KGaSi2O6, an I41/a tetragonal leucite analogue with possible tetrahedral site cation ordering?

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$KGaSi_2O_6$, an $I4_1/a$ tetragonal leucite analogue with possible tetrahedral site cation ordering?

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Introduction.

Synthetic anhydrous analogues of the silicate framework minerals **leucite** ($KAlSi_2O_6$) and **pollucite** ($CsAlSi_2O_6$) can be prepared with the general formulae $A_2BSi_5O_{12}$ and $ACSi_2O_6$, 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 and these materials are of potential technological interest as storage media for radioactive Cs from nuclear waste [1].

$ACSi_2O_6$ leucite structures are known for *A* = K, Rb, Cs; *C* = B, Al, Fe^{3+} [2-6], these structures are $I4_1/a$ tetragonal and *Ia*-3*d* or *I*-43*d* cubic, in all of these structures the trivalent C cations are disordered on the T-sites with Si However, no $ACSi_2O_6$ leucite structures are known where C = Ga although there is a Powder Diffraction File pattern [7] for $KGaSi_2O_6$. There is a published structure for $K_{0.8}Rb_{0.2}GaSi_2O_6$ [8], this structure **has some T-site cation ordering of Ga and Si.**

Synthesis.

$KGaSi_2O_6$ was prepared from appropriate stoichiometric mixtures of K_2CO_3, Ga_2O_3 and SiO_2. The mixture was initially heated at 1673K for 3 hours. The resultant material was then reground and heated at 1273K for 4 days, this produced a white powder.

Ambient temperature data collection and analysis.

The sample was then mounted on a low-background silicon wafer prior to ambient temperature X-ray powder diffraction. Data were collected with a PANalytical X'Pert Pro MPD using Cu Kα X-rays and an X'Celerator area detector. These data matched the Powder Diffraction File pattern for $KGaSi_2O_6$. Rietveld [9] refinements were done using FULLPROF [10]. Refinements were done using the structure of $KAlSi_2O_6$ [4] (Ga replacing Al) as a starting model. T-O distances were constrained to 1.68(2)Å (average distance for tetrahedral Si-O and Ga-O [11]) 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. Figure 1 shows the Rietveld difference plot for this refinement, $KGaSiO_4$ [12] was included as a second phase present at 3.0(2) wt.%. Figure 2 shows a VESTA [13] plot of the $KGaSi_2O_6$ crystal structure. Table 1 shows the comparison of some refined structural parameters for $KGaSi_2O_6$ and $K_{0.8}Rb_{0.2}GaSi_2O_6$, T-O distances are the mean of the 4 distances for each site.

High temperature data collection and analysis.

The Anton-Paar HTK1200N high temperature stage was then mounted on the X'Pert and XRD data were collected on $KGaSi_2O_6$ at 294K and in 100K steps from 373-1473K.

Figure 3 shows how the $I4_1/a$ tetragonal 004 and 040 Bragg reflections merge to a single peak on heating above 973K. There are 3 peaks at 773 and 873K, suggesting a 2-phase region. Figure 4 shows a Rietveld difference plot from $KGaSi_2O_6$ data collected at 1473K. This can be fitted with an *Ia*-3*d* cubic structure similar to pollucite, therefore the single high temperature peak can be indexed as *Ia*-3*d* cubic 400. Figure 5 shows a VESTA [13] plot of the $KGaSi_2O_6$ 1473K crystal structure. Table 1 also shows some refined structural parameters for $KGaSi_2O_6$ at 1473K.

