

High-pressure equation of state and phase transition in $\text{PbAl}_2\text{Si}_2\text{O}_8$ feldspar

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ABSTRACT

In situ high-pressure X-ray diffraction study was performed on synthetic lead feldspar with composition $\text{PbAl}_2\text{Si}_2\text{O}_8$ (PbFsp). The crystals were synthesized from the melt and thermally treated at $T = 1150$ °C for 12 h and at $T = 1000$ °C for 70 h. At room condition the unit-cell parameters are $a = 8.3936(4)$, $b = 13.0498(7)$, $c = 14.3258(8)$ Å, $\beta = 115.281(6)^\circ$, $V = 1418.9(1)$ Å³; space group: $I2/c$; $Q_{\text{od}} = 0.7$.

A single-crystal of lead feldspar was loaded in an ETH-type diamond-anvil cell and unit-cell parameters were measured at 26 different pressures up to 8.4 GPa at room T . The evolution with P of the unit-cell parameters and volume shows a strong discontinuity between 7.7 and 8.2 GPa indicating a first-order phase transition. The discontinuous character of the transition is especially noticeable in the behavior of the β angle, which decreases from 114.83° to 114.03° , and in the b parameter, which reduces from 12.746 to 12.567 Å.

In the P range 0.0001–7.72 GPa, the trend shown by the axial compressibility ($\beta_a > \beta_c > \beta_b$) is similar to that observed in the previous HP powder diffraction study, performed on lead feldspar using high-brilliance synchrotron radiation up to 7.1 GPa.

In the P range 0.0001–4.27 GPa at room T , the P - V data of the $I2/c$ lead feldspar were fitted with a second-order Birch-Murnaghan EoS. The parameters obtained are: $V_0 = 1422.2(1)$ Å³ and $K_{T0} = 76.4(9)$ GPa. At $P > 4.27$ GPa, the volume values deflect from the BM2 curve and show a volume softening, precursor of the reported HP phase transition. A volume softening was recently observed in strontium feldspar (SrFsp) above 4.2 GPa.

A second crystal of PbFsp was loaded in the DAC cell and in situ high-pressure X-ray diffraction intensities were measured at $P = 0.0001, 2.4, 3.1, 5.4, 6.0, 7.2, 8.4,$ and 9.7 GPa. The appearance of c and d -type reflections at 8.4 GPa, the analysis of the systematic absence and the structural refinements indicate the HP first-order transformation as an $I2/c$ - $P2_1/c$ phase transition. Structural results show that the main variations with compression in lead feldspar are in Pb-O bond lengths and in T-O-T bond angles, while T-O distances and O-T-O angles do not change meaningfully, indicating that the Si,Al tetrahedra behave with pressure as a rigid body. Changes observed in the compressional behavior of the structure between 3 and 5 GPa could explain the softening observed at $P > 4$ GPa in the volume compressibility.

The results obtained in the present work allow comparing the pressures of the HP $I2/c$ - $P2_1/c$ phase transition occurring in lead feldspar with those observed in alkaline-earth feldspars.

Keywords: Crystal structure, high-pressure studies, lead feldspar, equation of state, phase transition

INTRODUCTION

Several studies were performed on natural and synthetic feldspars to investigate their equations of state (EoS) and symmetry changes with pressure; however, taking into account the complexity of their potential chemical and structural arrangements, the number of high-quality data available in literature remains still limited. In a review on the behavior of feldspars at high-pressure conditions, Angel (1994) and Ross (2000) observed that the tetrahedra of the framework behave like almost a rigid body and the major compressional mechanism is the T-O-T bond bending. The degree of Al,Si order influences the HP elastic behavior of feldspars and, in particular, an increase of Al,Si disorder results in a small decrease in bulk modulus (Angel et al. 1988; Angel 1994; Downs et al. 1994; Allan and Angel 1997; Benusa

et al. 2005; Sochalski-Kolbus et al. 2010; Curetti et al. 2011b).

In feldspars with Al:Si ratio equal to 1:1, the symmetry at room condition is determined by the non-tetrahedral M cation: triclinic $P\bar{1}$ (or $\bar{1}$) space group is observed when the M-site is occupied by Ca (anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, An, Megaw et al. 1962), monoclinic $I2/c$ symmetry when the M-site is occupied by a larger cation as Sr, Pb, Ba (strontium feldspar, $\text{SrAl}_2\text{Si}_2\text{O}_8$, SrFsp, Chiari et al. 1975; lead feldspar, $\text{PbAl}_2\text{Si}_2\text{O}_8$, PbFsp, Bruno and Facchinelli 1972; $\text{BaAl}_2\text{Si}_2\text{O}_8$, celsian, Newman and Megaw 1960). Along the anorthite-strontium feldspar (An-SrFsp) join at ambient conditions, the structure of feldspars changes with composition from $P\bar{1}$ to $I2/c$, through an intermediate $\bar{1}$ structure. The $P\bar{1}$ - $\bar{1}$ phase transition occurs near $\text{An}_{50}\text{SrFsp}_{50}$ composition (Phillips et al. 1997; Tribaudino et al. 2000, 2005) and the $\bar{1}$ - $I2/c$ zone-center displacive ferroelastic transition, strongly affected by different Al,Si order (Tribaudino et al. 1993, 2009), was observed near $\text{An}_{10}\text{SrFsp}_{90}$ in ordered feldspars (Bambauer and Nager

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1981; McGuinn and Redfern 1994) and near $\text{An}_{20}\text{SrFsp}_{80}$ in more disordered samples (Bruno and Gazzoni 1968). The same $\bar{I}\bar{1}$ - $I2/c$ transition can be observed with increasing temperature in Sr-rich feldspars that are triclinic at room temperature and the temperature of the transition changes with the degree of order at constant composition (Bruno and Gazzoni 1968; Nager et al. 1969; Tribaudino et al. 1993; McGuinn and Redfern 1997; Benna and Bruno 2003).

Regard lead feldspar, Benna et al. (1996) synthesized both disordered ($C2/m$ space group, absence of b -type superlattice reflections, macroscopic order parameter $Q_{\text{od}} = 0$) and ordered ($I2/c$ space group, $Q_{\text{od}} = 0.9$) configurations. At room temperature, in the Pb-rich region of the anorthite-lead feldspar (An-PbFsp) join, the $\bar{I}\bar{1}$ - $I2/c$ phase transition occurs near $\text{An}_{10}\text{PbFsp}_{90}$ composition (Benna et al. 2000).

The volume compressibility of the Al:Si = 1:1 feldspars was frequently determined in a limited pressure range because these crystals experience phase transitions at low pressures. Angel et al. (1988) studied the compressibility of anorthite and found a reversible first-order $P\bar{1}$ to $\bar{I}\bar{1}$ phase transition between 2.6 and 3.0 GPa, by means of in situ HP investigations. An increase in the pressure of the $P\bar{1}$ - $\bar{I}\bar{1}$ transition with increasing disorder, together with a trend from first-order character to a more continuous transition, was observed by Angel (1992). Using in situ HP Raman spectroscopy, Daniel et al. (1995) observed in anorthite a further reversible transition at about 10 GPa, associated with drastic changes in the position of the vibrational modes, but the newly formed phase was not identified. In the $\text{An}_{20}\text{SrFsp}_{80}$ feldspar, triclinic at room temperature, Nestola et al. (2004) observed a first-order transformation from $\bar{I}\bar{1}$ to $I2/c$ at $P \sim 4.3$ GPa, and a further transition, strongly first order, from monoclinic $I2/c$ to monoclinic-II phase at $P \sim 7.3$ GPa. This second transformation was defined as an $I2/c$ - $P2_1/c$ transition by Benna et al. (2007) and the $P2_1/c$ configuration was studied by HP in situ single-crystal XRD. The volume bulk modulus of $P\bar{1}$ anorthite is 83.3 GPa (Hackwell and Angel 1992) and a value of around 82.5 GPa has been extrapolated for $\bar{I}\bar{1}$ anorthite from the compression behavior of plagioclases (Angel 2004). Since the volume bulk modulus of the triclinic $\text{An}_{20}\text{SrFsp}_{80}$ is 88.7 GPa, the substitution of 80% of $\text{SrAl}_2\text{Si}_2\text{O}_8$ component into the anorthite structure causes a slight increase in the bulk modulus (Pandolfo et al. 2011). In recent studies, Pandolfo et al. (2011) and Mrosko et al. (2011), with completely different analytical techniques (in situ single-crystal XRD and mid/far micro-FTIR spectroscopy), found in strontium feldspar a similar first-order $I2/c$ to $P2_1/c$ transition at $P = 6.6$ and 6.5 GPa, respectively. The bulk modulus of strontium feldspar is 90 GPa up to 3.7 GPa, with a volume softening for $P > 4.2$ GPa. In a preliminary study on HP behavior of barium feldspar, Curetti et al. (2011a) observed a similar phase transition between 5.5 and 5.9 GPa in natural celsian.

In conclusion, the pressure induced phase transitions until now known in Ca-Sr-Ba feldspars are the triclinic $P\bar{1}$ - $\bar{I}\bar{1}$ (anorthite), the triclinic $\bar{I}\bar{1}$ -monoclinic $I2/c$ ($\text{An}_{20}\text{SrFsp}_{80}$), and the monoclinic $I2/c$ - $P2_1/c$ transition (strontium feldspar, $\text{An}_{20}\text{SrFsp}_{80}$, celsian).

In situ HP powder diffraction study was performed on lead feldspar by Tribaudino et al. (1999), using high-brilliance synchrotron radiation. Two samples, with $Q_{\text{od}} = 0.68$ and 0.76, were compressed up to 11 GPa. Until $P = 7.1$ GPa the only phase present was lead feldspar. In the range 7.1–9.4 GPa, sudden changes in

the position of the reflections suggest the transformation of lead feldspar to a new phase (probably feldspar-like), but the powder diffraction data do not provide clear evidence of the transition.

