The synthesis and characterisation of Co_2X ($Ba_2Co_2Fe_{28}O_{46}$) and Co_2U ($Ba_4Co_2Fe_{36}O_{60}$) ferrite fibres, manufactured from a sol-gel process

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The X and U phases of hexagonal ferrites are notoriously difficult to make as pure materials, and what little data there is published regarding their physical or magnetic properties relates only to single crystals. Stoichiometric Co_2X and Co_2U fibres were made from a sol-gel based process, and the characteristics of the sols and fibres were studied using PCS, XRD, SEM and VSM. The evolution of the X and U fibres was studied, and shown to be similar that of the W and Z fibres whose structures they respectively resemble. Co_2X and Co_2U had been formed at 1200°C, and the morphology of the fibres was different from those of the W and Z phases. The magnetic properties, again while resembling the W and Z phases, were different to any of the other hexagonal ferrite fibres. The magnetic hysteresis loops of both fibres were magnetically as was, the Co_2X fibres having $M_s = 45.0$ emu g^{-1} and $H_c = 0.085$ T, and the Co_2U fibres having $M_s = 51.5$ emu g^{-1} and $H_c = 0.059$ T. © *2001 Kluwer Academic Publishers*

1. Introduction

A new class of hexagonal ferrites, containing both a group II metal ion and a divalent transition metal ion in addition to the Fe^{3+} ions, were discovered in the 1950's [1]. These magnetically soft compounds were named ferroxplana, as instead of having a uniaxial magnetic anisotropy along the *c*-axis, they have a preferred magnetic orientation either in a plane perpendicular to the *c*-axis, or in a cone at an angle to the *c*-axis. Many have been studied and characterised magnetically and physically, such as $Ba_2Co_2Fe_{12}O_{22}$ (Co_2Y), $BaCo_2Fe_{16}O_{27}$ (Co_2W) and $Ba_3Co_2Fe_{24}O_{41}$ (Co_2Z). These compounds were all found to be structurally related to the magnetically hard M ferrites, and any member of the hexagonal ferrite family can be made from combinations of the M, Y and spinel ferrite structures [2]. However, there has been little investigation into the characteristics of some ferroxplana ferrites, such as the X and U ferrites.

Co_2X ferrite has the chemical formula $Ba_2Co_2Fe_{28}O_{46}$, and its structure is very similar to that of Co_2W, being composed of one M and one W molecular unit [1]. Co_2X has a cone of magnetisation at an angle of 74° to the *c*-axis [3], and like the W ferrite it resembles, this cone changes to adopt a planar orientation parallel to the *c*-axis at a higher temperature, in this case 143°C [4]. The X ferrites are usually seen mixed with M and W phases, and are extremely hard to separate. Fe_2X was the first X ferrite to be produced as a pure single crystal sample only after 70 attempts, and even then a section of BaM phase had to be ground out of the crystal [2]. Pure Co_2X single crystals have also been grown from a flux [3], although the polycrystalline form appears not to have been investigated. Single crystal Co_2X has a magnetocrystalline anisotropy of 9.5 kOe, a high M_s of 57.1 emu g^{-1} and a very low H_c of only 0.005 T [3], and the Curie point has been measured as 467°C [4].

Co_2U ferrite, $Ba_4Co_2Fe_{36}O_{60}$, although identified at the same time as the other ferroxplana ferrites, has not been characterised much either structurally or magnetically, although the U ferrite structure has been found to consist of the molecular units Z + M (=M + Y + M) [5]. The U ferrites are extremely hard to make as a pure polycrystalline material, and with the exception of Zn_2U single crystals have only been seen as mixed phases with Z and Y ferrites [6]. There are no magnetic characteristics reported for Co_2U, except that it has a planar anisotropy at room temperature [6].

The authors have previously reported the synthesis and characterisation of a range of hexagonal ferrite fibres, including fibres of BaM [7], Co_2Y [8], Co_2W [9] and Co_2Z [10] ferrites. These fibres were produced from an aqueous sol-gel process involving the blow spinning of a continuous gel fibre precursor using an adapted commercial process, and were typically between

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3–7 μm in diameter. This paper reports the manufacture of polycrystalline fibres with Co_2X and Co_2U compositions, and their characterisation both physically and magnetically.

2. Experimental
2.1. Sol preparation and spinning
The spinning solutions were made from an acid peptised halogen stabilised iron(III) hydroxide sol. Stoichiometric amounts of the barium and cobalt salts were dissolved into solution with an organic liganding agent, before blending with the iron sol to give the required Co_2X and Co_2U compositions. Prior to spinning a small amount of a linear polymer spinning aid (polyethylene oxide) was added, and the sols were then concentrated, blow spun and collected as random gel fibres using a modified proprietary blow spinning process [11]. In this method the spinning solution is extruded through a row of holes on either side of which impinge parallel jets of attenuating air, the fibres being gelled by mixing in a stream of hot secondary air, and then collected and stored in a circulating oven at 110°C.

