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Magnetic wood-based biomorphic Sr₃Co₂Fe₂₄O₄₁ Z-type hexaferrite ecoceramics made from cork templates



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ABSTRACT

Ecoceramics (environmentally conscious ceramics) are biomimetic/biomorphic ceramics, which use a naturally occurring and sustainable material as a template for their unique morphology and structure. Usually woods (or lignocellulosics) are used, due to the inherent cellular nature of their microstructures. The wood is pyrolised and the resulting carbon skeleton impregnated with a fluid, and this is then heated to combust the carbon template and convert the fluid precursor into a ceramic, while maintaining the structure of the original natural template. For the first time, ecoceramics have been made from cork, a totally sustainable wood that is harvested without harming the tree. Also for the first time, ecoceramics have been made of soft magnetic Z-type hexaferrites, in this case the room temperature multiferroic strontium Z ferrite $Sr_3Co_2Fe_{24}O_{41}$ (SrZ). Cork powder was pyrolised at 1000 °C, infiltrated with an aqueous sol–gel SrZ precursor, and then heated at 1200 °C/2 h to produce the ecoceramic. The cellular structure of the cork was maintained, with a small reduction in the hexagonal cell dimension to 10 µm diameter, but the cell walls remained 1–2 µm thick, of a similar magnitude to the hexaferrite grain size. Both magnetic and XRD data agreed that there was a small portion of the SrW phase present in these ecoceramics as well, and the magnetic loop showed a magnetically soft ecoceramic with $M_s = 59.5 \text{ A m}^2 \text{ kg}^{-1}$ (at 3 T), and a low H_c of 16 kA m⁻¹.

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1. Introduction

Materials produced by land-based plants, or lignocellulosics, such as wood, palms, crops, grasses and vegetable fibres, are natural bioorganic composites which often exhibit porous, anisotropic morphologies, with excellent strength at low density, and high stiffness and elasticity [1]. The morphology of such bio-organic materials consists of a hierarchic system, with features ranging from millimetre (growth ring patterns in wood) to micron scales (cellulose fibres, wood cells). This hierarchical architecture has a cellular microstructure of high porosity, due to the specific functions of living cells, such as transportation of water and gasses, storage, and mechanical strength. These cells form a system of channels of pores, with a preferential orientation along an axial direction. This feature offers the possibility of using liquid infiltration techniques, either to fill these pores with liquid to form a "negative" microstructure of the original wood [2], or to impregnate the actual cellular structure of wood the wood and transform it into an inorganic copy of the original cellular structure [3]. In the first example, the existing cellular structure of the plant material is infiltrated with a liquid precursor, and the organic material is then burnt out and the solution converted to the inorganic phase by heating. In the second example, the structure is first pyrolised to a pure carbon skeleton which maintains the structure of the plant, and this then impregnated with a solution, which converts to the inorganic phase on heating in air with loss of the carbon. Both methods can be used as hierarchical templates for the synthesis of novel inorganic materials with highly anisotropic cellular micro-, meso-or macrostructures, a new class of ceramics now referred to as *Ecoceramics* [4]. By using such structural templates, a large variety of biomimetic materials can be created, which maintain the structure of the wood including carbides, oxide ceramics and composites, with tailored chemical, physical and mechanical properties [5].

Other advantages of using such bio-organic materials (e.g. wood, sawdust, organic fibres) are:

- They are low-cost materials, which are available on a commercial scale, and indeed often wastes or by-products can be used/recycled/valorised.
- The wood can easily be machined into complex threedimensional shapes before treatment begins.



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- A great variety of different microstructures exist in wood, allowing a great potential for materials selection, with large variations in density, porosity, cell diameter and shape, etc.
- For ceramics, different processing techniques can be applied, depending on the desired properties of the final ceramic, e.g. mechanical strength, specific surface area, porosity.

