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KGaSi₂O₆, an *I*₄/*a* tetragonal leucite analogue with possible tetrahedral site cation ordering?

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Introduction.

Synthetic anhydrous analogues of the silicate framework minerals **leucite** (KAlSi₂O₆) and **pollucite** (CsAlSi₂O₆) 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].

ACSi₂O₆ leucite structures are known for *A* = K, Rb, Cs; *C* = B, Al, Fe³⁺ [2-6], these structures are *I*₄/*a* tetragonal and *Ia-3d* or *I-43d* cubic, in all of these structures the trivalent *C* cations are disordered on the T-sites with Si. However, no ACSi₂O₆ leucite structures are known where *C* = Ga although there is a Powder Diffraction File pattern [7] for KGaSi₂O₆. There is a published structure for K_{0.8}Rb_{0.2}GaSi₂O₆ [8], this structure has some T-site cation ordering of Ga and Si.

Synthesis.

KGaSi₂O₆ was prepared from appropriate stoichiometric mixtures of K₂CO₃, Ga₂O₃ and SiO₂. 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.

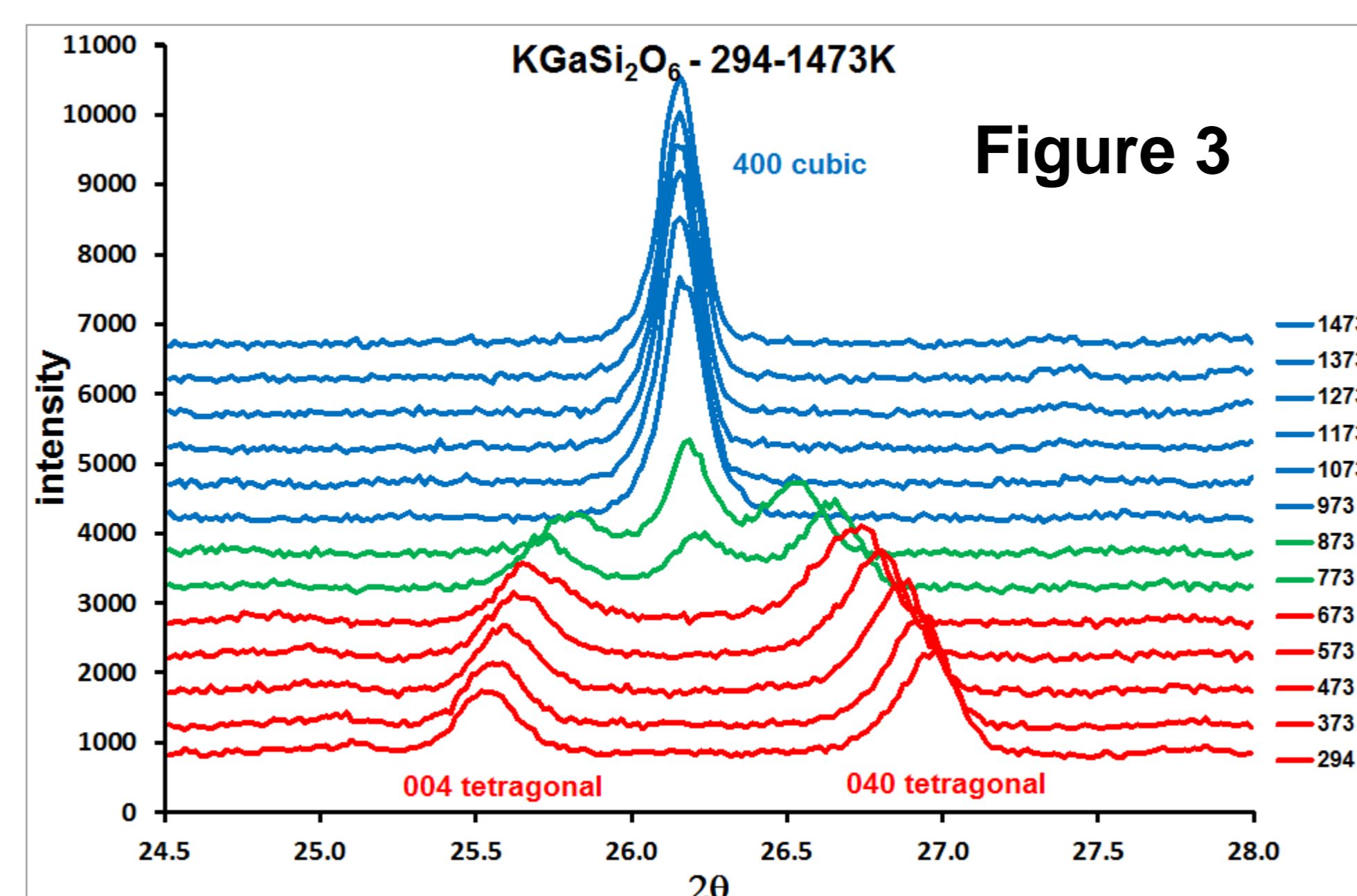
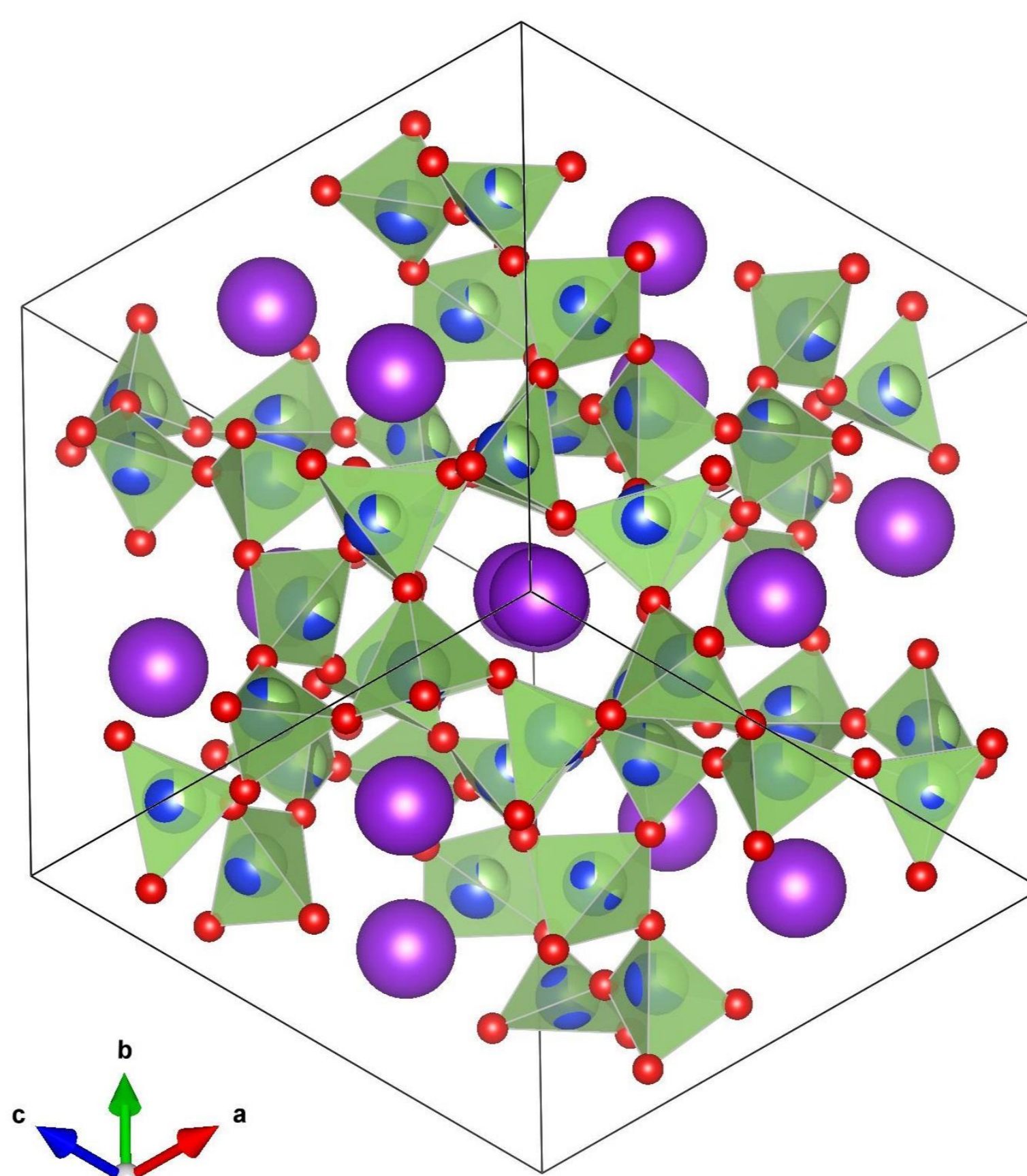
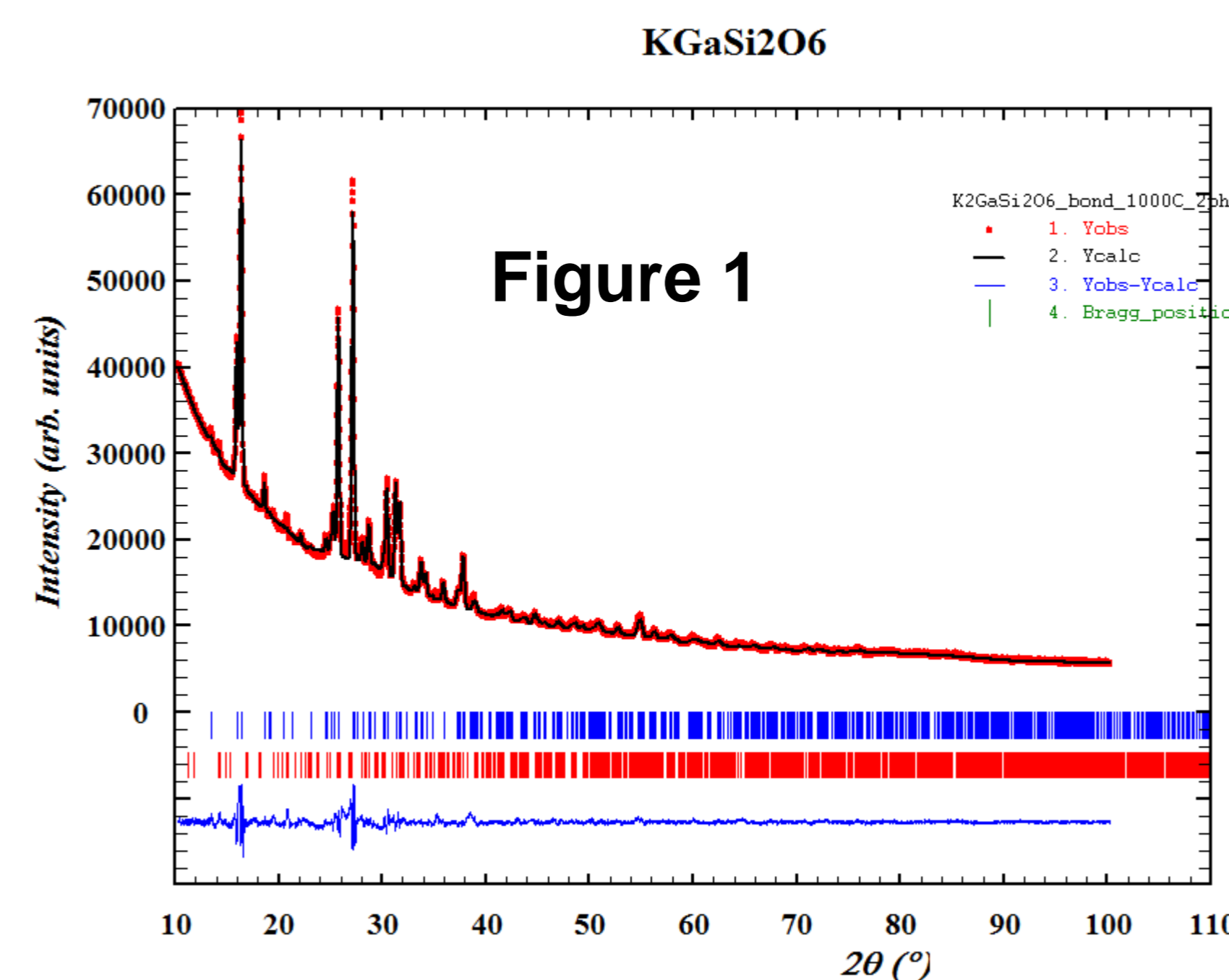
Ambient temperature data collection and analysis.

