American Mineralogist, Volume 82, pages 647–650, 1997

Crystal chemistry of superfluorous phase B ($Mg_{10}Si_3O_{14}F_4$): Implications for the role of fluorine in the mantle

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ABSTRACT

Single-crystal X-ray diffraction data have been obtained for crystals of the F analog of superhydrous phase B, $Mg_{10}Si_3O_{14}F_4$. Twinned crystals were synthesized using a split-sphere anvil apparatus (USSA-2000) at pressures between 17.8 and 22.3 GPa and temperatures between 1450 and 1600 °C. Orthorhombic (space group *Pnnm*) unit-cell parameters are $a = 5.050(3)$, $b = 13.969(2)$, and $c = 8.640(3)$ Å. The substitution of F for H results in minor crystal chemical changes. Notably, average Mg-F distances (1.95 Å) are shorter than the corresponding average of Mg-OH distances (1.98 Å). These differences are reflected in shortening of unit-cell axes *a* and *c* in superfluorous B by 0.6 and 0.8%, respectively, relative to superhydrous B, while the *b* axis is unchanged. The close similarities between superhydrous and superfluorous B phases suggest that F will usually substitute for OH^- in mantle phases.

INTRODUCTION

Hydrous high-pressure silicates have received considerable attention because of their presumed role in the hydrogen budget of the earth (Ringwood and Major 1967; Finger and Prewitt 1989; Thompson 1992; Gasparik 1993). Of special interest have been the high-pressure hydrous magnesium silicates phase B [$Mg_{12}Si_4O_{19}(OH)_2$] and superhydrous phase B [$Mg_{10}Si_3O_{14}(OH)_4$], which are members of a homologous series of dense phases in the $MgO\text{-}SiO_2\text{-}H_2O$ system (Finger and Prewitt 1989; Finger et al. 1989, 1991; Pacalo and Parise 1992; Kanzaki 1993; Kudoh et al. 1994). These high-pressure phases feature close-packed clusters of 13 O atom coordination octahedra, in which 12 Mg octahedra surround a silicate octahedron. These clusters are connected in part by silicate tetrahedra; each unit cell contains two Si1 octahedra and four Si2 tetrahedra. Such mixed fourfold- and six-fold-coordinated silicate structures are characteristic of pressures corresponding to the Earth's transition zone (Finger and Hazen 1991).

Whereas less effort has been devoted to high-pressure phases with volatiles other than H_2O, Gasparik (1990; 1993) completed several experiments on the systems $MgO\text{-}SiO_2\text{-}MgF_2$ and $MgO\text{-}SiO_2\text{-}H_2O\text{-}MgF_2$ at conditions corresponding to the Earth's transition zone. These experiments yielded a number of fluorine-bearing phases, including isomorphs of the hydrous phases B and superhydrous B. This report describes the crystal structure of superfluorous B synthesized by Gasparik and compares this structure with previous data for superhydrous B (Pacalo and Parise 1992).

The "alphabet phases," dense hydrous magnesium silicates (DHMS), synthesized originally by Ringwood and Major (1967), are of substantial interest because of their potential relevance as H-bearing phases in the mantle. However, the naming of these alphabetic phases has become awkward because additional phases with different letter designations, proposed by other investigators, have turned out to be the same as the ones reported by Ringwood and Major. One of these, superhydrous B, proposed by Gasparik (1990) was suggested by Kanzaki (1993) to be the same as Ringwood and Major's phase C. Moreover, its structure is substantially different from that of phase B, and other DHMS phases contain much more H than does superhydrous B. Superfluorous B, therefore, should be called fluorous C, but because the literature contains several papers that refer to data and interpretation of superhydrous B, we believe it is better to continue with this usage until all the complexities can be resolved on an international basis.