The first biomorphic ceramics produced were of "SiC wood", by Ota et al. in 1995 [6], who infiltrated charcoal with TEOS (tetraethyl orthosilicate) and then heated it under argon at 1400 °C to produce biomimetic SiC. In 1998, Greil et al. [7,8] investigated the pyrolysis under N₂ of several types of wood, as templates to create so-called SiC "ceramic wood" made from the simple impregnation of the pyrolysed wood with gaseous SiO₂, and subsequent heating under vacuum to 1600 °C. Since then, SiC and other carbides such as TiN have been produced from liquid or gas impregnated pyrolysed wood templates, as well as oxide ceramics such as TiO₂, Al₂O₃ and Al₆Si₂O₁₃ (mullite) [5], ZrO₂ [9], SiO₂ and CeO₂ [10]. In 2003, the name *Ecoceramics* was created by Singh of NASA and Martinez-Fernandez and de Arellano-Lopez of the Universidad de Sevilla, in their paper "Environmentally conscious ceramics (ecoceramics) from natural wood precursors" [4]. Singh has since reported the formation of both carbides and oxides [9]. However, to date the only magnetic oxide ecoceramics produced appear to be the spinel oxides $Mn_xZn_{1-x}Fe_2O_4$ [11] and Ni_xZn_{1-x}Fe₂O₄ [12], and the hexagonal ferrites BaFe₁₂O₁₉ [13] and $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ [14], all made using nitrate salt solutions to infiltrate the pyrolised wood, with subsequent heating in air. The wood-templated 500 nm diameter SrZnCoFe₁₆O₂₇ W ferrite rods made in Ref. [2] did not possess the morphology of the wood. The pyrolised wood converts to carbon typically above 400 °C, with most of the weight loss having occurred by then as cellulose and lignin are broken down, and H₂O, CO₂ and volatile compounds are lost [1]. Between 400 and 800 °C some anisotropic shrinkage (15-40%) also typically occurs with decomposition and rearrangement of the organic compounds, and release of residual hydrogen, but nevertheless the crystalline carbon framework retains the macro- and microstructure of the original wood or material. The resulting carbon skeleton has a high degree of nanoporosity, and can be impregnated by gasses, liquid, solutions or sols/colloids [1].

Many different soft and hard woods have been used as pyrolised templates for ecoceramics, as well as cellulose fibres and paper [5], charcoal [6], sawdust [4] and MDF (medium density fibreboard) [15]. In particular, cedar [11,12], pine [7,9,14], jelutong [9] and balsa [7,11] were used to make oxide ceramics, and maple, oak, beech, ebony [7], eucalyptus, satinwood, jelutong, jarrah, mahogany, mango, Brazilian rosewood, Californian Redwood, African Redwood and Bubinga [4], pear, elm, ash, wild cherry, black alder, Persian walnut and European hornbeam [16] have also been used to make SiC ecoceramics. However, cork has never previously been used as a precursor to make ecoceramics, despite its obvious suitability, and here we report cork based ecoceramics for the first time.

Cork is the bark of a slow growing, evergreen oak (*Quercus suber* L.), which grows only in specific regions of the Western Mediterranean (Portugal, Spain, Southern France, part of Italy, North Africa) and China. Europe has produces more than 80% of the world's cork, and Portugal is the major global cork producer (>50% of world output) and processor [17]. The bark is periodically harvested from the tree every 9–13 years, depending on the region, without harming the tree, which continues to live on as a carbon sink for hundreds of years, as cork trees have a productive life of up to 300 years [18]. Therefore, cork is an exceptionally sustainable and renewable resource, and furthermore, cork forests are one of the best examples of balanced conservation and development anywhere in the world. They play a key role in ecological processes

