Structural effects of the incorporation of large-radius alkalis in high cordierite

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Abstract

Single-crystal X-ray investigations of potassic high cordierite revealed reflections not compatible with space group $P6/mcc$, which is the space group previously accepted for all high cordierite. To obtain single crystals large enough for a structure determination using X-ray intensities, K-bearing high cordierite samples were synthesized from glass. After measuring X-ray intensities on a single-crystal diffractometer, the structure was refined in a number of subgroups of $P6/mcc$. The comparisons between the resulting R values and structure descriptions lead to the conclusion that only space group $P\bar{6}$ can describe the framework deformations induced by the presence of K in the structural channels at $z \approx 0.14$, which is a position of low symmetry. The redetermination of the space group of other high cordierite crystals either free of alkalis or containing Na or Cs revealed no deviation from space group $P6/mcc$. The refined structure of Cs-bearing high cordierite displayed framework deformations as a consequence of the presence of Cs in structural channels at $(0,0,\frac{1}{4})$. The high symmetry of this position does not lead to asymmetric forces on the framework, thus preserving the space group $P6/mcc$.

Introduction

Cordierite with the idealized formula $(Mg,Fe)_2[Al_4Si_5O_{18}]$ occurs essentially in two polymorphic modifications that are both closely related to the structure of beryl (Gibbs, 1966; Meagher and Gibbs, 1977). Six-membered rings of tetrahedra (T2) occupied by Al and Si are stacked to form structural channels parallel to the c axis. These ring stacks are interconnected in the third dimension by additional Al,Si tetrahedra (T1). Because of this topology octahedral sites are created that are occupied by Mg or Fe (Fig. 1). The high-temperature polymorph of cordierite is characterized by a more or less random distribution of Al and Si between the ring and the linking tetrahedra, thus leading to hexagonal symmetry and space group $P6/mcc$ (Meagher and Gibbs, 1977; Armbruster, 1985). Ordering of Si and Al in all tetrahedra produces the low-temperature polymorph that is orthorhombic with space group $Cccm$ (Gibbs, 1966). In this polymorph Al and Si do not strictly alternate but still obey the Al avoidance rule established by Loewenstein (1954).

The high-temperature polymorph (also called indialite) of the pure magnesium cordierite end-member $(Mg_2Al_4Si_5O_{18})$ is only stable in the interval between 1455 and 1465 °C at atmospheric pressure. Above this interval it melts incongruently to form mullite + melt, whereas below 1455 °C the ordered orthorhombic polymorph is the stable phase. Disordered high cordierite also crystallizes metastably from all temperatures below 1455 °C and can be retained by quenching (Schreyer and Schairer, 1961). Cordierite with states of Al,Si order intermediate between the high- and the low-temperature polymorphs can be produced by annealing metastable high cordierite at temperatures below 1455 °C (Putnis, 1980; Putnis et al., 1987).

Alkalis can be incorporated into the structural channels of cordierite. The electrostatic charge of these cations is often balanced by a concomitant change of the Al/Si ratio in the framework according to the equation $(K,Na)^+ + Al^{3+} \rightarrow Si^{4+}$.

Potassic cordierite was synthesized by annealing glass with a composition equivalent to cordierite with the formula $K_{0.1}Mg_2Al_{4.1}Si_{4.9}O_{18}$ for 3 d at 1460 °C. A single crystal of high cordierite was isolated under the polarizing microscope by breaking away the surrounding glass. The technical conditions for intensity measurements and the statistical treatment of R values resulting from structure refinements have been described elsewhere (Daniels, 1990). The comparison of R values led to the conclusion that potassic high cordierite must have one of the three space groups $P6$, $P\bar{6}$, and $P3$.

In order to determine the space group of high cordierite free of K, Na-substituted and alkali-free high cordierite were synthesized using the flux method proposed by Lee and Pentecost (1976). These syntheses yielded large single crystals. In all cases they showed no deviation from space group $P6/mcc$ even after exposure times of more than 150 h when examined with single-crystal X-ray film methods. Consequently it is the incorporation of K that is responsible for the appearance of extra X-ray reflections of type $h01$ and $hh1$ that are not compatible with space group $P6/mcc$.

