-D framework with alternating slabs of silicate and cerium polyhedra stacked in the c direction. The alkali cations lie between each set of three adjacent Ce polyhedra.

$K_2CeSi_3O_9$ crystallizes in a monoclinic distortion of the Wadeite structure with space group $P21/n$ and lattice parameters $a = 7.0801(2)$ Å, $b = 10.458(2)$ Å, $c = 12.238(2)$ Å and $\beta = 90.07(3)°$. The structure, shown in Fig. 3c and d, is very similar to that of the hexagonal Wadeite, however, the $Si_3O_9$ units are distorted, with the six atoms of the central $Si_3O_3$ ring no longer coplanar. The monoclinic distortion appears to occur when the A cation is too small to properly fit in the undistorted hexagonal Wadeite framework. The smaller $CeSi_3O_9$ framework can accommodate the Rb and Cs cations in the hexagonal structure and only has to monoclinically distort to accommodate the smaller K cation.