such as water retention, soil conservation and carbon storage, and as cork oak trees store carbon in order to regenerate their bark, a harvested cork oak tree absorbs up to five times more CO₂ than one that is left alone [19]. The cork oak forests of Portugal are also considered to be "Europe's Amazon forests", supporting the greatest bio-diversity anywhere in Europe, with up to 135 plant species/ m² [19]. Cork is made of about 45% suberin, 27% lignin, 12% celluloses, 6% waxes and 6% tannins [20]. It has a microstructure different from other lignocellulosic woods, being formed of hollow polyhedral prismatic cells, with a hexagonal honeycomb shape when viewed from the radial direction, and rectangular (resembling a brick wall) when viewed from the transverse directions [21]. The cells are on average 45 μ m long, with a hexagonal face of 15–20 μ m, and a cell wall thickness of 1–2 μ m [20], and there are up to 200 million cells per cm³ [22]. Due to this structure, cork exhibits exceptional thermal, acoustic and vibrational insulation. and very low density of 120–240 kg m⁻³ (0.12–0.24 g cm⁻³) [17], the higher densities occurring when the cell walls are corrugated. As such, it is an ideal natural template to form ecoceramics.

The hexagonal ferrites are magnetic iron(III)-based oxides with a hexagonal crystal structure, also known as hexaferrites. They have become massively important materials commercially and technologically, and hexaferrites are used in a multitude of applications, for example permanent magnets, electrical motors and transformers, actuators and sensors, information storage, mobile communications, transport, security, defence and aerospace [23]. They can absorb energy at microwave (GHz) frequencies, and therefore have applications as EM wave shielding, as well as in stealth and RAM (radar absorbing materials) technology. All hexaferrites have a strong magnetocrystalline anisotropy, but the Co₂Z ferrites are soft magnets, with the magnetisation locked in the hexagonal plane, but able to rotate within this plane, giving them low coercivity [23]. The best known Z ferrite is Ba₃Co₂Fe₂₄O₄₁ (Co₂Z), but in 2001 Pullar and Bhattacharya reported the strontium analogue Sr₃Co₂Fe₂₄O₄₁ (SrZ) for the first time [24], and this was found to be a potentially very useful room-temperature single phase multiferroic compound in 2010 by Kitagawa et al. [25] It is known that SrZ has only a narrow window of formation between 1180 and 1220 °C, and that with further heating it decomposes in the SrCo₂Fe₁₆O₂₇ W ferrite (SrW) [26]. In this paper, ecoceramics of a Z type hexaferrite are produced for the first time, namely the multiferroic strontium Z ferrite Sr₃Co₂Fe₂₄O₄₁, from a cork template.

2. Experimental

2.1. Synthesis

The precursor sol for $Sr_3Co_2Fe_24O_{41}$ (SrZ) was made from a nitrate-peptised inorganic aqueous sol, as detailed by Pullar and Bhattacharya [24]. In brief, a solution of iron(III) nitrate nonahydrate was precipitated with ammonia solution and then peptised with nitric acid, resulting in an iron oxy-hydroxide (FeOOH) sol, with a Fe concentration of ~10 wt% (1.8 M). To make the Z ferrite precursor sol, stoichiometric amounts of strontium nitrate and cobalt(II) nitrate hexahydrate solutions were added to the iron sol. The final precursor sol had a particle size between 8 and 12 nm [24]. All reagents were standard laboratory/ACS grade, e.g. 99% purity, and this sol is known to form the SrZ phase at 1200 °C/2 h in air.

Cork powder supplied by Amorim was used. This was pyrolised under argon in a graphite furnace at 1000 °C, while contained in alumina crucibles with loose-fitting lids. The heating rate was 5 °C/min to 150 °C, then 10 °C/min to 1000 °C with a dwell time at that temperature of 30 min, after which then samples were



Fig. 1. DTA/TGA plots of (a) untreated cork powder and (b) pure pyrolised cork powder, heated at 5 °C/min in air.

cooled down again at a rate of $10 \,^{\circ}$ C min. The pyrolised cork powder was then infiltrated with the sol under vacuum, on a rotary evaporator. The pyrolised cork was weighed (assuming it to be pure carbon), the number of moles of C present calculated, and the same number of moles of iron were added in the form of the sol (assuming the sol to be $10 \,$ wt% Fe). An excess of 10% over this stoichiometric amount of sol was added, to ensure full impregnation of the carbon template. The water was then removed from the sol under vacuum on a rotary evaporator (60 °C, 70 mPa, small 50 ml flask) to ensure optimum infiltration of the pyrolised cork template.

