

Ferroelastic phase transition in SrAl₂Si₂O₈ feldspar at elevated pressure

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Abstract

Synthetic end-member strontium feldspar (SrAl₂Si₂O₈) has been studied in a diamond-anvil cell at elevated pressures up to 10.3 GPa using energy-dispersive X-ray powder diffraction. Cell parameters have been refined between ambient pressure and 6 GPa. SrAl₂Si₂O₈ undergoes a ferroelastic phase transition from the ambient pressure monoclinic space group *I*2/*c* to the high-pressure triclinic space group $\bar{1}$ at 3.2 ± 0.4 GPa. The transition appears to be first-order and the ferroelastic and co-elastic components of the spontaneous strain tensor have been calculated.

KEYWORDS: strontium, feldspar, ferroelasticity, phase transition, diamond-anvil cell.

Introduction

STRONTIUM feldspar, SrAl₂Si₂O₈, is topologically isostructural with anorthite, CaAl₂Si₂O₈, with a three-dimensional framework of [SiO₄] and [AlO₄] tetrahedra in which divalent cations occupy large cavities (*M*-sites). In triclinic anorthite, all the *M*-sites are occupied by Ca²⁺ which has a smaller ionic radius than the ideal *M*-cation size for plagioclase (Jensen, 1973). The topochemical monoclinic symmetry of the framework is reduced to triclinic around these small Ca cations. On substitution of a larger cation such as Sr²⁺, the framework is held open about the *M*-sites, thereby maintaining the monoclinic symmetry. Feldspars in the Ca_{1-x}Sr_xAl₂Si₂O₈ solid solution therefore undergo a distortive phase transition from triclinic to monoclinic (Baubauer and Nager, 1981; McGuinn and Redfern, 1994) at room temperature as a result of increasing Sr-content. The critical composition for the transition in well-ordered samples is Ca_{0.09}Sr_{0.91}Al₂Si₂O₈ and the transition appears essentially second-order (although secondary ordering processes complicate the transition character; McGuinn and Redfern, 1993).

The same transition has been described as a function of temperature in triclinic samples of composition Ca_{0.90}Sr_{0.10}Al₂Si₂O₈ to Ca_{0.70}Sr_{0.30}Al₂Si₂O₈ (Bambauer and Nager, 1981) and the plane of the transition has been mapped in temperature-composition space.

Hazen (1977) has described the manner in which temperature, pressure and composition may be considered as analogue intensive parameters in

mineral systems such as the feldspars. This is particularly true for ferroelastic phase transitions (such as the *I*2/*c*- $\bar{1}$ transition in Ca_{1-x}Sr_xAl₂Si₂O₈) in these framework materials where the influence of internal pressure at the *M*-site (changing composition and temperature effects) often corresponds to the primary conjugate field acting on the order parameter (strain) in the same way as external pressure. Since this means that volume effects and hydrostatic pressure are essentially treated as identical, the general rule is that increasing pressure acts analogously to decreasing temperature. However, this cannot always be taken for granted. Angel (1988), for example, discovered that on increasing pressure, anorthite underwent a co-elastic distortive transition at around 2.55 GPa in ordered samples, the symmetry increasing from $\bar{1}$ to $\bar{1}$ on increasing pressure. This appears to be the same transition as that which is observed on heating anorthite above 510 K. However, recent single-crystal *in-situ* X-ray diffraction studies of the $\bar{1}$ to $\bar{1}$ transition suggest that the high-temperature, low-pressure structure differs from the high-pressure, low-temperature structure and that a crossover type transition exists between the two structures (Hackwell and Angel, 1993). This $\bar{1}$ to $\bar{1}$ transition presumably also occurs upon increasing Sr-content in Ca-rich anorthites, since Ca-Sr feldspars of intermediate composition and Sr-rich composition are identified as showing body-centred translational symmetry. This behaviour has yet to be verified, however, by experimental observation. This work focuses on