The aim of this work is to study at HP conditions in situ the synthetic partially ordered lead feldspar ($Q_{\text{od}} = 0.7$) by means of the single-crystal X-ray diffraction technique to investigate the high-pressure behavior of lead feldspar and to detail the possible presence of phase transitions.

EXPERIMENTAL METHODS

The lead feldspar studied in this work, with composition $\text{PbAl}_2\text{Si}_2\text{O}_8$, was synthesized from melt as in Benna et al. (1996). The sample was then annealed at $T = 1150$ °C for 12 h and further annealed at $T = 1000$ °C for 70 h in an electric furnace (SiC resistance, Pt-PtRh 10% thermocouple), using unsealed Pt tubes. X-ray powder diffraction revealed that lead feldspar was the only crystalline phase.

A single crystal of lead feldspar of size $150 \times 75 \times 50$ μm^3 was selected on the base of its optical features and its preliminary characterization was performed using a Gemini R Ultra single-crystal X-ray diffractometer equipped with a Ruby CCD detector, using monochromatic $\text{MoK}\alpha$ radiation and the tube operating at 50 kV and 40 mA (CrisDi Interdepartmental Center, University of Torino). A total of 202 frames were collected (frame width 1°, exposure time 9.1 s, sample-detector distance 55 mm) covering the whole accessible reciprocal space; 4312 reflections were measured, of which 2274 unique. The 171.36.24 version of CrysAlisPro software (Agilent Technologies) was used to integrate the intensity data and for analytical absorption and Lorentz-polarization correction. The data collection shows only a -type ($h + k = \text{even}$, $l = \text{even}$) and b -type ($h + k = \text{odd}$, $l = \text{odd}$) reflections, confirming the $I2/c$ space group as in Benna et al. (1996). With $F_o \geq 2\sigma(F_o)$, the number of a and b reflections observed is 1123 and 873, respectively. Unit-cell parameters at room conditions are $a = 8.3936(4)$, $b = 13.0498(7)$, $c = 14.3258(8)$ Å, $\beta = 115.281(6)^\circ$, $V = 1418.9(1)$ Å³. The structural data were refined starting from the fractional coordinates of lead feldspar reported in Benna et al. (1996) and using the neutral atomic scattering factor of the Pb, Si, Al, and O. The M-site was refined according to the “Pb split-atom model” (Tribaudino et al. 1998). The anisotropic refinement of 128 parameters converges at $R = 4.96\%$ for 1679 reflections with $F_o \geq 4\sigma(F_o)$ and $R = 7.15\%$ for all data. Structural details were refined using SHELX-97 package (Sheldrick 2008). The Pb coordination polyhedron shows a significant distortion, probably related to the lone-pairs effect (Benna et al. 1996; Tribaudino et al. 1998). The macroscopic order parameter Q_{od} , calculated from $\langle \text{T-O} \rangle$ bond lengths following Angel et al. (1990), is equal to 0.7 and indicates a partially ordered Al,Si distribution. The structural results obtained at room conditions agree with those reported by Tribaudino et al. (1998) for the PbF_1 64h sample, annealed at $T = 1000$ °C for 64 h, with a similar value of Q_{od} .

Afterward the room T characterization, the sample was loaded in an ETH-type diamond-anvil cell (DAC, hereafter) (Miletich et al. 2000). A foil of T301 steel 250 μm thick was used as a gasket to hold the crystal and it was pre-indented to 110 μm before drilling a hole by spark erosion (\emptyset 250 μm). A 16:3:1 mixture of methanol:ethanol:water was used as hydrostatic pressure-transmitting medium. The internal pressure was checked with Horiba-Jomin Micro-Raman spectrometer (Scansetti Interdepartmental Centre, University of Torino), by the shift of the fluorescence lines of five rubies (\emptyset 15 μm) scattered in the “hole” of the DAC. The uncertainty on P was estimated to be about 0.1 GPa (Mao et al. 1986). The unit-cell parameters were determined at room T in the P range 0.0001–8.4 GPa from the setting angles of 20–35 reflections centered in eight position (King and Finger 1979; Angel et al. 2000), using a Siemens P4 four circles X-ray diffractometer equipped with a point detector ($\text{MoK}\alpha$ radiation; Department of Earth Sciences, University of Torino) and with the SINGLE Control Program software (Angel and Finger 2011). The unit-cell parameters were measured at overall 26 different pressures, in both increasing- and decreasing- P , to check the reversal behavior of the sample. Unit-cell parameters are reported in Table 1. Measurements made on compression and decompression confirmed that the cell parameter changes are reversible with no pressure hysteresis.

Another crystal of lead feldspar of the same synthesis was selected (size $160 \times 80 \times 60$ μm^3) and loaded in the DAC cell to investigate the structural changes with increasing pressure. Unit-cell parameters at room conditions are $a = 8.3941(4)$, $b = 13.022(11)$, $c = 14.3153(7)$ Å, $\beta = 115.253(6)^\circ$, $V = 1415(1)$ Å³. Single-crystal diffraction intensities were collected with Gemini R Ultra X-ray diffractometer (see before) at $P = 0.0001$, 2.4, 3.1, 5.4, 6.0, 7.2, 8.4, and 9.7 GPa (16 runs with a total of 2116 frames, frame width 0.2°, exposure time 50 s, sample-detector distance 82 mm). Integrated intensities were corrected for the absorption of the DAC cell and

for the gasket shadow using ABSORB-7 software (Angel and Gonzalez-Platas 2013). Structural details were refined using SHELX-97 package (Sheldrick 2008). The measurements at room pressure and at $P = 2.4, 3.1, 5.4, 6.0,$ and 7.2 GPa showed only a - and b -type reflections confirming the $I2/c$ space group. At $P = 8.4$ and 9.7 GPa, the data collection also showed the presence of c ($h + k = \text{even}, l = \text{odd}$) and d -type reflections ($h + k = \text{odd}, l = \text{even}$) indicating a primitive lattice; reflection extinctions were accurately investigated and since reflections $h0l$ and $00l$ with $l = \text{even}$ only were observed (unfortunately, because of the shape and orientation of the crystal in the DAC, it has not been possible to measure $0k0$ diffractions to verify the presence of a screw axis along the b direction), the analysis of the systematic absences confirms the $P2_1/c$ symmetry at $P = 8.4$ and 9.7 GPa. In the $P2_1/c$ refinements all the atoms of $I2/c$ symmetry were splitted in two non-equivalent sites taking into account the change of origin by $1/4, 1/4,$ in the $P2_1/c$ space group. For all the refinements, anisotropic displacement parameters were introduced only for extra-framework Pb cations. Unit-cell parameters and refinements details are reported in Table 2. Fractional atomic coordinates and displacement parameters are shown in Tables 3 and 4. Pb-O interatomic distances and T-O-T bond angles are listed in Tables 5 and 6, respectively. (CIF¹ available.)

RESULTS AND DISCUSSION

Lattice deformation

The unit-cell parameters of lead feldspar up to $P = 8.35$ GPa are reported in Table 1 and the evolutions of the unit-cell parameters and volume with pressure are shown in Figures 1 and 2, respectively. A strong discontinuity is visible at about 8 GPa indicating a first-order phase transition at high pressure.

In the P range 0.0001–7.72 GPa the $a, b,$ and c parameters (Fig. 1) decrease with increasing pressure with a subtle change in the trend for P higher than 4 GPa. The linear parameters show a negative axial variation by 4.3, 2.4, and 3.6%, respectively, to the maximum pressure considered ($P = 7.72$ GPa). The axial compressibilities are $\beta_a = 5.57, \beta_b = 3.12, \beta_c = 4.72 \times 10^{-3} \text{ GPa}^{-1}$ [with $\beta = -(d - d_0)/d_0 \times 1/P$ where d is a unit-cell parameter] and show the typical trend previously observed in feldspars: $\beta_a > \beta_c > \beta_b$ (Angel et al. 1988). The comparison of the three linear compressibilities shows an axial anisotropy ($\Delta a/a_0; \Delta b/b_0; \Delta c/c_0 = 1.8:1:1.5$)

higher than in $I2/c$ $\text{An}_{20}\text{SrFsp}_{80}$ and SrFsp_{100} feldspars (1.2:1:1.2, Nestola et al. 2004; Pandolfo et al. 2011) and slightly higher than in anorthite (1.6:1:1.5, Angel et al. 1988), but lower than in overall alkali feldspars studied at HP, as anorthoclase (2.4:1:1.4, Nestola et al. 2008), analbite (2.4:1:1.2, Curetti et al. 2011b), low albite (3.3:1:1.3, Benusa et al. 2005), sanidine (5.2:1:2.4, Angel et al. 1988), and microcline (8.3:1:4.1, Allan and Angel 1997).

The lattice β angle weakly increases up to about 1.8 GPa reaching the maximum value of 115.32° and then as much weakly decreases for higher pressures (Table 1, Fig. 1). A similar trend in β angle was observed by Tribaudino et al. (1999) in lead feldspar up to 7.1 GPa in a HP powder diffraction study. Considering all the other feldspars till now examined at HP, the β angle decreases in anorthite, celsian (Curetti et al. 2011a), SrFsp_{100} , and $\text{An}_{20}\text{SrFsp}_{80}$ feldspars, while it increases in alkali feldspars with a plateau effect (Allan and Angel 1997; Nestola et al. 2008).

