Refinement of the crystal structure of celsian

DANA T. GRIFFEN[1] AND P. H. RIBBE

Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract

The crystal structure of celsian from Jakobsberg, Sweden, $(Ba_{0.95}K_{0.05}Al_{1.95}Si_{2.05}O_8$, $a = 8.622$, $b = 13.078$, $c = 14.411$ Å, $\beta = 115.09°$, space group $I2/c$) has been refined using 528 'a' reflections ($h+k$ even, l even) and 272 'b', reflections ($h+k$ odd, l odd) $> 1\hat{\sigma}$. The 'b' reflections were measured at one-quarter the rate of 'a' reflections to obtain a higher level of significance for these very much weaker 'difference' reflections whose intensities are related only to Al/Si ordering in the tetrahedral framework.

The Jakobsberg celsian is very similar to a celsian from Broken Hill, Australia, $(Cn_{\sim84}Or_{\sim18})$ refined by Newnham and Megaw (1960). The mean T–O distances for the symmetrically non-equivalent tetrahedral sites are $T_1O = 1.639$, $T_2z = 1.636$; $T_1z = 1.719$, $T_2O = 1.718$ Å, indicating that by comparison with fully ordered anorthite the Si-rich sites contain ~0.18 Al and the Al-rich sites ~0.79 Al. In the Broken Hill celsian the Al contents are ~0.17 and ~0.76, respectively, consistent with a somewhat lower Al/(Al+Si) ratio. These partially disordered Al/Si distributions are not in strict accord with the aluminum avoidance principle and may result from anti-phase domain textures as previously observed in bytownite and transitional anorthite.

Introduction

The first X-ray study of celsian ($BaAl_2Si_2O_8$, symbol: Cn) by Taylor *et al.,* (1934) showed it to be approximately isomorphous with the monoclinic K-feldspar orthoclase. Subsequently, Gay (1956) found that single crystal photographs of celsian showed a set of very weak diffraction maxima with $h+k$ odd, l odd, indicating that celsian is body-centered and that the c-dimension of its unit cell is ~14.4 Å, approximately twice that of the $C2/m$ orthoclase. The choice of the unconventional space group symbol $I2/c$ (*cf.* Fig. 1, Chiari *et al., 1975*) was made by Newnham and Megaw (1960) in order to preserve the axial orientation of celsian relative to orthoclase and other feldspars, some of which also have been assigned unconventional space group symbols (albite and microcline, $C\bar{1}$; bytownite, $I\bar{1}$).

Newnham and Megaw (1960) solved the structure of a celsian (approximate formula $Ba_{0.84}K_{0.18}Al_{1.90}Si_{2.11}O_8$) from Broken Hill, Australia, using intensities from five zero-layer Weissenberg photographs taken about

the zones [100], [010], [001], [110], and [111]. They first determined the "average" structure, using only the strong 'a'-type reflections ($h+k$ even, l even) and refining in space group $C2/m$ with $c = 7.2$ Å. This symmetrized unit cell has the Ba atom and one oxygen (O_A2) on the mirror plane, one oxygen (O_A1) on the two-fold axis through the origin, and the two tetrahedrally coordinated Al,Si "average" atoms (T_1 and T_2) and the other oxygens O_B, O_C, O_D in general positions. Having refined the "average" or symmetrized structure, they continued the refinement in space group $I2/c$ by including the weak 'b' reflections ($h+k$ odd, l odd) and doubling the c cell edge. The Ba, O_A1, and O_A2 atoms were shifted slightly from special to general positions. The tetrahedral and oxygen sites were "split" and given a notation which has since been simplified to T_1O, T_1z, T_2O, T_2z; O_BO, O_Bz; O_CO, O_Cz; O_DO, O_Dz to indicate that they are related by a pseudo-$c/2$ translation in the doubled cell.[2]

Newnham and Megaw found that the mean T–O

---

[2] This notation is modified somewhat and simplified from that suggested by Megaw (1956). It corresponds to that used by Chiari *et al.* (1975).

bond lengths at T_1O and T_2z (1.639 and 1.635Å) and at T_2O and T_1z (1.712 and 1.717 Å) indicated a highly ordered Al/Si distribution in celsian. In fact, since the variable y coordinate of the Ba atom remained 0.0000, indicating that the atom is located on the glide plane, it was evident that the weak 'b' reflections and the doubling of the c cell dimension resulted only from ordering of Al and Si atoms.