2.2. Heat treatments
The gel fibres were then heat treated in a muffle furnace, firstly being pre-fired to 400°C at 100°C/hr to remove water and organic compounds, and then further heat treated at 200°C/hr up to 1000°C in a re-crystallised alumina vessel for three hours. The fibres were further fired to between 1100–1200°C on a platinum foil sheet for three hours to form Co_2Z ferrite. Platinum was found to be necessary for the vessel material when firing above 1100°C to prevent cobalt migration into the alumina boat and the subsequent loss of stoichiometry.

2.3. Characterisation
2.3.1. Photon correlation spectroscopy (PCS)
The particle sizes of the sols were measured on a Malvern Instruments Lo-C Autosizer with series 7132 multi-8 correlator at an angle of 90°, using a 4 mw diode laser, 670 nm wavelength at 20°C. The PCS had been certified by the manufacturers to measure inorganic colloidal species of 3 nm diameter and above, provided the difference between the RI of the solvent and particle was sufficiently large. This was the case with our samples, the RI used being 1.33 for the solvent (water) and 1.89 for FeOOH. This piece of equipment conformed to the Methods of Particle Size Determination Standards ISO 13321, part 8-PCS (1996) and BS3406, part 8-PCS (1997) for determination of the Z Average calculated from the monomodal cumulants analysis. The volume and number distribution particle sizes and ranges were calculated from the cumulants results using the Malvern PCS software version 1.32 with contin algorithms. The volume distribution is a measure of the volume occupied by particles against their size, and the number distribution is a simple assessment of the particle size distribution, and these two values most accurately reflect the true nature of the sol.

It must be considered that as the PCS technique is unable to detect particles below the 3 nm threshold,

these measurements may be higher than the actual true figures. Also the sols were much too concentrated to be measured undiluted, and samples were made up typically as 5 drops of 10.5% Fe filtered sol in 2–3 cm^3 of water filtered through a 0.7 μm filter. This dilution did not destabilise the sols, and they showed no change over 1 day after being diluted.

2.3.2. X-ray powder diffraction (XRD)
XRD patterns of the samples treated at various temperatures were recorded in the region of $2\theta = 10\text{–}80°$ with a scanning speed of 0.25° min^{-1} on a Philips PW1710 diffractometer using Cu K$_\alpha$ radiation with a nickel filter. Philips APD 1700 software was used to calculate the average size of the crystallites in a sample using the Scherrer equation [12]:

$$D = K\lambda / h_{1/2} \cos\theta$$

where $D =$ average size of the crystallites, $K =$ Scherrer constant (0.9×57.3), $\lambda =$ wavelength of radiation (1.5405 Å), $h_{1/2} =$ peak width at half height and θ corresponds to the peak position. BaM powder samples made from standard ceramic methods were used as reference standards, and the Philips JPDS files were used for the reference patterns.

2.3.3. Scanning electron microscopy (SEM)
Scanning electron micrographs and analysis of the morphology of the samples was carried out on a Cambridge Instruments Stereoscan 90 SEM operating at 5–10 kV. Conducting samples were prepared by gold sputtering fibre specimens.

2.3.4. X-ray fluorescence spectrometry (XRF)
The elemental composition of the samples was measured on a Philips PW2400 sequential x-ray spectrometer fitted with a rhodium target end window x-ray tube, and Philips X-40 analytical software. The ferrite samples were analysed in the form of a fused bead, where 0.25–1 g of sample was fused with 10 g of lithium tetraborate flux at 1250°C for 12 minutes and then cast to form a glass bead. Stoichiometric standards for calibration of XRF analysis were made from stoichiometric amounts of α-Fe_2O_3, $BaCO_3$, and Co_3O_4, fired to 1000°C/3 hr. When looking for relative amounts of these four specific elements using these standards the statistical and sampling errors were about 1% for Fe and Ba and 2% for Co.

2.3.5. The vibrating sample magnetometer (VSM)
Magnetic measurements were taken on a Maglab VSM with a helium cooled 12 T superconducting magnet, supplied by Oxford Research Instruments. The apparatus was controlled by six independent Oxford units, which were managed by and the data collected using Oxford Object Bench software. The equipment was calibrated using a high purity (>99.99%) 2 mm nickel sphere supplied by Oxford for use in calibration when

measured in a fixed field of 0.6 T at 300 K, with a stated moment of 0.350 emu at 0.6 T.

2.3.6. VSM sample preparation and accuracy

A small mound of random ferrite fibre 3×3 mm square was weighed to ± 0.05 mg, placed on a piece of tissue paper, and soaked liberally with a casting resin, the surplus being absorbed by the tissue paper. This was then allowed to dry, trimmed to give a rigid square 1 mm wider than the fibre sample and mounted on a PEEK sample holder and secured with PTFE tape. Oxford Research Instruments state that the VSM is capable of producing reproducible results with an accuracy of 0.5% with a physically matched sample being measured at a fixed field over 1 hour. Errors in the weighing of the samples were crucial, since the equipment only measured the sample moment in emu, and M_s and M_r are expressed in units such as emu g^{-1} to have relevancy. The random fibre samples weighed at least 5 mg, so the percentage error in the weight was below 1% for random fibres. All samples demonstrated an excellent reproducibility even when removed from the sample holder and remounted.