The strain induced in lead feldspar by increasing pressure up to 7.72 GPa has been evaluated (Win_Strain4 program, Angel software 2011) to compare the magnitudes and the orientations of the principal axes of the strain ellipsoid with those observed in the other feldspars compressed at HP (Angel et al. 1988; Angel 1994). In lead feldspar the highest deformation occurs on the 010 plane, with the main axis ε_1 only slightly more compressible than the others (44% of the total strain), similarly to strontium feldspar (42%, Pandolfo et al. 2011). The strain ellipsoids in alkali feldspars and in anorthite are significantly more anisotropic and their orientation are quite different: in alkali feldspars some 55–65% of the volume compression is accommodated by the linear compression close to a^* (Angel et al. 1988; Allan and Angel 1997; Nestola et al. 2008; Curetti et al. 2011b) and in anorthite the maximum compression occurs close to the 001 plane with 70% of the total strain along ε_1 axis (Angel 1994).

Equation of state

Figure 2 shows that in the pressure range 0.0001–7.72 GPa in $I2/c$ lead feldspar at $P > 4.27$ GPa there is some evidence for a change in the compressional behavior of the unit-cell volume with pressure. So we have used a second-order Birch-Murnaghan Equation of State (BM2-EoS) to fit the P - V data only up to 4.27 GPa, using the EoSFit7c software (Angel et al. 2014) with the resulting EoS coefficients: $V_0 = 1422.2(1) \text{ \AA}^3, K_{T0} = 76.4(9) \text{ GPa}$. An attempt to fit the P - V data to a BM3-EoS or some other EoS in the P range 0.0001–4.27 GPa did not provide any reliable results, probably because of the too small pressure range. Fitting the P - V data to a BM2-EoS in the P range 4.79–7.72 GPa gives a lower bulk modulus, 63.2(2.3) GPa, confirming the anomalous volume behavior at $P > 4.27$ GPa. When our P - V data are reformulated as a normalized pressure-finite strain plot (F_E - f_E plot, Angel 2000), the values in the P range 0.0001–4.27 GPa lie on a horizontal line of constant F_E (indicating $K' = 4$) (Fig. 3), confirming that the data are adequately described by a BM2-EoS. The anomalous behavior of the volume values (Fig. 2), that deflect from the BM2 curve (solid line) at $P > 4.27$ GPa, could be defined as a volume softening. This softening, quite evident

TABLE 1. Unit-cell parameters of lead feldspar as a function of pressure ($\sigma P = 0.1$ GPa) (e.s.d. in parentheses)

P (GPa)	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
0.0001	8.4004(6)	13.0604(13)	14.3339(6)	115.268(3)	1422.1(2)
0.0001 ^a	8.4002(9)	13.0611(18)	14.3354(8)	115.278(4)	1422.2(2)
0.24	8.3950(5)	13.0544(13)	14.3270(5)	115.274(2)	1419.8(2)
0.28	8.3923(9)	13.046(2)	14.3221(9)	115.286(5)	1417.8(3)
0.50	8.3811(6)	13.0413(14)	14.3094(5)	115.295(3)	1414.1(2)
1.02	8.3604(9)	13.009(3)	14.2841(10)	115.302(5)	1404.5(3)
1.16	8.3502(4)	13.0107(10)	14.2698(4)	115.310(2)	1401.5(1)
1.79 ^a	8.3267(8)	12.9891(19)	14.2384(9)	115.315(5)	1392.1(2)
1.98	8.3197(6)	12.9775(16)	14.2278(6)	115.305(3)	1388.8(2)
2.09	8.3177(5)	12.9759(12)	14.2269(5)	115.309(2)	1388.1(2)
2.27 ^a	8.3042(9)	12.970(2)	14.2119(11)	115.291(6)	1383.9(3)
3.00	8.2763(21)	12.940(4)	14.174(3)	115.291(13)	1372.4(6)
3.06	8.2698(6)	12.9334(13)	14.1664(5)	115.282(3)	1370.1(2)
3.31 ^a	8.2585(6)	12.9266(15)	14.1490(8)	115.273(4)	1365.9(2)
3.83 ^a	8.2338(12)	12.903(3)	14.1172(13)	115.221(6)	1356.9(3)
4.27	8.2195(7)	12.8878(16)	14.0947(6)	115.195(3)	1351.0(2)
4.79	8.1905(17)	12.864(3)	14.0553(15)	115.168(8)	1340.4(4)
5.13	8.1720(9)	12.854(2)	14.0228(8)	115.098(5)	1333.9(3)
5.62	8.1448(10)	12.828(3)	13.9858(9)	115.043(5)	1323.8(4)
5.98	8.1201(9)	12.811(2)	13.9460(7)	114.994(4)	1314.9(3)
6.66	8.0875(10)	12.792(2)	13.8946(8)	114.933(5)	1303.5(3)
7.01	8.0722(10)	12.781(2)	13.8728(8)	114.907(5)	1298.1(3)
7.32	8.0562(11)	12.767(3)	13.8448(9)	114.870(5)	1292.0(3)
7.53	8.0501(14)	12.751(3)	13.8227(12)	114.842(6)	1287.6(4)
7.72	8.0391(15)	12.746(4)	13.8119(13)	114.830(7)	1284.5(5)
8.26 ^b	8.056(2)	12.567(3)	13.719(2)	114.028(11)	1268.6(5)
8.35 ^b	8.050(3)	12.554(5)	13.702(3)	113.980(14)	1265.1(6)

^a Measured in decreasing pressure. ^b $P2_1/c$ space group.

¹ Deposit item AM-15-75000, CIF. Deposit items are free to all readers and found on the MA web site, via the specific issue's Table of Contents (go to <http://www.minsocam.org/MSA/AmMin/TOC/>).

TABLE 2. Single-crystal data at different pressures

<i>P</i> (GPa)	0.0001 ^a	2.4	3.1	5.4	6.0	7.2	8.4	9.7
Space group	<i>I</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>					
<i>a</i> (Å)	8.3941(4)	8.3214(8)	8.2783(11)	8.160(3)	8.1063(13)	8.086(4)	8.057(1)	8.0401(15)
<i>b</i> (Å)	13.022(11)	12.979(14)	12.94(2)	12.84(3)	12.86(2)	12.73(4)	12.515(14)	12.41(2)
<i>c</i> (Å)	14.3153(7)	14.2352(14)	14.1774(18)	14.024(3)	13.920(3)	13.858(6)	13.7079(16)	13.593(2)
β (°)	115.253(6)	115.336(12)	115.269(16)	115.08(3)	114.94(2)	114.90(5)	114.116(14)	113.997(19)
<i>V</i> (Å ³)	1415(1)	1390(2)	1373(2)	1331(3)	1316(2)	1294(4)	1262(1)	1239(2)
Unique refl.	634	527	441	456	470	434	1120	842
Refl. $F_o \geq 4\sigma(F_o)$	537	432	376	354	357	416	743	575
$R F_o \geq 1\sigma(F_o)$	7.01	7.00	8.34	7.62	10.48	14.96	17.40	17.27
$R F_o \geq 4\sigma(F_o)$	5.67	4.80	6.55	5.27	7.18	14.48	10.38	11.23
Weight	0.12	0.11	0.15	0.14	0.17	0.32	0.25	0.27
Goodness of fit	1.29	1.28	1.27	1.04	1.16	1.16	1.14	1.20

^a Within the DAC; $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2]$, where $P = (F_o^2 + 2F_o^2)/3$.

TABLE 3. Atomic fractional coordinates and displacement parameters (Å²) for *I*2/*c* lead feldspar at different pressures

