Monoclinic-orthorhombic phase transition in the $K_2MgSi_5O_{12}$ leucite analog

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**ABSTRACT**

The high-temperature cell parameters of $K_2MgSi_5O_{12}$ have been measured by X-ray powder diffraction between room temperature and 842 K. A first-order ferroelastic phase transition between the room-temperature $P2_1/c$ structure and a high-temperature $Pbca$ structure occurs at 622 K. The spontaneous strain behaves as the order parameter for the transition, following a simple Landau model. Simple lattice dynamics simulation of the magnesiosilicate framework reveals that acoustic mode softening drives the elastic instability. The first-order character of the transition is attributed to a large excess volume, which arises from collapse of the framework around the alkali site. At higher temperatures the orthorhombic cell edges converge toward a metrically cubic structure, but this transformation requires Mg-Si disorder, which was not observed on the time scale of these experiments.

**FERROELASTICITY AND ORDER-DISORDER IN LEUCITE-RELATED FRAMEWORKS**

The leucite framework structure represents an extremely stable topological arrangement. Recent studies have shown that, although comparatively insignificant in nature, the known chemical extent of the leucite family of $X^i(Y^{ii}Z_{-x}^{ii})Si_{2x}O_6$ ($0 < x < 0.5$) compounds is expanding rapidly, with over 50 such compounds reported (Torres-Martinez and West 1989; Kohn et al. 1994). Recent investigations of leucite-related compounds have, for example, focused on their catalytic properties, especially those with transition metals substituting for Al and Si in the aluminosilicate tetrahedral framework (Heinrich and Baerlocher 1991). Investigations of synthetic leucite analogs with $X:K, Rb, Cs; Y: Mg, Zn, Cu, Cd; Z=Al, Fe$ have revealed a range of symmetrically distinct structures with the same leucite topology (Bell et al. 1994a, 1994b; Bell and Henderson 1994). These studies have highlighted the possible occurrence of three structural phenomena within anhydrous leucite and its related compounds: (1) Instabilities of the tetrahedral framework may lead to displacive transitions, (2) ordering of tetrahedral cations may occur on the T sites, and (3) the size and dynamic behavior of the alkali cation in the “W” site may influence either of the above processes (for details of leucite-site nomenclature and a more general discussion of the leucite structure type the reader is referred to the review by Galli et al. 1978).

Of these, the role of Al-Si order-disorder in natural leucite, and its relation to displacive distortions, has been the subject of much recent attention. In contrast to other framework aluminosilicates, in which strong coupling is often observed between displacive instabilities and Al-Si ordering (e.g., in feldspars, see Salje (1990) or Redfern (1995) for a review), it now seems clear that long-range Al-Si order is only weakly coupled (if at all) to the displacive cubic-tetragonal phase transition in $KAlSi_4O_8$ leucite (Dove et al. 1993). Dove et al. (1996) attributed this to a low ordering temperature for leucite, which they associated with dilution of Al in the tetrahedral network (in comparison with an Al:Si ratio of 1:1). On the basis of calculations of the exchange interaction for ordering, $J_1$ (equal to the energy difference between an Al-O-Al linkage plus Si-O-Si as against two Al-O-Si linkages), and estimates of the second-nearest-neighbor interaction, $J_2$, they used a modified Bragg-Williams approach to arrive at an order-disorder transition for leucite of 300 °C. They argued that the sluggishness of Al-Si ordering kinetics below such a low $T_c$ renders the process insignificant in leucite and explains why long-range Al-Si ordering is so limited in this mineral.

