American Mineralogist, Volume 65, pages 472–476, 1980

The crystal structure of a ternary (Ba,K,Na)-feldspar and its significance

KRISHNAMOORTHY VISWANATHAN AND KARL BRANDT

Mineralogisch-Petrographisches Institut
Technische Universität, Braunschweig
Federal Republic of Germany

Abstract

The crystal structure of a monoclinic ternary barium feldspar with the formula $(Ba_{0.19}K_{0.59}Na_{0.22})\,(Si_{2.82}Al_{1.13}Fe^{3+}_{0.05})O_8$ [a = 8.516(1), b = 13.023(2), c = 7.206(1)Å, β = 115.90(5)°, space group $C2/m$] has been refined to $R = 0.042$. The mean T–O distances are $(T_1\text{–}O) = 1.665$; $(T_2\text{–}O) = 1.636$Å, yielding the average Al contents: $Al_{T_1} = 0.405$, $Al_{T_2} = 0.185$.

If the structural state of the ternary feldspar is compared with those of pure potassium feldspars after normalizing the total Al in the tetrahedral sites of the former to the same amount as that possessed by the latter, the ternary feldspar has a disordered structural state similar to that of Spencer "C". As the investigated specimen occurs in the same metamorphic area where unmixed barium-rich feldspars have been found, it appears likely that the latter tend to reach the state of "maximum possible" order earlier and unmix earlier than the barium-poor varieties.

Introduction

Though alkali feldspars and plagioclases have been studied intensively, barium feldspars[1] have not been subjected to a similar examination, mainly because of their comparatively rare occurrence. The only detailed investigation is that of Gay and Roy (1968), who observed that barium feldspars are also influenced by the order/disorder of the Si/Al atoms, and that the lattice constants, especially c, behave similarly to those in other feldspars. Viswanathan (1978) and Viswanathan and Brandt (1978) showed that the barium feldspars from the highly metamorphosed manganese ore deposit of Otjosondu, Namibia, contain two interesting types: (1) barium-rich feldspars, which have unmixed into an almost pure celsian and a hyalophane of approximate composition $Or_{52}Cn_{44}Ab_4$ (wt%); and (2) ternary barium feldspars which contain, besides high Or contents, as much as 20% (wt%) Ab molecule.

Single-crystal studies of the ternary feldspar were undertaken for the following reasons:

(1) Homogeneous, natural ternary feldspars have not been observed in the corresponding plagioclase series and hence the barium analogs should provide useful information regarding the distribution of the Al and Si atoms in the different tetrahedral positions of such Al-rich feldspars.

(2) The influence of different parameters on the average (Si,Al)–O bond lengths in monoclinic potassium-rich feldspars has been investigated earlier (Phillips and Ribbe, 1973a). A structural investigation of Al-rich barium feldspars should reveal how far the results obtained with potassium feldspars are applicable to them.

Experimental and results

A typical feature of most barium feldspars from Otjosondu is that the cleavages, including (001), are usually not well developed. As a result the shape of the crystal used only approximates that of a parallelepiped (~0.06 × 0.14 × 0.28 mm). Precession and Weissenberg photographs of this crystal confirmed the absence of unmixed albite, though thin sections of bigger crystals showed occasional albite lamellae. Moreover, b-split reflections were not observed in spite of long exposures (maximum ≃72 hours). Hence the space group was determined as $C2/m$.

The chemical composition was determined on larger crystals with an electron microprobe. The

---

[1] The term "Ba-feldspars" has been used in this paper to designate all Ba–K-feldspars with or without sodium.

0003–004X/80/0506–0472$02.00

specimens were homogeneous except for occasional albite lamellae. The calculated formula is $(Ba_{0.19}K_{0.59}Na_{0.22})\,(Si_{2.82}Al_{1.13}Fe^{3+}_{0.05})O_8$ and is based on the average of six analyses carried out at six different points on a large single crystal. No attempt was made to determine the trace elements such as Sr, Rb, *etc.*

