The Refinement of the Crystal Structure of a Synthetic Non-Stoichiometric Sr Feldspar

H. D. Grundy,
Department of Geology, McMaster University,
Hamilton, Ontario, Canada L8S 4M1

AND JUN ITO
Department of Geological Sciences, Harvard University,
Cambridge, Massachusetts 02138

Abstract

The crystal structure of a synthetic Sr feldspar with vacancies on the alkali cation site has been refined in space group C2/m using 3-D counter diffractometer data and full-matrix least-squares methods. The chemical composition of the feldspar is Sr_{0.90}Na_{0.05}Al_{0.13}Si_{2.92}O_{8} with cell parameters a = 8.3282(8) Å, b = 12.9801(12), c = 7.1358(6), β = 115.599(3)°. The weights, 1/σ², were used throughout the refinement and the final weighted R-factor for 1193 non-equivalent reflections was 4.0 percent. The average Al/Si ratio over the Ti and T̄ sites determined by least-squares refinement are 0.48(8)Al and 0.39(8)Al, respectively.

Unit Cell and Space Group

Single-crystal precession photographs displayed diffraction symmetry C^*/. consistent with the space groups C2, Cm, and C2/m. As there is no evidence to suggest the absence of a center of symmetry, the space group C2/m was chosen in accord with other monoclinic feldspars. Long-exposure precession, rotation, and Weissenberg photographs taken with both CuKα and MoKα radiation showed that the space group C2/m was not violated by the presence of weak 'b' type reflections as appeared in stoichiometric Sr feldspar which assumes the space group I2/c (Bruno and Gazzoni, 1970). A single crystal which was unzoned, untwinned, and showed sharp optical extinction was selected for the intensity measurements; the unit cell parameters were determined by the least-squares method on 15 reflections collected on a 4-circle diffractometer. All relevant crystal data are presented in Table 1.

Intensity Data

The intensity data were collected on a Syntex P1 4-circle diffractometer using monochromatic MoKα radiation (graphite monochromator and λ = 0.71069) and the θ-2θ scan method. 1193 intensities were collected out to a 2θ of 65 degrees. Due to the highly absorbing nature of Sr, the data were corrected for absorption using an 8 point gaussian
H. D. GRUNDY, AND J. ITO

TABLE 1. Crystal Data

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>Atomic Ratios**</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Si 2.29</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Al 1.69</td>
</tr>
<tr>
<td>Fe²O₃</td>
<td>Fe³⁺ 0.00</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>V⁶⁺ 0.01</td>
</tr>
<tr>
<td>SrO</td>
<td>Sr 0.84</td>
</tr>
<tr>
<td>Na₂O</td>
<td>Na 0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>Ca 0.00</td>
</tr>
<tr>
<td>BaO</td>
<td>Ba 0.00</td>
</tr>
<tr>
<td>K₂O</td>
<td>K 0.00</td>
</tr>
</tbody>
</table>

Tetrahedral ions \( \Sigma = 3.99 \)

Space group: \( C2/m \)

Linear absorption coefficient: 79.60 cm\(^{-1}\)

Crystal size: \( 0.14 \times 0.10 \times 0.08 \) mm.

Radiation: Mo (\( \lambda = 0.71069 \))

No. of non equivalent reflections \( F_{\text{obs}} > 0 \): 893

Final R (weight 1/\( \sigma^2 \)): 4.0%

Density (calc): 2.98

Density (obs): 2.99

**Analysis by Jun Ito

***Mainly impurities (probe analyses by D. T. Griffith, personal communication P. H. Ribbe)

The extinction parameter as proposed by Zachariasen (1968) and resulted in a weighted \( R \)-factor of 4.0 percent (weight = 1/\( \sigma^2 \)) for the observed intensities. At this point, the population of the alkali cation site was set to agree with the chemical analysis and the population of the \( T_1 \) site was included as a variable; the refinement was continued with the bulk chemistry of the \( T_1 \) and \( T_2 \) sites constrained to the Al/Si ratio determined by the chemical analysis.

The structure converged with weighted and unweighted \( R \)-factors of 3.9 and 5.0 percent, respectively, for the observed 893 intensities and 4.0 and 7.3 percent for all of the 1193 intensities measured. The weighted \( R \)-factors for intervals of magnitude of \( F_{\text{obs}} \) showed no systematic effects; however, the weighted \( R \)-factors for intervals of \( \sin \theta/\lambda \) showed a slight systematic increase with increasing size of this parameter, probably because of imperfect correction for absorption.

The final positional parameters and equivalent isotropic temperature factors are presented in Table 3. Interatomic distances and angles were computed using the program ERRORS (Finger, 1969, personal communication) in which the associated standard deviations are those derived from the full matrices of

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1 X-Ray72 X-ray crystallographic system (Stewart et al, 1972).
errors both in the atomic positions and the cell parameters. These are listed in Tables 4 and 5 respectively.