The atomic coordinates resulting from refinements in the above-mentioned three space groups are listed in Ta-
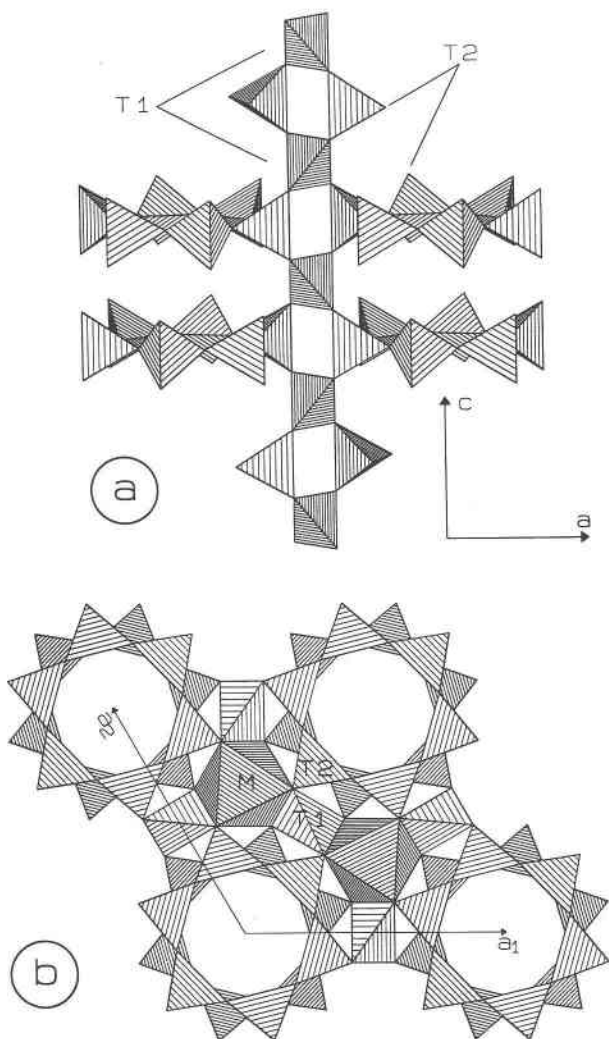
Fig. 1.   Schematic drawing of the three-dimensional arrangement of polyhedra in the structure of the high cordierite. The nomenclature is referenced in the text. (a) Ring and chain forming tetrahedra and (b) projection parallel to [001] that also shows the octahedra.

ble 1 together with the results for space group $P6/mcc$.[1] The origin along $\mathbf{c}$ was fixed in space groups $P6$ and $P3$ by keeping $z = \pm 1/4$ for the ring-connecting T1 tetrahedral positions and $z = 0$ or $z = 1/2$ for the T2 ring sites invariant. The positions did not move significantly when they were allowed to vary. In the case of space group $P6$ the same was found for the octahedrally coordinated positions M. The respective parameters could be fixed along $\mathbf{c}$ as well.

Because of strong parameter correlations, the positions of K for space groups $P6$ and $P3$ could only be refined

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[1] Copies of Tables 1–3 may be ordered as Document AM-92-490 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

when they were coupled to each other; however, the two independently refined values in space group $P\bar{6}$ show no significant deviation from the requirements of space group $P6/mcc$, so the appearance of reflections of type $h01$ and $hh1$ must have other structural causes. Since neither pure Mg- nor Na-substituted high cordierite produces these extra reflections, the presence of K in the channels of high cordierite must cause their appearance indirectly. Hence, the structural deviations from sapce group $P6/mcc$ should be sought in the positions of the O atoms of the first coordination sphere of K. Deviations in positions of these O atoms from positions required by space group $P6/mcc$ should in turn imply displacements in the whole framework of potassic high cordierite.

Neither the calculation of polyhedral distortions as proposed by Robinson et al. (1971) nor the calculation of bond-strength sums using the method of Brown and Shannon (1973) gave any evidence for the true space group of potassic high cordierite. Nevertheless, these calculations showed that the structure descriptions resulting from the refinements do not produce large deviations from polyhedral dimensions compared with the work of Robinson et al. (1971). Additionally, the refinement in space group $P\bar{6}$ resulted in a good agreement between observed and calculated structure amplitudes even for the weak additional reflections (Table 2).