A recent refinement of a synthetic $I2/c$ strontium feldspar ($SrAl_2Si_2O_8$, symbol: Srf) by Chiari *et al.* (1975) indicated that the smaller Sr cation was significantly shifted off the c-glide ($y = 0.0020$ [1]). The mean T–O bond lengths ($T_1O = 1.626$; $T_2z = 1.630$; $T_2O = 1.735$; $T_1z = 1.732$ Å), when compared to the grand mean Si–O bond length of 1.614Å and Al–O bond length of 1.747Å in ordered anorthite (Wainwright and Starkey, 1971) suggest ~10 percent Si in the Al-rich and ~10 percent Al in the Si-rich sites in Srf. By analogy there is ~24 percent Si in the Al-rich and ~17 percent Al in the Si-rich sites in the Broken Hill celsian, consistent with its $Cn_{\sim84}Or_{\sim18}$ composition.

It is the purpose of this refinement to provide precise structural data for a nearly pure celsian, for comparison with other aluminosilicate feldspar-type compounds ($I2/c$ Srf and ordered $P\bar{1}$ anorthite) and with synthetic $SrGa_2Si_2O_8$ and $BaGa_2Si_2O_8$, both of which crystallize in space group $I2/c$ and have similar highly ordered framework structures (Calleri and Gazzoni, 1975). Table 1 contains the crystal data for these compounds.

Experimental methods

The crystal used in this study was a clear cleavage fragment ($60 \times 60 \times 70\mu m$) from Jakobsberg, Sweden. It was provided by Mr. Timothy Grove from specimen #10062 of the Harvard Mineralogical Museum. Electron microprobe analysis indicated the approximate formula to be $Ba_{0.95}K_{0.05}Al_{1.95}Si_{2.05}O_8$ ($Cn_{\sim95}Or_{\sim5}$), which is similar to that of other celsians from the same locality studied by Gay and Roy (1968). The lattice parameters, listed in Table 1 with those of previously refined $M^{2+}T_2^{3+}T_2^{4+}O_8$ feldspar-type structures, were determined by least-squares refinement using 24 reflections measured on a fully-automated Picker four-circle diffractometer. They are within the range of those determined by Gay and Roy for other Jakobsberg celsians.

The computer programs used in this study, as listed in the *World List of Crystallographic Computer Programs* (Third Edition) were DATALIB, OR XFLS3, and OR FFE3. A total of 1054 intensities (557 'a' and 497 'b' reflections) were measured using Zr-filtered $MoK\alpha$ radiation in the range $0.1 < \sin\theta/\lambda < 1.2$ for 'a' reflections and $0.1 < \sin\theta/\lambda < 1.0$ for 'b' reflections; 'a' reflections were scanned at $1.0°2\theta/min$, and the weaker 'b' reflections at $0.25°2\theta/min$. In order to place the 'a' and 'b' reflections on the same scale, 20 weak 'a' reflections were measured at $0.25°2\theta/min$, and 20 strong 'b' reflections were measured at $1°2\theta/min$. The best-fit conversion factor for scaling the raw 'b' intensities to a $1°2\theta/min$ scan rate was then deter-