Tetrahedral cation ordering is observed in certain leucite analogs, however. For example, although it appears that $Al^{3+}$ shows only limited ordering over the three T sites of natural $I4_1/a$ $KAlSi_4O_8$, studies of synthetic Fe analogs (KFeSi$_2$O$_6$) show that Fe$^{3+}$ tends to order preferentially on T$_1$ and T$_2$ rather than T$_3$ (Bell and Henderson 1994; Brown et al. 1987). More dramatic, however, is the behavior of tetrahedral cations in certain $K_2Y$-$Si$O$_4$ leucite analogs ($Y^{2+}= Mg, Zn$, and Cd; Bell et al. 1993; Kohn et al. 1994). When synthesized hydrothermally at relatively low temperatures each of these compounds crystalizes as a well-ordered low-symmetry leucite framework, whereas high-temperature dry synthesis from oxides tends to yield disordered structures, isomorphous with the $Ia3d$ high-temperature structure of natural $KAlSi_4O_8$. Coupling between tetrahedral ordering and macroscopic strain in these leucite analogs is very strong indeed, as is evidenced by crystallization of or-
ordered polymorphs in low-symmetry monoclinic and orthorhombic structures with strains of a few percent compared with the disordered \( \text{Ia3d} \) aristotype. Why does their behavior appear to be so different from that of natural \( \text{KAlSiO}_6 \) leucite?

The arguments of Dove et al. (1996) point to dilution of Al with respect to the ideal 1:1 Al:Si ratio (pertinent to traditional Bragg-Williams models) as the reason for the low ordering temperature of \( \text{KAlSiO}_6 \). It seems paradoxical, therefore, that the \( \text{K,Y}^{2+}\text{Si}^{5+}\text{O}_{12} \) ordered leucite analogs have \( \text{Y}:\text{Si} \) ratios corresponding to even greater dilution, yet they seem to have higher temperature order-disorder transitions. To provide further light on the nature and role of order-disorder, its dependence on T-site chemistry, and its coupling to elastic transitions in these framework structures, we studied the high-temperature behavior of the \( \text{K,MgSiO}_6 \) leucite analog. This material is related to natural leucite by the coupled substitution

\[
2\text{Al}^{3+} \rightarrow \text{Mg}^{2+} + \text{Si}^{4+}
\]

The relationship between the tetrahedrally ordered \( \text{P2}_1/c \) structure and the disordered \( \text{Ia3d} \) polymorph of this compound is illustrated in Figure 1. The hydrothermally synthesized monoclinic polymorph has 12 symmetrically distinct tetrahedral sites, whereas the cubic structure has just one. Another leucite-related compound \( \text{Cs,CdSiO}_6 \) crystallizes as an ordered \( \text{Pbca} \) structure, with six T sites, and possible relations among these polymorphs are shown in Figure 2. It is clear that order-disorder processes and ferroelastic phase transitions both play important roles in controlling the high-temperature behavior of these materials.

### Figure 1
Crystal structures of the monoclinic (right) and cubic (left) polymorphs of the \( \text{K}_2\text{MgSiO}_6 \) leucite analog. K atoms are shown as circles, \( \text{MgO}_4 \) tetrahedra are shown unshaded, and \( \text{SiO}_4 \) tetrahedra (and \( \text{TO}_4 \) tetrahedra in the disordered cubic phase) are shown shaded.

### Figure 2
Relationships among tetrahedral sites in the monoclinic \( \text{K}_2\text{MgSiO}_6 \) leucite analog and its higher symmetry parents. Site occupancies for \( \text{P2}_1/c \) \( \text{K}_2\text{MgSiO}_6 \) and \( \text{Pbca} \) \( \text{Cs,CdSiO}_6 \) are from Bell et al. (1994a, 1994b). The transitions between \( \text{P2}_1/c-\text{Pbca} \) and \( \text{Ibca-Ia3} \) are expected to be displacive in character, whereas \( \text{Pbca-Ibca} \) involves order-disorder of the tetrahedral cations.