<i>P</i> (GPa)	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}/U_{eq}^a	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
0.0001	Pb	0.2726(1)	-0.0041(2)	0.0718(1)	0.0523(17)					
2.4		0.2707(1)	-0.0005(6)	0.0699(1)	0.0519(15)					
3.1		0.2702(2)	-0.0032(9)	0.0696(1)	0.054(3)					
5.4		0.2690(2)	-0.0045(6)	0.0700(1)	0.0463(16)					
6.0		0.2684(2)	-0.0049(9)	0.0701(1)	0.067(3)					
7.2		0.2675(4)	-0.0039(8)	0.0704(2)	0.062(5)					
0.0001	T1(0)	0.0048(5)	0.1862(13)	0.1097(3)	0.0124(9)	T1(z)	0.0046(5)	0.1732(15)	0.6151(3)	0.0091(10)
2.4		-0.0006(11)	0.165(2)	0.1077(6)	0.019(3)		0.0028(9)	0.194(2)	0.6156(5)	0.006(2)
3.1		-0.0080(17)	0.160(3)	0.1090(9)	0.022(4)		0.0058(15)	0.198(3)	0.6145(8)	0.006(3)
5.4		0.0102(11)	0.1751(19)	0.1165(6)	0.017(2)		-0.0275(16)	0.188(2)	0.6051(7)	0.026(3)
6.0		0.0114(13)	0.178(2)	0.1162(8)	0.023(2)		-0.0297(15)	0.184(2)	0.6061(8)	0.021(2)
7.2		0.0009(14)	0.174(3)	0.1080(8)	0.004(3)		-0.031(2)	0.186(3)	0.6166(13)	0.026(4)
0.0001	T2(0)	0.6957(5)	0.1170(12)	0.1729(3)	0.0089(8)	T2(z)	0.6867(5)	0.1159(12)	0.6725(3)	0.0136(8)
2.4		0.6893(11)	0.127(2)	0.1725(7)	0.012(3)		0.6863(12)	0.1039(19)	0.6719(7)	0.017(3)
3.1		0.6855(19)	0.134(3)	0.1723(10)	0.021(4)		0.6875(15)	0.105(3)	0.6726(8)	0.014(3)
5.4		0.6687(13)	0.113(2)	0.1704(7)	0.022(3)		0.6967(14)	0.124(2)	0.6747(7)	0.022(2)
6.0		0.6702(17)	0.123(3)	0.1698(11)	0.033(4)		0.6941(15)	0.114(3)	0.6756(9)	0.028(3)
7.2		0.675(2)	0.118(4)	0.1773(14)	0.035(5)		0.6910(17)	0.113(3)	0.6719(10)	0.019(3)
0.0001	OA(1)	-0.0032(12)	0.134(3)	-0.0015(7)	0.0157(19)	OA(2)	0.5984(13)	-0.005(3)	0.1460(7)	0.020(2)
2.4		-0.015(3)	0.139(3)	-0.0070(14)	0.015(3)		0.5945(16)	0.008(3)	0.1472(9)	0.018(3)
3.1		-0.007(6)	0.140(5)	-0.003(2)	0.023(5)		0.595(3)	0.011(4)	0.1481(16)	0.028(5)
5.4		-0.021(2)	0.140(3)	-0.0059(13)	0.014(4)		0.590(3)	-0.013(3)	0.1554(19)	0.055(7)
6.0		-0.022(3)	0.140(4)	-0.0035(19)	0.027(5)		0.596(5)	-0.002(4)	0.158(3)	0.072(10)
7.2		0.014(4)	0.146(6)	-0.002(2)	0.025(9)		0.571(8)	-0.004(4)	0.145(5)	0.08(2)
0.0001	OB(0)	0.8258(13)	0.129(3)	0.1095(7)	0.022(2)	OB(z)	0.8108(14)	0.134(3)	0.6130(8)	0.027(3)
2.4		0.823(3)	0.112(5)	0.111(2)	0.039(9)		0.806(2)	0.144(4)	0.6080(13)	0.015(5)
3.1		0.811(3)	0.106(5)	0.1071(17)	0.007(5)		0.807(6)	0.145(8)	0.607(3)	0.055(15)
5.4		0.794(3)	0.161(5)	0.1031(18)	0.033(6)		0.810(3)	0.102(4)	0.6019(18)	0.033(6)
6.0		0.796(3)	0.172(7)	0.104(2)	0.048(9)		0.803(3)	0.098(4)	0.600(2)	0.035(7)
7.2		0.807(7)	0.152(14)	0.112(5)	0.09(2)		0.796(4)	0.097(5)	0.596(2)	0.015(8)
0.0001	OC(0)	0.0240(18)	0.310(4)	0.1283(10)	0.036(4)	OC(z)	0.0150(12)	0.301(3)	0.6278(7)	0.011(2)
2.4		0.004(4)	0.293(3)	0.128(2)	0.053(10)		0.014(2)	0.321(3)	0.6281(13)	0.012(4)
3.1		0.008(6)	0.284(4)	0.128(4)	0.073(19)		0.004(3)	0.327(3)	0.629(2)	0.016(6)
5.4		-0.013(3)	0.302(3)	0.1156(19)	0.033(6)		0.006(3)	0.317(3)	0.641(2)	0.039(7)
6.0		-0.017(5)	0.305(4)	0.115(3)	0.060(12)		0.008(4)	0.316(3)	0.636(2)	0.042(8)
7.2		-0.012(3)	0.303(4)	0.1190(19)	0.000(6)		0.013(6)	0.315(4)	0.649(4)	0.056(15)
0.0001	OD(0)	0.1874(13)	0.128(3)	0.1973(7)	0.021(2)	OD(z)	0.1952(13)	0.121(3)	0.7003(7)	0.020(2)
2.4		0.193(2)	0.134(4)	0.1934(13)	0.016(5)		0.185(2)	0.127(4)	0.7064(14)	0.020(5)
3.1		0.176(3)	0.110(5)	0.2034(15)	0.011(6)		0.203(4)	0.138(6)	0.6985(19)	0.023(7)
5.4		0.175(5)	0.109(6)	0.200(3)	0.095(19)		0.185(2)	0.134(4)	0.7011(11)	0.012(4)
6.0		0.168(4)	0.107(5)	0.204(2)	0.051(11)		0.190(3)	0.143(6)	0.6983(18)	0.030(7)
7.2		0.164(5)	0.102(6)	0.196(2)	0.038(11)		0.188(7)	0.145(11)	0.703(4)	0.08(2)

Note: All atoms except for Pb were refined with isotropic displacement parameters. ^a U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

near 6 GPa and over, could be a precursor of the HP first-order phase transition observed at about 8 GPa. In strontium feldspar too, a volume softening within the *I*2/*c* symmetry above 4.2 GPa was recently observed by Pandolfo et al. (2011).

The volume bulk modulus of lead feldspar, 76.4(9) GPa, is clearly lower than that of strontium feldspar [90(1) GPa by using a BM3-EoS; 84(1) GPa by using a BM2-EoS, Pandolfo et al. 2011], but meaningfully higher than those reported for alkali feldspars (all in the range 50–60 GPa, Angel 1994). In the HP powder diffraction study performed by Tribaudino et al. (1999)

on two samples of lead feldspar with different degree of Al,Si order, the bulk modulus, calculated by using a BM2-EoS in the *P* range 0.0001–7.1 GPa, was 71.0(9) for the PbF1 sample ($Q_{od} = 0.68$) and 67.6 (1.2) for the PbF2 ($Q_{od} = 0.76$) sample, respectively. To compare the results obtained in the present work with those of Tribaudino et al. (1999), we have fitted our *P*-*V* data in all the *P* range 0.0001–7.72 GPa by using a BM2-EoS: the resulting volume bulk modulus, 66(1) GPa, is quite in agreement with the results of Tribaudino et al. (1999).

Compressibilities of unit-cell axes of lead feldspar were de-

TABLE 4. Atomic fractional coordinates and displacement coefficients (\AA^2) for $P2_1/c$ lead feldspar at different pressures

Site	$P = 8.4$ GPa				$P = 9.7$ GPa			
	x	y	z	$U_{\text{iso}}/U_{\text{eq}}^a$	x	y	z	$U_{\text{iso}}/U_{\text{eq}}^a$
Pb(0)	0.2878(2)	-0.0035(7)	0.0695(1)	0.050(3)	0.2882(3)	-0.0091(11)	0.0691(2)	0.063(5)
Pb(i)	0.7604(2)	0.5024(6)	0.5689(1)	0.051(3)	0.7610(3)	0.4999(10)	0.5683(2)	0.075(5)
T1(00)	0.9968(13)	0.173(2)	0.1187(7)	0.011(2)	0.012(3)	0.178(5)	0.1155(19)	0.041(7)
T1(0i)	0.4838(17)	0.683(3)	0.6108(10)	0.026(3)	0.480(3)	0.678(5)	0.6088(17)	0.029(6)
T1(z0)	-0.001(3)	0.173(4)	0.6114(15)	0.053(6)	-0.013(3)	0.166(5)	0.6214(16)	0.023(5)
T1(zi)	0.4779(16)	0.711(3)	0.0962(10)	0.021(3)	0.474(3)	0.709(6)	0.0941(19)	0.034(7)
T2(00)	0.6916(12)	0.121(2)	0.1838(7)	0.0024(19)	0.696(2)	0.129(3)	0.1886(11)	0.004(3)
T2(0i)	0.184(3)	0.618(4)	0.6743(14)	0.049(5)	0.165(5)	0.614(6)	0.674(3)	0.060(10)
T2(z0)	0.695(3)	0.120(5)	0.6736(17)	0.076(7)	0.690(4)	0.109(6)	0.671(2)	0.058(9)
T2(zi)	0.1702(14)	0.627(3)	0.1711(8)	0.015(2)	0.177(2)	0.631(4)	0.1676(13)	0.013(4)
OA(10)	-0.016(4)	0.135(6)	-0.0055(18)	0.021(7)	-0.020(6)	0.125(7)	-0.013(3)	0.025(12)
OA(1i)	0.495(4)	0.645(8)	0.499(2)	0.041(10)	0.488(5)	0.639(9)	0.488(3)	0.016(10)
OA(20)	0.622(5)	0.008(5)	0.199(3)	0.052(9)	0.609(7)	-0.003(6)	0.198(4)	0.054(15)
OA(2i)	0.081(4)	0.505(5)	0.632(2)	0.035(7)	0.075(6)	0.513(6)	0.625(4)	0.050(14)
OB(00)	0.777(8)	0.144(14)	0.082(5)	0.13(3)	0.796(8)	0.153(16)	0.095(5)	0.07(2)
OB(0i)	0.315(4)	0.642(7)	0.619(2)	0.027(7)	0.291(8)	0.693(11)	0.622(6)	0.07(2)
OB(z0)	0.812(3)	0.107(5)	0.6094(17)	0.012(5)	0.806(9)	0.078(10)	0.609(6)	0.09(3)
OB(zi)	0.271(3)	0.640(6)	0.024(2)	0.023(7)	0.292(6)	0.636(9)	0.096(4)	0.032(12)
OC(00)	0.992(4)	0.296(5)	0.156(2)	0.032(8)	0.990(5)	0.296(6)	0.161(3)	0.015(9)
OC(0i)	0.494(7)	0.806(6)	0.622(4)	0.09(2)	0.496(5)	0.809(6)	0.629(3)	0.023(11)
OC(z0)	0.985(3)	0.308(5)	0.6279(19)	0.013(6)	-0.013(5)	0.300(6)	0.624(3)	0.010(8)
OC(zi)	0.497(4)	0.848(5)	0.113(2)	0.035(9)	0.477(6)	0.851(7)	0.093(4)	0.032(13)
OD(00)	0.187(4)	0.111(6)	0.2036(19)	0.024(7)	0.186(5)	0.100(8)	0.200(3)	0.024(11)
OD(0i)	0.679(5)	0.680(9)	0.692(3)	0.068(14)	0.663(7)	0.708(9)	0.701(4)	0.052(19)
OD(z0)	0.208(6)	0.114(9)	0.701(3)	0.067(14)	0.215(10)	0.185(14)	0.709(5)	0.13(5)
OD(zi)	0.663(4)	0.657(7)	0.203(2)	0.040(9)	0.656(9)	0.630(12)	0.198(4)	0.07(2)

Notes: All atoms except for Pb were refined with isotropic displacement parameters. ^a U_{eq} defined as one third of the trace of the orthogonalized U_i tensor. The coordinates of the $P2_1/c$ model have been reported without the $1/4, 1/4, 1/4$ origin shift to compare our data with those of other feldspar structures. The symmetry operators for this non-standard setting must be changed accordingly.