the less subtle behaviour of Sr-feldspars at the ferroelastic $I\bar{1}$ to $I2/c$ transition. While this transition has been observed as a function of temperature and composition in Ca-containing members of the solid solution, the question of the stability of monoclinic 2:2 (Al:Si) feldspars at high pressure has not been addressed. The purpose of this work is to ascertain whether or not pure $\text{SrAl}_2\text{Si}_2\text{O}_8$ feldspar behaves according to Hazen's (1977) prediction and undergoes a monoclinic-triclinic symmetry reduction on increasing pressure. Since only 9% of the M -cations need be replaced by Ca to induce this distortion at room temperature, the stability of the $I2/c$ polymorph might reasonably be expected to be restricted. We have explored such stability in a powder diffraction study of $\text{SrAl}_2\text{Si}_2\text{O}_8$ held in the diamond anvil cell at pressures up to 10 GPa.

Experimental methodology

Synthesis. The $\text{SrAl}_2\text{Si}_2\text{O}_8$ sample used in this experiment was prepared using the pyrosynthesis technique outlined by McGuinn and Redfern

(1994). The sample was prepared by accurately weighing out a stoichiometric mixture of the component oxides Al_2O_3 , SiO_2 , and SrCO_3 (the Sr component was included in the initial mixtures as the carbonate due to the extremely hygroscopic nature of the oxide). The mixture was then finely ground by hand in an agate mortar and annealed at 1 atmosphere in a Pt crucible. The sample was heated at 1073 K for 24 hours, then at 1573 K for 24 hours to remove the CO_2 from the SrCO_3 before the mixture was finally annealed at 1773 K for 72 hours. The sample was air-cooled without any specific additional quench. The synthesis products were slightly sintered and were disaggregated by crushing in an agate mortar. Room-temperature powder diffraction confirmed the sample as single phase $\text{SrAl}_2\text{Si}_2\text{O}_8$ feldspar with cell parameters in agreement with those reported by Bambauer and Nager (1981).

High-pressure X-ray powder diffraction. The sample was pressurized using a lever-arm diamond-anvil cell and energy-dispersive X-ray diffraction spectra of the sample were recorded at pressures between ambient and 10 GPa. The

