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Structure of a new upper-mantle, magnetoplumbite-type phase, $Ba[Ti_3Cr_4Fe_4Mg]O_{19}$

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ABSTRACT

The new phase, ideally $Ba[Ti_3Cr_4Fe_4Mg]O_{19}$, is found in metasomatized lithosphere–derived harzburgite, in the Kimberley district of South Africa. It has hexagonal symmetry, space group $P6_3/mmc$, with $a = 5.871(2)$ and $c = 23.06(2)$ Å. The crystal structure has been refined to $R = 0.044$ for 368 independent reflections $[I > 3\sigma(I)]$ collected on a Siemen's AED diffractometer using Mo$K\alpha$ radiation. The new mineral has the magnetoplumbite-type structure, with a statistical disorder of the cations occupying the bipyramidal site, in positions displaced by 0.2 Å on either side of the mirror plane. Cation ordering in the structure is consistent with a genesis model in which the new mineral derives from magnesiochromite spinel by periodic replacement of the mixed octahedral, tetrahedral $(111)_{sp}$ layer with a segment of hexagonal $BaTiO_3$.

INTRODUCTION

The new phase (phase N) was discovered during a study of metasomatized lithosphere–derived harzburgite samples collected from the waste dumps (Bultfontein Floors) that resulted from early diamond mining in the Kimberley district of South Africa (Haggerty et al., 1986). It is intimately associated with magnesiochromite spinel and is rimmed with lindsleyite; it is distinguished from other opaque oxides in the samples by very high BaO (14 wt% max.). A preliminary X-ray diffraction examination of the new phase by the precession method showed that it was in oriented intergrowth with the spinel and had a magnetoplumbite-type hexagonal unit cell. Electron-microscope, electron-microprobe, and XRD studies suggested that the phase was derived from spinel through interaction with metasomatic fluids containing Ba and Ti. We report here the structure refinement of the new phase using single-crystal X-ray intensity data.

CHEMICAL COMPOSITION

Average microprobe analyses are given in Table 1. The analyses were performed on the sample from which fragments were taken for the XRD studies. The XRD studies confirm that the structure of the new phase is of the magnetoplumbite (MP) type (Adelsköld, 1938) and thus has an ideal composition $AM_{12}O_{19}$, where A = large cations with 12-fold coordination and M = small cations with 4-, 5-, and 6-fold coordination by oxygen. In the second column of Table 1, the number of atoms has been scaled to 12 small cations, with the Fe^{2+}/Fe^{3+} ratio adjusted to give charge balance relative to 19 oxygens. The composition of the new phase is $(Ba_{0.85}K_{0.12})[Cr_{4.68}Ti_{3.00}Fe^{3+}_{1.48}Fe^{2+}_{2.01}Mg_{0.80}Mn_{0.02}Nb_{0.01}]O_{19}$.

PRELIMINARY XRD STUDIES

A large composite grain, comprising the new phase with spinel and lindsleyite, was extracted from the thin section and fragmented. The individual fragments were studied in a scanning-electron microscope fitted with backscattered-electron and X-ray detectors. A few fragments that showed no *exposed* phases other than the new mineral were selected for X-ray diffraction studies. Precession photographs for these grains show spinel as the only impurity phase, in oriented intergrowth with the new phase. The diffraction patterns display hexagonal symmetry with approximate unit-cell parameters $a = 5.87$ and $c = 23.0$ Å. The systematic extinctions, $(hh\,2\bar{h}\,l)$, $l = 2n + 1$, are consistent with space groups $P6_3/mmc$, $P6_3mc$, and $P\bar{6}2c$. The cell dimensions, symmetry, and intensity distribution in the diffraction patterns are consistent with the phase being isostructural with barium ferrite, $BaFe_{12}O_{19}$ (Townes et al., 1967), having the magnetoplumbite structure (Adelsköld, 1938). The orientation relationship of the new phase to the intergrown spinel phase is $[0001] \parallel [111]_{spinel}$, $(30\bar{3}0) \parallel (22\bar{4})_{spinel}$. From measurements taken from the precession photographs (calibrated using the new phase as a standard), the cell parameter of the spinel phase is 8.380(5) Å.