TABLE 1. Crystal data for $M^{2+}T_2^{3+}T_2^{4+}O_8$ feldspar-type compounds

	Celsian $(Cn_{\sim95}Or_{\sim5})$	Celsian $(Cn_{\sim84}Or_{\sim18})$	$SrAl_2Si_2O_8$	$CaAl_2Si_2O_8$	$SrGa_2Si_2O_8$	$BaGa_2Si_2O_8$
Source, reference*	(1)	(2)	(3)	(4)	(5)	(6)
Space group	$I2/c$	$I2/c$	$I2/c$	$P/\bar{1}$	$I2/c$	$I2/c$
a	8.622(4)**	8.627	8.388(3)	8.173(1)	8.481(2)	8.727(5)
b	13.078(6)	13.045	12.974(4)	12.869(1)	13.142(2)	13.240(6)
c	14.411(8)	14.408	14.263(6)	14.165(1)	14.444(3)	14.608(6)
α	90	90	90	93.11(1)	90	90
β	115.09(2)	115.2	115.2(1)	115.91(1)	115.48(4)	115.00(6)
γ	90	90	90	91.26(1)	90	90
Volume	1471.6	1467.0	1404.4	1337.7	1453.3	1530.0

*(1) Jakobsberg, Sweden, this work; (2) Broken Hill, N.S.W., Newham and Megaw (1960)--standard errors not determined; (3) synthetic, Chiari et al. (1975); (4) Val Pasmeda, Italy, Wainwright and Starkey (1971); (5) synthetic, Calleri and Gazzoni (1975).
**e.s.d.'s, given in parentheses, refer to last decimal place.

mined, and the 'b' $|F_{obs}|$ were later multiplied by it during the refinement. Lorentz-polarization and absorption corrections ($\mu_1 = 61.3$ cm^{-1}) based on the actual crystal shape were applied using the data reduction program DATALIB. Of the measured intensities 538 'a' and 331 'b' reflections had non-zero values of $|F_{obs}|$; of these, 528 and 272, respectively, had $|F_{obs}|$ values greater than $1\hat{\sigma}$, where $\hat{\sigma}$ is the estimated standard error of the observation; only the statistically observed measurements were included in the refinement.

Refinement of the structure was carried out in space group $I2/c$ with the full-matrix least-squares computer program OR XFLS3. The final atomic coordinates of Newnham and Megaw (1960) were used as starting parameters. The $|F_{obs}|$ were weighted proportionally to $1/\hat{\sigma}^2$.

Using isotropic temperature factors for all atoms, the refinement converged to an unweighted residual of 0.049 ($wR = 0.052$). Upon attempting refinement with anistropic temperature factors, the R-value dropped to 0.037, but the thermal parameter for $O_A 1$ became non-positive definite. Careful examination of the data disclosed a single obviously erroneous 'b' reflection (077; $|F_{obs}| = 42$, $F_{calc} = 3$). Removal of this reflection permitted full anisotropic refinement. The final unweighted residual for reflections with $|F_{obs}| > 1\hat{\sigma}$ was 0.034 ($wR = 0.037$). The inclusion of all 869 non-zero intensities yielded $R = 0.037$ ($wR = 0.045$). $|F_{obs}|$ and F_{calc} values are listed in Table 2.[3]

Atomic coordinates, temperature factors, and r.m.s. components of thermal displacement with thermal ellipsoid orientations are listed in Tables 3 and 4. Table 5 contains the important interatomic distances and angles calculated using the crystallographic function and error program OR FFE3. It is worth noting that the removal of the erroneous 'b' reflection mentioned above had a marked effect on the calculated interatomic distances. The calculated ⟨Si–O⟩ increased and ⟨Al–O⟩ decreased by 0.013Å, while the esd's of all distances decreased by approximately 30 percent.