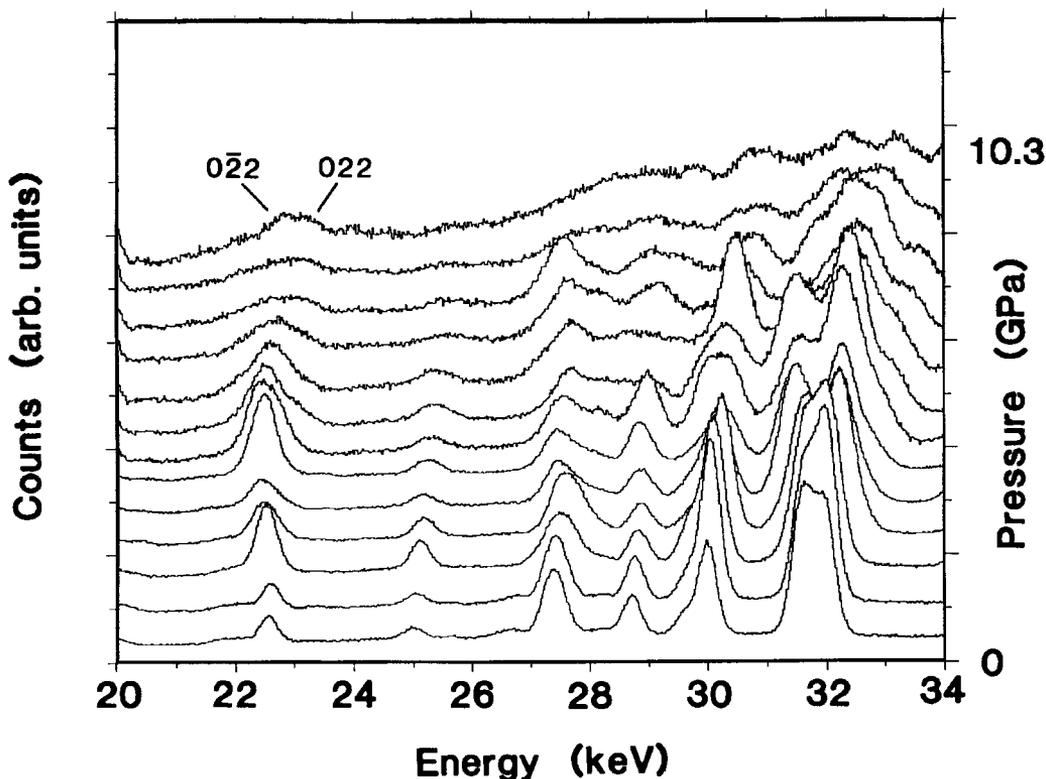


FIG. 1. Part of (20–34 keV) the energy-dispersive powder diffraction patterns of $\text{SrAl}_2\text{Si}_2\text{O}_8$ between ambient pressure and 10.3 GPa. Splitting of the 022 reflection corresponds to a monoclinic-triclinic phase transition.

TABLE 1. High-pressure unit cell parameters of $\text{SrAl}_2\text{Si}_2\text{O}_8$

P(GPa)	a	b	c	α	β	γ	Volume
0.00	8.384(4)	12.965(7)	14.258(8)	90.00	115.37(4)	90.00	1400(1)
0.52	8.364(6)	12.96(1)	14.24(1)	90.00	115.40(7)	90.00	1395(1)
1.18	8.353(6)	12.95(1)	14.22(1)	90.00	115.4(1)	90.00	1389(1)
2.76	8.33(1)	12.93(1)	14.19(2)	90.00	115.4(1)	90.00	1381(1)
3.48	8.33(1)	12.96(1)	14.14(2)	90.3(1)	115.2(1)	90.14(9)	1382(1)
3.67	8.32(1)	12.94(2)	14.15(2)	90.6(1)	115.1(1)	90.3(1)	1380(1)
4.53	8.32(1)	12.94(2)	14.13(2)	90.9(1)	115.1(1)	90.4(1)	1379(1)
5.30	8.33(1)	12.93(2)	14.14(2)	91.0(1)	115.1(1)	90.4(1)	1379(1)

sample was mixed with a small amount of NaCl, which acted as an internal pressure calibrant, and the mixture was ground by hand using an agate pestle and mortar. The mixture was mounted in a

pre-indented Inconel steel gasket of internal diameter 150 μm . A wet 4:1 methanol-ethanol mixture was used as a hydrostatic pressure transmitting medium. This mixture is hydrostatic