3. Results and discussion
3.1. Sol characterisation and stability

When spinning gel fibres from an inorganic sol, the existence of any large species, even in small numbers, inhibits spinning, blocks spinnerets and cause shot to form, resulting in a poor quality fibre product. Also very important for spinning is the degree to which the sol can be concentrated without flocculating or gelling, the minimum and optimum levels varying with each sol, but generally requiring at least 10 wt% metal ions. It has been found that the ferrite precursor sols usually require a volume distribution upper limit of <50 nm and a concentration of at least 13% Fe to be spinnable, much stricter requirements than those normally needed in sol-gel work.

The characteristics of the Co_2X and Co_2U precursor sols are compared to those of the previously reported Co_2Y [8], Co_2Z [10] and Co_2W [9] precursor sols in Table I. It can be seen that the Co_2X sol closely resembled the other ferroxplana ferrite sols with a Z average of 7.6 nm, and the volume distribution showed that 99.2% was within 3.4–21.5 nm with an average of 7.7 nm and an upper limit of 33.0 nm. The number distribution had an average 6.0 nm, an upper limit of 17.1 nm and 99.3% was within 3.4–10.8 nm, and these distributions are shown in Fig. 1. The sol gelled at a concentration of 16.2%, and appeared to be well

TABLE I Comparison of stoichiometric Co_2Y [8], Co_2Z [10], Co_2W [9], Co_2X and the Co_2U ferrite sols at a concentration of 10.5% iron

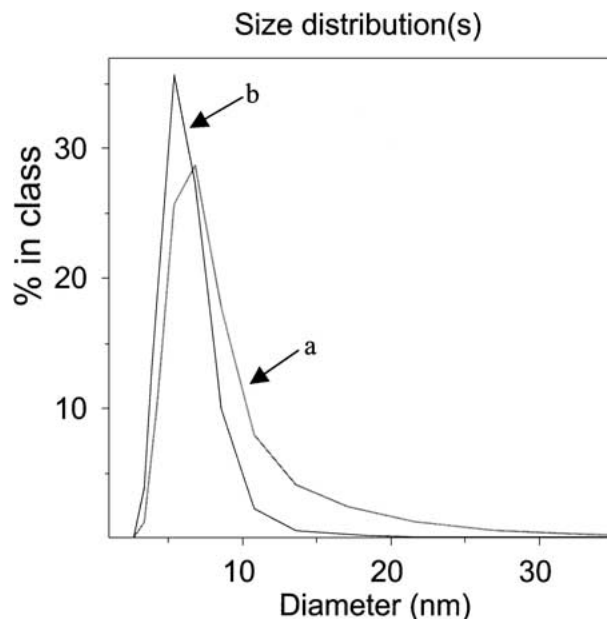| Sol	Y	Z	W	X	U
Z Av./nm	8.2	9.3	6.8	7.6	16.3
Vol Av./nm	7.5	8.1	6.6	7.7	9.4
Vol upper/nm	36.8	33.0	30.9	33.0	32.6
No. Av./nm	5.9	7.5	5.2	6.0	7.5
No. upper/nm	17.4	20.8	15.5	17.1	18.7
Range/nm	2.6–27.1	3.1–27.5	2.8–23.4	2.3–25.3	6.1–33.1

Figure 1 Volume (a) and number (b) distributions of the Co_2X sol.

within spinnable limits. The fibres produced contained some shot, indicating some structuring within the sol, but despite this no blockages or stoppages occurred during spinning, and smooth, 5–6 μm diameter fibres were produced. The fibre radii were measured on an optical microscope at $1000\times$ magnification using a graticule.

The Co_2U sol had a much larger Z average of 16.3 than the other ferrite sols, and a larger volume average of 9.4 nm, although the upper limit of 32.6 nm was in line with the rest and 99.3% was within 5.6–22.5 nm. Similarly the number average was high at 7.5 nm and with 99.3% being between 5.6–14.1 nm, but the upper limit was a lower 18.7 nm (Fig. 2). This sol appeared to lack the smaller sized fraction, thus raising the average values but not the more important upper limits, which are vital for successful spinning. The sol demonstrated differences in concentration too, becoming viscous at only 10.0% Fe and gelling at 12.5% Fe. The
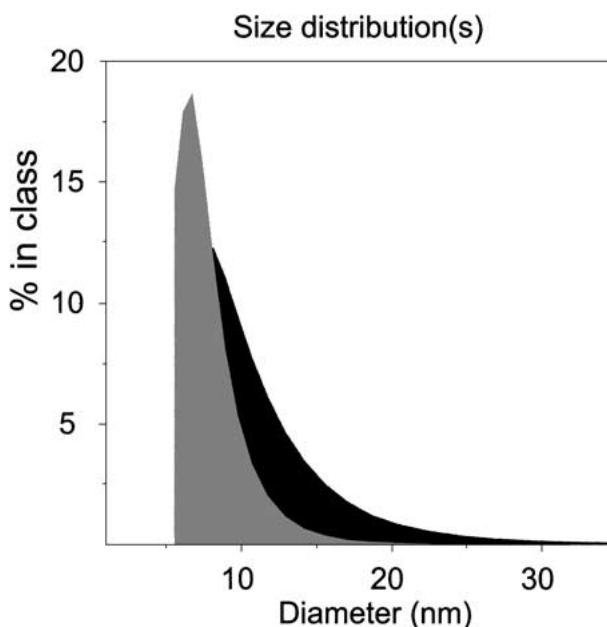