EXPERIMENTAL METHODS

Single crystals of $Mg_{10}Si_3O_{14}F_4$ were synthesized in a split-sphere anvil apparatus (USSA-2000) as part of a study of the role of volatiles in the transition zone (Gasparik 1993). The largest crystals, up to 150 μm in diameter, were produced in a 10 min experiment (SUNY exp. 1474) at 17.8 GPa. This experiment was conducted with a 200° temperature gradient, from approximately 1450 to 1650 °C. Superfluorous B crystals occurred in the portions corresponding to temperatures from about 1450 to 1600 °C. Additional specimens were obtained

0003–004X/97/0506–0647$05.00

TABLE 1. Atomic positional and displacement parameters of superfluous phase B

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{iso}
Si1	½	0	0	0.0043(10)	0.0008(1)	0.0010(3)	0.0001(5)	0	0	0.45(4)
Si2	0.4892(5)	0.3758(1)	0	0.0058(6)	0.0005(1)	0.0012(2)	−0.0006(3)	0	0	0.45(3)
Mg1	0.1657(5)	0.1711(2)	0	0.0059(9)	0.0009(1)	0.0019(3)	−0.0001(3)	0	0	0.62(4)
Mg2	0.1543(3)	0.3241(1)	0.3205(2)	0.0060(6)	0.0007(1)	0.0020(2)	−0.0001(2)	0.0002(3)	0.0001(1)	0.59(3)
Mg3	½	½	0.3180(3)	0.0053(8)	0.0005(1)	0.0022(3)	0.0008(3)	0	0	0.54(4)
Mg4	½	0	0.3454(2)	0.0051(8)	0.0007(1)	0.0020(3)	−0.0002(3)	0	0	0.57(4)
O1	0.3297(6)	0.4101(2)	0.1580(3)	0.0072(13)	0.0009(1)	0.0009(4)	0.0005(5)	0.0001(7)	0.0000(2)	0.57(5)
O2	0.4914(13)	0.2561(3)	0	0.0068(19)	0.0004(2)	0.0016(5)	−0.0014(7)	0	0	0.50(8)
O3	0.7887(9)	0.4196(3)	0	0.0016(18)	0.0007(2)	0.0027(6)	−0.0002(5)	0	0	0.49(8)
O4	0.3541(6)	0.0732(2)	0.1453(3)	0.0041(12)	0.0003(2)	0.0019(4)	−0.0001(4)	−0.0001(7)	0.0001(2)	0.41(5)
F5	−0.0101(7)	0.2439(2)	0.1633(3)	0.0100(12)	0.0017(1)	0.0034(3)	0.0008(5)	−0.0001(8)	−0.0006(2)	1.12(5)
O6	0.1917(10)	−0.0797(3)	0	0.0061(21)	0.0004(2)	0.0030(6)	−0.0000(6)	0	0	0.61(8)

Notes: Mo$K\alpha_1$ radiation, $\lambda = 0.7093$ Å; data collection from $0° \leq 2\theta \leq 60°$; $a = 5.050(3)$, $b = 13.969(2)$, $c = 8.640(3)$ Å, $V_{cell} = 609.5(4)$ Å^3. Space group *Pnnm*, $Z = 2$, formula weight = 627.37 g, $\rho_{calc} = 3.418$ g/cm^3, $\mu = 10.318$ cm^{-1}. Two data octants measured, $R_{merge} = 0.034$. Full-matrix least squares refinement on F with $R_w = 0.023$ and $R = 0.031$ for 655 reflections with $I > 2\sigma_I$. The weighting factor $w = 1/\sigma_F^2$. The goodness of fit = 0.96 with anistropic displacement parameters (Å) for all atoms.

from SUNY experiment 1241 (6 min, 22.3 GPa); superfluorous B crystals were extracted from the cooler end (approximately 1850 °C) of this experiment, which had a temperature gradient from 1850 to 2050 °C. These experiments also yielded wadsleyite (β-Mg_2SiO_4), silicate spinel (γ-Mg_2SiO_4), fluorous B ($Mg_{12}Si_4O_{19}F_2$), anhydrous B ($Mg_{14}Si_5O_{24}$), periclase (MgO), and sellaite (MgF_2).