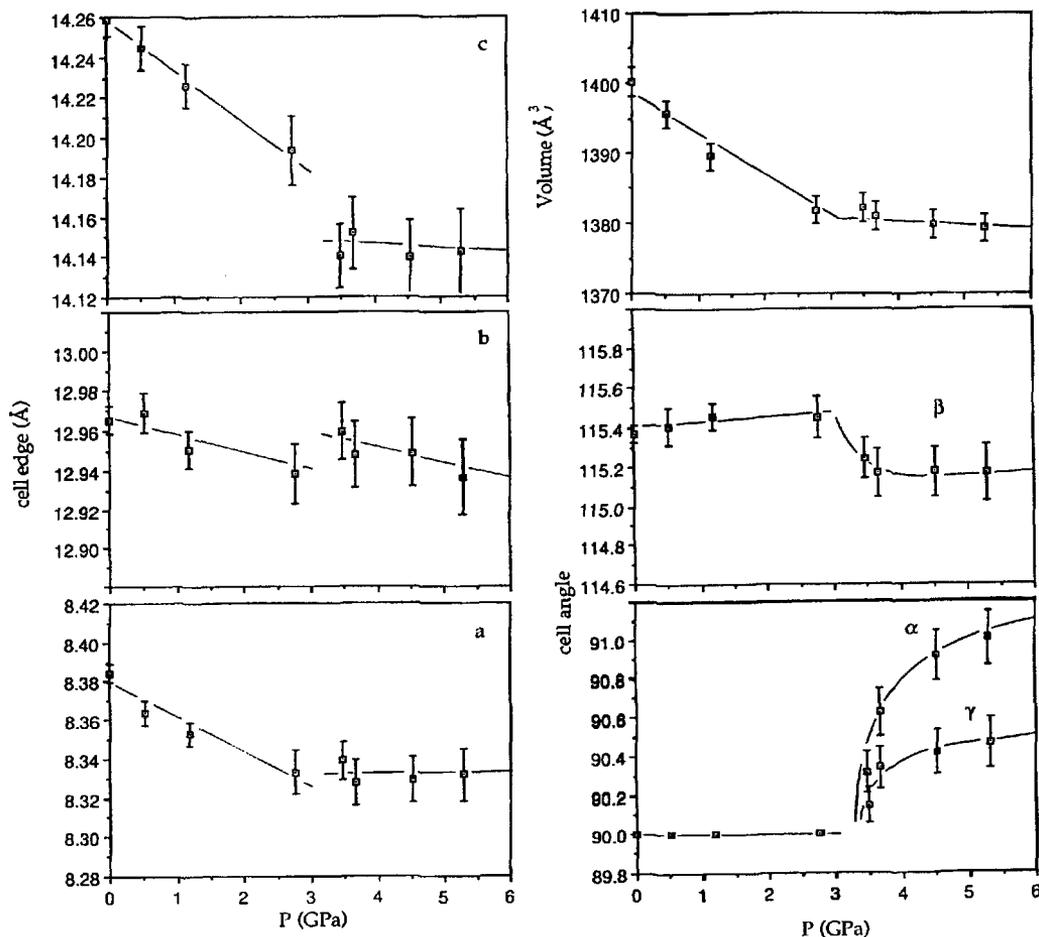


FIG. 2. Unit-cell parameters of $\text{SrAl}_2\text{Si}_2\text{O}_8$ as a function of pressure. Error bars indicate $\pm 1\sigma$.

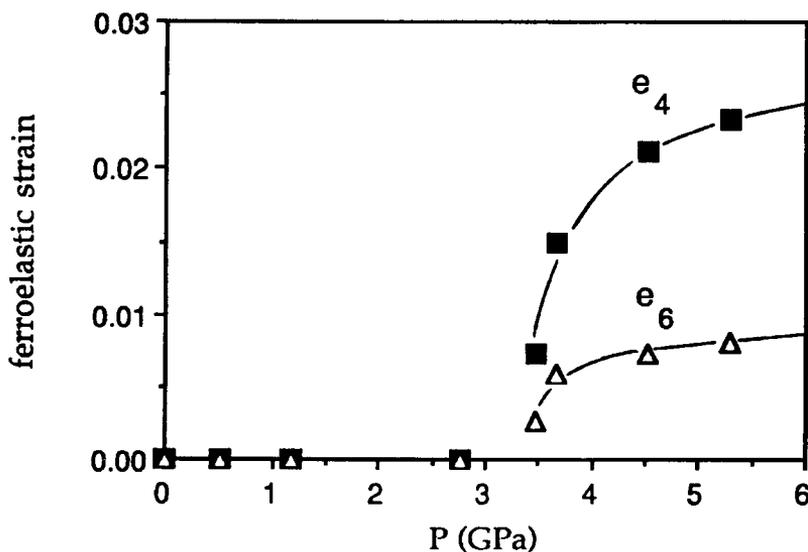


FIG. 3. Ferroelastic components of the spontaneous strain above the $I2/c-\bar{1}$ transition in $\text{SrAl}_2\text{Si}_2\text{O}_8$. This strain is coupled linearly to the order parameter, Q , for the transition.

at pressures beyond 10 GPa (Piermarini *et al.*, 1973). The high-pressure X-ray powder diffraction was performed on Wiggler 9.7 at the SERC synchrotron radiation source, Daresbury UK.

