Crystal structures and X-ray powder diffraction data for Cs$_2$NiSi$_5$O$_{12}$, RbGa$_2$O$_6$, and CsGa$_2$Si$_2$O$_6$ synthetic leucite analogues

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Leucites are tetrahedrally coordinated silicate framework structures with some of the silicon framework cations partially replaced by divalent or trivalent cations. These structures have general formulae $A_2BSi_3O_12$ and $ACSi_3O_6$; where $A$ is a monovalent alkali metal cation, $B$ is a divalent cation, and $C$ is a trivalent cation. In this paper, we report the Rietveld refinements of three more synthetic leucite analogues with stoichiometries of Cs$_2$NiSi$_5$O$_{12}$, RbGa$_2$O$_6$, and CsGa$_2$Si$_2$O$_6$. Cs$_2$NiSi$_5$O$_{12}$ is Ia$3d$ cubic and is isostructural with Cs$_2$CuSi$_5$O$_{12}$. RbGa$_2$O$_6$ is $I4_1/a$ tetragonal and is isostructural with KGa$_2$Si$_2$O$_6$. CsGa$_2$Si$_2$O$_6$ is $I43d$ cubic and is isostructural with RbBSi$_2$O$_6$.

I. INTRODUCTION

Synthetic anhydrous analogues of the silicate framework minerals leucite (KAlSi$_2$O$_6$) and pollucite (CsAlSi$_2$O$_6$) can be prepared with the general formulae $A_2BSi_3O_12$ and $ACSi_3O_6$; where $A$ is a monovalent alkali metal cation, $B$ is a divalent cation, and $C$ is a trivalent cation. These structures all have the same topology with $B$ and $C$ cations partially substituting onto tetrahedrally coordinated sites (T-sites) in the silicate framework and charge balancing $A$ cations sitting in extra-framework channels. The $A$ cations can be replaced by ion exchange, Cs containing silicate framework minerals are of potential technological interest as storage media for radioactive Cs from nuclear waste (Gatta et al., 2008).

We have used X-ray and neutron powder diffraction to determine and Rietveld refine the ambient temperature crystal structures of leucite analogues with the general formulae $A_2BSi_3O_12$ and $ACSi_3O_6$. Crystal structures have been refined in the $Ia3d$ cubic and $I4_1/a$ tetragonal space groups ($A = K$, Rb, Cs; $B = Mg$, Mn, Co, Cu, Zn; $C = Fe^{2+}$, Ga; Bell and Henderson, 1994a, 1994b, 2018, 2020; Bell et al., 1994a, 2010). These structures all have disordered T-site cations and also have A cation sites fully occupied with either K, Rb, or Cs. Cs$_2$ZnSi$_5$O$_{12}$ undergoes a reversible phase transition from $Pbca$ to $Pna2_1$ on heating to 566 K (Bell and Henderson, 2012). K$_2$MgSi$_5$O$_{12}$ and K$_2$ZnSi$_5$O$_{12}$ both undergo phase transitions from $P2_1/c$ to $Pbca$ on heating to 622 K (K$_2$MgSi$_5$O$_{12}$; Redfern and Henderson, 1996) and over the temperature range 843–868 K (K$_2$ZnSi$_5$O$_{12}$; Bell et al., 2021). KGa$_2$Si$_2$O$_6$ undergoes a phase transition from $I4_1/a$ to $Ia3d$ over the temperature range 673–970 K (Bell and Henderson, 2020). Cs$_2$X$^{2+}$Si$_3$O$_6$ ($X = Cd, Cu, Zn$) all retain the cation ordered $Pbca$ orthorhombic structure below 10 K (Bell, 2021).

RbCsX$^{2+}$Si$_3$O$_6$ ($X = Mg, Ni, Cd$) leucite analogues, with two different extra-framework alkali metal cations, all have the $Pbca$ structure with ordered T-site cations (Bell and Henderson, 2019). For $X = Ni$ and $Cd$, these structures have disordered extra-framework cations, but, for $X = Mg$, there is partial extra-framework cation ordering.