Figure 2 Volume (black) and number (grey) distributions of the Co_2U sol.
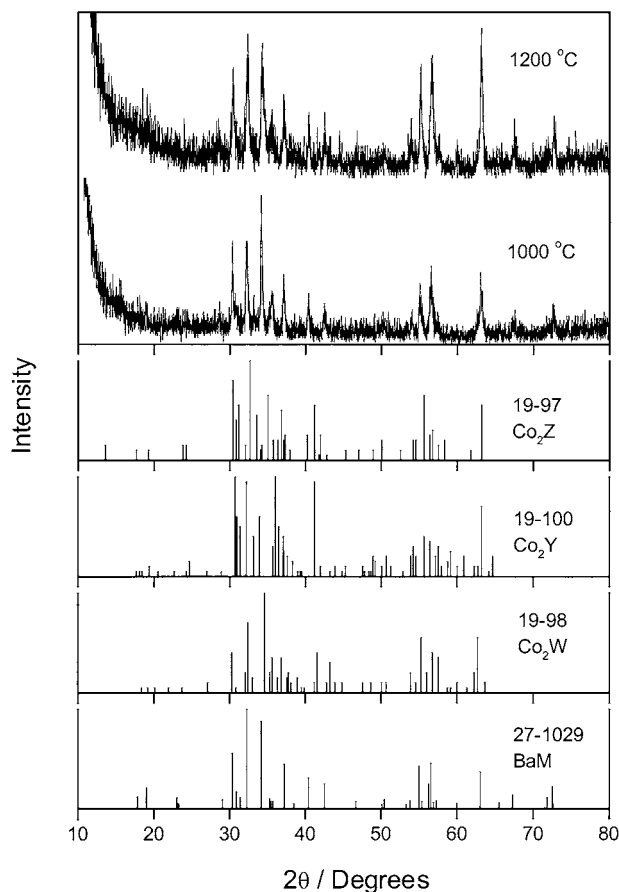
Figure 3 XRD pattern of the Co$_2$X fibres fired to 1000 and 1200°C/3 hr.

3.2. Physical characteristics

The XRD patterns for the Co$_2$X composition fibres fired to 1000°C and 1200°C/3 hr are shown in Fig. 3. Although there are no published patterns of Co$_2$X, the patterns of M, Y. W and Z ferrites are shown for comparison. At 1000°C the fibres consisted of only BaM and CoFe$_2$O$_4$, and did not contain any Co$_2$Y which was seen as a precursor phase to in the Co$_2$Z fibres [10], but not in the Co$_2$W fibres [9]. The microstructure also resembled that of the previously reported BaM fibres at this temperature [7] rather than the Co$_2$Y [8] or Co$_2$Z fibres [10], consisting of grains below 1 μm, although the fibre did appear to be more porous than the M ferrite fibres (Fig. 4). At 1200°C an unidentified phase had formed. It can be seen from XRD that the pattern does not match BaM or Co$_2$W, which when combined form the Co$_2$X structure, or any other identified hexagonal ferrite phases. However, as would be expected of Co$_2$X, it does resemble the M and W phases patterns, and is clearly a hexagonal ferrite. The fibres had experienced grain growth with most grains being 1–2 × 0.2–0.4 μm (Fig. 5), and even though some were as large as 15 μm the exaggerated growth observed in Z and W ferrites had not occurred. XRF analysis showed the composition to be close to that of the X ferrite at Ba$_{1.98}$Co$_{1.85}$Fe$_{28}$O$_{45.83}$. As the M, Y, Z and W phases have all been formed and identified from stoichiometric fibres manufactured by this method, the XRD, SEM and XRF results are evidence that Co$_2$X had been formed.