The detector angle was kept constant at $2\theta = 6.866^\circ$, determined from the diffraction peak positions of a silicon standard. Each energy-dispersive X-ray diffraction spectrum was measured between 5 and 120 keV, with the most significant diffraction information occurring between 20 and 60 keV. Bragg reflections were measured by fitting Gaussian curves to the corrected background diffracted intensity. The patterns were indexed according to the cell reported by Bruno and Gazzoni (1970). The NaCl peaks were measured separately from the feldspar peaks and the cell parameters of each phase calculated by a least squares refinement. The NaCl cell parameters were used to determine the pressure for each spectrum from the equation of state for NaCl of Decker (1971). Unfortunately it was not possible to refine feldspar cell parameters at higher pressures due to a combination of reduced signal:noise ratio caused by scattering from the diamond and the complex interference of the splitting diffraction peaks. Lower-pressure diffraction patterns were indexed, however, with up to 40 recorded Bragg reflections used for refinement. The lowest pressure data were initially fitted constraining α and γ to monoclinic values.

Results

The recorded X-ray diffraction spectra are shown in Fig. 1.

The NaCl peaks are easily distinguishable from the feldspar reflections. They show no significant broadening, suggesting that pressure conditions remained reasonably hydrostatic, even up to the highest pressures. Increasing pressure has two effects on the appearance of the spectra. Firstly, the feldspar diffraction becomes weak and impossible to index at high pressures (between 6.0 and 10.3 GPa). This may indicate incipient amorphization. Lowering of the pressure to ambient results in the return of a strong diffraction pattern. More importantly, for the purposes of this investigation, certain Bragg reflections in the lower-pressure monoclinic diffraction pattern are seen to split in the high-pressure spectra. This is apparent, for example, in the pressure-dependent behaviour of the monoclinic 022 peak, which splits to a triclinic pair (022 and $0\bar{2}2$) on increasing pressure. Such peak-splitting is interpreted, therefore, in terms of a distortive transition from the low-pressure $I2/c$ monoclinic structure to a triclinic cell (almost certainly $\bar{1}$) on increasing pressure. The refined cell parameters are shown in Fig. 2 and Table 1. The refined cell angles provide the best evidence of the existence of a transition and the pressure-

dependence of the triclinic distortion. The α and γ angles increase from 90° at ambient to 91.0° and 90.5° respectively at 5.3 GPa. The first deviation from 90° occurs at around 3.3 ± 0.3 GPa and is a sharp discontinuous break, suggesting a first-order character to the transition. The β cell angle also shows a discontinuity at approximately 3.3 ± 0.3 GPa.

Within experimental error, the cell edges all decrease linearly with increasing pressure and show breaks in the rate of decrease at about 3.0 ± 0.3 GPa. There is a resultant volume decrease with a marked change in slope at about 3.0 ± 0.3 GPa. These results would place the transition at 3.2 ± 0.4 GPa.

Discussion

The $I2/c-I\bar{1}$ symmetry reduction in $\text{SrAl}_2\text{Si}_2\text{O}_8$ conforms with the Aizu group $2/mF\bar{1}$ (Aizu, 1970) and is therefore potentially ferroelastic. The spontaneous strain which arises in the low-symmetry triclinic phase as a result of the ferroelastic transition can be used as a primary order-parameter for the transition. The only symmetry-allowed ferroelastic strain components for a monoclinic-triclinic transition are e_4 and e_6 , which relate to shears in the (100) and (001) planes respectively. The ferroelastic strain components have been calculated using the equations of

Redfern and Salje (1987) and are shown in Fig. 3. Both ferroelastic strain components show a small discontinuous (first-order) increase from zero at the transition; e_4 then increases continuously to approximately 0.025 at 6.0 GPa while e_6 is smaller, only increasing to approximately 0.009 at 6.0 GPa.