In this paper, we report the Rietveld refinements (Rietveld, 1969) of three more T-site cation-disordered synthetic leucite analogues with stoichiometries of Cs$_2$NiSi$_5$O$_{12}$, RbGa$_2$O$_6$, and CsGa$_2$Si$_2$O$_6$.

II. EXPERIMENTAL

A. Sample synthesis

All three samples were prepared from appropriate stoichiometric mixtures of Rb$_2$CO$_3$, Cs$_2$CO$_3$, SiO$_2$, NiO, and Ga$_2$O$_3$. The starting mixture for Cs$_2$NiSi$_5$O$_{12}$ was loaded into a platinum crucible and heated for 24 h at 873 K to decompose the carbonate. The mixture was then heated at 1673 K for 90 min before quenching by dipping the base of the crucible in water. The resultant glass was then reground and heated at 1393 K for 5 days; this produced a dark blue

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powdered sample. The starting mixtures for RbGaSi$_2$O$_6$ and CsGaSi$_2$O$_6$ were also loaded into platinum crucibles. Both mixtures were heated at 10 K min$^{-1}$ from room temperature to 873 K; the temperature was then maintained at 873 K for 12 h, in order to decompose carbonates. The mixtures were then heated to 1473 K at 10 K min$^{-1}$ and the temperature was then maintained at 1473 K for 10 h. Each crucible was removed from the furnace and quenched by dipping the base of the crucible in water. The resultant glasses were then reground and heated up at 1473 K for 7 days before cooling at 2 K min$^{-1}$ to room temperature. This produced white powdered samples.

B. X-ray powder diffraction data collection

After heating the samples were removed from the metal capsules, ground with a mortar and pestle and then mounted on low-background silicon wafers with a drop of acetone prior to ambient temperature X-ray powder diffraction (XRD).

For Cs$_2$NiSi$_3$O$_{12}$, data were collected on a PANalytical Empyrean diffractometer using CoK$_\alpha$ X-rays with an iron $\beta$-filter and a 3.3473° 2$\theta$ wide 255 channel PIXCEL-3D area detector. Data were collected in a single scan over 66 h using Data Collector 5.1a (PANalytical, 2014). These data were collected over the range 12–140° 2$\theta$ with a step width of 0.0131° 2$\theta$ and an effective counting time of 5998 s per point. The beam size was defined with a 20 mm mask, fixed divergence anticrystal (¼°) slit and automatic divergence slit with a 15-mm long beam footprint. These diffracted intensities were converted from the automatic divergence slit mode to the fixed divergence slit mode in HighScore Plus (PANalytical, 2009) prior to data analysis.

For the RbGaSi$_2$O$_6$ and CsGaSi$_2$O$_6$ samples, data were collected on a PANalytical X’Pert Pro MPD using CuK$_\alpha$ X-rays, with a nickel $\beta$-filter and a 3.3473° 2$\theta$ wide 255 channel PIXCEL-1D area detector. Data were collected in the range 8–100° 2$\theta$ with a step width of 0.0131° 2$\theta$ using Data Collector 5.5a (PANalytical, 2017). The beam size was defined with a 20 mm mask, fixed anticrystal (¼°) and divergence (¼°) slits. For RbGaSi$_2$O$_6$, a single-scans were collected lasting 33 h and an effective counting time of 4175 s per point. For CsGaSi$_2$O$_6$, a single-scans was collected lasting 24 h and an effective counting time of 3035 s per point.

No smoothing or $\alpha_2$ stripping was done on any of these data. Both diffractometers were calibrated with an external NIST 640e silicon standard.