The infiltrated cork was then heated in air to 1200 °C, the temperature known to be required to form SrZ from the sol precursor [24], at 5 °C/min with a dwell time of 2 h at 1200 °C, followed by



Fig. 2. SEM images of (top row) untreated cork powder and (bottom row) cork powder after pyrolysis at 1000 °C.

natural cooling. The carbon template skeleton was fully combusted, leaving just a pure hexaferrite ecoceramic.

2.2. Characterisation

Differential thermal analysis and thermogravimetric analysis (DTA/TGA) was carried out on a Setaram Setsys 16/18, under flowing air. Scanning Electron Microscopy (SEM) was carried out on a Hitachi S-4100 at 25 kV on samples coated with a thin layer of a gold/platinum mix. The crystal structure of the ecoceramic was identified using X-ray diffraction (XRD, Rigaku Geigerflex D/max Series) with Cu K_{α} radiation. The JCPDF standard files used were 19-97 for Ba₃Co₂Fe₂₄O₄₁ (Co₂Z) and 54-106 for SrCo₂Fe₁₆O₂₇ (SrW). There is no standard file for SrZ, but the pattern reported by Kikuchi et al. in [26] was also used to identify the phase, although this only consisted of peaks up to 45°. The magnetic properties were measured using a vibrating sample magnetometer (VSM, Cryogenics), at 300 K and magnetic fields up to 3 T. The sample temperature was stabilized at 300 K, and the maximum field ramp rate was 0.25 T min⁻¹. The device sensitivity is rated up to 10.6 emu, and maximum recorded temperature drift was ±0.05 K, with typical values of ±0.01 K.

3. Results and discussion

Prior to pyrolysis, DTA/TGA analysis of the combustion of cork in air was carried out, to investigate what temperature is required to remove the components of cork. As can be seen in Fig. 1a, there was a slow initial weight loss of \sim 4% up to 200 °C (attributed to loss of moisture), followed by a more rapid weight loss of a further 55% between 200 and 460 °C, signalled by an exotherm around 340 °C. It is known that the polysaccharides, celluloses and carbohydrates in cork degrade between 200 and 360 °C, with a loss of around 30 wt% and a darkening of the colour. Above 350 °C lignin and suberin begin to degrade, and above 400 °C only coke (from decomposed suberin) and lignin remain [21]. There was then a steady, slower weight loss of 32.6% to 910 °C, after which there was no further weight change. The total weight lost at 910 °C

was 91.6%, and the remaining 8.4% was ash. This cork was not treated with acid or base to remove surface chemical groups, a process which is often used to produce activated carbon during pyrolysis [21], and which would reduce the amount of ash. Clearly this is not identical to the pyrolysis process without oxygen present, but it is suggested that a temperature of 1000 °C would be sufficient for full pyrolysis to be achieved. In actual fact, we have since discovered that a temperature of only 800 °C is sufficient, and pyrolysis temperatures as low as 700 °C have been reported for cork [20].

The DTA/TGA of pure pyrolised cork (not infiltrated with a sol) heated in air is shown in Fig. 1b, and it can be seen that the major weight loss begins at 300 °C, and is completed at 820 °C, by which point a weight loss of 93% has occurred. We were unable to measure the sol impregnated pyrolised cork by DTA/TGA, as the ferrite reacts with the platinum of the sample holder. Nevertheless, it is clear that 900 °C would be a sufficient temperature to combust all of the carbon template skeleton.

The untreated cork powder was coarse by the standards of the industry, with particle sizes between 250 and 500 µm, but containing typically sized cells of around 15–20 µm diameter (Fig. 2). Cork powder is a low cost and environmentally friendly by-product of the cork industry, and in 1997 it was estimated that 32–37,000 tonnes were produced annually in Portugal, and 50,000 tonnes globally [27]. It can also be seen in Fig. 2 that the pyrolised cork has maintained the cork macro- and microstructure, with cell dimensions and cell wall widths being retained.