The lattice constants determined with a Guinier powder pattern are as follows: $a = 8.516(1)$, $b = 13.023(2)$, $c = 7.206(1)$Å and $\beta = 115.90(5)°$. The intensity data were collected on a Stoe 4-circle automatic single-crystal diffractometer with Mo*Kα* radiation and a graphite monochromator. Altogether 2812 reflections were measured in the 2θ range 0–65°, which were then reduced to 1346 independent reflections. The data were corrected for Lorentz, polarization, and absorption effects ($\mu = 24.4$). Atomic scattering factors given for neutral atoms in the international tables and anomalous scattering factors given by Cromer and Liberman (1970) were used while refining with an ORFLS program[2] (Busing *et al.*, 1962). At the beginning of the refinement a completely disordered arrangement of Al and Si atoms in the tetrahedral positions was assumed. Subsequently the values in T_1 and T_2 sites were calculated on the basis of the average T–O bond lengths. Isotropic and anisotropic refinements were carried out using 1346 reflections which included the unobserved ones.[3] The final residuals arrived at, using the isotropic and anisotropic temperature factors, were 0.066 and 0.042 respectively. Only unit weights were used throughout the refinement. The atomic coordinates (Table 1) and the important bond lengths and interatomic angles (Table 2) were taken from the anisotropic refinements. The temperature factors and the r.m.s. equivalents are listed in Table 3.

The specimen was then ion-exchanged in KCl melt at 900°C. This exchange involved replacing sodium in the structure by potassium without disturbing the Al/Si distribution in the tetrahedral framework.

Discussion

Colville and Ribbe (1968) determined the structures of two potassium feldspars, Spencer "B" and Spencer "C", which show different structural states. As the observed atomic parameters and interatomic distances of the ternary Ba-feldspars are very similar to those of Spencer "C" the relevant parameters of the latter are also included in all the tables for a comparison. A perusal of the atomic coordinates reveals relatively large movements of oxygen atoms $O_A(2)$. This results in the comparatively short (K,Na,Ba)–O bond of 2.647Å. All the other (K,Na,Ba)–O bonds are comparable to those of Spencer "C". The average (K,Na,Ba)–O distance of 2.939Å, calculated assuming a coordination number of nine for (K,Na,Ba), appears to be in accordance with the average occupancy of the respective site.

The average T–O and O–O distances of the T_1 and T_2 tetrahedra reflect the average size of the tetrahedral ion occupying the respective sites. The average Al content of the tetrahedra has been calculated on the basis of the differences of the average T–O bond lengths from the formulae of Ribbe (1975, p. R22).

The temperature factors of the ternary feldspars (Table 3) are distinctly larger than those of Spencer "B" and are comparable to those of Spencer "C"—a fact which is in tune with its disordered state.

Conclusions

Viswanathan and Brandt (1978) plotted the *c* parameter of many barium feldspars and their K-exchanged equivalents against their volume. The figure is reproduced here in a modified form (Fig. 1). The investigated ternary feldspar falls between the plots of Spencer "B" and Spencer "C", which suggests the likelihood of its being disordered, and is now confirmed by the structure determination.

It is interesting to compare Al/Si distributions with those of both the monoclinic potassium feldspars (Table 4). Order/disorder is judged from the relative distributions of Si/Al atoms in different tetrahedral positions and not from their absolute values. Hence the total Al in the tetrahedral sites should be normalized to the same amount as that possessed by one of the end members (Table 5), in order to make the comparison of the structural states of feldspars with different Al contents easier and meaningful. It must, however, be admitted that this type of normalization does not accurately model the physical reality of somewhat ordered feldspars of intermediate composition (Al:Si between 1:3 and 2:2), especially of those showing diffuse or well-defined *b*-split reflections.

The specimen studied corresponds to Spencer "C" in its structural state, though it falls nearer to "B" in the *c–V* plot (Fig. 1). This should not be surprising

---

[2] Fe^{3+} was included with Al^{3+} during the refinement of the structure, *i.e.* total Al = 1.18 in T sites.

[3] To receive a copy of the observed and calculated structure factors, order Document AM-80-132 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Table 1. Fractional atomic coordinates of ternary barium feldspar and Spencer "C"

Atom	Barium feldspar			Spencer C		
	x	y	z	x	y	z
$O_A(1)$	0	.1429(2)	0	0	.1459(8)	0
$O_A(2)$	.6273(4)[a]	0	.2864(4)	.6346(11)	0	.2851(13)
O_B	.8260(3)	.1422(2)	.2270(3)	.8280(7)	.1470(7)	.2282(9)
O_C	.0308(3)	.3101(2)	.2567(3)	.0349(6)	.3106(5)	.2607(9)
O_D	.1841(3)	.1254(2)	.4045(3)	.1815(6)	.1258(5)	.4065(7)
T_1	.0087(1)	.1831(1)	.2240(1)	.0095(3)	.1844(2)	.2239(3)
T_2	.7046(1)	.1175(1)	.3445(1)	.7089(2)	.1178(2)	.3443(3)
K(Na,Ba)	.2826(1)	0	.1345(1)	.2838(3)	0	.1373(4)

[a] Standard errors X10^{-4}, are in parentheses.

because the changes in the lattice parameter *c* are effected by different causes:

(1) The change in *c* (Δc = 0.006Å) as the composition varies from the KCl-exchanged Ba-feldspar (Ba + KC1) to the original sample (Ba) is caused only by ionic substitution.