At 1000°C the Co$_2$U fibre resembled the Z precursor fibres at the same temperature [10], with the BaM, Co$_2$Y and CoFe$_2$O$_4$ phases coexisting with another unidentified phase that resembled Co$_2$Z. This would be a remarkably low temperature for Z ferrite to have formed even as a mixed phase, as the Z phase has never been observed previously without the exaggerated discontinuous grain growth (DGG) occurring [10, 13], in which
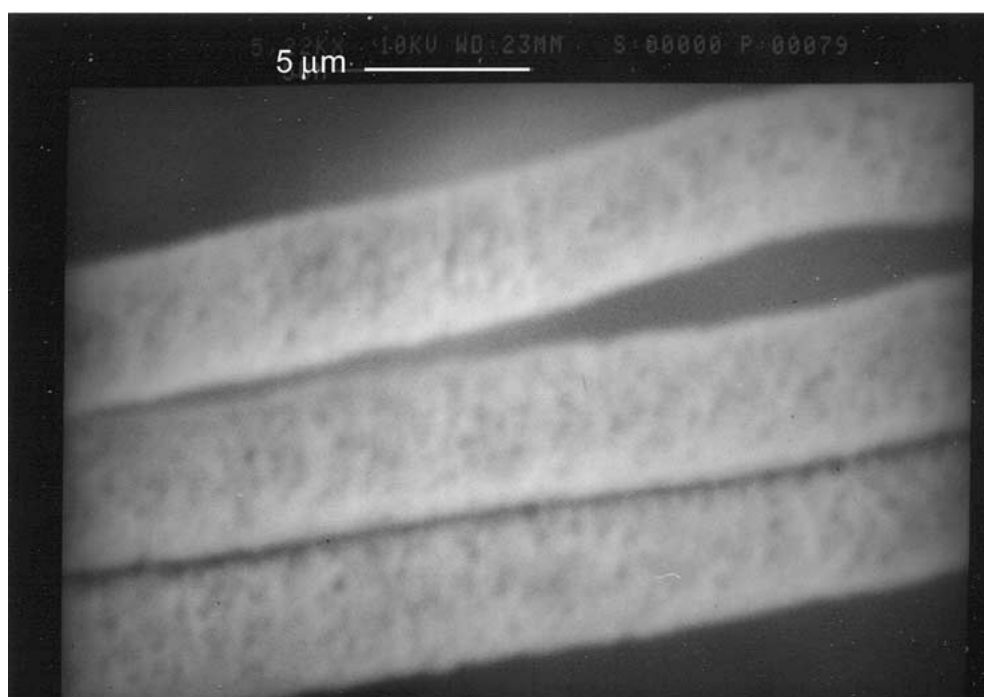
spinning solution was concentrated only to a normally unspinnable 11.9% Fe, but the increased viscosity of the Co$_2$U sol rendered the sol just spinnable. A smooth, clear and structureless fibre resulted, but unfortunately a large proportion of the solution was lost as shot, and this reduced the diameter of the fibre to only 3–4 μm.

Figure 4 SEM micrograph of the Co$_2$X fibres fired to 1000°C/3 hr.

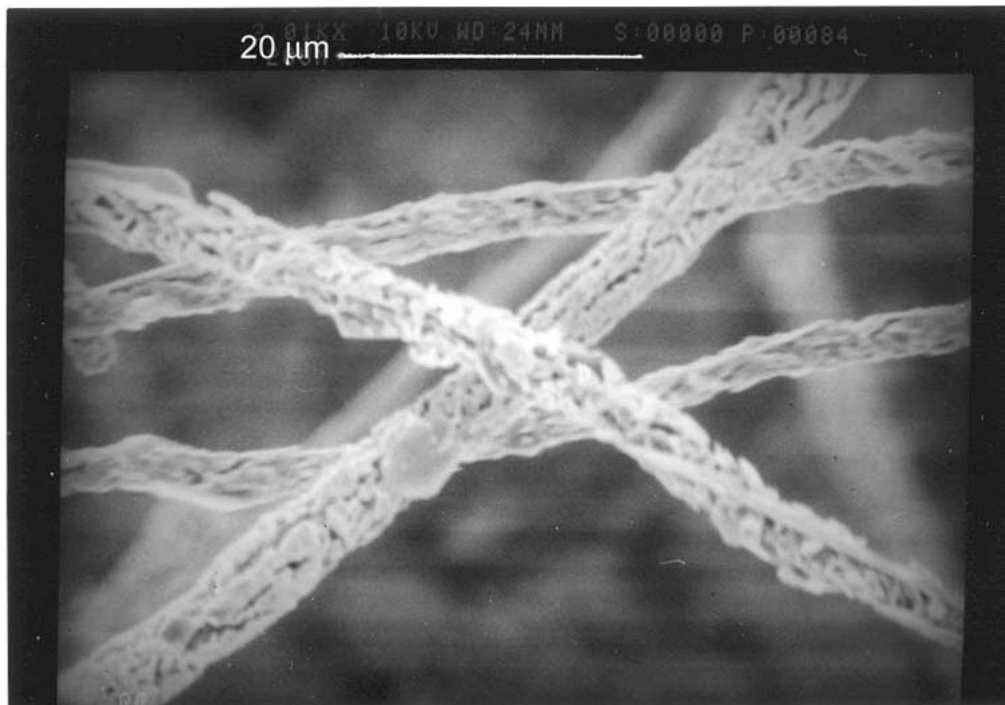*Figure 5* SEM micrograph of the Co$_2$X fibres fired to 1200°C/3 hr.