### High-Temperature Powder Diffraction of \( \text{K}_2\text{MgSiO}_6 \)

The sample used for the high-temperature study was from the same batch studied by Bell et al. (1994b) and Kohn et al. (1994) and was crystallized from glass by hydrothermal synthesis at 600 °C and 0.5 kbar for 7 d. High-temperature powder X-ray diffraction patterns were collected between room temperature and 842 K using a Huber high-temperature Guinier camera. Monochromatic CuKα radiation was selected from a bent quartz monochromator. Diffraction patterns were collected on single-sided emulsion film from a thin powdered sample held in a platinum wire loop in transmission geometry.
Si powder was mixed with the sample to act as an internal 2θ standard, enabling film shrinkage corrections and zero-point corrections to be made for each exposure. The furnace stability was better than ±1 K at the lower range of the heating experiments, worsening to ±2 K at the upper end of the temperature range, with the control thermocouple positioned <1 mm from the sample. The set temperatures were independently calibrated by a secondary type-K thermocouple placed in the sample position. Diffraction patterns were collected under isothermal conditions at varying temperature intervals (Table 1), but an additional continuous heating film was recorded, which shows the behavior of Bragg reflections on heating through the temperature interval of interest in this material (Fig. 3).

Furnaces were scanned on a flat-bed scanner and positions of Bragg reflections were determined in a manner like that described by O’Neill et al. (1993). The temperature evolution of the 400, 040, and 004 group of peaks reveals the first-order nature of the phase transition, showing coexisting monoclinic and orthorhombic peaks at \( T_c \pm 20 \) K (Fig. 4) and a step in peak positions. Typically, approximately 30 Bragg peaks below 60° 2θ were measured and used for cell-parameter determination. Cell parameters were determined by least-squares refinement of measured 2θ positions, with maximum deviations between observed and calculated values ≤0.02° 2θ. The refined cell parameters are given in Table 1 and presented as a function of temperature in Figure 5. Discontinuities in all cell edges as well as the cell angle \( \beta \) are apparent at the transition point.

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**Table 1. High-temperature cell parameters of \( K_2MgSi_5O_{12} \)**

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*Note: Figures in parentheses represent one standard-deviation error.*

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**Figure 3.** Continuous-heating diffraction patterns of ordered \( K_2MgSi_5O_{12} \). Split pairs of peaks in the room-temperature monoclinic structure converge in the high-temperature orthorhombic structure. Orthorhombic peaks likewise converge to a higher symmetry structure on increasing temperature, but the material melts incongruently before a further transition occurs. The asterisk marks the position of an Si line.

**Figure 4.** Scans of the 400, 040, and 004 group of peaks in monoclinic and orthorhombic \( K_2MgSi_5O_{12} \) across the phase transition, obtained at equally spaced temperature intervals between 671 and 646 K. The coexistence of the two polymorphs across an extended temperature range near \( T_c \) and the step in peak position are both indicative of the first-order character of the transition.
magnesiosilicate framework resulting from its topological connectivity and provides an energy spectrum of the polyhedral tilt distortions, or rigid-unit modes, that the framework may undergo. Such rigid-unit mode analysis of our orthorhombic leucite structure reveals that the lowest lying acoustic branch of the tetrahedral frame-
ion that appears to control the thermodynamic order of this transition in these materials, and we might expect chemical substitution on the alkali site to modify its character. The volume collapse may be regarded in terms of secondary elastic order parameter, $Q_2$. Because volume strain is invariant under the action of symmetry operators that are lost upon the phase transition from the high-symmetry paraelastic state to the low-symmetry ferroelastic state (unlike the ferroelastic strain, which changes from $+Q$ to $-Q$ under the operation of these “lost” symmetry elements), volume strain behaves as the square of the primary ferroelastic order parameter, $Q_1$. This is a general result for any ferroelastic transition and means that the volume strain couples to the primary order parameter, $Q_1$, through a linear-quadratic term of the form $\lambda Q_1^2 Q_2$, which enters Equation 2 above. A plot of $\cos^2 \beta^*$ against cell volume confirms this linear-quadratic relationship between ferroelastic and volume strain (Fig. 8), showing the linear-quadratic coupling of the two processes.