C. XRD data analysis

All powder diffraction data were using HighScore Plus and the ICCD Powder Diffraction File. Analysis of the powder diffraction data for Cs$_2$NiSi$_3$O$_{12}$ showed that this sample was single-phase cubic and the position of the Bragg reflections in the powder diffraction data matched the cubic pattern PDF# 00-037-0335 for Cs$_2$NiSi$_3$O$_{12}$. However, analysis of the powder diffraction data for RbGaSi$_2$O$_6$ showed that this sample consisted of two phases. The main phase was $I4_1/a$ tetragonal RbGaSi$_2$O$_6$ PDF# 00-037-0350 with $C2/m$ monoclinic Ga$_2$O$_3$ PDF# 00-043-1012 as a minor phase. A similar analysis of CsGaSi$_2$O$_6$ also showed $I4_3d$ cubic pattern PDF# 00-050-0175 for CsGaSi$_2$O$_6$ as the main phase and $C2/m$ monoclinic Ga$_2$O$_3$ PDF# 00-043-1012 as a minor phase.

Rietveld refinements were done using FULLPROF (Rodríguez-Carvajal, 1993). Backgrounds were fitted by linear interpolation between a set of background points with refinable heights. The Thompson-Cox-Hastings Pseudo-Voigt function (van Laar and Yelon, 1984), convoluted with asymmetry due to axial divergence (Finger et al., 1994), was used to model the profile shape.

The crystal structure of Cs$_2$NiSi$_3$O$_{12}$ was refined using the $Ia\overline{3}d$ cubic structure of Cs$_2$CuSi$_3$O$_{12}$ (Bell et al., 2010) as the starting model. In this starting model, Ni replaced Cu on the disordered T-site. In this crystal structure, there is one $Ia\overline{3}d$ 16h Wyckoff special position site which is 100% occupied by Cs, there is one 48g special position site which is 1/6th occupied by Ni and 5/6th by Si (T-site occupancies were not refined) and there is a 96 h general position 100% occupied by O. A stoichiometry of Cs$_2$NiSi$_3$O$_{12}$ was assumed. The isotropic temperature factors of the T-site atoms Si and Ni were constrained to be the same. It should be noted that one of the authors (AMTB) published a $Pbca$ orthorhombic structure for Cs$_2$NiSi$_3$O$_{12}$, with ordered T-site cations and $a$, $b$, and $c$ being very close but slightly different (Bell and Henderson, 1996). However, the XRD data for this sample did not show the slight orthorhombic distortion that was seen in the synchrotron XRD data used for the earlier structure refinement.

The crystal structure of RbGaSi$_2$O$_6$ was refined using the $I4_1/a$ structure of KGaSi$_2$O$_6$ (Bell and Henderson, 2020) as the starting model with Rb replacing K on the extra-framework cation site. In this crystal structure, all atoms were located on the $I4_1/a$ 16f Wyckoff general position. There is one 16f position for Rb, three 16f positions for T-sites (disordered 1/3rd Ga and 2/3rd Si, T-site occupancies were not refined), and six 16f positions for O. The isotropic temperature factors of the T-site atoms Si and Ga were constrained to be the same on each T-site but were allowed to vary between different T-sites. All isotropic temperature factors for the six O sites were constrained to have the same value. As was done for KGaSi$_2$O$_6$ the T–O interatomic distances were soft constrained to be 1.68 ± 0.02 Å (the average bond distance for tetrahedral Si–O and Ga–O) assuming complete T-site disorder (1/3Ga:2/3Si) on each T-site as it was not possible to refine chemically sensible T-site occupancies. Rietveld refinements in noncubic leucite structures without soft interatomic distance constraints tend to give unrealistic interatomic T–O distances.