Discussion

Ordering in the tetrahedral sites of celsian analogs

Anorthite, CaAl$_2$Si$_2$O$_8$, has frequently served as a standard for the determination of ordering in alu-

---

[3] To obtain a copy of this table, order Document AM-76-017 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

TABLE 3. Fractional atomic coordinates

Atom	x	y	z
Ba	0.2827(1)*	0.0000(1)	0.0653(0)
T_1O	.0096(3)	.1820(2)	.1103(2)
T_1z	.0076(3)	.1830(2)	.6148(2)
T_2O	.7054(4)	.1214(2)	.1730(2)
T_2z	.7019(3)	.1163(2)	.6743(2)
O_A1	.0005(9)	.1377(4)	−.0002(5)
O_A2	.6206(7)	−.0003(5)	.1438(4)
O_BO	.8349(8)	.1368(5)	.1119(5)
O_Bz	.8198(8)	.1370(5)	.6136(5)
O_CO	.0220(8)	.3062(5)	.1210(5)
O_Cz	.0293(8)	.3120(5)	.6312(5)
O_DO	.1836(8)	.1296(5)	.1958(5)
O_Dz	.1900(8)	.1231(5)	.7017(5)

*e.s.d.'s, given in parentheses, refer to last decimal place.

minosilicate feldspars. Its Al:Si ratio is 1:1, and every oxygen atom forms a bridge between an AlO$_4$ and an SiO$_4$ tetrahedron. The mean Al–O distance in ordered anorthite is 1.747Å; the mean Si–O distance is 1.614Å (Wainwright and Starkey, 1971). Recently, the structures of two $I2/c$ celsian analogs, both of them synthetic compounds containing Ga and Si in a 1:1 ratio, have been refined by Calleri and Gazzoni (1975), and one of them, SrGa$_2$Si$_2$O$_8$, has mean Si–O and Ga–O distances of 1.614 and 1.821Å, respectively. By comparison with anorthite, Si is presumed to be completely ordered into the T_1O and T_2z sites, and Ga must therefore be ordered into T_1z and T_2O. By contrast, the mean Si–O and Ga–O distances in BaGa$_2$Si$_2$O$_8$ are 1.634Å and 1.805Å, respectively, strongly suggesting partial Ga/Si disorder.

In 1962 Megaw et al. pointed out that it is statistically invalid to base conclusions about ordering on mean bond length differences which are of the same order of magnitude as the r.m.s. deviations of individual bond lengths from those means. Because the differences between corresponding mean bond lengths in the two gallosilicates are approximately equal to the r.m.s. values for bond length deviations (~0.02Å), and because the temperature factors of the tetrahedral atoms are smaller than those in anorthite (Wainwright and Starkey, 1971) and similar to each other, Calleri and Gazzoni have concluded that the postulate of partial disorder in their BaGa$_2$Si$_2$O$_8$ is unnecessary.

At least three circumstances speak against their conclusion. First, with one exception the temperature factors for the T-atoms of Cn$_{\sim95}$Or$_{\sim5}$, which must

TABLE 4. Isotropic and anisotropic temperature factors

Atom	B(Å)	Anisotropic temperature factors ($\times 10^4$)					
		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	0.99(1)*	28(1)	14(1)	19(1)	−1(1)	7(1)	−1(1)
T_1O	0.70(5)	28(5)	9(2)	12(2)	−1(3)	8(2)	−1(2)
T_1z	0.49(5)	13(5)	7(2)	8(2)	−4(3)	2(3)	0(2)
T_2O	0.51(5)	22(5)	4(2)	9(2)	3(3)	5(3)	1(2)
T_2z	0.54(5)	16(4)	7(2)	10(2)	−1(3)	4(2)	1(2)
O_A1	0.70(10)	47(9)	5(3)	8(3)	−5(7)	6(5)	0(4)
O_A2	0.84(10)	31(9)	2(3)	22(4)	8(6)	5(5)	4(4)
O_BO	1.40(13)	64(14)	15(4)	27(5)	−11(6)	22(7)	−2(4)
O_Bz	1.04(12)	39(12)	9(4)	16(4)	4(6)	4(6)	−1(3)
O_CO	1.21(13)	55(13)	9(4)	22(5)	−3(6)	12(7)	1(4)
O_Cz	1.08(12)	24(12)	19(4)	22(4)	−1(6)	16(6)	4(4)
O_DO	1.13(12)	38(12)	19(4)	17(4)	−2(6)	6(6)	−3(4)
O_Dz	1.14(12)	41(12)	22(5)	16(5)	8(6)	12(6)	3(4)