TABLE 1. Microprobe analysis of the new phase

Element	wt%*	Atoms†
K	0.46	0.12
Ba	11.21	0.85
Cr	23.30	4.68
Ti	13.75	3.00
Fe	18.65	1.48 (Fe^{3+}) 2.01 (Fe^{2+})
Mg	1.85	0.80
Mn	0.09	0.02
Nb	0.11	0.01

* Average of 11 point analyses.

† Atoms normalized to 12 small cations; Fe^{2+}/Fe^{3+} adjusted to correspond to 19 oxygens.

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TABLE 2. Coordinates and isotropic thermal parameters

Atom	Wyckoff position	Site occupancy	*x*	*y*	*z*	*B* (Å²)
A	2 *d*	$0.85\ Ba^+ + 0.12\ K^+$	⅓	⅔	¼	0.70(5)
M(1)	2 *d*	Cr^{3+}	0	0	0	0.36(5)
M(2)	4 *e*	$0.5\ Fe^{3+}$	0	0	0.2571(3)	0.70(9)
M(3)	4 *f*	$0.64(2)\ Fe^{2+} + 0.36\ Mg^{2+}$	⅓	⅔	0.0268(1)	0.49(5)
M(4)	4 *f*	Ti^{4+}	⅓	⅔	0.1888(1)	0.35(4)
M(5)	12 *k*	Cr*	0.1662(2)	0.3324	−0.1063(1)	0.44(2)
O(1)	4 *e*		0	0	0.1512(5)	0.44(18)
O(2)	4 *f*		⅓	⅔	−0.0599(5)	0.43(17)
O(3)	6 *h*		0.1878(13)	0.3756	¼	1.36(19)
O(4)	12 *k*		0.1483(7)	0.2966	0.0548(2)	0.39(9)
O(5)	12 *k*		0.5020(8)	1.0040	0.1508(3)	0.49(9)

* Dominant element occupation of M(5) is approximately 0.62Cr + 0.17Ti + 0.21Fe, for which the scattering curve for Cr was used in the refinement.

DATA COLLECTION AND STRUCTURE REFINEMENT

For the structure determination, a crystal fragment was selected that appeared to be free from intergrown spinel phase. The crystal, measuring 0.130 × 0.088 × 0.035 mm, was mounted parallel to its long dimension on a Siemen's AED diffractometer. Ten reflections with $24° < 2\theta < 50°$ (Mo$K\alpha$) were centered, and the 2θ values were used in a refinement of the cell parameters, giving a = 5.871(2) and c = 23.06(2) Å. Operating conditions were θ–2θ scan; 2θ range 6–60°; scan speed, $0.03°(2\theta)\ s^{-1}$. A total of 4197 reflections was measured for $h = -7$ to 7, $k = 0$ to 7, $l = -32$ to 32. A standard reflection measured every 3 h showed less than 2% intensity variation. The data were corrected for absorption, $\mu = 126.3\ cm^{-1}$, maximum and minimum transmission coefficients 0.65 and 0.34, and reduced to 442 unique structure amplitudes, $R_{int} = 0.041$, of which 368, with $I > 3\sigma(I)$, were used in the structure refinement.

