Feldspars with trivalent non-tetrahedral cations: Experimental studies in the system NaAlSi3O8 – CaAl2Si2O8 – LaAl3SiO8

HANS-JÜRGEN KNEIP* and FRIEDRICH LIEBAU

Mineralogisches Institut der Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany
* Present address: Geschwister-Scholl-Str. 13, D-37081 Göttingen, Germany

Dedicated to Dr. Helen D. Megaw and the late Dr. William H. Taylor, pioneers in feldspar crystal chemistry

Abstract: Feldspars with up to about 45% trivalent cations on M positions were synthesized by heating gels of composition Ca_{6-x}Na_xLa_xAl_{16}Si_{16}O_{64} at 1300°C and 1 bar. In the range 0 < x(gel) ≤ 3, these feldspars can be derived from anorthite Ca[Al_{2}Si_{2}O_{8}] by the substitution 2Ca^{2+} → Na^{+} + La^{3+}; at x(gel) ≥ 3 this substitution is accompanied by the substitution Ca^{2+} + Al^{3+} → Na^{+} + Si^{4+}. As x increases, the triclinic anorthite structure gradually becomes monoclinic at x(gel) = 3.05(3). Electron diffraction indicates transformation from P1 through I1 to I2/c with increasing x. 29Si MAS NMR spectra indicate considerable Al/Si disorder, as well as low long- and medium-range order of the Q4 (4Al) units. The latter is due to distortion of the [SiO4] tetrahedra and considerable variation of the Si–O–T angles caused by rotation of the [TO4] tetrahedra as they adjust to the different M cations.

Key-words: lanthanum sodium feldspar, sodium lanthanum feldspar, feldspar, anorthite, albite.

I. Introduction

The feldspar structure type is energetically very favourable, as can be seen from the wide range of temperatures, pressures and chemical compositions over which feldspar-type phases are known to exist. With regard to composition, end-member feldspars of general formula

$$M^{7+}T_{4}^{4+}O_{8}$$

have been described in which the tetrahedrally coordinated cations are:

- T4+: T3+ = B, Al, Ga, Fe,
- T4+ = Si, Ge;

but also:
- T2+ = Fe, Mg
- T5+ = P

and have been reported.

The larger cations are:
- M+ = Na, K, Rb, NH4, Tl,
- M2+ = Ca, Sr, Ba, Pb, Eu, Mn.

Recently, even feldspars with M = H+, Li+, and Ag+ have been synthesized, although they are metastable under all P, T conditions (Deubener et al., 1991). Here, the term “end-member” applies to the more detailed formula

$$M^{7+}T_{m}T_{n}^{''}T_{4-m-n}^{'''}O_{8}$$

with m, n = 0, 1, 2. Prior to 1976, only end-member feldspars with mono- and divalent M cations were known, while trivalent M in feldspars had only been detected at the ppm level (Smith & Brown, 1988, pp. 377–384). In order to test whether the feldspar structure can accommodate considerable amounts of trivalent cations into the M position, Bettermann & Liebau (1976) tried to synthesize lanthanum feldspars because La3+ has nearly the same size (r[7+] = 1.10 Å) (Shannon, 1976) and electronegativity (χ = 1.08) (Allred & Rochow, 1958) as Ca2+ (r[2+] = 1.06 Å, χ = 1.04) and Na+ (1.12 Å, 1.01). In agreement with predictions based on Loewenstein’s (1954) aluminium avoidance rule,