r.m.s. components of thermal displacement along principal axes (r) and thermal ellipsoid orientation for Ba

r	r.m.s. displacement	Angle (°) with respect to		
		a	b	c
1	0.093(2)	27(3)	84(5)	89(2)
2	0.109(2)	81(4)	169(4)	99(4)
3	0.133(1)	115(2)	99(4)	9(4)

e.s.d.'s, given in parentheses, refer to last decimal place.

necessarily be partially disordered due to its composition, are also lower than any of those for tetrahedral sites in anorthite and are similar to each other. Arguments based on comparisons of temperature factors from one structure and composition to another are tenuous in any case. Second, ⟨Si–O⟩ increases from $SrGa_2Si_2O_8$ to $BaGa_2Si_2O_8$ by about the same amount that ⟨Ga–O⟩ decreases, a highly fortuitous circumstance if $BaGa_2Si_2O_8$ is not partially disordered. Third, Phillips and Kroll (personal communication) have completed the refinement of another synthetic $BaGa_2Si_2O_8$ in which the ⟨Si–O⟩ distances are shorter and the ⟨Ga–O⟩ distances are longer than in the specimen of Calleri and Gazzoni. Statistical theory notwithstanding, it would seem reasonable to postulate ~10 percent disorder in this structure.

A similar degree of disorder was observed in one synthetic $SrAl_2Si_2O_8$ (Chiari *et al.,* 1975), but another synthesized by Pentinghaus and investigated by Kroll and Phillips (personal communication) shows weak '*c*' (*h*+*k* even, *l* odd) and '*d*' (*h*+*k* odd, *l* even) reflections indicative of space group $P\bar{1}$ and (possibly) complete Al/Si order. This specimen would be analogous to $P\bar{1}$ anorthite, $CaAl_2Si_2O_8$, which has always proven to be completely ordered (Megaw *et al.,* 1962;

Wainwright and Starkey, 1971; Czank, 1973; Foit and Peacor, 1973; J. R. Smyth, personal communication).

TABLE 5. Interatomic distances (Å) and angles (°)

	T–O distances		O–O distances	O–T–O angles
T_1O tetrahedron				
T_1O–O_A1	1.664(6)*	O_A1–O_BO	2.570(8)	102.7(3)
–O_BO	1.628(7)	–O_CO	2.768(8)	114.4(3)
–O_CO	1.630(7)	–O_DO	2.589(9)	103.4(3)
–O_DO	1.634(7)	O_BO–O_CO	2.710(8)	112.6(3)
		–O_DO	2.725(9)	113.3(4)
		O_CO–O_DO	2.676(9)	110.1(4)
Mean	1.639		2.673	109.4
T_1z tetrahedron				
T_1z–O_A1	1.727(6)	O_A1–O_Bz	2.686(8)	102.4(3)
–O_Bz	1.721(7)	–O_Cz	2.900(8)	115.5(3)
–O_Cz	1.701(7)	–O_Dz	2.669(9)	101.1(3)
–O_Dz	1.728(7)	O_Bz–O_Cz	2.859(8)	113.3(3)
		–O_Dz	2.898(8)	114.3(3)
		O_Cz–O_Dz	2.804(9)	109.6(3)
Mean	1.719		2.803	109.4
T_2O tetrahedron				
T_2O–O_A2	1.728(7)	O_A2–O_BO	2.749(9)	106.5(3)
–O_BO	1.702(6)	–O_CO	2.654(8)	100.7(3)
–O_CO	1.719(7)	–O_DO	2.788(9)	107.8(3)
–O_DO	1.722(7)	O_BO–O_CO	2.856(8)	113.2(3)
		–O_DO	2.843(8)	112.3(3)
		O_CO–O_DO	2.904(9)	115.1(3)
Mean	1.718		2.799	109.3
T_2z tetrahedron				
T_2z–O_A2	1.650(7)	O_A2–O_Bz	2.639(9)	107.6(3)
–O_Bz	1.621(6)	–O_Cz	2.561(8)	102.1(3)
–O_Cz	1.643(7)	–O_Dz	2.668(9)	108.9(3)
–O_Dz	1.630(7)	O_Bz–O_Cz	2.707(7)	112.0(3)
		–O_Dz	2.706(8)	112.6(3)
		O_Cz–O_Dz	2.727(9)	112.8(3)
Mean	1.636		2.668	109.3