TABLE 5. Pb-O interatomic distances (\AA)

P (GPa)	0.0001	2.4	3.1	5.4	6.0	7.2
Space group	$I2/c$	$I2/c$	$I2/c$	$I2/c$	$I2/c$	$I2/c$
Pb-OA(1)	2.65(2)	2.63(3)	2.65(5)	2.53(3)	2.51(4)	2.75(6)
Pb-OA(1i)	2.76(2)	2.81(3)	2.78(5)	2.84(3)	2.83(4)	2.67(6)
Pb-OA(2)	2.48(1)	2.44(1)	2.44(2)	2.38(3)	2.41(3)	2.23(6)
Pb-OB(0)	2.87(2)	2.76(4)	2.66(3)	3.02(5)	3.11(7)	3.00(14)
Pb-OB(z)	3.02(3)	2.99(4)	3.00(8)	2.60(3)	2.55(4)	2.49(4)
Pb-OC(0)	3.17(4)	3.21(4)	3.35(6)	3.06(4)	3.02(5)	3.03(4)
Pb-OC(z)	3.14(3)	2.95(3)	2.82(4)	2.89(4)	2.90(4)	2.94(6)
Pb-OD(0)	2.79(3)	2.74(4)	2.76(4)	2.69(6)	2.74(5)	2.60(5)
Pb-OD(z)	2.67(2)	2.85(4)	2.75(5)	2.78(3)	2.78(5)	2.83(11)
<Pb-O>	2.84	2.82	2.80	2.75	2.76	2.73

P (GPa)	8.4	9.7	8.4	9.7	
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	
Pb(0)-OA(10)	2.64(5)	2.58(7)	Pb(i)-OA(10)	2.66(5)	2.59(7)
Pb(0)-OA(1i)	2.79(7)	2.74(7)	Pb(i)-OA(1i)	2.60(7)	2.52(8)
Pb(0)-OA(20)	2.55(3)	2.46(5)	Pb(i)-OA(20)	2.93(3)	2.91(5)
Pb(0)-OA(2i)	3.33(3)	3.26(5)	Pb(i)-OA(2i)	2.36(3)	2.33(5)
Pb(0)-OB(0i)	2.93(5)	3.32(11)	Pb(i)-OB(00)	2.68(13)	2.81(14)
Pb(0)-OB(zi)	2.66(6)	2.74(8)	Pb(i)-OB(z0)	2.62(4)	2.45(8)
Pb(0)-OC(0i)	2.89(7)	2.92(8)	Pb(i)-OC(00)	3.07(5)	3.08(7)
Pb(0)-OC(zi)	2.41(6)	2.24(8)	Pb(i)-OC(z0)	2.94(5)	2.98(7)
Pb(0)-OD(00)	2.70(5)	2.62(6)	Pb(i)-OD(0i)	3.02(9)	3.42(10)
Pb(0)-OD(z0)	2.55(7)	3.11(16)	Pb(i)-OD(zi)	3.03(6)	2.76(10)
<Pb-O>	2.75	2.80	<Pb-O>	2.79	2.78

terminated by fitting a BM2-EoS to a , b , and c parameters in the range 0.0001–4.27 GPa (gray symbols and lines in Fig. 4). The coefficients obtained are: $a_0 = 8.4008(6)$ \AA , $1/3 M_0 = 59.2(9)$ GPa; $b_0 = 13.0609(10)$ \AA , $1/3 M_0 = 99.4(1.5)$ GPa; $c_0 = 14.3347(6)$ \AA , $1/3 M_0 = 79.5(1.2)$ GPa (with $M_i = \beta_i^{-1}$, Angel et al. 2014). The linear moduli indicate an axial compression anisotropy with $\beta_a > \beta_c > \beta_b$. Therefore, the b axis is less compressible than the c axis, which in turn is less compressible than the a axis. The anomalous compressional pattern at P higher than 4 GPa, especially evident in a and c axes, could indicate a pre-transition elastic softening. In a recent paper on compression of cordierite,

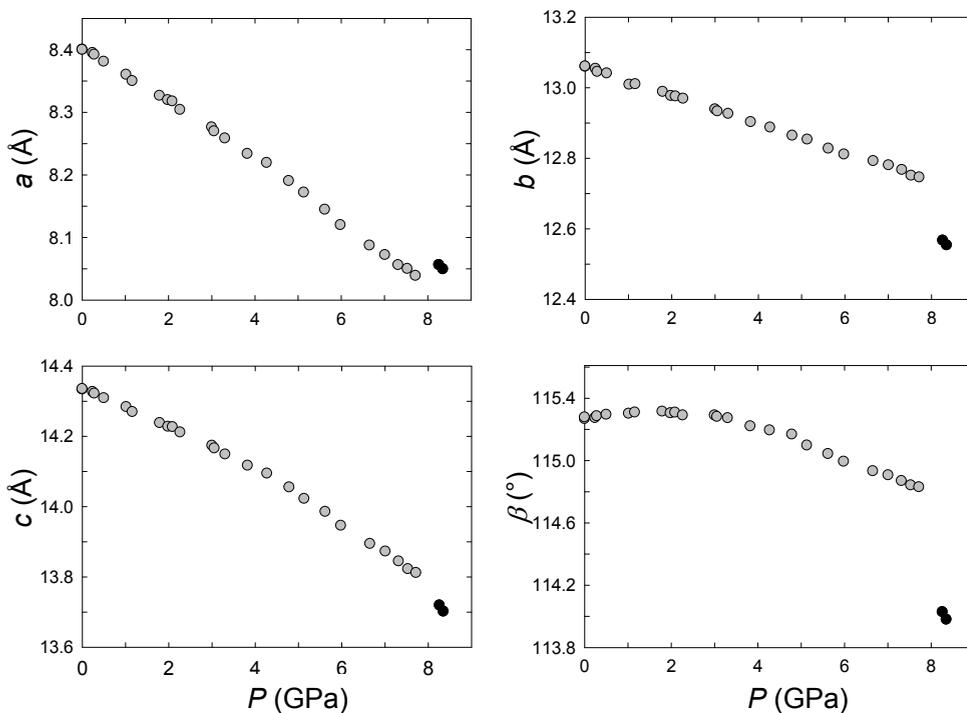
Miletich et al. (2014) observed, at pressures above ~ 4 GPa, for a axis the conventional stiffening with pressure, but b and c axes reveal anomalous behavior and seem “involved in elastic softening associated with an upcoming structural instability.” The elastic softening phenomenon, indicated by the negative values for $\partial(\beta^{-1})/\partial P$ coefficients, is typically associated with first-order transitions (Miletich et al. 2014).

Phase transition

Only two sets of unit-cell parameters were measured at pressure higher than 7.7 GPa (Table 1). At about 8 GPa the evolution of the unit-cell parameters shows a significant discontinuity (Fig. 1). The β angle suddenly decreases from 114.83 to 114.03° (Table 1); both b and c parameters experience a significant compression at this pressure and their relative plots show a clear step, whereas a parameter at about 8 GPa suddenly increases (Fig. 1). The unit-cell volume vs. pressure plot (Fig. 2) does not emphasize so much the discontinuity because the volume values “merge” the two opposite trends (decrease in b and c , increase in a). A similar strong discontinuity in the behavior of unit-cell parameters and volumes was observed in $\text{Ca}_{0.2}\text{Sr}_{0.8}\text{Al}_2\text{Si}_2\text{O}_8$ feldspar at $P > 7.3$ GPa and in strontium feldspar at $P > 6.6$ GPa, indicating the occurrence of a phase transition strongly first-order in character (Nestola et al. 2004; Pandolfo et al. 2011). The discontinuities observed in lead feldspar in the present work indicate the occurrence of an analogous phase transition and allow restricting its P range between 7.72 and 8.26 GPa. The presence of a possible phase transition for $P > 7.1$ GPa in lead feldspar had been suggested by Tribaudino et al. (1999) in a HP powder diffraction study. The authors observed a single monoclinic phase up to 7.1 GPa; at higher pressures, in the range 7.1 and 9.4 GPa, sudden changes in the position of the reflections occurred and some reflections appeared split, suggesting the transformation of lead feldspar to

TABLE 6. T-O-T angles (°)

<i>P</i> (GPa)	0.0001	2.4	3.1	5.4	6.0	7.2		8.4	9.7
Space group	<i>I</i> 2/ <i>c</i>		<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>					
T1(0)-OA(1)-T1(z)	139(2)	143(2)	145(4)	138(2)	138(3)	150(6)	T1(00)-OA(10)-T1(zi)	130(4)	120(5)
							T1(z0)-OA(1i)-T1(0i)	150(7)	150(7)
T2(0)-OA(2)-T2(z)	130(1)	130(1)	132(2)	131(2)	134(2)	122(4)	T2(00)-OA(20)-T2(z0)	128(3)	122(3)
							T2(zi)-OA(2i)-T2(0i)	128(2)	126(3)
T2(0)-OB(0)-T1(0)	145(2)	139(3)	132(3)	142(2)	141(3)	153(4)	T1(00)-OB(00)-T2(00)	119(3)	130(4)
							T1(0i)-OB(0i)-T2(0i)	156(3)	135(8)
T1(z)-OB(z)-T2(z)	150(1)	148(1)	147(3)	120(3)	121(3)	114(3)	T1(z0)-OB(z0)-T2(z0)	133(4)	117(6)
							T1(zi)-OB(zi)-T2(zi)	132(3)	137(5)
T1(0)-OC(0)-T2(0)	131(2)	127(2)	133(4)	123(2)	117(3)	124(2)	T1(00)-OC(00)-T2(0i)	119(2)	114(3)
							T1(0i)-OC(0i)-T2(00)	125(4)	122(4)
T1(z)-OC(z)-T2(z)	132(1)	130(2)	122(2)	124(2)	131(3)	132(4)	T1(z0)-OC(z0)-T2(zi)	117(3)	122(3)
							T1(zi)-OC(zi)-T2(z0)	110(4)	107(5)
T2(0)-OD(0)-T1(0)	140(2)	140(2)	139(4)	141(5)	136(4)	136(4)	T1(00)-OD(00)-T2(0i)	137(4)	134(6)
							T1(0i)-OD(0i)-T2(00)	139(5)	129(6)
T1(z)-OD(z)-T2(z)	138(2)	148(2)	139(2)	142(2)	141(2)	141(4)	T1(z0)-OD(z0)-T2(zi)	133(5)	127(6)
							T1(zi)-OD(zi)-T2(z0)	162(3)	151(8)



◀ **FIGURE 1.** The variations of the *a*, *b*, *c*, and β unit-cell parameters of lead feldspar with pressure. Gray circle = *I*2/*c* phase. Black circle = *P*2₁/*c* high-pressure phase. Experimental uncertainties are smaller than symbols.

a new phase (probably feldspar-like).