The crystal structure of CsGaSi$_2$O$_6$ was refined using the $I4_3d$ cubic structure of RbBSi$_2$O$_6$ (Filatov et al., 2011) as the starting model. This matched the space group assignment of the CsGaSi$_2$O$_6$ PDF# 00-050-0175. In this starting model, Ga replaced B on the disordered T-site, which is occupied by 1/3rd Ga and 2/3rd Si (T-site occupancies were not refined), and Cs replaced Rb on the extra-framework cation site. In this crystal structure, there is one $I4_3d$ 16c Wyckoff special position site which is 100% occupied by Cs. There are also three $I4_3d$ 48e Wyckoff general position sites, one of these is occupied by the disordered Ga/Si T-site and two are 100% occupied by O. The Rietveld refinements for RbGaSi$_2$O$_6$ and CsGaSi$_2$O$_6$ both used the crystal structure of Ga$_2$O$_3$ (da Silva et al., 2012) to fit the minor phase. The RbGaSi$_2$O$_6$ sample contained 11.8(1) wt.% Ga$_2$O$_3$, and the CsGaSi$_2$O$_6$ sample contained 9.2(1) wt.% Ga$_2$O$_3$. 

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Table I. Refined lattice parameters compared with those for starting structures

| Stoichiometry           | Space group | a (Å)               | b (Å)               | c (Å)               | V (Å³)  |
|-------------------------|-------------|---------------------|---------------------|---------------------|---------|
| Cs₂NiSi₅O₁₂             | Ia₃d        | 13.4694(9)          | 13.4694(9)          | 2541.59(3)          |         |
| Cs₂CuSi₅O₁₂             | Ia₃d        | 13.6322(4)          | 13.6322(4)          | 2533.42(4)          |         |
| RbGaSi₂O₆               | I₄₁/a       | 13.3703(2)          | 13.7983(2)          | 2466.66(7)          |         |
| KGaSi₂O₆                | I₄₁/a       | 13.1099(4)          | 13.8100(4)          | 2373.50(12)         |         |
| CsGaSi₂O₆               | I₄3d        | 13.72124(8)         | 13.72124(8)         | 2583.33(2)          |         |
| RbBSi₂O₆                | I₄3d        | 12.7898(1)          | 12.7898(1)          | 2092.14(5)          |         |

Table II. Refined interatomic distances, Ia₃d cubic structures

|                  | A–O x6 (Å) | A–O x6 (Å) | T–O x2 (Å) | T–O x2 (Å) |
|------------------|------------|------------|------------|------------|
| Cs₂NiSi₅O₁₂      | 3.547(4)   | 3.357(4)   | 1.629(4)   | 1.655(4)   |
| Cs₂CuSi₅O₁₂      | 3.528(5)   | 3.363(5)   | 1.631(4)   | 1.652(5)   |

Table III. Refined interatomic angles, Ia₃d cubic structures

|                  | O–T–O x2 (°) | O–T–O x2 (°) | O–T–O (°) | O–T–O (°) |
|------------------|--------------|--------------|-----------|-----------|
| Cs₂NiSi₅O₁₂      | 113.0(4)     | 111.9(3)     | 105.0(3)  | 102.3(4)  |
| Cs₂CuSi₅O₁₂      | 112.6(3)     | 112.0(3)     | 106.4(4)  | 101.3(4)  |

VESTA (Momma and Izumi, 2011) was used to plot crystal structures.

III. RESULTS AND DISCUSSION

Crystal structures have been refined for Cs₂NiSi₅O₁₂, RbGaSi₂O₆, and CsGaSi₂O₆ leucite analogues from XRD data. All refined structures have disordered T-site cations. Cs₂NiSi₅O₁₂ is isomorphous with Ia₃d cubic Cs₂CuSi₅O₁₂; RbGaSi₂O₆ is isostructural with I₄₁/a tetragonal KGaSi₂O₆; and CsGaSi₂O₆ is isostructural with I₄3d cubic RbBSi₂O₆. Table I shows the comparison of the refined lattice parameters for Cs₂NiSi₅O₁₂, RbGaSi₂O₆, and CsGaSi₂O₆ with the Cs₂CuSi₅O₁₂ (Bell et al., 2010), KGaSi₂O₆ (Bell and Henderson, 2020), and RbBSi₂O₆ (Filatov et al., 2011) starting structures used for Rietveld refinement. Tables II–VII similarly show refined interatomic distances and angles; the mean T–O distances are close to the constraint distances, the mean O–T–O angles are close to the ideal tetrahedral angle of 109.47°. Table VIII similarly shows the tetrahedral angle variances for the T-sites (Robinson et al., 1971) in the silicate framework structures.