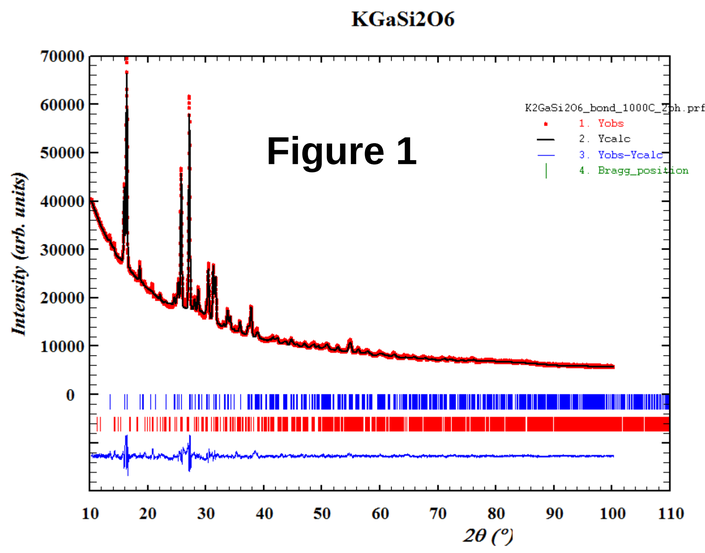


Figure 1

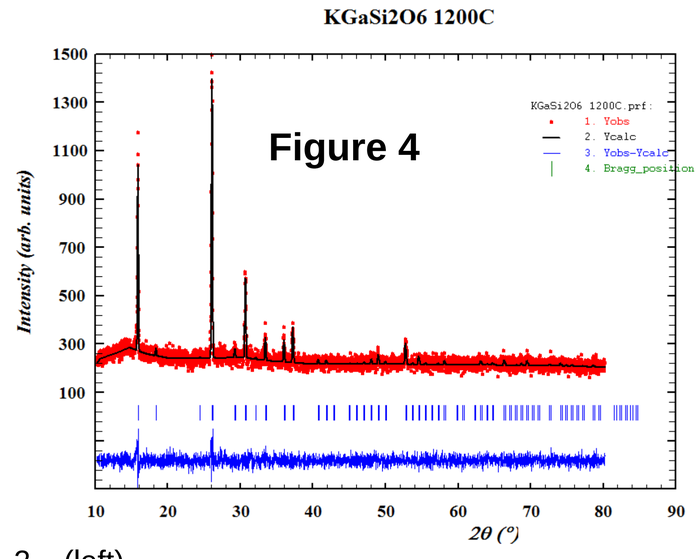


Figure 4

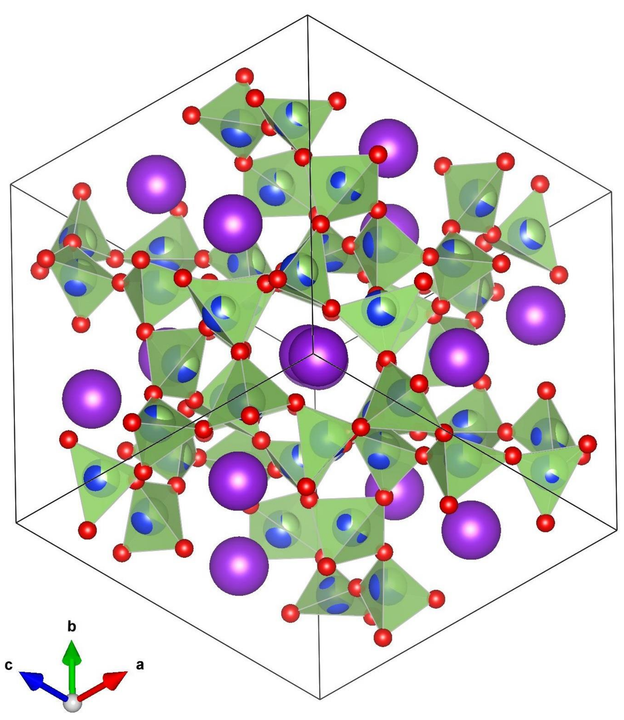
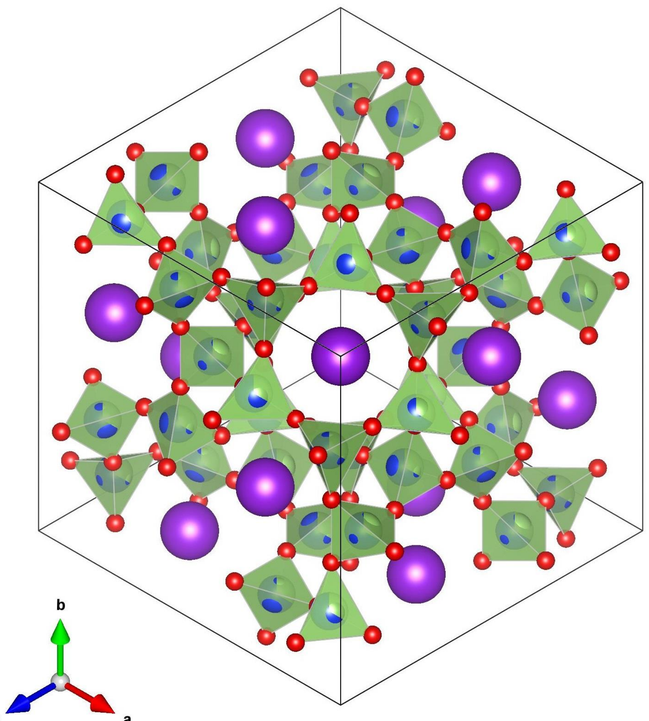


Figure 2 (left) shows the 294K $I4_1/a$ tetragonal structure for $KGaSi_2O_6$. Figure 5 (right) shows the I473K *Ia*-3*d* cubic structure for $KGaSi_2O_6$. Purple spheres = K cations. Green and blue spheres = disordered Si/Ga cations. Red spheres = O anions. Green polyhedra = $(Si,Ga)O_4$ units.