**Discussion**

The structure of the Sr feldspar is very similar to the structures of the monoclinic K feldspars. This can be illustrated most easily by a comparison of the results of a bond strength calculation (Brown and Shannon, 1973) made on representative monoclinic K feldspars (see Table 5 for references). To emphasize the great similarities, bond strengths were normalized by dividing them by the sum of the bond strengths around the cation and expressing them as a percentage (Table 6). A more detailed examination of the table reveals that, in the case of Sr feldspar, the $O_A2$ anion site deviates somewhat from the general pattern. This is not unexpected because the differing chemistry of the alkali cation site produces a small change in the internal geometry which is reflected in the lattice parameters. Due to the similar ionic sizes of Sr$^{2+}$ and K$^+$ (Shannon and Prewitt, 1969), the lattice parameters of sanidine ($a$ 8.546, $b$ 13.037, $c$ 7.178, $\beta$ 115.97, Weitz, 1972) and Sr feldspar (Table 1) are comparable. However, in the Sr feldspar, the effective increase in bond strength between $O_A1$, $O_A2$ and $O_B$ and Sr leads to a shortening of the $a$ and $b$ dimensions and a rotation of the tetrahedron causing a decrease in $c$ and $\beta$ relative to sanidine. The shortening of the $a$ dimension is further enhanced by vacancies on the alkali cation site, to which it appears to be par-

**Table 2. Structure Factors for Synthetic Sr Feldspar**

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>F(OBS)</th>
<th>F(CALC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5407</td>
<td>0.5407</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.6007</td>
<td>0.6007</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.5407</td>
<td>0.5407</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.5407</td>
<td>0.5407</td>
</tr>
</tbody>
</table>
particularly sensitive, as may be seen by a comparison of the lattice parameters of this feldspar with those of a stoichiometric Sr-feldspar ($a$ 8.389; $b$ 12.972; $c$ 14.262; $\beta$ 115.43) examined by Nager, Hoffman, and Nissen (1969).

**Tetrahedral Cation Sites**

The Al content of each of the tetrahedral sites $T_1$ and $T_2$ was determined during the least-squares refinement by varying the population of Al on the $T_1$ site while applying the following constraints:

<table>
<thead>
<tr>
<th>Table 3. Site Population Atomic Coordinates and Temperature Factors$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
</tr>
<tr>
<td>$T_1$</td>
</tr>
<tr>
<td>$T_2$</td>
</tr>
<tr>
<td>$T_3$</td>
</tr>
<tr>
<td>$T_4$</td>
</tr>
<tr>
<td>$T_5$</td>
</tr>
<tr>
<td>$T_6$</td>
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<tr>
<td>$T_7$</td>
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<tr>
<td>$T_8$</td>
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<tr>
<td>$T_9$</td>
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<tr>
<td>$T_{10}$</td>
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<tr>
<td>$T_{11}$</td>
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<tr>
<td>$T_{12}$</td>
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<tr>
<td>$T_{13}$</td>
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<tr>
<td>$T_{14}$</td>
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<tr>
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<tr>
<td>$T_{17}$</td>
</tr>
<tr>
<td>$T_{18}$</td>
</tr>
<tr>
<td>$T_{19}$</td>
</tr>
<tr>
<td>$T_{20}$</td>
</tr>
</tbody>
</table>

$^*$defined as $\exp[\frac{1}{2}(\beta_1 x^2 + \beta_2 y^2 + \beta_3 z^2 + \beta_{12} xy + \beta_{13} xz + \beta_{23} yz)]$
Table 4. Bond Multiplicities and Interatomic Distances (Å)

<table>
<thead>
<tr>
<th></th>
<th>T₁ Tetrahedron</th>
<th>T₂ Tetrahedron</th>
<th>SR Polyhedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁ - O₁</td>
<td>1.679(2)</td>
<td>1.505(2)</td>
<td>2.660(4)</td>
</tr>
<tr>
<td>T₁ - O₂</td>
<td>1.625(4)</td>
<td>1.616(2)</td>
<td>2.446(6)</td>
</tr>
<tr>
<td>T₁ - O₃</td>
<td>1.580(3)</td>
<td>1.708(2)</td>
<td>2.843(5)</td>
</tr>
<tr>
<td>T₁ - O₄</td>
<td>1.542(3)</td>
<td>2.548(2)</td>
<td>2.314(8)</td>
</tr>
</tbody>
</table>

Mean T₁ - O 1.670

Mean T₂ - O 1.677

Table 5. Tetrahedral Interatomic Angles (°)

<table>
<thead>
<tr>
<th></th>
<th>T₁ Tetrahedron</th>
<th>T₂ Tetrahedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₁₁ - O₂</td>
<td>2.604(5)</td>
<td>2.659(5)</td>
</tr>
<tr>
<td>O₁₁ - O₃</td>
<td>2.830(5)</td>
<td>2.617(7)</td>
</tr>
<tr>
<td>O₁₁ - O₄</td>
<td>2.769(5)</td>
<td>2.785(7)</td>
</tr>
<tr>
<td>O₂ - O₃</td>
<td>2.735(5)</td>
<td>2.735(5)</td>
</tr>
</tbody>
</table>