In the present work, the appearance of *c*- and *d*-type reflections at $P > 8$ GPa, the analysis of the systematic absences and the structural refinements at $P = 8.4$ and 9.7 GPa (Table 2) indicate that the phase transition occurs from *I*2/*c* to *P*2₁/*c* symmetry. The $I/\sigma(I)$ ratios of the *a*, *b*, *c*, and *d* superlattice reflections, collected in lead feldspar just before and just after the *I*2/*c*-*P*2₁/*c* phase transition, are listed in Table 7. The ratios are compared with those of $\text{An}_{20}\text{SrFsp}_{80}$, which is the only structure with *P*2₁/*c* symmetry until now published in feldspars (Benna et al. 2007). Table 7 shows that the scheme of intensity of the different reflections in *P*2₁/*c* lead feldspar is $a > d > b \geq c$, in agreement with the results observed for $\text{An}_{20}\text{SrFsp}_{80}$.

Structural modifications

***I*2/*c* phase.** In the *P* range 0.0001–7.2 GPa, the structural results show that the lead feldspar retains *I*2/*c* symmetry with

increasing pressure and the main variations are in Pb-O bond lengths and in T-O-T bond angles (Tables 5–6), while T-O distances and O-T-O angles does not change meaningfully, indicating that the Si,Al tetrahedra behave with pressure as a rigid body, only flexing the T-O-T angles.

The average $\langle \text{Pb-O} \rangle$ distances decrease with pressure, but some of the individual length shows an irregular evolution with a change in their compressional trend between 3 and 5 GPa (Table 5, Fig. 5). While the $\text{Pb-O}_D(0)$ distance slightly decreases and $\text{Pb-O}_D(z)$ distance shows a small increase in all the *P* range, the $\text{Pb-O}_B(z)$ remains quite constant until about 3 GPa, then significantly decreases (Fig. 5). The $\text{Pb-O}_C(0)$ distance increases until 3 GPa and then decreases; on the contrary, the $\text{Pb-O}_B(0)$ and $\text{Pb-O}_C(z)$ distances decrease and then increase. All the Pb-O_A distances show a variation in the trend at about 6 GPa. In all the *P* range investigated, considering all individual Pb-O bond distances smaller than 2.94 Å, the coordination of the Pb site

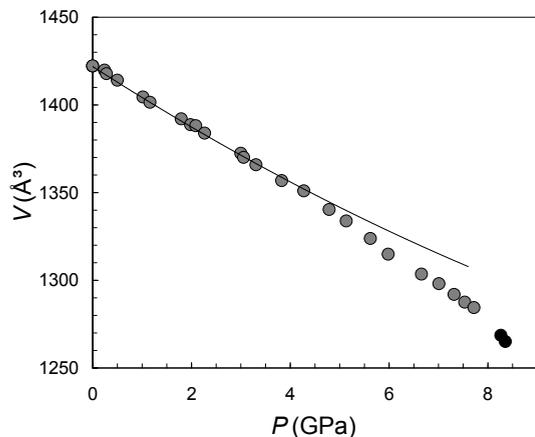


FIGURE 2. The variation of the unit-cell volume of lead feldspar with pressure. Symbols as in Figure 1. The line shows the second-order Birch-Murnaghan equation of state (BM2-EoS) in the P range 0.0001–4.27 GPa. Experimental uncertainties are smaller than symbols.

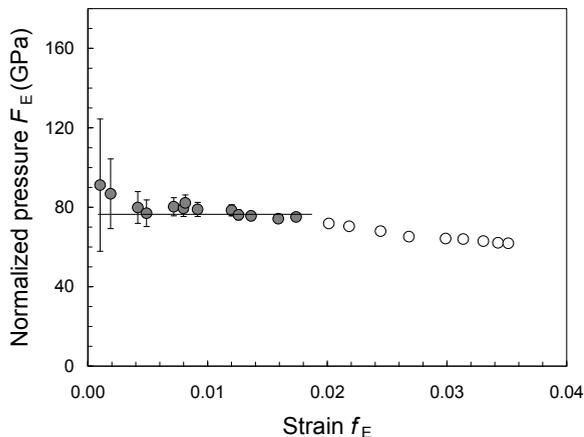


FIGURE 3. Evolution of the normalized pressure F_E vs. Eulerian finite strain f_E in lead feldspar. $F_E = P/3 \times f_E \times (1 + 2f_E)^{3/2}$ and $f_E = [(V_0/V)^{2/3} - 1]/2$ (Angel 2000). The horizontal line of constant F_E indicates that the P - V data (gray circles, P range 0.0001–4.27 GPa) could be fitted by a second-order truncation of the BM-EoS. Open circles = P - V data in the range 4.79–7.72 GPa.

increases from sixfold at room condition (Benna et al. 1996) to a irregular sevenfold configuration at 7.2 GPa (Table 5).

The change in the compressional behavior of the Pb polyhedron is obviously related to changes occurring in the T-O-T angles, because the rearrangement of the framework mainly occurs by the rotation of the essentially rigid tetrahedra, forming the characteristic crankshaft-chains running parallel to a axis of the feldspar structure.

While the decrease of the average \langle T-O-T \rangle angle with pressure is relatively small (Table 6), individual T-O-T bond angles show different variations, with some increasing and some decreasing, as typical for other feldspars studied at high pressures (Ross 2000). In the four-membered rings of tetrahedra lying on the 010 plain, forming chains parallel to c , the $T_1(0)$ - $O_B(0)$ - $T_2(0)$ angle significantly decreases up to 3 GPa and then increases

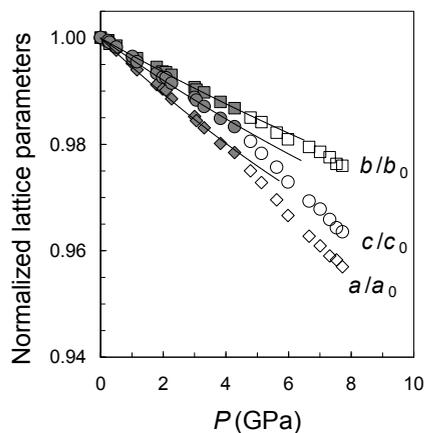


FIGURE 4. The variations of the a , b , and c lattice edges of lead feldspar as a function of pressure, normalized to their room pressure values. Diamonds = a/a_0 ; squares = b/b_0 ; circles = c/c_0 . Lines correspond to linear fits in the P range 0.0001–4.27 GPa (gray symbols) with linear moduli $M_i = 177.5(2.7)$, 298.1(4.6), 238.5(3.6) GPa, respectively (with $i = a, b, c$, and $M_i = \beta_i^{-1}$, Angel et al. 2014). Open circles = normalized parameters the range 4.79–7.72 GPa. Experimental uncertainties are smaller than symbols.

TABLE 7. Number of a , b , c , and d reflections and $l/\sigma(l)$ ratios for lead feldspar and monoclinic $An_{20}SrF_{80}$ feldspar^a at different pressures

	P (GPa)	Space group	No. refl. $l/\sigma(l) > 1$	No. refl. x/a	$l/\sigma(l)$ mean	$l/\sigma(l)$ max
PbAl ₂ Si ₂ O ₈	0.0001 ^b	$I2/c$				
a refl.			389	1.0	23.5	121.0
b refl.			243	0.62	2.9	14.9
Total			632	–	–	–
PbAl ₂ Si ₂ O ₈	7.2	$I2/c$				
a refl.			258	1.0	12.7	110.1
b refl.			176	0.68	4.2	8.9
Total			434	–	–	–
PbAl ₂ Si ₂ O ₈	8.4	$P2_1/c$				
a refl.			370	1.0	9.7	54.4
b refl.			181	0.49	2.2	8.3
c refl.			201	0.54	2.0	6.5
d refl.			342	0.92	5.0	21.0
Total			1094	–	–	–
Ca _{0.2} Sr _{0.8} Al ₂ Si ₂ O ₈	4.4	$I2/c$				
a refl.			226	1.0	24.2	85.1
b refl.			83	0.37	4.7	28.6
Total			309	–	–	–
Ca _{0.2} Sr _{0.8} Al ₂ Si ₂ O ₈	7.4	$P2_1/c$				
a refl.			242	1.0	24.0	71.8
b refl.			150	0.62	6.5	46.4
c refl.			114	0.47	5.0	25.2
d refl.			241	1.0	13.6	57.0
Total			747	–	–	–

^a Benna et al. (2007). ^b Within the DAC.

while $T_1(z)$ - $O_B(z)$ - $T_2(z)$ angle slightly decreases up to 3 GPa and then slumps. The $T_1(0)$ - $O_D(0)$ - $T_2(0)$ and $T_1(z)$ - $O_D(z)$ - $T_2(z)$ angles remain practically constant in all the investigated P range.