The refinement was initiated using the refined coordinates for $BaFe_{12}O_{19}$ (Obradors et al., 1985) as starting values. Ba and K were distributed at the Ba site according to the atom contents determined from the microprobe analysis (Table 1), and the scattering curve for Cr (representing an average of the main elements, Ti, Cr, and Fe) was used for all metal-atom sites. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974), and all computing was done with the SHELX76 programs (Sheldrick, 1976). Refinement of coordinates and isotropic thermal parameters (unit weights) converged at R = 0.050. At this stage, bond lengths were calculated and used to compute bond-valence sums at the different atomic sites, using the empirical parameters of Brown and Wu (1976). These data, together with the thermal parameters and information on cation distributions in related structures (e.g., spinels, $BaTiO_3$, MP) were used to establish a model for cation ordering at the different sites. This involved ordering of Cr at the octahedral site M(1), Fe at the trigonal bipyramid site M(2), divalent Fe plus Mg at the tetrahedral site M(3), and Ti at the face-shared octahedral site M(4). Refinement of the site occupancies of the sites with mixed atoms led to a reduction in R to 0.048. The occupancies were then fixed, and refinement of all coordinates and isotropic temperature factors converged at R = 0.047. These refinements included a statistically disordered M(2) at site 4(e) with the metal atom displaced by 0.20 Å on either side of the mirror plane at z = ¼, as found in $BaFe_{12}O_{19}$ (Obradors et al., 1985). A second refinement in which M(2) was constrained to the 2(b) site at (0,0,¼) converged to an R factor of 0.064, and a difference Fourier synthesis showed peaks at $\pm(0,0,z)$, $z \simeq 0.26$.

For the split M(2) atom model, the refinement was continued, with fixed occupancies and conversion to anisotropic thermal parameters, resulting in convergence at $R = 0.044$ for the 368 reflections with $I > 3\sigma(I)$. For all 442 reflections, the final R factor was 0.066. The number of parameters refined in the final cycle was 43 and the maximum Δ/σ was 0.10. A difference Fourier map showed a peak at (0,0,0.10) as the only significant feature ($0.7\ e \cdot Å^{-3}$). This does not correspond to a physically reasonable site and may reflect disorder due to stacking faults, which commonly occur in these types of compounds.

Final coordinates and isotropic thermal parameters are given in Table 2, and important bond lengths and angles are listed in Table 3. Anisotropic thermal parameters and observed and calculated structure factors have been deposited.[1]

DISCUSSION

The MP structure type has been described in detail by Townes et al. (1967) and Obradors et al. (1985). Briefly, the structure is composed of slabs of spinel-type structure, which are four anion-layers thick, intergrown with perovskite-like AO_3 close-packed layers parallel to $(111)_{spinel}$. The AO_3 layers lie on mirror planes at $z = \pm$¼. The anion stacking sequence is (cchh′h . . .) where h′ corresponds to

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[1] To obtain tables of these data, order Document AM-87-340 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 3. Interatomic distances (Å) and angles (°)

		Ba polyhedron				M(4) octahedron	
			O–M–O				O–M–O
Ba–O(5)	(×6)	2.835(7)		M(4)–O(5)	(×3)	1.926	
–O(3)	(×6)	2.943(10)		–O(3)	(×3)	2.045	
O(3)–O(3)′	(×3)	2.56(2)	51.6(2)	O(3)–O(3)′	(×3)	2.56(2)	77.6(4)
O(3)–O(5)	(×12)	2.80(1)	57.9(2)	O(3)–O(5)	(×6)	2.80(1)	89.5(4)
O(5)–O(5)′	(×6)	2.90(1)	61.5(2)	O(5)–O(5)′	(×3)	2.97(1)	100.9(3)
O(3)–O(3)″	(×3)	3.31(2)	68.4(2)				
		M(1) octahedron				M(5) octahedron	
				M(5)–O(5)	(×2)	1.975	
M(1)–O(4)	(×6)	1.968(6)	83.2(2)	–O(1)		1.982	
O(4)–O(4)′	(×6)	2.61(1)	96.8(2)	–O(4)	(×2)	1.998	
O(4)–O(4)″	(×6)	2.943(8)		–O(2)		2.008	
				M(2) bipyramid			
M(2)–O(1)		2.115(13)		O(4)–O(4)′		2.61(1)	81.6(4)
–O(1)′		2.442(13)		O(2)–O(5)		2.68(1)	84.7(3)
–O(3)	(×3)	1.917(13)		O(1)–O(4)		2.69(1)	84.9
				O(4)–O(5)		2.856(9)	91.9(3)
O(1)–O(3)	(×3)	2.97(1)	94.9(2)	O(5)–O(5)′		2.90(1)	94.5(4)
O(1)′–O(3)	(×3)	2.97(1)	85.1(2)	O(1)–O(5)		2.936(7)	95.8(3)
O(3)–O(3)′	(×3)	3.31(2)	119.28(6)	O(2)–O(4)		2.943(6)	94.6(2)
				M(3) tetrahedron			
M(3)–O(4)	(×3)	1.989(7)		O(2)–O(4)	(×3)	3.25(1)	108.9(1)
–O(2)		2.00(1)		O(4)–O(4)′	(×3)	3.26(1)	110.0(1)