The fact that K causes a reduction of symmetry in high cordierite raises the question whether there are other large-radius alkali ions that may also occupy channel positions and lead to deviations from space group $P6/mcc$. Consequently, Cs-bearing high cordierite crystals were synthesized and their structure refined.

Cs-SUBSTITUTED HIGH CORDIERITE

Experimental

Natural Cs-substituted cordierite has not been found, but Evans et al. (1980) synthesized such cordierite and discovered large differences between the powder diffraction profiles of this and of pure magnesium cordierite.

In order to locate the Cs, which cannot be placed at 0,0,0 because its radius of about 1.69 Å is too large for this constricted position, and to find simultaneously the reason for the differences in the powder diffraction pattern (Evans et al., 1980), single crystals of Cs-substituted high cordierite were synthesized. This was accomplished using the PbO-V$_2$O$_5$ flux method described by Lee and Pentecost (1976) modified with respect to the desired cordierite composition, $Cs_{0.5}Mg_2Al_{4.5}Si_{4.5}O_{18}$, as consistent with the substitution mechanism Cs + Al → Si. Using this method, hexagonal prisms with lengths up to 200 μm were grown. Their quality was checked optically and by means of single-crystal X-ray film methods. Weissenberg photographs of $hk1$ layers of such crystals did not show any deviation from space group $P6/mcc$ even after exposure times of more than 150 h.

A single crystal was mounted on a Syntex R3 four-circle diffractometer and centered optically. The automatic

centering of 25 reflections and the subsequent refinement of the dimensions of a C-centered orthorhombic unit cell led to the lattice parameters $a = 16.976(10)$ Å, $b = 9.801(5)$ Å, and $c = 9.381(6)$ Å and a ratio $a/b\sqrt{3} = 1.0001(8)$, which perfectly describe an orthohexagonal cell corresponding to a truly hexagonal cell with $a = 9.801$ Å and $c = 9.381$ Å. On the basis of the orthohexagonal unit cell, intensities for reflections with $-6 \leq h < 27$, $-14 \leq k \leq 14$, and $0 \leq l \leq 15$ and $2\theta \leq 70°$ were measured using graphite monochromatized $MoK\alpha$ radiation. Three out of every 50 intensities measured were for standard reflections 004, 402, and 044.

After scaling the intensities to the standard reflections and correcting for Lorentz and polarization factors, resultant structure amplitudes were reindexed according to the truly hexagonal unit cell and merged using the Laue symmetry $6/mmm$. This gave rise to 556 unique observed structure amplitudes with $|F|_o > 3\sigma_{|F|_o}$ and a merging R value of 4.6% for the subsequent calculations, which were all performed using the program SHELX76 (Sheldrick, 1976).

As starting parameters the atom positions obtained for potassic cordierite in space group $P6/mcc$ were used. The refinement using weighted structure amplitudes ($w = 1/\sigma^2$) converged rapidly, but the final R_w value $\{R_w = [\Sigma\sqrt{w} \cdot (|F|_o - |F|_c)]/[\Sigma\sqrt{w} \cdot |F|_o]\}$ was only 15.6%. In a difference Fourier synthesis a large maximum was found at 0,0,¼, which was taken to be the position of the Cs cation. After including the Cs on this position, which is fixed by the symmetry of space group $P6/mcc$, and refining its site occupancy factor and its anisotropic temperature factors, the R_w value decreased to 3.91%. Observed and calculated structure factors are listed in Table 3. The refined occupancy factor corresponds to 0.281(2) Cs per formula unit (pfu) and a cordierite formula of $Cs_{0.28}Mg_2Al_{4.28}Si_{4.72}O_{18}$. The occupancies of the tetrahedral sites were chosen to give Al/Si ratios of 1/3 for the T2 tetrahedra and 5/1 for the T1 tetrahedra. These ratios had been found to be an optimum for high cordierite by Armbruster (1985) using a distance least-squares refinement. In order to take the Cs concentration and the resultant changed overall Al/Si ratio into account, only the Al/Si ratio for the T1 positions was changed to about 13/1, which approximately reflects the above-mentioned formula.