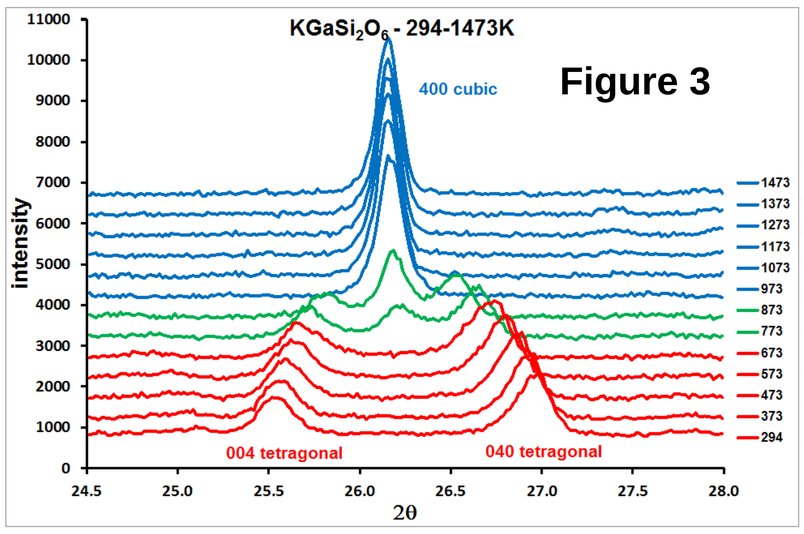


Figure 3

Table 1 - SG = space group and sof = site occupation factor

	$KGaSi_2O_6$ 294K [this work]	$K_{0.8}Rb_{0.2}GaSi_2O_6$ 294K [8]	$KGaSi_2O_6$ 1473K [this work]
SG	$I4_1/a$	$I4_1/a$	*Ia*-3*d*
a(Å)	13.1099(4)	13.157	13.6521(7)
c(Å)	13.8100(4)	13.897	
V(Å)³	2373.49(12)	2405.66	2544.5(2)
T1-O(Å)	1.61(2)	1.68(1)	1.73(3) & 1.58(4)
T2-O(Å)	1.68(2)	1.65(3)	
T3-O(Å)	1.65(2)	1.71(2)	
T1 sof	1/3Ga:2/3Si	1/3Ga:2/3Si	1/3Ga:2/3Si
T2 sof	1/3Ga:2/3Si	1/4Ga:3/4Si	
T3 sof	1/3Ga:2/3Si	1/2Ga:1/2Si	

Discussion.

Ambient temperature XRD on a synthetic leucite sample of $KGaSi_2O_6$ shows that this material has an $I4_1/a$ tetragonal structure, similar to that for $KAlSi_2O_6$ leucite. The refined mean T-O distances (see Table 1) for the 3 different tetrahedrally coordinated sites in the silicate framework structure are all different, similar to the published structure of $K_{0.8}Rb_{0.2}GaSi_2O_6$, which has partial T-site order. The longer the T-O distance then the more Ga on the T-site, this could suggest some partial T-site order in the ambient temperature crystal structure of $KGaSi_2O_6$. However, no chemically sensible site occupancies could be refined so the T-site occupancies were fixed at 1/3Ga:2/3Si, any partial T-site ordering is not conclusive.

High temperature XRD on $KGaSi_2O_6$ shows a previously unknown phase transition from $I4_1/a$ tetragonal to *Ia*-3*d* cubic between 773 and 973K, this structure is maintained to 1473K. Figures 2 and 5 show how the shape of the extraframework channel in the silicate framework structure becomes less distorted on heating.

Conclusions and future work.

The ambient temperature crystal structure for the synthetic leucite $KGaSi_2O_6$ is $I4_1/a$ tetragonal structure, similar to that for $KAlSi_2O_6$ leucite. There is some evidence for partial T-site order in this structure but this is not conclusive.

High temperature XRD on $KGaSi_2O_6$ shows a phase transition from $I4_1/a$ tetragonal (leucite structure) to *Ia*-3*d* cubic (pollucite structure) between 773 and 973K.

When the Anton-Paar HTK1200N high temperature stage is repaired then more high temperature XRD measurements are to be done to further study this phase transition.

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