In the other type of four-membered rings of tetrahedra, approximately normal to a axis, the T_1 - O_C - T_2 angles connect the 010 tetrahedral rings along b direction, forming the crankshaft-chains parallel to a . In the low albite at HP (Benusa et al. 2005) these angles well describe the shear of the rings with increasing pressure. In lead feldspar the shear is not evident: the $T_1(0)$ - $O_C(0)$ -

at $P > 8$ GPa with the pressures of the transitions occurring in the other feldspars with Al:Si ratio equal to 1:1 (i.e., alkaline-earth feldspars). As seen, the different space groups observed until now in Ca-Sr-Ba-Pb feldspars, by varying the pressure and/or the composition, are: $P\bar{1}$, $\bar{1}$, $I2/c$, and $P2_1/c$. While at room and low pressures the $P\bar{1}$, $\bar{1}$, and $I2/c$ phases are observed, the $P2_1/c$ phase seems to be stable only at very high pressures.

In alkaline-earth feldspars there seems to be a possible correlation between the pressure of the $I2/c$ - $P2_1/c$ transition and the dimension of the cation in the M-site. Indeed, the pressure of the transition seems to increase with the decrease of the mean ionic radius of the M cation (Ba, Sr, Ca). The $I2/c$ - $P2_1/c$ transition occurs in barium feldspar between 5.5 and 5.9 GPa (Curetti et al. 2011a), while in strontium feldspar (with Sr^{2+} cation smaller than Ba^{2+}) it occurs at about 6.6 GPa (Pandolfo et al. 2011). The substitution of 20% of $\text{CaAl}_2\text{Si}_2\text{O}_8$ component into the strontium feldspar structure (with a decrease in the mean ionic radius) causes an increase of the transition pressure: in the $\text{Ca}_{0.2}\text{Sr}_{0.8}\text{Al}_2\text{Si}_2\text{O}_8$ feldspar the $I2/c$ - $P2_1/c$ transition occurs at about 7.3 GPa (Nestola et al. 2004). Moreover, Pandolfo et al. (2011) hypothesized that, along the An-SrFsp join, at $\sim\text{An}_{30}\text{SrFsp}_{70}$ composition “there could be a triple point where $P2_1/c$, $\bar{1}$ and $P\bar{1}$ phases coexist at about 7.5 GPa.” Finally, Daniel et al. (1995) observed that anorthite remains $\bar{1}$ up to 10 GPa and then transforms into a phase of higher symmetry.

The results obtained in the present work indicate that in lead feldspar the $I2/c$ - $P2_1/c$ transition occurs at about 8 GPa, a pressure

higher than in strontium feldspar (6.6 GPa), although the ionic radii of Sr and Pb are similar ($r^{\text{VII}}\text{Sr}^{2+} = 1.21 \text{ \AA}$, $r^{\text{VII}}\text{Pb}^{2+} = 1.23 \text{ \AA}$, according to Shannon 1976). Hence, lead feldspar has a higher transition pressure than could be inferred by considering only the size of the ionic radius. It is known in literature that the significant deviations of lead feldspar from trends of unit-cell parameters vs. volume or ionic radius have been attributed to an effect of the lone-pair (Ribbe 1994). In lead feldspar the relatively high value of the pressure of the $I2/c$ - $P2_1/c$ transition with respect to alkaline-earth feldspars could be ascribed, besides the specific nature of Pb^{2+} as a lone-pair bearing cation, also to the degree of Al,Si order. We must consider that, in the lead feldspar studied at HP in the present work, the Al,Si configuration is only partially ordered ($Q_{\text{od}} = 0.7$), while the Ca-Sr-Ba feldspars studied at HP are almost completely ordered, with a $Q_{\text{od}} = 0.9$. The partial disorder occurring in lead feldspar could affect the pressure of the transition, as it was observed in anorthite, in which small amounts of disorder can affect dramatically its phase transition behavior at HP. Indeed, the effect of decreasing Al,Si order on the $P\bar{1}$ - $\bar{1}$ transition in anorthite was found to be an increase in the P_{tr} and a change in the character of the transition itself (Angel 1994).

IMPLICATIONS

Feldspars are major igneous and metamorphic rock-forming minerals and are among the most abundant minerals within the Earth’s crust. Their HP and HT behavior is crucial for the understanding of most petrological, geochemical, and thermodynamic processes. While the behavior of feldspars at elevated temperatures has been the subject of intensive investigations, yet few detailed studies have been made at elevated pressures. Pressure-induced phase transitions are very complex to model because they are “non-quenchable” and therefore require “in situ” studies at HP for their characterization. Although feldspars are stable in an extremely limited pressure range under geological conditions, compressional studies and investigations on phase transitions induced by pressure can provide more accurate EoS data on thermodynamic properties useful for petrological applications (Angel 1994).

In the present work, we have measured the compressibility of lead feldspar by single-crystal in situ XRD techniques and we have found a new $P2_1/c$ phase at $P > 8$ GPa. The experimental findings of this study improve the knowledge on the elastic behavior at HP of feldspars with Al:Si ratio equal to 1:1 and provide new compressibility data for their thermodynamic characterization, as well as a basis for further HP structural studies. As the state of Al,Si order can affect the elastic properties and EoS (e.g., the bulk modulus increases from sanidine to microcline), we suggest that the different degree of Al,Si order may also affect the pressure of the $I2/c$ - $P2_1/c$ displacive transition that occurs at very high pressure in Ca-Sr-Pb-Ba-feldspars. Further investigations at HP on lead feldspar with different degrees of Al,Si order are needed, with the aim to study the interactions between slow order-disorder processes and fast displacive phase transitions.

To extend our investigation’s implications to the geological context, lead feldspar represents a useful model for characterizing the thermodynamic behavior of anorthite and anorthite-bearing feldspars. Indeed, it is well known that anorthite retains an ordered Al,Si configuration up to a temperature close to the melting point,

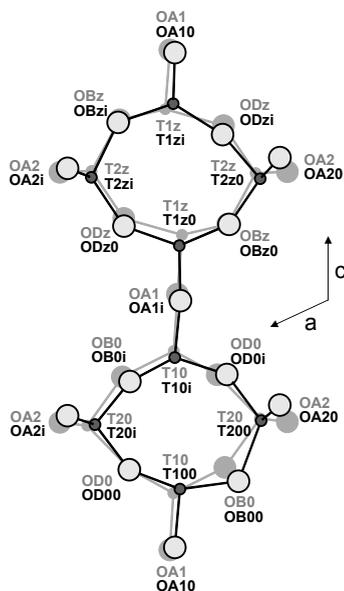


FIGURE 7. The four-membered rings of tetrahedra with 010 as the ring-plane, forming chains parallel to c . Projection on the 010 plane (thickness $\sim 5 \text{ \AA}$). O_c oxygen atoms are not shown. Atoms in the shadow: $P = 7.2$ GPa, $I2/c$ space group; the twofold rotation axes, parallel to b , are at the centers of the rings formed by the two pairs of equivalent tetrahedra. Atoms in close-up: $P = 8.4$ GPa, $P2_1/c$ space group; the rings consist of four symmetrically non-equivalent tetrahedra, as the twofold rotation axes are lost; the structure is more free and the rings become more irregular. The largest angles are $T_1(0i)\text{-}O_b(0i)\text{-}T_2(0i)$ (156°) and $T_1(\text{zi})\text{-}O_b(\text{zi})\text{-}T_2(\text{z}0)$ (162°).

and only limited changes in Al,Si ordering can be achieved by extreme heating (Benna et al. 1985; Carpenter 1992). On the contrary, in lead feldspar the Al,Si ordering kinetics are significantly faster and a significant degree of Al,Si disorder (that cannot be reached in anorthite) can be easily achieved at low temperatures by varying the annealing conditions (Tribaudino et al. 1998).