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 K α X-rays and an X'Celerator area detector. These data matched the Powder Diffraction File pattern for KGaSi₂O₆. Rietveld [9] refinements were done using FULLPROF [10]. Refinements were done using the structure of KAlSi₂O₆ [4] (Ga replacing Al) as a starting model. T-O distances were constrained to 1.68(2) \AA (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, KGaSi₂O₆ [12] was included as a second phase present at 3.0(2) wt.%. Figure 2 shows a VESTA [13] plot of the KGaSi₂O₆ crystal structure. Table 1 shows the comparison of some refined structural parameters for KGaSi₂O₆ and K_{0.8}Rb_{0.2}GaSi₂O₆, 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 KGaSi₂O₆ at 294K and in 100K steps from 373-1473K. Figure 3 shows how the *I*₄/*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 KGaSi₂O₆ data collected at 1473K. This can be fitted with an *Ia-3d* cubic structure similar to pollucite, therefore the single high temperature peak can be indexed as *Ia-3d* cubic 400. Figure 5 shows a VESTA [13] plot of the KGaSi₂O₆ 1473K crystal structure. Table 1 also shows some refined structural parameters for KGaSi₂O₆ at 1473K.

References:- [1] Gatta, G. D. *et al.* (2008). *Phys. Chem. Miner.* 35, 521–533. [2] Filatov, S.K. *et al.* (2011) *Zeitschrift für Kristallographie - Crystalline Materials* 226(7), 602-612. [3] Derkacheva, E.S. *et al.* (2011) *Glass Physics and Chemistry* 37(5), 572-578. [4] Gatta, G. D. *et al.* (2008). *American Mineralogist* 93, 1588-1596. [5] Palmer, D.C. *et al.* (1997). *American Mineralogist* 82, 16-29. [6] Bell, A. M. T. & Henderson, C. M. B. (1994). *Acta Cryst.* C50, 1531–1536. [7] Torres-Martinez, L. & West, A.R. (1986). *Powder Diffraction File pattern* 37-349. [8] Klaska, R. (1978) *Naturwissenschaften* 65, 592-593. [9] Rietveld, H. M. (1969). *J. Appl. Cryst.* 2, 65–71. [10] Rodríguez-Carvajal, J. (1993). *Phys. B: Condens. Matter*, 192, 55–69. [11] Shannon, R.D. (1976). *Acta Cryst.* A32 751-767. [12] Barbier, J. & Fleet, M.E. (1987) *Journal of Solid State Chemistry* 71, 361-370. [13] Momma, K. & Izumi, F. (2008). *J. Appl. Cryst.* 41, 653–658.



Discussion.

Ambient temperature XRD on a synthetic leucite sample of KGaSi₂O₆ shows that this material has an *I*₄/*a* tetragonal structure, similar to that for KAlSi₂O₆ 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}GaSi₂O₆, 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 KGaSi₂O₆. 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 KGaSi₂O₆ shows a previously unknown phase transition from *I*₄/*a* tetragonal to *Ia-3d* 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 KGaSi₂O₆ is *I*₄/*a* tetragonal structure, similar to that for KAlSi₂O₆ leucite. There is some evidence for partial T-site order in this structure but this is not conclusive.

High temperature XRD on KGaSi₂O₆ shows a phase transition from *I*₄/*a* tetragonal (leucite structure) to *Ia-3d* 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.

Figure 2 (left) shows the 294K *I*₄/*a* tetragonal structure for KGaSi₂O₆. Figure 5 (right) shows the 1473K *Ia-3d* cubic structure for KGaSi₂O₆. Purple spheres = K cations. Green and blue spheres = disordered Si/Ga cations. Red spheres = O anions. Green polyhedra = (Si,Ga)O₄ units.

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

	KGaSi ₂ O ₆ 294K [this work]	K _{0.8} Rb _{0.2} GaSi ₂ O ₆ 294K [8]	KGaSi ₂ O ₆ 1473K [this work]
SG	<i>I</i> ₄ / <i>a</i>	<i>I</i> ₄ / <i>a</i>	<i>Ia-3d</i>
<i>a</i> (\AA)	13.1099(4)	13.157	13.6521(7)
<i>c</i> (\AA)	13.8100(4)	13.897	
<i>V</i> (\AA^3)	2373.49(12)	2405.66	2544.5(2)
T1-O(\AA)	1.61(2)	1.68(1)	1.73(3) & 1.58(4)
T2-O(\AA)	1.68(2)	1.65(3)	
T3-O(\AA)	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	