Optical examination revealed that all superfluorous B crystals possess lamellar twins, similar in appearance to the albite twinning displayed by plagioclase feldspars. Crystals selected for further X-ray examination displayed sharp extinction and a minimal number of narrow twin lamellae.

Several crystals from both experiments were examined by X-ray precession photography and by X-ray diffractometry, conducted on a Rigaku AFC-5R single-crystal diffractometer with rotating-anode generator and graphite-monochromatized Mo$K\alpha_1$ radiation ($\lambda = 0.7093$ Å), operated at 45 kV and 180 ma.

Whereas most crystals had diffraction maxima too broad for satisfactory results, orthorhombic unit-cell parameters (space group *Pnnm*) were determined on two crystals, one from each synthesis experiment. The first crystal, from experiment 1241, was elongate: approximately 30 × 30 × 60 μm. Orthorhombic (space group *Pnnm*) unit-cell parameters were determined using the multiple peak centering procedure of Ralph and Finger (1982) from positions of 12 reflections between 20 and 30° 2θ [$a = 5.051(3)$, $b = 13.970(9)$, $c = 8.644(4)$ Å, $V = 609.9(6)$ Å^3]. Examination of diffraction peak shapes for this crystal revealed numerous broad and doublet peaks, unsuitable for intensity measurements.

A second specimen, a plate-like crystal approximately 75 × 75 × 25 μm, was selected from experiment 1474. This crystal was distinguished by having only one thin twin lamella, less than 5 μm wide, suggesting a twin fraction less than 0.05. Unit-cell parameters, determined from positions of 25 reflections between 26 and 29° 2θ [$a = 5.050(3)$, $b = 13.969(2)$, $c = 8.640(3)$ Å, $V = 609.5(4)$ Å^3], agree within one estimated standard deviation with lattice parameters of the first crystal. Diffraction peaks were sharper and displayed less prominent doublets than other crystals examined. Intensity data were obtained with ω step scans, and reflections were integrated with the algorithm of Lehmann and Larsen (1974).

Crystal structure refinements were performed with a modified version of the program RFINE4 (Finger and Prince 1975) using neutral atom scattering factors from *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). All atoms were refined with anisotropic displacement parameters, and we included an isotropic extinction parameter (Becker and Coppens 1974). Table 1 records refinement conditions, refined positional parameters, and anisotropic displacement parameters.

Although the space group determined for superhydrous B by Pacalo and Parise (1992) was *Pnmn*, Kudoh et al. (1994) observed reflections violating the n glide normal to a and proposed that the correct space group is $P2_1mn$ (note that in this study we use the different space group orientation, as suggested by Finger et al. 1991). We thought initially that the extra reflections seen in superfluorous B diffraction patterns because of twinning could explain the Kudoh et al. observations, but careful examination showed that the reflections caused by twinning were not consistent with this idea. We did not observe reflections that violate the n glide, and our R factors are lower than those obtained by Kudoh et al. (Rw = 0.023 and R = 0.031 in this study, compared to Rw = 0.087 and R = 0.078 for Kudoh et al. 1994). Thus, it appears that the centrosymmetric space group is the correct one for superfluorous B.

RESULTS AND DISCUSSION

Selected interatomic distances and angles are listed in Tables 2 and 3, respectively. Structural details are, for the most part, similar to those of superhydrous B (Pacalo and Parise 1992). Most bond distances, for example, are within 0.01 Å of those observed in superhydrous B. The mean Si-O distances in the Si1 octahedron and Si2 tetrahedron of superfluorous B are 1.824 and 1.654 Å, respectively; those in superhydrous B are 1.819 and 1.645 Å. Mean Mg-O distances in Mg3 and Mg4 octahedra are 2.100 and