Ba polyhedron		**T–O–T angles**	
Ba–O_A2	2.641(5)	T_1O–O_A1–T_1z	139.6(3)
–O_A1	2.847(6)	T_2O–O_A2–T_2z	133.9(3)
–O_A1	2.854(6)	T_1O–O_BO–T_2O	149.9(5)
–O_Dz	2.903(6)	T_1z–O_Bz–T_2z	148.9(4)
–O_BO	2.916(6)	T_1O–O_CO–T_2O	127.0(4)
–O_DO	2.924(7)	T_1z–O_Cz–T_2z	130.3(4)
–O_Bz	2.949(6)	T_1O–O_DO–T_2O	139.4(4)
–O_Cz	3.124(6)	T_1z–O_Dz–T_2z	137.8(4)
–O_CO	3.150(7)		
Mean	2.862 (CN=7)		138.4
	2.923 (CN=9)		

e.s.d.'s, given in parentheses, refer to last decimal place.

Ordering in the tetrahedral sites of natural celsians

The results of our structure refinement of $Cn_{\sim95}Or_{\sim5}$ are surprisingly similar to those obtained for $Cn_{\sim84}Or_{\sim18}$ by film methods (Newnham and Megaw, 1960), particularly with regard to the tetrahedral $O \cdots O$ distances, $O-T-O$ angles, and mean $T-O$ and Ba,K–O bond lengths. Only for T_2O do the corresponding $\langle T-O \rangle$ distances in the two structures differ by more than 0.002Å. Despite the difference in chemical composition, the mean Ba,K–O distances are also statistically identical, whether the M-site is considered 7- or 9-coordinated. As in $Cn_{\sim84}Or_{\sim18}$ the Ba,K and O_A2 atoms lie statistically on the c-glide, and O_A1 is on the pseudo-diad axis. Thus the intensities of the 'b' reflections are due entirely to the doubling of the c axis introduced by Al/Si ordering in the tetrahedral sites.

The ordering scheme in celsian does not appear to be as straightforward as that in primitive anorthite and $SrGa_2Si_2O_8$. In both $Cn_{\sim84}Or_{\sim18}$ and $Cn_{\sim95}Or_{\sim5}$ some degree of disorder is inevitable since the Al:Si ratios are 1.84:2.16 and 1.95:2.05, respectively. But even after the silicon atoms in excess of 2.00 in the formula are assigned to the Al sites, the mean T–O bond lengths, when compared to those in anorthite (see the first paragraph of this Discussion), indicate the presence of an additional ~0.35 silicon atoms in the Al sites and the same amount of Al in the Si sites of both structures. There appears to be no obvious reason to expect Al/Si disorder beyond that due to the Or content, and it is particularly surprising that the amount of this "excess" disorder is the same in two such chemically different celsians from different localities and geologic environments.