all grains grow to plates at least 20 μm wide, and a few even greater still. The microstructure resembled that of the Co$_2$Z precursor and Co$_2$Y fibres at 1000°C, with hexagonal plates up to 3 μm wide and 0.5 μm thick. This suggests that the unidentified Z-like phase may be Co$_2$U beginning to form at this point, although it is admittedly hard to judge from the muddled XRD data. As with Co$_2$X, there are no published XRD patterns for Co$_2$U ferrite, and the XRD pattern at 1200°C (Fig. 6) was different from those of BaM and Co$_2$Z, or any other identified hexagonal ferrite phase. As would be expected of Co$_2$U, it does resemble the M and Z phases, and is again clearly a hexagonal ferrite. At 1200°C DGG had not occurred despite the large grain size of up to 10 μm, as the grains were all roughly of equal dimension (Fig. 7), indicating that the material was the U phase and not a mixture of M and Z, the later only ever forming after the onset of DGG. At 1250°C the XRD pattern observed at 1200°C had become better resolved, but DGG had occurred, in which some grains had grown to proportionately huge sizes at the expense of others, so that the fibres became assemblies of elongated, planar crystals (Fig. 8). This resulted in a very mechanically weak fibre, and some of the grains had begun to fuse together. The composition was confirmed by XRF to be Ba$_{4.30}$Co$_{2.13}$Fe$_{36}$O$_{60.43}$, close to that of Co$_2$U.

3.3. Magnetic properties

The magnetic characteristics of other hexagonal ferrite fibres, with definite proven phases, have been investigated previously by the authors, and are currently in the publication process [14–16]. These are summarised in Table II, and can be compared to the Co$_2$X and Co$_2$U fibres to aid phase determination.
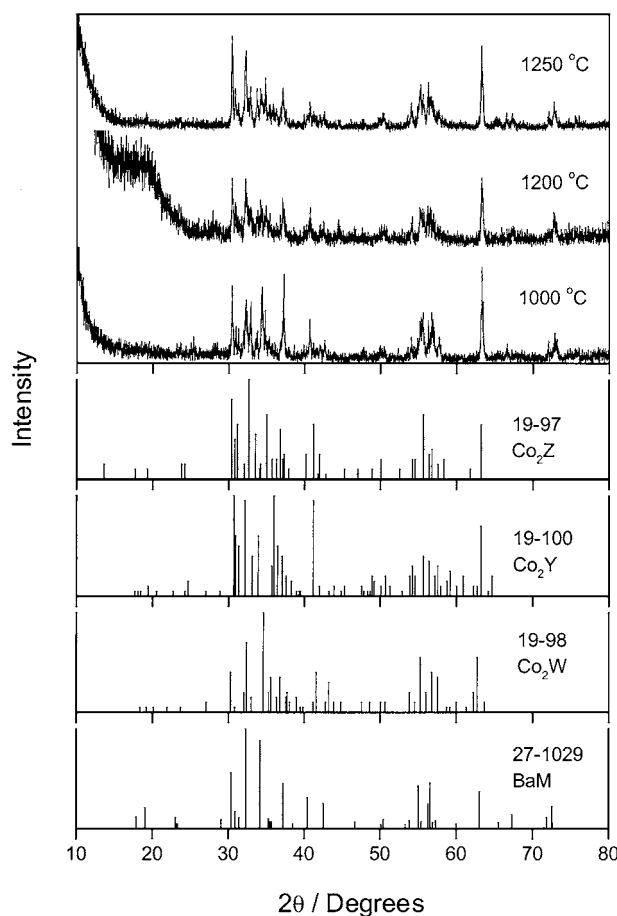

Figure 6 XRD pattern of the Co$_2$U fibres fired to 1000, 1200 and 1250°C/3 hr.

Single crystal Co$_2$X has a high M_s of 57.1 emu g^{-1}, and a very low H_c of only 0.005 T in single crystal samples [3]. It can be seen in Fig. 9 that the fibres had not reached these values. At 1000°C/3 hr the fibre was
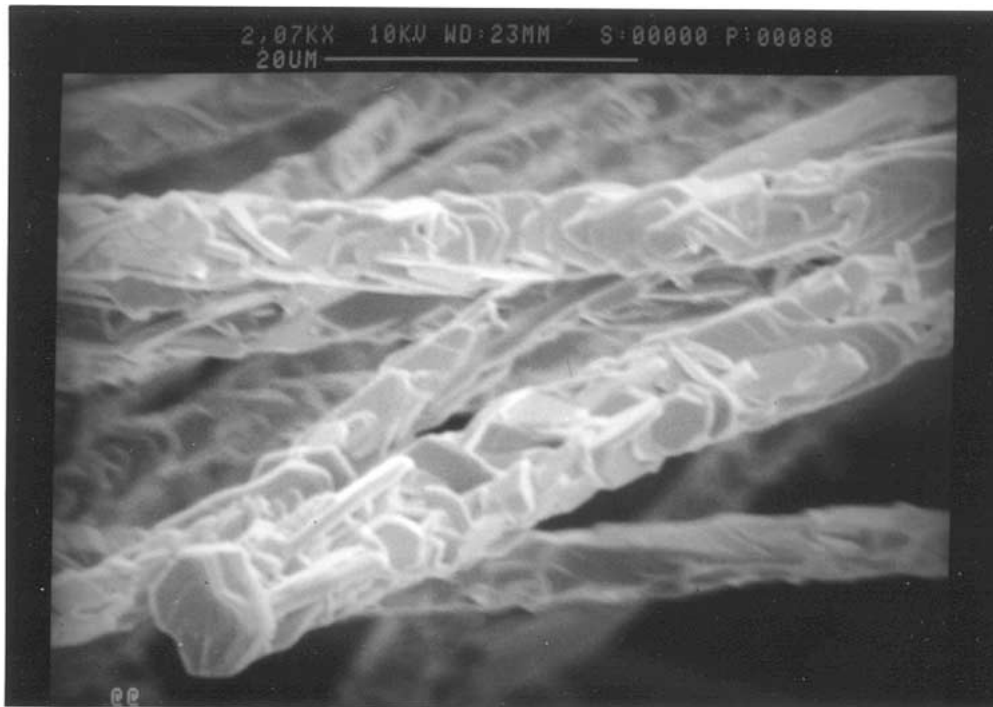
Figure 7 SEM micrograph of the Co_2U fibres fired to 1200°C/3 hr.