TABLE 2. Selected interatomic distances (Å) in superfluorous phase B

Si1-O4 × 4	1.779(3)	[1.777(1)]*	Si2-O1 × 2	1.656(3)	[1.649(1)]
Si1-O6 × 2	1.914(5)	[1.903(1)]	Si2-O2	1.672(3)	[1.639(1)]
Avg.	1.824	[1.819]	Si2-O3	1.632(5)	[1.642(1)]
			Avg.	1.654	[1.645]
Mg1-O2	2.029(6)	[2.036(1)]	Mg3-O1 × 2	2.056(3)	[2.064(1)]
Mg1-O4 × 2	2.086(3)	[2.111(1)]	Mg3-O4 × 2	2.084(3)	[2.102(1)]
Mg1-F5 × 2	1.953(3)	[2.005(1)]	Mg3-O6 × 2	2.156(4)	[2.152(1)]
Mg1-O6	2.211(5)	[2.277(1)]	Avg.	2.099	[2.106]
Avg.	2.053	[2.091]			
Mg2-O1	2.049(3)	[2.117(1)]	Mg4-O1 × 2	2.086(3)	[2.081(1)]
Mg2-O2	2.083(4)	[2.095(1)]	Mg4-O3 × 2	2.046(3)	[2.108(1)]
Mg2-O4	2.108(3)	[2.127(1)]	Mg4-O4 × 2	2.140(3)	[2.126(1)]
Mg2-F5	1.947(3)	[1.962(1)]	Avg.	2.091	[2.105]
Mg2-F5	1.948(4)	[1.963(1)]			
Mg2-O6	2.195(3)	[2.179(1)]			
Avg.	2.055	[2.074]			

* Data in brackets are for superhydrous phase B (Pacalo and Parise 1992).

2.091 Å in superfluorous B, and 2.106 and 2.105 Å in superhydrous B.

Polyhedral distortions in the two structures are also similar. Notably, whereas all adjacent O-Si1-O angles in the silicate octahedra of both structures are within 0.2° of 90°, both of these octahedra are significantly elongated. In superfluorous B, two apical Si1-O6 bonds are 1.914 Å, compared to 1.779 Å for four in-plane Si1-O4 bonds. In superhydrous B, corresponding bond distances are 1.903 and 1.777 Å, respectively.

The most significant differences between the two structures occur in the Mg1 and Mg2 octahedra, which have a single Mg-F bond in superfluorous B and a single Mg-OH bond in superhydrous B. The Mg-F bonds are significantly shorter than Mg-OH bonds, which contributes to the smaller size of the Mg1 and Mg2 octahedra (average distances = 2.053 and 2.055 Å, respectively, in superfluorous B, compared to 2.091 and 2.074 Å in superhydrous B). These small differences are consistent with distances for Mg-F and Mg-OH calculated from ionic radii (Shannon and Prewitt 1970), which differ by 0.04 Å.

TABLE 3. Selected interatomic angles (°) in superfuorous phase B

O4-Si1-O4′	90.2(2)	O1-Si2-O1	111.1(2)
O4′-Si1-O4″	89.8(2)	O1-Si2-O2	107.0(2)
O4-Si1-O6	89.9(1)	O1-Si2-O3	110.0(1)
O4′-Si1-O6	90.1(1)	O2-Si2-O3	111.6(3)
O2-Mg1-O4	90.8(2)	O1-Mg3-O1′	95.5(2)
O2-Mg1-F5	93.7(2)	O1-Mg3-O4	99.3(1)
O2-Mg1-O6	179.5(2)	O1-Mg3-O4′	92.5(1)
O4-Mg1-O4′	74.0(2)	O1-Mg3-O6	89.3(1)
O4-Mg1-F5	96.5(1)	O1-Mg3-O6′	173.4(1)
O4-Mg1-F5′	169.6(2)	O4-Mg3-O4′	162.5(2)
O4-Mg1-O6	89.6(2)	O4-Mg3-O6	91.2(2)
F5-Mg1-F5′	92.5(2)	O4-Mg3-O6′	76.0(2)
F5-Mg1-O6	86.0(2)	O4′-Mg3-O6	86.4(2)
O1-Mg2-O2	175.1(2)		
O1-Mg2-O4	90.5(1)		
O1-Mg2-F5	92.5(1)	O1-Mg4-O1′	178.4(2)
O1-Mg2-F5′	87.7(1)	O1-Mg4-O3	85.6(2)
O1-Mg2-O6	88.4(1)	O1-Mg4-O3′	95.5(2)
O2-Mg2-O4	88.7(2)	O1-Mg4-O4	88.6(1)
O2-Mg2-F5	92.4(2)	O1-Mg4-O4′	90.1(1)
O2-Mg2-F5′	91.6(2)	O3-Mg4-O3′	98.5(2)
O2-Mg2-O6	86.7(2)	O3-Mg4-O4	165.9(1)
O4-Mg2-F5	100.5(1)	O3-Mg4-O4′	94.9(1)
O4-Mg2-F5′	161.4(1)	O4-Mg4-O4′	72.2(2)
O4-Mg2-O6	74.9(2)		
F5-Mg2-F5	98.1(1)		
F5-Mg2-O6	175.3(2)		
F5-Mg2-O6	86.5(2)		