the AO_3 layer. Using the nomenclature developed for the spinel-related nigerite and hogbomite polytypes (Grey and Gatehouse, 1979), the cation-layer sequence is $O_cT_2O_cT_1T_1$ and the complete sequence is (h-O_c-c-T_2-c-O_c-h-T_1-h′-T_1 . . .). Here, O_c and T_2 are the all-octahedral and octahedral-tetrahedral cation (111) layers of the spinel structure, and T_1 is the octahedral-tetrahedral cation (001) layer of the nolanite structure (Grey and Gatehouse 1979, Fig. 1).

The special structural features that characterize the MP structure type are associated with the cation sites M(2) and M(4), which are the tetrahedral and octahedral sites in the T_1 layers. These occur in pairs across the AO_3 layers, with resulting face-sharing of the polyhedra. The pairs of tetrahedra (trigonal bipyramid) are statistically half-occupied by atoms that are displaced by ~0.2 Å along **c** from the mirror plane. The face-shared octahedra are analogous to those in hexagonal $BaTiO_3$ (Burbank and Evans, 1948).

The new mineral is considered to be derived from chromian spinel in the upper mantle by metasomatism involving fluids rich in elements such as Ti, Ba, and K. The composition of the spinel coexisting with the new mineral is approximately $[(Mg_{0.7}Fe_{0.3})Cr_2O_4]_{0.7}[Fe(Fe_{0.67}Ti_{0.33})_2O_4]_{0.3}$, corresponding to a mixture of magnesiochromite with minor magnetite-ulvöspinel. A comparison of the analyses for the new mineral and the spinel shows that the main composition changes are due to replacement of Cr and Mg in the spinel by Ti and Ba. To a first approximation, the structure of the new mineral can thus be considered to be derived from that of the spinel by periodic replacement of the octahedron and one tetrahedron from the spinel T_2 cation layer (containing mainly Cr and Mg, respectively) by a segment of hexagonal $BaTiO_3$. The site occupancies of the various cation sites (Table 2) are consistent with this simple model. In Table 4, the average bond lengths to oxygen for the individual cation sites are compared with the corresponding values for $BaFe_{12}O_{19}$ (Obradors et al., 1985) in which all M sites are occupied by Fe^{3+}. There are significant differences for some sites because of ordering of divalent and tetravalent cations in the new mineral. Thus ⟨M(3)–O⟩ is 0.1 Å greater in the new mineral owing to ordering of Fe^{2+} and Mg^{2+} at this spinel tetrahedral site. The octahedral spinel-site cations M(1) (in the T_2 layer) and M(5) (in the O_c layer) are each ~0.04 Å shorter in the new mineral owing to ordering of the smaller Cr^{3+} cation at these sites. Similarly,

TABLE 4. Comparison of average bond lengths for the new phase and $BaFe_{12}O_{19}$ (Obradors et al., 1985)