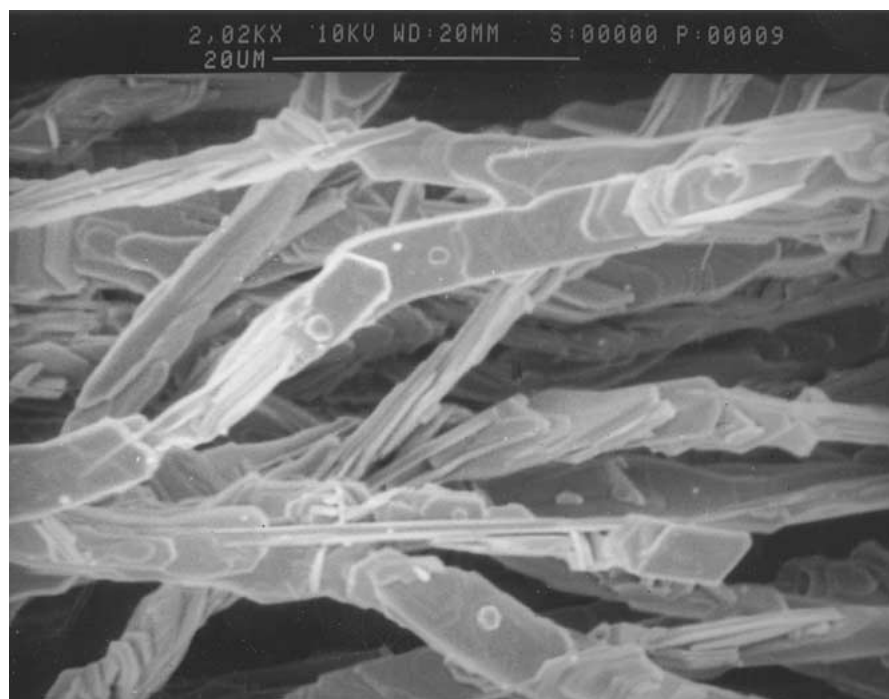*Figure 8* SEM micrograph of the Co_2U fibres fired to 1250°C/3 hr.

TABLE II Summary of magnetic properties of random hexagonal ferrite fibres

Ferrite Fibre	Temp./°C	M_s/emu g^{-1}	H_c/T	M_r/M_s
BaM [14]	1000	62.5	0.523	0.50
Co_2Y [15]	1000	35.8	0.045	0.46
Co_2Z [17]	1250	50.8	0.038	0.18
Co_2W [16]	1250	44.3	0.025	0.56
Co_2X	1200	45.0	0.085	0.38
Co_2U	1200	51.5	0.059	0.26