At higher temperatures, the orthorhombic cell edges tend to converge toward a higher symmetry structure (Fig. 5A). The framework is prohibited from transforming to the cubic phase unless the Mg$^{2+}$ and Si$^{4+}$ cations disorder on the tetrahedral sites (defined by an order parameter $Q_{ad}$). Both $Q_{ad}$ and the displacive order parameter for the transition, $Q_1$, behave in the same way under the operation of the symmetry elements lost at the transition (they behave as the active representation for the phase transition): They couple bilinearly. Under equilibrium both $Q_1$ and $Q_{ad}$ would fall to zero at $T_c$ on increasing temperature, but this does not appear to happen on the time scale of our high-temperature diffraction experiments because of the kinetic control on cation order-disorder on the tetrahedral sites. If, however, the cell parameters shown in Figure 5 represent those of the equilibrium or near-equilibrium state, and some disorder has occurred, then the extrapolation of the square of the $m3mFmmm$ scalar spontaneous strain to zero provides an estimate of the temperature of the Mg-Si order-disorder transformation in K$_2$MgSi$_3$O$_8$. Scalar strain has been defined for the lowest-symmetry case by Redfern and Salje (1987). Because it is the magnitude of the spontaneous strain (a second-rank tensor property) that varies critically below a phase transition, the reduction of strain to this scalar quantity provides a convenient measure of an order parameter as a function of temperature. From Figure 9 it thus appears that the transformation to cubic symmetry would occur at 1028 K, but because of the bilinear coupling between $Q_{ad}$ and $Q_1$ and the relatively low temperatures, which make disordering times very long, this transformation has not yet been observed experimentally, not least because K$_2$MgSi$_3$O$_8$ melts at relatively low temperatures (we have not determined the melting point accurately, but our studies so far suggest that K$_2$MgSi$_3$O$_8$ melts incongruently at temperatures between 800 and 900 °C). Nonetheless, the dry-synthesized K$_2$MgSi$_3$O$_8$ leucite analog does show cubic symmetry, even at room temperature, indicating the influence of $Q_{ad}$ on the high-temperature and quench behavior of this framework structure. The transition temperature and thermodynamic character of the $P2_1/c-Pbca$ phase transition are expected to show a strong dependence on $Q_{ad}$. Furthermore, the large strain that $Q_{ad}$ induces might be expected to result in the development of tweed microstructures in ordering and disordering experiments on these leucite analogs. These experiments with K$_2$MgSi$_3$O$_8$ are difficult to conduct because of its low melting point, but investigations into the ordering and disordering of tetrahedral cations in the Rb$_2$ZnSi$_3$O$_8$ isomorph (which has a higher melting point,
allowing faster Zn-Si exchange kinetics) are currently underway.

It remains to be seen why K₂MgSi₅O₁₂ can order its tetrahedral cations but KAlSi₅O₁₂ cannot, despite the higher dilution of the ordering cation (Mg) in the former. The answer is expected to lie in the relative magnitudes of the J₁ and J₂ (nearest- and next-nearest-neighbor) exchange interaction terms. The monoclinic ordered structure of K₂MgSi₅O₁₂ reveals that Mg-Mg repulsion acts well beyond nearest- and next-nearest-neighbor tetrahedra as all MgO₄ tetrahedra are separated by two SiO₄ tetrahedra. The MgO₄ tetrahedron is considerably larger than the AlO₄ tetrahedron, leading to an enhanced avoidance rule in K₂MgSi₅O₁₂ in comparison with KAlSi₅O₁₂, and this appears to be the most important control on Tc for ordering (and hence kinetic accessibility of ordered and disordered states) in this suite of materials. This illustrates the importance of the relationship between ordering and elastic interactions in framework minerals.

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**REFERENCES CITED**


Kohn, S.C., Henderson, C.M.B., and Dupree, R. (1994) NMR studies of the leucite analogues X₂YSi₅O₁₄, where X = K, Rb, Cs; Y = Mg, Zn, Cd. Physics and Chemistry of Minerals, 21, 176-190.


Torres-Martinez, L.M., and West, A.R. (1989) Pollucite-related and leucite-related phases (ABA₂X₂O₆ and A₂BX₃O₉; A = K, Rb, Cs; B = Be, Mg, Fe, Co, Ni, Cu, Zn, Cd; C = B, Al, Ga, Fe, Cr; X = Si, Ge). Zeitschrift für anorganische und allgemeine Chemie, 576, 223-230.