Cation site	Coordination	New phase No. atoms*	New phase ⟨M–O⟩ (Å)	$BaFe_{12}O_{19}$ No. atoms	$BaFe_{12}O_{19}$ ⟨M–O⟩ (Å)
M(1)	octahedral	$2Cr^{3+}$	1.968	$2Fe^{3+}$	2.000
M(2)	tetrahedral	$2Fe^{3+}$	1.967	$2Fe^{3+}$	1.932
M(3)	tetrahedral	$2.5Fe^{2+} + 1.5Mg^{2+}$	1.992	$4Fe^{3+}$	1.894
M(4)	octahedral	$4Ti^{4+}$	1.986	$4Fe^{3+}$	2.021
M(5)	octahedral	$7Cr^{3+} + 2Ti^{4+} + Fe^{3+} + 1.5Fe^{2+} + 0.5Mg^{2+}$	1.989	$12Fe^{3+}$	2.028
A	12-fold	$1.7Ba^{+} + 0.2K^{+}$	2.889	2Ba	2.909

* Number of atoms rounded off; minor elements not shown.

ordering of Ti^{4+} at the face-shared octahedral site M(4) results in a decrease in ⟨M(4)–O⟩ by ~0.03 Å, relative to Fe^{3+} at this site.

A feature that differs from reported refinements of other MP-related structures is the thermal parameter for O(3), which is a factor of 3 higher than the corresponding parameter for the other oxygens (Table 2). O(3) forms the triangular grouping of bridging oxygens for both the face-shared half-occupied tetrahedral site M(2) and the face-shared octahedral site M(4). O(3) lies in the mirror-planes at $z = \pm 1/4$ and is situated on the line joining M(2) to M(4). It also forms bonds to the A cation lying in the same mirror plane. The anisotropic thermal ellipsoid for O(3) is elongated within the mirror plane and probably reflects correlated substitutions of different cations at M(2) and M(4), related to the change of the A cation from Ba to K.

Note that in a related paper on metasomatic titanate minerals in the upper mantle (Haggerty et al., 1986), we commented on the possibility of tetravalent Ce in the new phase. We have subsequently found that the microprobe evidence for Ce was erroneous, owing to interference from Ba.

REFERENCES

Adelsköld, V. (1938) X-ray studies on magneto-plumbite, $PbO \cdot 6Fe_2O_3$, and other substances resembling 'beta-alumina', Na_2O, $11Al_2O_3$. Arkiv för Kemi Mineralogioch Geologi, Series A-12, no. 29, 1–9.

Brown, I.D., and Wu, K.K. (1976) Empirical parameters for calculating cation-oxygen bond valences. Acta Crystallographica, B32, 1957–1959.

Burbank, R.D., and Evans, H.T., Jr. (1948) The crystal structure of hexagonal titanate. Acta Crystallographica, 1, 330–336.

Grey, I.E., and Gatehouse, B.M. (1979) The crystal structure of nigerite-24R. American Mineralogist, 64, 1255–1264.

Haggerty, S.E., Erlank, A.J., and Grey, I.E. (1986) Metasomatic mineral titanate complexing in the upper mantle. Nature, 319, 761–763.

Ibers, J.A., and Hamilton, W.C., Eds. (1974) International tables for X-ray crystallography, vol. 4. Kynoch Press, Birmingham, England.

Obradors, X., Collomb, A., Pernet, M., Samaras, D., and Joubert, J.C. (1985) X-ray analysis of the structural and dynamic properties of $BaFe_{12}O_{19}$ hexagonal ferrite at room temperature. Journal of Solid State Chemistry, 56, 171–181.

Sheldrick, G. M. (1976) SHELX-76: A programme for crystal structure determination. University of Cambridge, Cambridge, England.

Townes, W.D., Fang, J.H., and Perrotta, A.J. (1967) The crystal structure and refinement of ferrimagnetic barium ferrite, $BaFe_{12}O_{19}$. Zeitschrift für Kristallographie, 125, 437–449.

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