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REFERENCES CITED

- Allan, D.R., and Angel, R.J. (1997) A high-pressure structural study of microcline (KAlSi₃O₈) to 7 GPa. *European Journal of Mineralogy*, 9, 263–275.
- Angel, R.J. (1992) Order-disorder and the high-pressure *P1- $\bar{1}$* transition in anorthite. *American Mineralogist*, 77, 923–929.
- (1994) Feldspars at high pressure. In I. Parsons, Ed., *Feldspars and their Reactions*, p. 271–312. Kluwer, Dordrecht, The Netherlands.
- (2000) Equations of state. *Reviews in Mineralogy and Geochemistry*, 41, 35–59.
- (2004) Equations of state of plagioclase feldspars. *Contributions to Mineralogy and Petrology*, 146, 506–512.
- Angel, R.J., and Finger, L.W. (2011) SINGLE: a program to control single-crystal diffractometers. *Journal of Applied Crystallography*, 44, 247–251.
- Angel, R.J., and Gonzalez-Platas, J. (2013) ABSORB-7 and ABSORB-GUI for single-crystal absorption corrections. *Journal of Applied Crystallography*, 46, 252–254.
- Angel, R.J., Hazen, R.M., McCormick, T.C., Prewitt, C.T., and Smyth, J.R. (1988) Comparative compressibility of end-member feldspars. *Physics and Chemistry of Minerals*, 15, 313–318.
- Angel, R.J., Carpenter, M.A., and Finger, L.W. (1990) Structural variation associated with compositional variation and order-disorder behavior in anorthite-rich feldspars. *American Mineralogist*, 75, 150–162.
- Angel, R.J., Downs, R.T., and Finger, L.W. (2000) High-temperature-high-pressure diffraction. *Reviews in Mineralogy and Geochemistry*, 41, 559–596.
- Angel, R.J., Ross, N.L., and Zhao, J. (2005) The compression of framework minerals: beyond rigid polyhedra. *European Journal of Mineralogy*, 17, 193–199.
- Angel, R.J., Gonzalez-Platas, J., and Alvaro, M. (2014) EoSFit7c and a Fortran module (library) for equation of state calculations. *Zeitschrift für Kristallographie*, 229, 405–419.
- Bambauer, H.U., and Nager, H.E. (1981) Gitterkonstanten und displazive Transformationen synthetischer Erdalkalfeldspäte. I. System Ca[Al₂Si₂O₈]-Sr[Al₂Si₂O₈]-Ba[Al₂Si₂O₈]. *Neues Jahrbuch für Mineralogie Abhandlungen*, 141, 225–239 (in German).
- Benna, P., and Bruno, E. (2003) Single-crystal in situ high-temperature structural investigation of the $\bar{1}$ -*I2/c* phase transition in Ca_{0.2}Sr_{0.8}Al₂Si₂O₈ feldspar. *American Mineralogist*, 88, 1532–1541.
- Benna, P., Zanini, G., and Bruno, E. (1985) Cell parameters of thermally treated anorthite. Al, Si configurations in the average structures of the high temperature calcic plagioclases. *Contributions to Mineralogy and Petrology*, 90, 381–385.
- Benna, P., Tribaudino, M., and Bruno, E. (1996) The structure of ordered and disordered lead feldspar (PbAl₂Si₂O₈). *American Mineralogist*, 81, 1337–1343.
- (2000) $\bar{1}$ -*I2/c* ferroelastic phase transition in the Ca_{0.2}Pb_{0.8}Al₂Si₂O₈ feldspar as a function of temperature. *Mineralogical Magazine*, 64, 285–290.
- Benna, P., Nestola, F., Boffa Ballaran, T., Balić-Žunić, T., Fahl Lundegaard, L., and Bruno, E. (2007) The high-pressure structural configurations of Ca_{0.2}Sr_{0.8}Al₂Si₂O₈ feldspar: the $\bar{1}$ -*I2/c* and *I2/c-P2₁/c* phase transitions. *American Mineralogist*, 92, 1190–1199.
- Benusa, M.D., Angel, R.J., and Ross, N.L. (2005) Compression of albite NaAlSi₃O₈. *American Mineralogist*, 90, 1115–1120.
- Bruno, E., and Facchinelli, A. (1972) Al, Si configurations in lead feldspar. *Zeitschrift für Kristallographie*, 136, 296–304.
- Bruno, E., and Gazzoni, G. (1968) Feldspati sintetici della serie CaAl₂Si₂O₈-SrAl₂Si₂O₈. *Atti dell'Accademia delle Scienze di Torino*, 102, 881–893 (in Italian).
- Carpenter, M.A. (1992) Equilibrium thermodynamics of Al/Si ordering in anorthite. *Physics and Chemistry of Minerals*, 19, 1–24.
- Chiari, G., Calleri, M., Bruno, E., and Ribbe, P.H. (1975) The structure of partially disordered synthetic strontium feldspar. *American Mineralogist*, 60, 111–119.
- Curetti, N., Benna, P., Nestola, F., and Bruno, E. (2011a) High-pressure structural configurations of celsian. *Geotitalia 2011*, VIII Forum Italiano di Scienze della Terra (FIST), Epitome, 213, 4, Torino.
- Curetti, N., Sochalski-Kolbus, L., Angel, R.J., Benna, P., Nestola, F., and Bruno, E. (2011b) High-pressure structural evolution and equation of state of analbite. *American Mineralogist*, 96, 383–392.
- Daniel, I., Gillet, P., and Ghose, S. (1995) A new high pressure phase transition in anorthite (CaAl₂Si₂O₈) revealed by Raman spectroscopy. *American Mineralogist*, 80, 645–648.
- Downs, R.T., Hazen, R.M., and Finger, L.W. (1994) The high pressure crystal chemistry of low albite and the origin of the pressure dependency of Al-Si ordering. *American Mineralogist*, 79, 1042–1052.
- Hackwell, T.P., and Angel, R.J. (1992) The comparative compressibility of reedmergnerite, danburite and their aluminium analogues. *European Journal of Mineralogy*, 4, 1221–1227.
- King, H.E., and Finger, L.W. (1979) Diffracted beam crystal centering and its application to high pressure crystallography. *Journal of Applied Crystallography*, 12, 374–378.
- Mao, H.K., Xu, J., and Bell, P.M. (1986) Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *Journal of Geophysical Research*, 91, 4673–4676.
- McGuinn, M.D., and Redfern, S.A.T. (1994) Ferroelastic phase transition along the join CaAl₂Si₂O₈-SrAl₂Si₂O₈. *American Mineralogist*, 79, 24–30.
- (1997) High-temperature ferroelastic strain below the *I2/c- $\bar{1}$* transition in Ca_{1-x}Sr_xAl₂Si₂O₈ feldspars. *European Journal of Mineralogy*, 9, 1159–1172.
- Megaw, H.D., Kempster, C.J.E., and Radoslovich, E.W. (1962) The structure of anorthite CaAl₂Si₂O₈. II. Description and discussion. *Acta Crystallographica*, 15, 1017–1035.
- Miletich, R., Alla, D.R., and Kuhs, W.F. (2000) High pressure single-crystal technique. *Reviews in Mineralogy and Geochemistry*, 41, 445–520.
- Miletich, R., Gatta, G.D., Willi, T., Mirwald, P.W., Loti, P., Merlini, M., Rotiroli, N., and Loerting, T. (2014) Cordierite under hydrostatic compression: Anomalous elastic behavior as a precursor for a pressure-induced phase transition. *American Mineralogist*, 99, 479–493.
- Mrosko, M., Koch-Muller, M., and Schade, U. (2011) In-situ mid/far micro-FTIR spectroscopy to trace pressure-induced phase transitions in strontium feldspar and wadsleyite. *American Mineralogist*, 96, 1748–1759.
- Nager, H.E., Hoffmann, W., and Nissen, H.U. (1969) Die Mischreihe (Ca,Sr)[Al₂Si₂O₈]. *Naturwissenschaften*, 56, 136 (in German).
- Nestola, F., Boffa Ballaran, T., Benna, P., Tribaudino, M., and Bruno, E. (2004) High-pressure phase transitions in Ca_{0.2}Sr_{0.8}Al₂Si₂O₈ feldspar. *American Mineralogist*, 89, 1474–1479.
- Nestola, F., Curetti, N., Benna, P., Ivaldi, G., Angel, R.J., and Bruno, E. (2008) Compressibility and high-pressure behavior of Ab_{0.3}Or_{0.7}An_{1.0} anorthoclase. *Canadian Mineralogist*, 46, 1443–1454.
- Newman, R.E., and Megaw, H.D. (1960) The crystal structure of celsian (barium feldspar). *Acta Crystallographica*, 13, 303–312.
- Pandolfo, F., Boffa Ballaran, T., Nestola, F., Koch Muller, M., Mrosko, M., and Bruno, E. (2011) High-pressure *I2/c-P2₁/c* phase transformation in SrAl₂Si₂O₈ feldspar. *American Mineralogist*, 96, 1182–1185.
- Phillips, B.L., McGuinn, M.D., and Redfern, S.A.T. (1997) Si-Al order and the $\bar{1}$ -*I2/c* structural phase transition in synthetic CaAl₂Si₂O₈-SrAl₂Si₂O₈ feldspar: A ²⁹Si MAS-NMR spectroscopy study. *American Mineralogist*, 82, 1–7.
- Ribbe, P.H. (1994) The crystal structures of the aluminum-silicate feldspars. In I. Parsons, Ed., *Feldspars and Their Reactions*, p. 1–49. Kluwer, Dordrecht.
- Ross, N.L. (2000) Framework structures. *Reviews in Mineralogy and Geochemistry*, 41, 257–287.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, 32, 751–767.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, A64, 112–122.
- Sochalski-Kolbus, L.M., Angel, R.J., and Nestola, F. (2010) The effect of Al/Si disorder on the bulk moduli of plagioclase feldspars. *Mineralogical Magazine*, 74, 943–950.
- Tribaudino, M., Benna, P., and Bruno, E. (1993) $\bar{1}$ -*I2/c* phase transition in alkaline-earth feldspars along the CaAl₂Si₂O₈-SrAl₂Si₂O₈ join: Thermodynamic behaviour. *Physics and Chemistry of Minerals*, 20, 221–227.
- (1998) Structural variations induced by thermal treatment in lead feldspar (PbAl₂Si₂O₈). *American Mineralogist*, 83, 159–166.
- Tribaudino, M., Benna, P., Bruno, E., and Hanfland, M. (1999) High pressure behaviour of lead feldspar (PbAl₂Si₂O₈). *Physics and Chemistry of Minerals*, 26, 367–374.
- Tribaudino, M., Benna, P., and Bruno, E. (2000) TEM observations on the $\bar{1}$ -*I* phase transition in feldspars along the join CaAl₂Si₂O₈-SrAl₂Si₂O₈. *American Mineralogist*, 85, 963–970.
- Tribaudino, M., Benna, P., Nestola, F., Meneghini, C., and Bruno, E. (2005) Thermodynamic behaviour of the high-temperature *P1- $\bar{1}$* phase transition along the CaAl₂Si₂O₈-SrAl₂Si₂O₈ join. *Physics and Chemistry of Minerals*, 32, 314–321.
- Tribaudino, M., Zhang, M., and Salje, E.K.H. (2009) Cation ordering and phase transitions in feldspars along the join CaAl₂Si₂O₈-SrAl₂Si₂O₈: a TEM, IR and XRD investigation. *Mineralogical Magazine*, 73, 119–130.

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