Unless an anti-phase domain texture similar to that postulated for bytownite (Megaw, 1962; Fleet *et al.*, 1966) and transitional anorthite (Ribbe, 1963; Foit and Peacor, 1973) occurs in the $SrAl_2Si_2O_8$ of Chiari *et al.* (1975) and these two celsian structures, there is no obvious rationalization of their partial disorder. Lacking any direct diffraction evidence for a domain texture, it might be concluded that the nearly sacrosanct aluminum avoidance principle (Lowenstein, 1954; Goldsmith and Laves, 1955) so clearly applicable to plagioclase feldspars (Smith and Ribbe, 1969) is not operative in these compounds, or by extension, in $BaGa_2Si_2O_8$. But the recent success of Bailey (1975) in using a distance least-squares refinement program in determining that sheet silicates, whose 'average' structures were apparently disordered, in fact have ordered Al/Si distributions, has encouraged us to try the same approach with celsian and other aluminosilicates which appear to violate the aluminum avoidance principle. This will be reported in a later publication.

References

BAILEY, S. W. (1975), Cation ordering and pseudosymmetry in layer silicates: Presidential Address, 1974. *Am. Mineral.* **60,** 175–187.

CALLERI, M. AND G. GAZZONI (1975) The structures of (Sr,Ba) $[(Al,Ga)_2(Si,Ge)_2O_8]$. I. The crystal structures of synthetic feldspars $SrGa_2Si_2O_8$ and $BaGa_2Si_2O_8$. *Acta Crystallogr.* **B31,** 560–568.

CHIARI, G., M. CALLERI, E. BRUNO AND P. H. RIBBE (1975) The structure of partially disordered synthetic strontium feldspar. *Am. Mineral.* **60,** 111–119.

CZANK, M. (1973) Strukturuntersuchungen von Anorthit in Temperaturbereich von 20°C bis 1430°C. Doctoral dissertation, Eidgenössischen Technischen Hochschule, Zurich, 75 p.

FLEET, S. G., S. CHANDRASEKHAR AND H. D. MEGAW (1966) The structure of bytownite ('body-centered anorthite'). *Acta Crystallogr.* **21,** 782–801.

FOIT, F. F. AND D. R. PEACOR (1973) The anorthite crystal structure at 410 and 830°C. *Am. Mineral.* **58,** 665–675.

GAY, P. (1956) A note on celsian. *Acta Crystallogr.* **9,** 474.

——— AND N. N. ROY (1968) The mineralogy of the potassium-barium feldspar series III. Subsolidus relationships. *Mineral. Mag.* **36,** 914–932.

GOLDSMITH, J. R. AND F. LAVES (1955) Cation order in anorthite $(CaAl_2Si_2O_8)$ as revealed by gallium and germanium substitutions. *Z. Kristallogr.* **106,** 213–226.

LOWENSTEIN, W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. *Am. Mineral.* **39,** 92–96.

MEGAW, H. D. (1956) Notation for felspar structures. *Acta Crystallogr.* **9,** 56–60.

——— (1962), Order and disorder in felspars. *Norsk Geol. Tidsskr.* **42,** 104–137.

———, C. J. E. KEMPSTER AND E. W. RADOSLOVICH (1962) The structure of anorthite, $CaAl_2Si_2O_8$. II. Description and discussion. *Acta Crystallogr.* **15,** 1017–1035.

NEWNHAM, R. E. AND H. D. MEGAW (1960) The crystal structure of celsian (barium felspar). *Acta Crystallogr.* **13,** 303–312.

RIBBE, P. H. (1963) Structural studies of plagioclase felspars. Ph.D. dissertation, Cambridge University, p. 159–222.

SMITH, J. V. AND P. H. RIBBE (1969) Atomic movements in plagioclase feldspars: kinetic interpretation. *Contrib. Mineral. Petrol.* **21,** 157–202.

TAYLOR, W. H., J. A. DARBYSHIRE AND H. STRUNZ (1934) An X-ray investigation of the felspars. *Z. Kristallogr.* **87,** 464–498.

WAINWRIGHT, J. E. AND J. STARKEY (1971) A refinement of the structure of anorthite. *Z. Kristallogr.* **133,** 75–84.