A. Cs₂NiSi₅O₁₂ structure

Figures 1 and 2 respectively show the Rietveld difference and the VESTA crystal structure plots for the refined crystal structure of Cs₂NiSi₅O₁₂. Table I shows that this crystal structure has a unit cell volume that is slightly larger than the isostructural Cs₂CuSi₅O₁₂ which was used as a starting model for Rietveld refinement. However, the ionic radius (Shannon, 1976) for Ni²⁺ (0.69 Å) is smaller than that for Cu²⁺ (0.71 Å), it would be expected that the smaller ionic radius for Ni²⁺ would result in a smaller unit cell compared with the one synthesized for Cs₂CuSi₅O₁₂. This discrepancy may be due to Cs₂NiSi₅O₁₂ not having the assumed stoichiometry. Table II shows that one set of Cs–O distances is slightly larger for Cs₂NiSi₅O₁₂ compared with Cs₂CuSi₅O₁₂. However, the other set of Cs–O distances are equivalent between error limits. Table II also shows that both sets of T–O distances are equivalent between error limits for Cs₂NiSi₅O₁₂ and Cs₂CuSi₅O₁₂. Table III shows that two of the six O–T–O angles are different between error limits for Cs₂NiSi₅O₁₂ and Cs₂CuSi₅O₁₂, but the T–O–T angles are equivalent between error limits for Cs₂NiSi₅O₁₂ and Cs₂CuSi₅O₁₂. Table VIII shows that tetrahedral distortions for Cs₂NiSi₅O₁₂ and Cs₂CuSi₅O₁₂ are very close.

B. RbGaSi₂O₆ structure

Figures 3 and 4 respectively show the Rietveld difference and the VESTA crystal structure plots for the refined crystal structure of RbGaSi₂O₆. Note that Figure 4 shows that this tetragonal crystal structure has a slightly collapsed silicate

Table IV. Refined interatomic distances (Å)

|                  | A = K       | A = Rb      |
|------------------|-------------|-------------|
| A                | O1          | 3.51(3)     | 3.21(2)     |
| A                | O2          | 3.24(3)     | 3.20(2)     |
| A                | O3          | 3.92(3)     | 3.43(2)     |
| A                | O4          | 3.38(3)     | 3.34(1)     |
| A                | O5          | 3.33(3)     | 3.32(2)     |
| A                | O6          | 3.17(3)     | 3.66(1)     |
| A                | O7          | 2.87(3)     | 3.20(1)     |
| A                | O8          | 3.90(3)     | 3.60(1)     |
| A                | O9          | 2.93(3)     | 3.18(2)     |
| A                | O10         | 3.39(3)     | 3.98(1)     |
| A                | O11         | 3.44(2)     | 3.65(2)     |
| A                | O12         | 3.41(3)     | 3.28(2)     |
| mean A–O        | 3.374(29)   | 3.423(15)   |
| T1               | O1          | 1.63(2)     | 1.72(2)     |
| T1               | O2          | 1.61(2)     | 1.62(2)     |
| T1               | O3          | 1.63(2)     | 1.76(2)     |
| T1               | O4          | 1.58(2)     | 1.59(1)     |
| T1               | O5          | 1.73(2)     | 1.64(2)     |
| T1               | O6          | 1.65(2)     | 1.79(1)     |
| T1               | O7          | 1.60(2)     | 1.54(1)     |
| T1               | O8          | 1.73(1)     | 1.62(1)     |
| T1               | O9          | 1.66(2)     | 1.64(1)     |
| T1               | O10         | 1.70(2)     | 1.68(1)     |
| T1               | O11         | 1.60(2)     | 1.53(2)     |
| T1               | O12         | 1.66(2)     | 1.76(2)     |
| mean T1–O       | 1.648(20)   | 1.658(14)   |
| mean T2–O       | 1.614(19)   | 1.672(15)   |
| mean T3–O       | 1.677(20)   | 1.649(14)   |
| mean T–O        | 1.655(20)   | 1.654(15)   |

