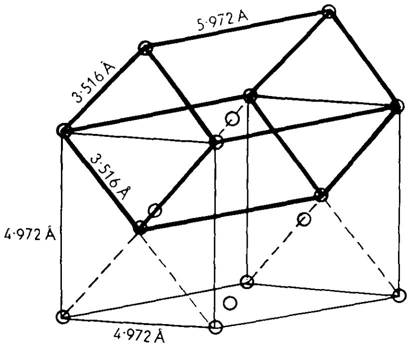

Fig. 3. Uranium atoms in the UC_2 tetragonal cell.

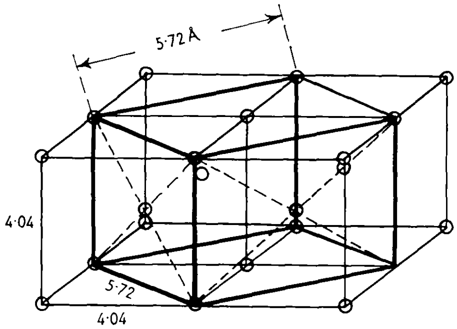

Fig. 4. Transformation to body centred cubic by homogeneous shear.

In Fig. 3 the thick lines denote a body-centred tetragonal UC_2 cell with the uranium atoms shown in their positions on the lattice. By a suitable homogeneous shear (001) [100], the tetragonal prism shown by thinner lines can be transformed to another prism of dimensions $4{\cdot}04 \times 5{\cdot}75 \times 5{\cdot}97$ Å. This is equivalent to changing the square small face of the UC_2 cell into a rhomb of angle 70°. The construction in Fig. 4 shows that by a rotation of two axes by 45°, the structure becomes body-centred cubic with a cell edge of 4·04 Å, following a slight contraction of the long axis.

This has not quite reached the U_2C_3 structure (Fig. 2) however, but the U_2C_3 structure could be converted into the b.c.c. structure by giving it a parameter $x = 0{\cdot}25$ instead of $x = 0{\cdot}20$. This is equivalent to moving each uranium atom by $0{\cdot}05 \times \sqrt{3} \times 8{\cdot}09 = 0{\cdot}7$ Å.

This transformation could thus be regarded as one in which there is little or no interchange in the positions of neighbouring uranium atoms, a feature which is normally regarded as a characteristic of martensitic transformations. It may be noted that although this change of structure bears a close resemblance to the well known kinds of martensitic transformations (see, for example, Bilby & Christian, 1956), a b.c.t. to b.c.c. transformation is rather uncommon in this field. It would be interesting to see if habit-plane relationships can be found experimentally for the UC_2/U_2C_3 transformation, although it is one which proceeds by nucleation and growth of the new phase, and goes to completion isothermally; the movement of carbon atoms by interstitial diffusion may alone be responsible for this. Another feature which this transformation has in common with martensitic ones is that some cold working as well as heat treatment appears to be desirable to form U_2C_3.

The UC structure, which is cubic, can also be related to the UC_2 tetragonal structure by a rotation of 45° and an extension of some 20% in the [100] direction, carbon atoms moving into the spaces associated with the extension.

Thus all the uranium–carbon compounds can be regarded as structures containing carbon atoms arranged in the interstices of approximately similar networks of uranium atoms. The possibility that a whole range of non-stoichiometric compounds occurs should not be overlooked.

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Dendritic crystals of cubic (Ba, Bi)FeO_3.

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Recent studies (Tauber, Savage, Gambino & Whinfrey, 1962) at this Laboratory have concerned the growth of large crystals of hexagonal ferrites for microwave applications. The work has involved synthesis of such phases as $Ba_2Zn_2Fe_{12}O_{22}$, $BaZn_2Fe_{16}O_{27}$ (known as Zn*Y* and Zn*W*, respectively; Braun, 1957), etc., by slow-cooling melts containing fluxes of Na_2FeO_4 and Bi_2O_3. While using the latter flux in the growth of Zn*Y*, minute dendritic crystals of a bronze-colored phase were obtained in several experiments as a minor reaction product. This proved to be a Ba, Bi, Fe oxide, having an X-ray powder diffraction pattern almost identical with that of cubic $BaFeO_3$.

Polycrystalline $BaFeO_3$ has previously been prepared as cubic, tetragonal, and hexagonal phases (Erchak, Fankuchen & Ward, 1946; Scholder, 1952; Kedesdy & Malinofsky, 1954; Scholder, Kindervater & Zeiss, 1956; Fesenko & Prokopalo, 1956; Prokopalo & Fesenko, 1958). $BiFeO_3$, recently prepared in polycrystalline form by Venevtsev *et al.* (1960), is a rhombohedrally-distorted perovskite phase. Based on X-ray diffraction data, the material described in the present study was initially thought to represent the first synthesis of cubic $BaFeO_3$ in single-crystal form. Subsequent preparation of additional crystals, however, permitted spectrochemical analysis, which showed substantial bismuth and demonstrated that the material was actually a cubic phase in the $BaFeO_3$–$BiFeO_3$ series. Since there appeared to be no earlier studies in this series, it was considered of interest to further characterize the dendritic single crystals.