DISCUSSION

The K position

The K has been located in the structural channels of potassium cordierite at $z = 0.14$, $z = 0.36$, $z = 0.64$, $z = 0.86$ (Kim et al., 1984; this work, Table 1). These positions are symmetrically equivalent in space group $P6/mcc$, divide into two symmetrically nonequivalent positions in space group $P\bar{6}$, and are independent in space groups $P6$ and $P3$. The positions with $z = 0.14$ and $z = 0.36$ are located in one large cage of the cordierite channel and are separated by approximately 2.06 Å. This distance is small compared with the diameter of a K cation of 2.66 Å. Consequently, K cannot be located at both positions in one cage at the same time. The same applies to the positions at $z = 0.64$ and $z = 0.86$. The channel positions at $z = 0.14$ and $z = -0.14$ (above and below a six-membered tetrahedral ring) are approximately 2.62 Å apart in different cages and cannot be occupied by K at the same time either. Hence, the position of a K cation in one cage is not independent of the occupancy of the next cage by K. When the K concentration exceeds a certain value, an ordering of the cations should become observable. This was not the case in this work because the concentration of K (0.1 pfu) leads to an occupancy of only 10% of the cages.

The K at $z = 0.14$ is primarily coordinated by O2 O atoms at $z = 0$ that form the inner O ring of the six-membered tetrahedral rings (Fig. 1). The distance between K and these O atoms is approximately 3.02 Å. When the O radius is taken to be 1.40 Å, this distance gives an ionic radius of 1.62 Å for K. This value corresponds well with the effective ionic radii observed for K with seven or eight coordinating anions (Shannon, 1976). The electrostatic valence of the K cation is rather badly compensated in the positive direction of the c axis. The O2 O atoms of the next ring ($z = 0.5$) are 4.33 Å from the site at $z = 0.14$. In the plane perpendicular to the c axis, the K cation is surrounded by the O1 O atoms. Since their distance from the site at $z = 0.14$ is approximately 4.23 Å and since the K-T2 distance is appreciably smaller (3.50 Å), the O1 O atoms are shielded by the Al or Si atom in the T2 positions. The fact that the observed K radius is slightly larger than the one expected for six-coordinated K leads to the assumption that there must still be some bonding between the K cation and O atoms other than those at $z = 0$. Hence, the coordination sphere of K may be described as $^{[6+6+6+6]}$K indicating that K at $z = 0.14$ is more or less strongly bonded to the four six-membered O rings at $z = 0$, $z \approx 0.14$, $z \approx 0.36$, and $z = ½$. This bonding is expected to cause distortions of the structure, finally leading to the appearance of X-ray reflections that otherwise would be extinct.

Comparing the lattice dimensions of pure Mg- and K-substituted high cordierite (Kim et al., 1984; this study), it becomes evident that the unit-cell volume increases when K is present. Since the K cation occupies a position in the channel that is large enough to accommodate it, the expansion of the unit cell must be due to changes in the framework itself. Two mechanisms may be responsible for such changes. The first is that the Al/Si ratio is increased by the substitution K + Al → Si. This leads to increased mean tetrahedra sizes. The second mechanism is the slight change of relative positions of the framework atoms when K is introduced into the structure, which may also cause expansion in the unit cell. The two mechanisms cannot be distinguished because no substitution is known that allows the incorporation of K without changing the chemical composition of the framework.