The XRD pattern of the cork-based SrZ ecoceramics fired at 1200 °C/2 h is shown in Fig. 3. The indexed peaks attributed to SrZ from Ref. [26] are shown in red above the spectra, and remaining Z phase peaks that can be attributed to Co_2Z are shown in blue above the spectra. The main difference between the two structures is the substitution of barium by the smaller strontium, so their patterns will be very similar, as can bee seen when the two standards are compared in Fig. 3. SrZ has an extremely narrow formation window of about 20–30 °C between 1280 and 1210 °C, and it is very difficult to make as a totally pure phase. SrM hexaferrite (SrFe₁₂O₁₉) is a precursor phase, and it is known to decompose to



Fig. 3. XRD pattern of the cork-based SrZ ecoceramics fired at 1200 °C/2 h. The indexed peaks are attributed to SrZ (in red above the spectra), Co₂Z (in blue above the spectra) and SrW (in green below the spectra). Below are the three standard patterns. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

form SrW (SrCo₂Fe₁₆O₂₇) above 1200 °C. There does not seem to be any of the SrM phase present, but there are indications that there may be a small amount of the SrW phase present – in particular, the 008 and 116 peaks, and perhaps the 110, 1010 and 202 peaks appearing as shoulders (marked in green below the spectra). Nevertheless, this appears to be a largely good quality SrZ specimen, and magnetic measurements will help confirm its precise nature. There is an unidentified peak at around 44.6°. This is where the secondary peak for poorly crystalline active carbon may be expected to appear (resolving into the crystalline graphite 101 peak at higher temperatures), but it does seem unusually crystalline, and there is an absence of any other graphite peaks, or the large amorphous carbon peak which occurs at around 25° [28].

The SEM images of the SrZ ecoceramics after firing to 1200 °C/2 h are shown in Fig. 4. It can clearly be seen that the cellular structure of the cork has been maintained, with a clear hexagonal aspect, but the diameter of the cells appears to have been reduced to around $10 \mu m$ (Fig. 4a and b). The cell walls seem to have the same dimensions of $1-2 \mu m$, but that width is now made up of just one or two discrete hexaferrite grains. This is not surprising, because like most hexaferrites, the grain size of SrZ ferrite is $1 \mu m$ and larger, and such micron-sized grains can also be single magnetic domains [23]. It can be seen that the cell walls consist of randomly oriented, clearly hexagonal, planar grains, or up to $2 \mu m$ diameter and 200–300 nm thick, with sharp edges and clear

evidence of hexagonal growth in layers on the surface of the plane (Fig. 4c and d). Such a microstructure is also typical of SrZ hexaferrite, which does not undergo the exaggerated discontinuous grain growth found in Co_2Z ferrite. It can also be seen that this grain growth has led to the formation of large pores or gaps between the crystals, hundreds of nm in scale, so the cells walls are no longer smooth and continuous. This means that such ecoceramics will more permeable to water and other fluids or gasses, unlike cork wood, and this may be advantageous for applications which rely on continuous open porosity and increased surface area.

The magnetic hysteresis loop (measured at room temperature) of the SrZ ecoceramics is shown in Fig. 5. SrZ is known to be a soft ferrite (low coercivity, narrow loop), with a saturation magnetisation (M_s) of 48.5–50.5 A m² kg⁻¹ [24,26], and a very low coercivity (H_c) of 6–11 kA m⁻¹ [24,26]. However, the measured loop of the ecoceramics had a higher M_s (at 3 T) of 59.5 A m² kg⁻¹, and although it had a low H_c of 16 kA m⁻¹at zero T, the loop also showed an unusual "lobing" or widening of the loop. This was caused by a less rapid decrease magnetisation when the field was being reduced, compared to a rapid increase in magnetisation once the orientation of all magnetic domains was overcome (at zero M_s) and a reverse coercive field was applied. This form of loop can be caused by two effects: either alignment of the orientation of the magnetic domains (i.e., grains), or the existence of a secondary magnetic phase [29,30].