(2) The change in *c* (Δc = 0.034Å) as one goes from Ba + KCl to Spencer "C" is produced by the coupled substitution BaAl → KSi under monoclinic symmetry. That this line runs approximately parallel to that of monoclinic, disordered (synthetic) Ba–K feldspars (shown as black squares in Fig. 1) suggests that the trend is plausible.

Note that the investigated specimen "Ba", after a cationic exchange reaction with KCl melt, plots near the boundary line for Ba–K feldspars with maximum possible order [this boundary line has been drawn on the reasonable assumption that the Ba-poor end

Table 2. Interatomic distances (Å) and angles (degrees). Estimated standard errors are in brackets and refer to the last decimal place

	Barium feldspar	Spencer C		Barium feldspar	Spencer C
T_1-$O_A(1)$	1.668(1)[a]	1.654(4)	$O_A(1)$-O_B	2.644(2)	2.642(6)
-O_B	1.653(2)	1.641(6)	$O_A(1)$-O_C	2.795(3)	2.774(11)
-O_C	1.670(2)	1.661(7)	$O_A(1)$-O_D	2.649(2)	2.655(5)
-O_D	1.670(2)	1.666(5)	O_B-O_C	2.747(3)	2.712(10)
			O_B-O_D	2.752(2)	2.735(7)
Mean T_1-O	1.665	1.656	O_C-O_D	2.722(4)	2.700(7)
T_2-$O_A(2)$	1.646(2)	1.641(3)	Mean O-O tetrahedron 1	2.718	2.703
-O_B	1.629(2)	1.620(6)			
-O_C	1.631(2)	1.631(6)			
-O_D	1.637(2)	1.621(5)	$O_A(2)$-O_B	2.666(3)	2.674(10)
			$O_A(2)$-O_C	2.584(3)	2.586(7)
Mean T_2-O	1.636	1.628	$O_A(2)$-O_D	2.661(3)	2.648(8)
			O_B-O_C	2.687(2)	2.677(8)
K-$O_A(1)$	2.856(2)	2.893(7)	O_B-O_D	2.702(3)	2.678(8)
-$O_A(2)$	2.647(2)	2.711(9)	O_C-O_D	2.715(3)	2.685(7)
-O_B	2.995(2)	3.045(7)			
-O_C	3.119(2)	3.129(6)			
-O_D	2.930(2)	2.945(7)	Mean O-O tetrahedron 2	2.669	2.658

T-O-T angles	Ba-Fs	Spencer 'C'	O-T-O angles	Ba-Fs	Spencer 'C'	O-T-O angles	Ba-Fs	Spencer 'C'
T_1-$O_A(1)$-T_1	143.4(3)	144.8(7)	$O_A(1)$-T_1-O_B	105.5(1)	106.6(3)	$O_A(2)$-T_2-O_B	109.0(1)	110.2(5)
T_2-$O_A(2)$-T_2	136.8(2)	137.8(5)	$O_A(1)$ O_C	113.7(1)	113.6(4)	$O_A(2)$ O_C	104.2(1)	104.4(4)
T_1-O_B-T_2	152.2(1)	153.3(4)	$O_A(1)$ O_D	105.0(1)	106.2(3)	$O_A(2)$ O_D	108.3(1)	108.5(4)
T_1-O_C-T_2	130.9(1)	131.1(4)	O_B O_C	111.5(1)	110.4(4)	O_B O_C	111.0(1)	110.8(4)
T_1-O_D-T_2	141.0(2)	141.6(4)	O_B O_D	111.8(1)	111.5(3)	O_B O_D	111.7(1)	111.4(3)
			O_C O_D	109.2(1)	108.5(3)	O_C O_D	112.4(1)	111.3(3)
Mean T-O-T	140.9	141.7						
			Mean	109.5	109.5	Mean	109.4	109.4

[a] Estimated standard errors are in brackets and refer to the last decimal place.