No differences between the four K positions in one unit cell could be detected (Table 1). This means that the K

TABLE 4. Refined positional and thermal parameters for Cs-substituted high cordierite

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M	⅓	⅔	¼	119(6)	U_{11}	179(11)	0	0	½U_{11}
T1	½	½	¼	96(4)	U_{11}	129(7)	0	0	½U_{11}
T2	0.3735(1)	0.2663(1)	0	115(6)	92(4)	143(5)	0	0	62(5)
O1	0.4844(2)	0.3489(2)	0.1439(2)	163(9)	132(9)	169(9)	−1(8)	−28(9)	90(8)
O2	0.2299(4)	0.3070(4)	0	196(16)	232(17)	312(17)	0	0	155(14)
Cs	0	0	¼	406(14)	U_{11}	558(22)	0	0	½U_{11}

Note: Thermal parameters are multiplied by 10^4. They are defined by $\exp(-2\pi^2 h_i h_j a_i^* a_j^* U_{ij})$.

positions can be described as being related by a horizontal mirror plane, as it is present in space group $P6/mcc$. Only one of the three possible space groups, namely $P\bar{6}$, relates the K positions above and below a six-membered tetrahedral ring by a mirror plane while simultaneously leaving enough degrees of freedom for the framework to account for the presence of a cation at 0,0,0.14.

Cs-substituted high cordierite

The large differences between the R_w values of the structure refinements of Cs-bearing cordierite with and without considering the Cs show the strong influence of Cs on the X-ray intensities. Hence, the changes in intensities of a powder diffraction pattern of cesium cordierite found by Evans et al. (1980) compared with pure magnesium cordierite are primarily caused by the large Cs cation.

The refined parameters are listed in Table 4. The atom positions are not exceptional when compared with other high cordierite structures like those of potassic high cordierite (this work) or pure magnesium cordierite (Armbruster, 1985). The O2 O atoms display the largest standard deviations for their positional as well as for their vibrational parameters not only compared to the framework cations but also in comparison to the O1 O atoms (Table 4). The same could be observed for K-substituted cordierite (Table 1) but not for pure magnesium cordi-

erite (Armbruster, 1985). This may be due to the partial occupancy of the alkali positions and resultant variation in T2-O2 distances (Table 5).

The Cs atom is located in the large cage of the structural channel of cordierite at $z = \frac{1}{4}$ surrounded by 24 O atoms. This sphere is composed of four six-membered rings, namely the two O1 rings at $z \approx 0.14$ and $z \approx 0.36$ and the two O2 rings at $z = 0$ and $z = \frac{1}{2}$. Since the Cs-O1 distance is large (4.358 Å) compared with the Cs-O2 distance (3.586 Å), the coordination can be regarded as being 12-fold. The O2 rings are farther apart than in the case of pure magnesium cordierite, although one might expect a contraction due to the coulombic forces between Cs$^+$ and O2^{2-}; obviously the repulsion between Cs$^+$ and the cations in T2 positions is stronger in this case (for distances see Table 5).

In a structural model constructed of solid balls instead of atoms, the Cs ion would just touch the O2 atoms if it had a radius of 2.185 Å. This is about 16% larger than the radius found by Shannon (1976) for 12-fold coordinated Cs (1.88 Å). This discrepancy is due to the fact that the O1 O atoms also belong to the coordination sphere of Cs and hence contribute to its coordination and bonding.

The presence of Cs in the channel cages of cordierite leads to an increased coordination number for the O2 O atoms, which in turn form the main coordination of Cs. Consequently, the mean T2-O2 distances are larger and the O2-T2-O2 angles (Table 5) are smaller than in pure magnesium cordierite (Armbruster, 1985). These changes can also be due to the increased Al/Si ratio in the tetrahedral framework, but the additional Al introduced by the substitution Cs + Al → Si is most probably located on the T1 sites (Daniels and Gies, 1991). The O2-O2 distances and the distances between O2 and the central axis of the channel are not changed. In addition, the T2 positions are changed relative to their two coordinating O2 O atoms, leading to a larger difference between the two nonequivalent T2-O2 distances. This may be due to an improved shielding between T2 and Cs$^+$. The T2-Cs and O1-Cs distances increase for the same reason. These small changes lead to distortion of the T2 tetrahedra in the direction of an ideal tetrahedron.