a hard ferrite with $M_s = 54.4$ emu g^{-1}, $H_c = 0.282$ T and $M_r/M_s = 0.48$, the coercivity being about half of that seen in the pure BaM fibres [14]. It resembled the mixed phase precursor fibres seen before the formation of Co_2Z, but the microstructure was similar to the M ferrites. After heating to 1200°C/3 hr the material had become a soft ferrite, with a reduction of M_s to 45.0 emu g^{-1} (0.8% error), $H_c = 0.085$ T and $M_r/M_s = 0.38$. As BaM has a higher M_s than Co_2X, the loss of this phase would result in the lowering of
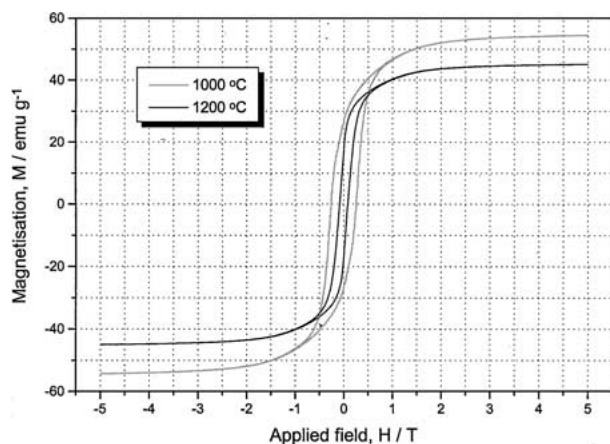
Figure 9 Hysteresis loops of the Co_2X fibres fired at 1000 and 1200°C/3 hr.
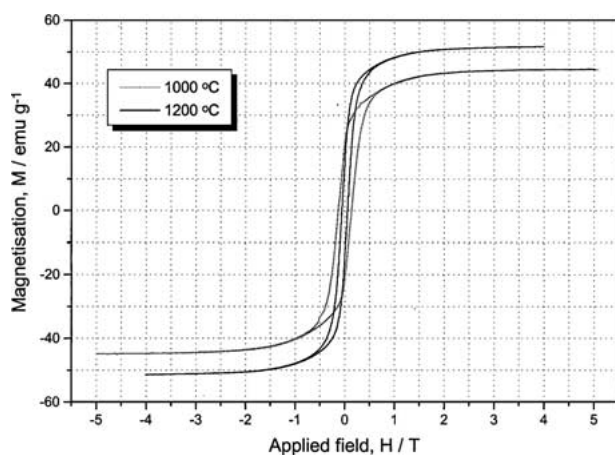

Figure 10 Hysteresis loops of the Co_2U fibres fired at 1000 and 1200°C/3 hr.

M_s. The lower coercivity also proved that there was no BaM in the material, as it is a very hard magnet, and as expected the loop shape did not resemble those of Co_2Y or Co_2Z. Although the M_s value was similar to that of Co_2W, the coercivity was much greater, and the loop had a different shape, the Co_2W loop having "lobes" around 0.2 T which were several times wider than the loop width at 0 T. The XRD pattern also clearly showed that the fibre was not pure Co_2W. Therefore the Co_2X fibre was magnetically different compared to the other ferrite fibres. The lower M_s and higher H_c those reported for single crystals could be due to the polycrystalline nature of the fibre and small phase impurities.

The only known property of Co_2U is that is ferroxplana [2], and will therefore be a soft ferrite, but it could reasonably be expected to resemble Co_2Z. The hysteresis loops of Co_2U random fibres fired to 1000 and 1200°C are shown in Fig. 10. At 1000°C/3 hr the fibre was already a soft ferrite, the loop having straight and smooth sides and a much smaller H_c than the Co_2X fibres fired to the equivalent temperature. This indicated the absence of BaM, and suggested that the U phase may indeed have already begun to form at this temperature. By 1200°C/3 hr the material resembled Co_2Z, but with an even sided and wider loop, whereas the Co_2Z loop had small "lobes" around 0.25 T [17]. M_s was similar to Co_2Z at 51.5 emu g^{-1} (0.3% error), but H_c was twice

as high at 0.059 T. The loop shape, together with lack of DGG, indicated that the Z phase had not formed, and Co_2Y and Co_2W have even larger "lobes" in their loops. Therefore the Co_2U fibre again seemed to be a magnetically different material to the other hexagonal ferrite fibres characterised previously, as well as the Co_2 fibre. After firing to 1250°C DGG had begun, but there was little change in the magnetic properties, with $M_s = 52.0$ emu g^{-1}, $H_c = 0.050$ T and $M_r/M_s = 0.32$, and there were still no "lobes", indicating that the pure phase had been obtained at 1200°C.

4. Conclusions

Stable stoichiometric precursor sols of Co_2X and Co_2U were made and characterised by PCS. The X sol resembled the other ferroxplana ferrite sols characterised previously, while the U sol, despite having a larger average particle size, still had the same upper size limit of around 30 nm. Therefore both sols were spinnable, and random gel fibres were blow spun of each. The XRD patterns of both samples were unclear due to their polycrystalline and fibrous nature, but they appeared to form new and distinct crystalline phases which have been tentatively identified as the X and U phases. As expected, the evolution of the Co_2X fibres resembled that of the similar Co_2W fibres, while the Co_2U fibres shadowed the development of the Co_2Z fibres reported previously. In neither Co_2X or Co_2U fibres was the exaggerated grain growth normally associated with Z and W ferrites observed at 1200°C, again indicating that these were the X and U phases. In the Co_2U fibres DGG had occurred by 1250°C, but with no change of crystalline phase. The magnetic hysteresis loops of both fibres were magnetically soft at 1200°C, as was expected of the X and U phases. The Co_2X fibres had an M_s of 45 mu g^{-1}, similar to that of the Co_2W fibres, but a higher H_c of 0.085 T and a more even loop shape. The Co_2U fibres also resembled the Co_2Z fibres with an M_s of 51.5 emu g^{-1}, but with again with a higher H_c of 0.059 T, and a very parallel sided loop shape. These two materials were therefore shown not to magnetically match any of the other hexagonal ferrite fibres investigated previously, adding further evidence that the X and U phases had been formed.

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