Table 3. Temperature factors and r.m.s. displacements

Atom	Isotropic B(Å^2)	r.m.s. displacement (Å)			Anisotropic (x 10^4)					
					Barium feldspar					
$O_A(1)$	1.80(6)	88	139	267	107(5)	23(2)	94(6)	0	55(5)	0
$O_A(2)$	1.80(6)	112	116	241	93(5)	16(1)	109(6)	0	29(5)	0
O_B	2.08(5)	83	179	274	89(3)	37(1)	120(5)	-6(2)	64(3)	0(2)
O_C	1.71(5)	95	136	240	81(3)	22(1)	100(4)	-5(2)	38(3)	-5(2)
O_D	1.70(5)	96	143	218	85(3)	24(1)	72(4)	-3(2)	23(3)	4(2)
T_1	0.95(2)	59	107	189	55(1)	14(0)	41(1)	-5(1)	27(1)	-3(0)
T_2	0.95(2)	70	100	186	52(1)	12(0)	52(1)	0(0)	24(1)	1(1)
K,Na,Ba	1.94(2)	99	167	230	67(1)	33(1)	114(1)	0	31(1)	0
					Spencer 'C'[a]					
$O_A(1)$	1.8(1)	129	129	160						
$O_A(2)$	1.8(2)	104	129	170						
O_B	2.2(1)	124	159	173						
O_C	1.7(1)	111	134	149						
O_D	1.6(1)	121	137	156						
T_1	0.91(3)	85	92	106						
T_2	0.80(3)	83	91	98						
K	2.23(6)	138	175	176						

a Anisotropic temperature factors for Spencer 'B' are not available.

member of the unmixed specimen (Viswanathan, 1978) represents a Ba-feldspar with maximum possible order]. As the Al/Si distribution in the feldspar framework is not disturbed during the ion exchange process, this observation leads to the conclusion that the "maximum possible order" for Ba-rich feldspars probably represents only a particular disordered distribution of Al and Si atoms depending upon the Al content—a result which has already been noted in plagioclase feldspars (Viswanathan, 1972; Ribbe, 1975, p. R29, R30). The very fact that the investigated specimen and a more Ba-rich but unmixed feldspar occur in the same metamorphic region probably means that the Ba-rich feldspars become unstable even at a relatively higher disordered state as compared to the Ba-poorer ones and hence they start unmixing somewhat earlier. Apparently a relationship exists between this observation and the results of Eberhard (1967), who by studying the rates of ordering in An_0, An_{10}, and An_{20} inferred that the ability to order declines with increasing anorthite content. With our present knowledge the same result can be interpreted to mean that because the maximum possible order for An-rich feldspars corresponds to relatively higher disordered states, they tend to reach their state of maximum possible order comparatively sooner than the An-poor ones and hence are unable to order further without unmixing. This interpretation is probably applicable to Ba-feldspars also, in which the unmixing is likely to take place more

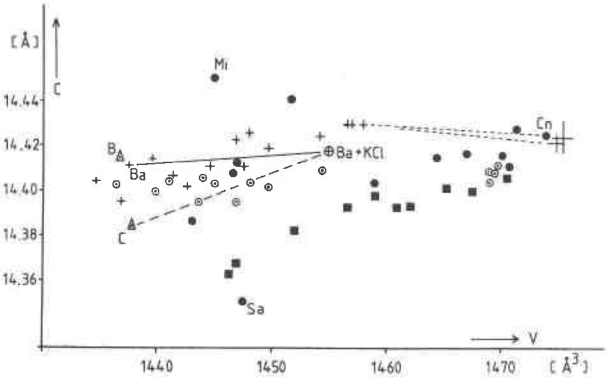

Fig. 1. Variation of the lattice parameter c of barium feldspars with volume ($c \simeq 14$Å has been assumed for all feldspars with space group $C2/m$).

+ : Natural barium feldspars from Otjosondu, Namibia;
⊕ : Na/K exchanged barium feldspar (Ba + KCl);
● : Natural feldspars of Gay and Roy (1968);
⊙ : Natural feldspars of Gay and Roy (1968) for which the lattice constants were again determined by the authors;
■ : Synthetic feldspars of Gay and Roy (1968);
△ : Monoclinic potassium feldspars (Colville and Ribbe, 1968);
Ba : Barium feldspar under investigation.