The combination of the effects mentioned above causes an expansion of the unit cell in all directions, although the positions of the O2 O atoms are not changed in the a,b plane. This means that the observed changes of T2

TABLE 5. Distances and angles in the tetrahedral framework of Cs-substituted high cordierite

	Distances (Å)			Angles	
	Cs-cord.	Mg-cord.*		Cs-cord.	Mg-cord.*
T1-O1	1.727(2)	1.723(1)	O1-T1-O1	123.5(1)	123.83(3)
O1-O1	3.043(3)	3.039(1)	O1-T1-O1	109.6(1)	109.60(3)
O1-O1	2.821(3)	2.815(1)	O1-T1-O1	96.5(1)	96.19(3)
O1-O1	2.576(4)	2.564(1)			
T1-Cs	4.900(1)				
O1-Cs	4.358(2)				
T2-O1	1.668(2)	1.666(1)	O1-T2-O1	108.2(1)	107.35(2)
T2-O2	1.644(3)	1.629(1)	O1-T2-O2	108.2(1)	108.26(3)
T2-O2	1.630(3)	1.620(2)	O1-T2-O2	110.2(1)	109.83(2)
			O2-T2-O2	111.9(1)	113.14(5)
T2-Cs	4.021(1)	3.997(1)			
O1-Cs	4.358(2)	4.345(2)			
O2-Cs	3.586(2)	3.579(2)			
T2-c	3.265(2)	3.243(1)			
O1-c	4.242(2)	4.230(2)			
O2-c	2.711(3)	2.712(2)			

* Data taken from Armbruster (1985).

and O1 positions are not caused by the size of the Cs ion but merely by the presence of a positive charge at 0,0,¼. On the other hand, a large radius is required for location of a cation in this position.

The changes of the T1 tetrahedral dimensions and distortions as a consequence of Cs incorporation are small compared with those of the T2 tetrahedra. The positions of the O1 O atoms forming the coordination of the T1 sites are the only ones in Cs-substituted high cordierite that are not constrained by the symmetry of space group *P6/mcc*. As a consequence, the T1 tetrahedron can adapt to small structural changes without change in its dimensions. The slightly increased T1-O1 bond lengths (Table 5) may be due to the positional changes of O1 caused by the distortion of the T2 tetrahedra but may also be caused by the increased Al/Si ratio (Cs + Al → Si) leading to a higher Al concentration on T1 positions and a larger overall tetrahedral volume.

CONCLUSIONS

As the two structure refinements described above have shown, both K and Cs incorporation influence the whole framework of high cordierite. In both cases, the structural changes can be viewed as being caused by repulsive and attractive forces between the added cation and the framework cations and O atoms, respectively. This means that the structural changes are merely caused by the electrostatic charge of the channel cation.

The channel position actually occupied by a cation is a compromise of the charge and the size of the cation, the available space in the channel, and the preference of any cation to be placed at 0,0,0, which is caused by different electrostatic potentials along the channel axis. This position is occupied by Na (Meagher, 1967), but it is too small for the two cations K and Cs considered in this work. The K position dictated by the K radius (too large for $z = 0$ and too small for $z = ¼$) leads to asymmetric coulombic forces on the framework anions and cations and finally to displacements of framework atoms that are no longer compatible with space group *P6/mcc*. On the other hand, the Cs position (0,0,¼) is highly symmetric. Hence, the surrounding framework is deformed according to this symmetry, and no deviations from space group *P6/mcc* are necessary for the formation of a locally charge-balanced coordination sphere.

These results lead to a number of new and unexpected questions. The transformation of high into low pure magnesium cordierite is combined with a symmetry reduction from space group *P6/mcc* to *Cccm* (Gibbs, 1966; Meagher and Gibbs, 1977). The group theoretical relation between these two space groups (*Cccm* is a subgroup of *P6/mcc*) allows the application of Landau theory to this transformation process (Salje, 1987). If K-substituted low cordierite crystallizes with space group *Cccm,* this theory may not be applicable. If, on the other hand, potassic low cordierite crystallized with a subgroup of *P6̄*, Landau theory might lead to different conclusions about the nature of the high-low transformation process.

Another question concerns the ordering of Al and Si during the transformation. An ordering scheme with strictly alternating Al and Si occupancy of all tetrahedra is theoretically possible when the Al/Si ratio is exactly 1/1, which is perhaps possible in cordierite with 0.5 alkali cations pfu and a Si/Al ratio of 4.5/4.5. This kind of ordering would also lead to a structure with a trigonal symmetry.

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