As with the $I2/c-I\bar{1}$ transition in room-temperature Sr-Ca feldspars, the ferroelastic framework collapse is not the only process which operates at the transition; there are secondary co-elastic processes operating which contribute to the spontaneous strain (although it is not certain whether the same co-elastic processes which operate in the room-temperature transition are operating in the high-pressure transition). Since these co-elastic processes are not subject to the same symmetry restrictions as the ferroelastic processes, they can manifest themselves as strain components which are not required for the ferroelastic process. Such 'non-symmetry breaking' strain components (i.e. e_1 , e_2 , e_3 , and e_5) are observed at the high-pressure transition and are shown in Fig. 4. The are around an order of magnitude smaller than the ferroelastic components. Both e_5 and e_3 show discontinuities at the transition before increasing to 0.005 and 0.003 respectively at 6.0 GPa. Curiously, e_1 and e_2 show no evidence of a discontinuous increase at the transition but seem to increase continuously and linearly straight from the transition to 0.004 and 0.001 respectively at 6.0 GPa.

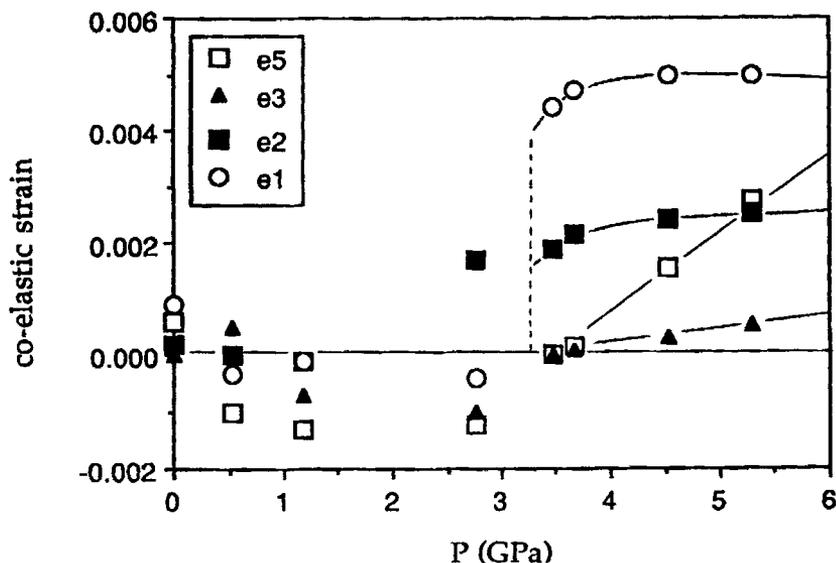


FIG. 4. Co-elastic components of the spontaneous strain above the $I2/c-I\bar{1}$ transition, which couple in the lowest order as $e \propto Q^2$ above the transition point.

To conclude, a previously undescribed monoclinic–triclinic transition has been observed at elevated pressure in strontium feldspar. The transition occurs at 3.2 ± 0.4 GPa and is first-order, although the step in the order parameter, ΔQ , at the transition is relatively small. The structure of strontium feldspar appears to be incompressible relative to the common end-member feldspars, and hardens at the phase transition. These results show that energy-dispersive powder diffraction may usefully be applied to high-pressure studies of poorly-scattering low-symmetry solids. This technique is especially useful in pinpointing ferroelastic transitions such as the $I2/c$ – I transition reported here, since ferroelastic twinning in the high-pressure (low-symmetry) phase does not compromise the powder diffraction data. The essential order parameters are revealed in the macroscopic strain determined from cell parameters. A detailed microscopic analysis of the $I2/c$ – I transition in $\text{SrAl}_2\text{Si}_2\text{O}_8$, however, awaits further single-crystal studies. These authors have recently grown single-crystals of strontium feldspar hydrothermally, and these should prove amenable to detailed structural analysis.

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