Table 4. Al/Si distributions in barium feldspar and Spencer "C"

Specimen	t_1	t_2	Σ Al in T-sites
Spencer "B"	0.39	0.11	1.0
Spencer "C"	0.35	0.15	1.0
Ternary Ba-feldspar (Ba)	0.405	0.185	1.18
Ternary Ba-feldspar	0.343*	0.156*	1.0*

* Total Al normalized to 1.0 see "conclusions".

rapidly because of the difference in the size of the bigger cations.

It is relevant perhaps to point out what is meant by "relatively higher disordered state." Hereby only one ordering scheme, the "microcline ordering" scheme, is considered for the whole series with *c* repeat distance of ~7Å and only the relative distributions of Al/Si atoms, obtained using the normalization method, are compared. According to this scheme it is possible to define Ba-feldspars with different Al contents but with "similar" structural states. It must be admitted that the term "similar" structural state considers only structural details and should not be correlated to any particular temperature and pressure conditions, which can be entirely different for the different feldspars. It must be also noted that "similar structural state" must be distinguished from "same" or "identical" structural states, which ion-exchanged feldspars are supposed to possess.

In order to test the applicability of the equations of Phillips and Ribbe (1973a), the T–O bond lengths of the ternary feldspar were calculated using their coefficients. The values calculated for T_1–$O_A(1)$, T_1–O_B, T_1–O_C, and T_1–O_D are 1.665, 1.659, 1.669, and 1.666Å respectively, whereas those calculated for T_2–O_A (2), T_2–O_B, T_2–O_C, and T_2–O_D are 1.643, 1.622, 1.632, and 1.629Å respectively. A comparison with the observed bond lengths (Table 2) reveals that the agreement is good in the case of five T–O bonds, but the three others show fairly large discrepancies. There is a slight improvement in these values if the inductive effect on the T–O bond of the divalent cation is also considered, as done by Phillips and Ribbe (1973b) for sodic plagioclase feldspars. No attempt is made to carry out a regression analysis for the eight T–O bonds of the barium feldspar as we feel the data are too scanty to draw significant conclusions.

Acknowledgments

We are indebted to Professor E. Woermann, Mineralogical Institute Aachen, for lending the specimen and to Professor E. Eberhard, Hannover, Professor M. Okrusch, Braunschweig, and Dr. H. Kroll, Münster, for critically reading the manuscript. Thanks are also due to Dr. P. Gay, Cambridge, England, for lending ten samples of barium feldspars from his collection. The suggestions and constructive criticisms of Dr. M. W. Phillips, University of Toledo, are gratefully acknowledged.

References

Busing, W. R., K. O. Martin and H. A. Levy (1962) A Fortran crystallographic least-squares program. *U. S. Atomic Energy Commission Rep. 6RNL-TM-305.*

Colville, A. A. and P. H. Ribbe (1968) The crystal structure of an adularia and a refinement of the structure of orthoclase. *Am. Mineral., 53,* 25–37.

Cromer, D. T. and D. Liberman (1970) Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys., 53,* 1891–1898.

Eberhard, E. (1967) Zur Synthese der Plagioklase. *Schweiz. Mineral. Petrogr. Mitt., 47,* 385–398.

Gay, P. and N. N. Roy (1968) The mineralogy of the potassium–barium feldspar series III: subsolidus relationships. *Mineral. Mag., 36,* 914–932.

Phillips, M. W. and P. H. Ribbe (1973a) The structures of monoclinic potassium-rich feldspars. *Am. Mineral., 58,* 263–270.

——— and ——— (1973b) The variation of tetrahedral bond lengths in sodic plagioclase feldspars. *Contrib. Mineral. Petrol., 39,* 327–339.

Ribbe, P. H. (1975) (Ed.) *Feldspar Mineralogy.* Mineralogical Society of America Short Course Notes, Vol. 2.

Viswanathan, K. (1972) Kationenaustausch an Plagioklasen. *Contrib. Mineral. Petrol., 37,* 277–290.

——— (1978) Intergrowth of Ba-rich and Ba-poor phases in barium feldspars from Otjosondu, South-West Africa. *Mineral. Mag., 42,* 294.

——— and K. Brandt (1978) Geordnete und entmischte Barium Feldspäte aus Otjosondu/Südwestafrika (abstr.). *Fortschr. Mineral., 56/1,* 140.

Manuscript received, July 16, 1979;
accepted for publication, December 26, 1979.