The principal components of Mg1-F and Mg2-F bonds lie in the (010) plane, near $y = 1/4$ and 3/4. The substitution of F for OH, therefore, is reflected principally by a shortening of the a and c axes, while b remains unchanged.

Refinement included a parameter for a fractional twin component; the crystal selected for data collection had a relatively low refined fractional twin component of 0.024(8), compared to values near 0.50 (estimated optically) for several other crystals. The twin operator is a mirror parallel to (101). This pseudomerohedral twinning is a consequence of the approximate unit-cell relationship $4/c^2 = (1/c^2 + 1/a^2)$. In a twinned crystal, one-half of the reciprocal lattice points may be doubled as a result of this near equivalence. In the case of superfluorous B, $4/c^2$ and $(1/c^2 + 1/a^2)$ agree within about 1.8%, leading to a close but imprecise match of reciprocal lattices, and thus to peak broadening and doubling. This type of twinning was not reported for superhydrous B (Pacalo and Parise 1992), which has a slightly larger 2.1% lattice mismatch.

This (101) twinning may be recognized by the presence of weak additional reflections with h and l fractional indices of ±0.5, ±1.5, and so on. These extra twin reflections have $(h + l)$ equal to an even integer, such as 0.5,0,1.5 and 0.5,0,-0.5. Extra reflections with $(h + l)$ odd are absent for that twin component. Twin-related peak broadening or doublets may be observed for normal reflections with $(h + l)$ even, such as 101 or 002, while $(h + l)$ odd reflections will be unaffected by this twin component.

The twin composition plane, measured optically on an oriented crystal, is indistinguishably close to (010). This plane is also the close-packed O layer, which defines the stacking of octahedral layers. The (101) mirror operation maintains close packing of O atoms, while altering the distribution of occupied octahedral sites. The presence of macroscopic twinning suggests that stacking faults and other types of layer disorder might occur in the phase B-related structures at a microscopic scale as well.

CONCLUSIONS

End-member superfluorous B, though stable under a range of conditions appropriate to the Earth's transition zone, is not a likely candidate as a mantle mineral. However, the crystal chemical similarities of superfluorous B and superhydrous B, coupled with the slightly smaller size of F, suggest that F will readily substitute for OH in hydrous phases, at least throughout the upper mantle and transition zone. As increasing attention is paid to novel high-pressure hydrous phases and their possible deep-earth roles in rheological processes, melt generation, and deep-focus earthquakes, attention should be paid to the modifying effects of F solid solution, as well.

ACKNOWLEDGMENTS

X-ray diffraction work at the Geophysical Laboratory is supported by NSF grant EAR9218845 and by the Carnegie Institution of Washington. High-pressure studies are supported in part by the NSF Center for High Pressure Research.

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MANUSCRIPT RECEIVED FEBRUARY 19, 1997
MANUSCRIPT ACCEPTED MARCH 27, 1997