The grains appear to be randomly oriented from the SEM images, and the low remnant magnetisation $(M_r, M$ when the field = 0) of 15 A $m^2 kg^{-1}$ when the field is being reversed also suggests that there is no orientation of the domains. The M_s of SrZ is \sim 50 A m² kg⁻¹ [24]. However, the larger-than-expected M_s value of 59.5 A m^2 kg⁻¹ observed here suggests that there is a second phase present. The two possible choices could be the precursor SrM ferrite, or the decomposition product SrW ferrite – both have *M*_s values larger than SrZ. However, SrM is a very hard ferrite, with $M_{\rm s} \sim 72-74 \,{\rm A}\,{\rm m}^2\,{\rm kg}^{-1}$ and $H_{\rm c}$ values >300 kA m⁻¹ [23], and this would lead to a broadening of the loop as well as increased H_c . Similarly, the presence of the $CoFe_2O_4$ spinel precursor phase would also lead to major loop broadening, as it also has a large H_{c_1} and it would not be expected to be found in a Z ferrite sample heated as high as 1200 °C. There was no evidence of any SrM or CoFe₂O₄ phases in the XRD patterns, and this is supported by the magnetic data.

There appear to be no published H_c values for SrW, but all known Co₂ hexaferrites have hexaplana (in-plane) magnetocrystalline anisotropy, and so they are all soft ferrites [23]. Therefore, we would also expect $SrCo_2W$ to be a soft ferrite, with low H_c . It is reported that SrW has a high M_s of 77 A m² kg⁻¹ [31], and the same authors claim it becomes uniaxial above 500 K, further supporting the fact that it has planar (i.e., soft) anisotropy at room temperature. Such a high M_s would have a large contribution to the magnetisation, raising it above the expected values for SrZ, and the reversal with field of two different species of magnetic domain (Z and W) could cause the "lobed" loop observed here. The W phase is the usual decomposition phase formed from Z ferrites at higher temperatures, and it is known that SrZ has a very narrow formation and stability range, of around 1180-1200 °C, so these samples heated to 1200 °C are right on the limits of this, and it is likely they could contain some W phase [23].

Therefore, both magnetic and XRD data agree that there is a small portion of the SrW phase present in these ecoceramics as well, certainly more than was formed from the pure sol precursor when heated to 1200 °C [24]. This suggests that the combustion of the carbon skeleton may aid in the formation of the SrW phase at lower temperature than normal, and further investigations need to be made into the exact formation kinetics of this system.



Fig. 4. SEM images of SrZ ecoceramics fired at 1200 °C/2 h.



Fig. 5. Magnetic hysteresis loop of SrZ ecoceramics fired at 1200 $^{\circ}C/2$ h. Inset plot shows expanded view of the loop between applied fields of -0.3 and 0.3 T.

4. Conclusions

For the first time, ecoceramics have been made from cork wood, and ecoceramics have been made of soft magnetic Z-type hexaferrites, in this case the room temperature multiferroic material, SrZ (Sr₃Co₂Fe₂₄O₄₁). Cork powder was pyrolised at 1000 °C under argon, and maintained its macro- and microstructure. This was infiltrated with an aqueous sol–gel SrZ precursor, and then heated at 1200 °C/2 h to produce the ecoceramic. SEM images showed that the cellular structure of the cork was maintained, although there was a small reduction in the dimension of these hexagonal cells to about 10 μ m in diameter. The cell walls remained 1–2 μ m thick, of a similar magnitude to the hexaferrite grain size. Both magnetic and XRD data agree that there is a small portion of the SrW phase present in these ecoceramics as well, and the magnetic loop showed a magnetically soft ecoceramic with M_s = 59.5 A m² kg⁻¹ (at 3 T), and a low H_c of 16 kA m⁻¹.

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