Mean O - O 2.723

The results are given in Table 7. In order to test the validity of these, the Al content of each tetrahedral site was calculated from the mean T-O bond length using the equations of Ribbe and Gibbs (1969) and Jones (1968); these are also shown in Table 7, and the agreement is fairly good. A further estimate of the Al content is available from the bond strength calculation made on this feldspar (Table 6); this correlates quite well with the value determined by least-squares refinement. From these results and comparable results on a number of amphiboles (Hawthorne and Grundy, 1973a, b), it is apparent that although the difference between the Al and Si scattering factor curves is extremely small, meaningful estimates may be obtained by this method providing that the major sources of systematic error have been removed from the data. The T₁ site is enriched in Al relative to the T₂ site as is the case in orthoclase.

The equivalent isotropic temperature factors of the tetrahedral sites (Table 3) are appreciably larger than in anorthite (Wainwright and Starkey, 1971), but comparable with those observed in the monoclinic K feldspars (references, Table 6). This effect can be attributed in part to the Al/Si disorder which exists on both the T₁ and T₂ sites. The anisotropic nature of the vibrational ellipsoids (Table 8, Fig. 1) is probably the result of positional disorder. The
the space group C2/m, then the resulting positional disorder would produce ellipsoids with elongations on the T1 and T2 sites of 0.074 Å and 0.070 Å, respectively. These values are close enough to the r.m.s. values for the feldspar under study (Table 8) so as not to preclude the possibility that a disorder of this type contributes to the anisotropy on the tetrahedral sites; the absence of reflections which violate the C2/m symmetry, however, suggests that any deviation from C2/m symmetry must be small and that the high degree of long-range order observed in celsian is not present in this non-stoichiometric feldspar. The presence of short-range order is to be expected because of the clustering of the silica-rich tetrahedra about any vacant alkali cation sites.

Alkali Cation Site

The Sr cation is markedly anisotropic (Table 8, Fig. 1); however, Fourier and difference-Fourier sections through the site reveal no unusual features; its largest vibrations are in directions of least electrostatic resistance, similar to the K feldspars (Brown and Bailey, 1964).

Stoichiometry in the Feldspars

The possibility of non-stoichiometric feldspars has been a much discussed topic since Schwantke (1909) proposed a theory for the origin of myrmekite by the dissociation of the phase Ca(AlSiO₃)₂ into anorthite and quartz according to the reaction

\[ \text{Ca(AlSiO₃)₂} \rightarrow \text{CaAl₂Si₂O₈} + 4\text{SiO₂} \]

He argued that such a phase was present in many feldspars which, on chemical analysis, showed an excess of silica.

More recent work on the chemical composition has confirmed that many feldspars do have an excess of silica which cannot be attributed to analytical error (Perry, 1968, p. 211; Sturt, 1970, p. 824; Weill et al, 1970; Wenk and Wilde, 1973). Carman and Tuttle (1967) reported on the basis of their experimental work on the alkali feldspar solvus that sanidine can indeed tolerate small amounts of silica in solid solution; in the case of the alkali feldspars this results in an Al/Si ratio less than one-third and
a deficiency of alkali cations. An alternative interpretation of their synthetic data is that the appearance of quartz during the reheating process was due to leaching of the alkalies; however, Morse (1969) discounts this criticism and suggests that the alkali feldspars can indeed be non-stoichiometric.

Preliminary annealing experiments made at 1000°C for two weeks on large crystals of non-stoichiometric Sr feldspar resulted in the appearance of very weak b-type reflections on precession photographs exposed for 24 hours (MoKα radiation). The crystals lost some transparency but no clearly exsolved SiO₂ phase could be detected optically. Similar annealing experiments using a non-stoichiometric synthetic anorthite (J. Ito, in preparation) produced a change in the space group of the anorthite from C1 to P1 and finally P1 and the appearance of a clearly visible exsolved phase, presumably SiO₂. A possible mechanism by which non-stoichiometric Sr and Ca feldspar could exsolve SiO₂ may involve the onset of long range order and thereby generation of stoichiometric Sr and Ca feldspars; the vacant cation sites with the expected short-range ordering of the silica-rich tetrahedra about them would act as nucleation centers for the myrmekitic type intergrowths.

This work provides crystallographic evidence for the existence of a non-stoichiometric feldspar. Although this particular feldspar is not representative of naturally-occurring feldspar compositions and has been grown under somewhat specialized conditions, it seems highly probable that naturally occurring feldspars with a partially-vacant alkali cation site can and do exist, and serious consideration should be given to the effect of these on the physical and chemical properties of feldspar.

Acknowledgments

One of the authors (H. D. Grundy) is grateful to the National Research Council of Canada for research grants awarded to assist this work. The authors are indebted to Drs. B. J. Burley, C. Calvo, and F. C. Hawthorne for critical review and discussion of the manuscript.

References


Manuscript received, January 22, 1974; accepted for publication July 2, 1974.