I₄₁/a tetragonal structures. AGaSi₂O₆ (A = K, Rb). T = disordered Si/Ga.
However, the ambient temperature heated the cations (Shannon, 1976). RbGaSi2O6 has a larger unit cell volume than that of KGaSi2O6, which was used as a starting model for Rietveld refinement, this reflects the differences in the ionic radii for Rb+ (1.72 Å) and K+ (1.64 Å) cations (Shannon, 1976). However, the ambient temperature c/a ratio for RbGaSi2O6 is 1.032, which is smaller than the ambient temperature c/a ratio for KGaSi2O6, which is 1.053. When KGaSi2O6 is heated the c/a ratio decreases before a phase transition from Ia3d to I43d over the temperature range 673–970 K (Bell and Henderson, 2020). It would be interesting to do a high-temperature XRD experiment on RbGaSi2O6 as this smaller c/a ratio would suggest that this leucite analogue would undergo a phase transition from I41/a to Ia3d at a lower temperature than KGaSi2O6. Table IV shows larger A–O distances for A = Rb compared with A = K, also reflecting the ionic radii difference. The mean T–O distances for RbGaSi2O6 and KGaSi2O6 are the same within error limits. Table IV shows that the mean O–T–O and T–O–T angles for RbGaSi2O6 and KGaSi2O6 are the same within error limits. Table VIII shows that mean tetrahedral distortion for KGaSi2O6 is larger than that for RbGaSi2O6, this reflects the greater collapse (Taylor and Henderson, 1968) of the silicate framework structure with the smaller K+ cation compared with the larger Rb+ cation.

### C. CsGaSi2O6 structure

Figures 5 and 6 respectively show the Rietveld difference and the VESTA crystal structure plots for the refined crystal structure of CsGaSi2O6. Table I shows that the crystal structure of CsGaSi2O6 has a larger unit-cell volume than that of RbBSi2O6 which was used as a starting model for Rietveld refinement, this reflects the differences in the ionic radii for Cs+(2.02 Å), Ga3+ (0.61 Å), Rb+ (1.86 Å), and B3+ (0.25 Å) cations (Shannon, 1976). CsGaSi2O6 has the I43d cubic crystal structure, unlike RbGaSi2O6, which has the I41/a tetragonal structure. These differences in cation size mean that the silicate framework for the RbGaSi2O6 is more collapsed (Taylor and Henderson, 1968) than for CsGaSi2O6, and consequently, there is a lowering of symmetry for the crystal structure. Table VI shows that for CsGaSi2O6 the A–O and T–O distances are larger than those for the RbBSi2O6 due to the differences in ionic radii for the cations present in these crystal structures. Table VII shows that three of the six O–T–O angles are...
Figure 1. Rietveld difference plot for $\text{Cs}_2\text{NiSi}_5\text{O}_{12}$. Red circles represent observed data points, the blue line represents calculated data points, the green line represents difference curve, and black crosses represent positions of Bragg reflections. $R$-factors for this refinement were: $R_p = 21.5314\%$, $R_{wp} = 11.5115\%$, $R_{exp} = 4.7035\%$, $\chi^2 = 6.2111$.

Figure 2. VESTA la3d cubic structure plot for $\text{Cs}_2\text{Ni}^{2+}\text{Si}_5\text{O}_{12}$, viewed down [111] showing a channel for extra-framework light blue Cs$^+$ cations. Disordered (Si/Ni)O$_4$ tetrahedra are shown in gray with O$^{2-}$ anions are shown in red.
Figure 3. Rietveld difference plot for RbGaSi₂O₆. Red circles represent observed data points, the blue line represents calculated data points, and the green line represents difference curve. The upper line of black crosses represent positions of Bragg reflections for RbGaSi₂O₆ and the lower line of black crosses represent positions of Bragg reflections for Ga₂O₃ impurity. \( R \)-factors for this refinement were: \( R_p = 10.1855\% \), \( R_{wp} = 8.2308\% \), \( R_{exp} = 2.7240\% \), \( \chi^2 = 9.2667 \).

