Crystal chemistry of synthetic Mn-bearing anorthite: Incorporation of MnAl$_2$Si$_2$O$_8$ end-member into feldspar

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Abstract: A representative series of feldspars with intermediate compositions along the join CaAl$_2$Si$_2$O$_8$ (anorthite)-MnAl$_2$Si$_2$O$_8$ has been synthesized by heating stoichiometric mixtures of chemical reagents under an N$_2$ atmosphere. Morphological comparison with synthetic Mn-free anorthites suggests that Mn may play a role as a mineralizer for megacrystallization of anorthite. The reciprocal relationship between the Mn and Ca contents of these anorthites and the variation of the unit-cell parameters provides strong evidence that the Mn is incorporated into the extra-framework M site of the feldspar structure. The maximum limit of solubility of MnAl$_2$Si$_2$O$_8$ is about 25 mol% in CaAl$_2$Si$_2$O$_8$. Gradual decreases in the unit-cell dimensions and unit-cell volume with Mn content are similar to those observed in the CaAl$_2$Si$_2$O$_8$-SrAl$_2$Si$_2$O$_8$ series.

The crystal structure of synthetic Mn-bearing anorthite, Ca$_{0.725}$Mn$_{0.195}$Na$_{0.045}$Al$_{0.865}$Si$_{2.135}$O$_8$ (square represents an M site vacancy) with cell parameters $a = 8.131(2)$ Å, $b = 12.847(3)$ Å, $c = 7.069(1)$ Å, $\alpha = 94.03(1)^\circ$, $\beta = 115.89(1)^\circ$, $\gamma = 90.72(1)^\circ$, $V = 661.8(2)$ Å$^3$, space group C1, $Z = 4$, has been refined to an R-index of 3.9% using 2109 X-ray reflection intensities collected with MoKα radiation. The structure is isotypic with high albite NaAl$_2$Si$_3$O$_8$, but has the M site (containing Ca, Mn and Na) split into three sites (M1, M2, M3) with unequal occupancies: Mn/Ca/Na = 0.144/0.358/0.021 (M1), 0.0/0.179/0.0 (M2), 0.052/0.179/0.024 (M3). The Al/Si distributions calculated from the T-O bond lengths are as follows: Al/Si = 0.557/0.443 (T1o site) 0.434/0.566 (T1m), 0.455/0.545 (T2o) and 0.465/0.535 (T2m). The distribution of the Mn$^{2+}$ and Ca$^{2+}$ over the three split M sites, together with the disordered Al/Si distribution can give rise to many different locally ordered configurations. Spatial disorder of these configurations accounts for the reduction of the c axis to 7 Å in Mn-bearing anorthite. In addition, solid solution of the square Si$_8$O$_{24}$ end-member (the excess silica component) contributes to the shrinkage of the M site making it more favourable for Mn to enter the anorthite structure.

The crystal-chemical conditions promoting incorporation of Mn into anorthite are therefore (1) a highly disordered Al/Si distribution, (2) solid solution of square Si$_8$O$_{24}$ end-member, (3) crystallization from anhydrous melt at high temperature and (4) rapid cooling after crystallization. The rarity of Mn feldspars in nature cannot therefore be attributed to an intrinsic exclusion of Mn from the feldspar structure, but to the unusual combination of temperature, pressure and chemical conditions required for its crystallization.

Key-words: anorthite, MnAl$_2$Si$_2$O$_8$, synthesis, solid solution, crystal structure.

Introduction

The presence of numerous minor end-member components in natural feldspars has received considerable attention in the past two decades (Smith & Brown, 1988; Ribbe, 1994). Aluminosilicates with the feldspar topology have been synthesized by substituting Na, K, Rb, NH$_4^+$, Ca, Sr, Ba, Pb, Eu, La, H, Li and Ag into the M sites and P, Ge, B, Ga, Fe$^{3+}$, Mg and Fe$^{2+}$ into the tetrahedral sites. Ionic radii of the former group (except H) range from 0.92 to 1.61 Å, while those of the latter range from 0.11 to 0.63 Å (Shannon, 1976). Since the ionic radius of Mn$^{2+}$ is 0.96 Å in eight-fold coordination and 0.66 Å in tetrahedral coordination (Shannon, 1976), it is to be expected that Mn$^{2+}$ should, at least partially, substitute into the M site of the feldspar structure. In practice, the radius of...