From a typical Zn*Y* synthesis consisting of an 80 g. batch (30 mol.% Bi_2O_3 flux) in a platinum crucible, 100 mg. of the dendritic phase were recovered by leaching with dilute nitric acid. The crystals occurred principally at the interface between a solid Bi_2O_3 cake at the bottom of the crucible and the overlying mass of hexagonal ferrite crystals, flux, etc. Dendritic clusters were extremely fragile and measured typically 0·5 mm. by 0·05 mm. They were red in transmitted light and not attracted to a magnet at room temperature. Microchemical analyses* of a 50 mg. sample averaged 15·1% Ba, 47·9% Bi, and 18·4% Fe by weight, which gives a Ba:Bi:Fe atomic ratio of close to 1:2:3. Reduced to an ABO_3 stoichiometry, with no oxygen deficiency, this corresponds to $(Ba_{0\cdot33}Bi_{0\cdot67})(Fe^{III}_{0\cdot67}Fe^{IV}_{0\cdot33})O_3$. Crystal chemical reasoning precludes an alternative cationic distribution. Compositional singularity is indicated by the sharpness of the resolved $\alpha_1\alpha_2$ doublets in the X-ray powder pattern back-reflection region. The presence of trivalent Fe is supported by the color of the material. There exists the possibility that the phase is somewhat oxygen-deficient, which would diminish the requisite amount of tetravalent iron. This situation is considered unlikely, however, since it has been our experience that bismuth trioxide in the present studies causes an oxidizing environment.

Rotation and Weissenberg single-crystal X-ray patterns of minute crystallites showed the space group *Pm*3*m*, or a sub-group, and demonstrated that the phase has a cubic perovskite-type structure. Close examination of the films showed no departure from cubic symmetry. The dendritic growth directions were found to be octahedral. An X-ray powder diffraction pattern of selected crystals gave a cell dimension of $3\cdot999\pm0\cdot002$ Å. The rhombohedral cell dimensions of pseudocubic $BiFeO_3$ are $\alpha=89°\ 24'$, $a_0=3\cdot963$ Å. $BaFeO_3$ literature values are 4·007 Å with a firing temperature of 950 °C. and 4·010 Å with 1150 °C. (Fesenko & Prokopalo, 1956) and 4·013 Å, averaged from data of Derbyshire, Fraker & Stadelmaier (1961).* Neglecting the slightly non-cubic nature of $BiFeO_3$ and assuming a linear composition versus cell dimension relationship in $BaFeO_3$–$BiFeO_3$, the cell edge observed in the dendritic crystals would indicate a composition close to the $BaFeO_3$ end. This would appear to be supported by the fact that no departure from cubic symmetry is evident. It appears significant, then, that although the phase is compositionally closer to $BiFeO_3$, its structure is that of $BaFeO_3$ and its cell edge approaches that of the Ba compound. In other words, cubic $BaFeO_3$ can tolerate a large amount of bismuth with essentially no dimensional change.

A logical question concerns the stoichiometry: What is the significance of the 1:2 Ba:Bi ratio in view of the fact that the dendritic phase apparently formed in the presence of a vast excess of Bi_2O_3? Occupancy of the *A* sites is statistical because powder X-ray diffraction films showed no evidence for ordering. In an ideally cubic perovskite-type structure, the *A* sites have twelve nearest neighbor oxygens. The dendritic phase, with 2/3 of the *A* sites occupied by Bi, shows no distortion, while end-member $BiFeO_3$ has a rhombohedral distortion. Somewhere between the two compositions, then, the deviation from cubic symmetry must have its onset. Since the phase observed admitted no more than 2/3 Bi into the *A* sites, it seems likely that under the experimental conditions used the statistical replacement of 2/3 of the Ba–O bonds by Bi–O represents a saturation beyond which the structure distorts. Further studies, outside the scope of the present note, are needed to confirm this point.

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* These authors were apparently unaware of the Russian syntheses of cubic $BaFeO_3$ having a perovskite-type structure (Fesenko & Prokopalo, 1956; Prokopalo & Fesenko, 1958). Furthermore, the failure of Derbyshire, Fraker & Stadelmaier to prepare such a compound by reacting oxides and carbonates of Ba and Fe is not supported by Fesenko & Prokopalo, who synthesized the phase from $BaCO_3$ and Fe_2O_3.