Figure 4. VESTA \( H_4/a \) tetragonal structure plot for RbGaSi₂O₆ viewed down \([1\text{–}11]\) showing a channel for extra-framework pink Rb⁺ cations. Disordered (Si/ Ga)O₄ tetrahedra are shown in light green with O²⁻ anions are shown in red.
Figure 5. Rietveld difference plot for CsGaSi2O6. Red circles represent observed data points, the blue line represents calculated data points, and the green line represents difference curve. The upper line of black crosses represent positions of Bragg reflections for CsGaSi2O6 and the lower line of black crosses represent positions of Bragg reflections for Ga2O3 impurity. R-factors for this refinement were: $R_p = 9.9377\%$, $R_{wp} = 8.0887\%$, $R_{exp} = 2.5680\%$, $\chi^2 = 10.4871$.

Figure 6. VESTA $I\overline{4}3d$ cubic structure plot for CsGaSi2O6, viewed down [111] showing a channel for extra-framework light blue Cs$^+$ cations. Disordered (Si/Ga)O$_4$ tetrahedra are shown in light green with O$^{2-}$ anions are shown in red.
different between error limits for CsGaSi$_2$O$_6$ and RbBSi$_2$O$_6$. The mean T–O–T angles for CsGaSi$_2$O$_6$ are smaller than those for RbBSi$_2$O$_6$, reflecting the greater framework collapse of RbBSi$_2$O$_6$ compared with CsGaSi$_2$O$_6$. Table VIII shows that tetrahedral distortion for CsGaSi$_2$O$_6$ is larger than that for RbBSi$_2$O$_6$. This reflects the greater distortion of the silicate framework structure by incorporation of the larger Ga$^{3+}$ cation into the framework compared with the smaller B$^{3+}$ cation.

The R-factors for this refinement of the CsGaSi$_2$O$_6$ crystal structure in I43d were: $R_p = 9.9377\%$, $R_wp = 8.0887\%$, $R_exp = 2.5680\%$, $\chi^2 = 10.4871$. However, it should be noted that a refinement of the CsGaSi$_2$O$_6$ crystal structure in Ia3d, using the cubic structure of CsAlSi$_2$O$_6$ (Yanase et al., 1997) as a starting structure, gave the following R-factors: $R_p = 10.3604\%$, $R_wp = 8.4084\%$, $R_exp = 2.5708\%$, $\chi^2 = 11.5234$. These R-factors are only slightly worse than those for I43d, suggesting that the crystal structures in these two different space groups show some similarities. Ia3d is a supergroup of I43d, it would also be interesting to try a high-temperature XRD experiment on CsGaSi$_2$O$_6$ to see if there might be a phase transition from I43d to Ia3d.

IV. CONCLUSIONS

Crystal structures have been refined for Cs$_2$NiSi$_3$O$_12$, RbGaSi$_2$O$_6$, and CsGaSi$_2$O$_6$ synthetic leucite analogues. All refined structures have disordered T-site cations. Cs$_2$NiSi$_3$O$_12$ is isostructural with Ia3d cubic Cs$_2$CuSi$_3$O$_12$; RbGaSi$_2$O$_6$ is isostructural with I41/a tetragonal KGaSi$_2$O$_6$, and CsGaSi$_2$O$_6$ is isostructural with I43d cubic RbBSi$_2$O$_6$.

V. DEPOSITED DATA

 CIF files with information related to crystal structure, interatomic distances, and angles, and powder diffraction data for Cs$_2$NiSi$_3$O$_12$, RbGaSi$_2$O$_6$, and CsGaSi$_2$O$_6$ synthetic leucite analogues were deposited with the ICDD. You may request these data from ICDD at info@icdd.com.

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