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Synthesis of multifunctional photonic crystals

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A method for the synthesis of three-dimensionally ordered macroporous crystals from materials that exhibit additional functionality using a hetero-metallic precursor is reported.

The interest in three-dimensionally ordered macroporous materials for photonic crystals has developed rapidly during the last decade.[1] A number of recent publications have demonstrated that template-directed synthesis is an elegant and simple route to the formation of this class of materials.[2] The template consists of a close-packed array of mono-disperse polymer spheres. The interstices of the template are filled with a precursor to form a composite structure, which is subsequently calcined to convert the precursor to the desired solid compound and simultaneously remove the template. This synthetic protocol is analogous to removal of the template molecules used as structure-directing agents in zeolite synthesis. To date almost all of the three-dimensionally ordered macroporous (3-DOM) solids formed in this way are either elements or binary compounds *e.g.* TiO_2, ZrO_2, Al_2O_3, Si, C and GaN.[2] However, many of the technologically important compounds used in advanced applications contain two or more metals in a specific ratio. If the functionality of such materials is to be incorporated into 3-DOM structures in order to form, for example, a multifunctional photonic crystal, the synthetic route must be refined to ensure chemical homogeneity of the product. In this communication a protocol for the formation of multi-component 3-DOM solids is reported. In the research described in this communication barium titanate ($BaTiO_3$) was used as the target compound although the procedures developed are applicable to the synthesis of a wide range of multi-functional 3-DOM materials.

In solid state chemistry the simplest approach to the formation of advanced multi-component materials is to combine binary precursors in the correct ratio. The finely ground mixture is heated at high temperatures and the desired compound forms by solid-state diffusion. Utilisation of a polymer template in the synthesis of 3-DOM solids precludes the use of high temperatures as the template would be removed before the desired compound is formed and in the absence of the template the periodic arrangement of the pores would be lost. In some cases a sol–gel route can be used to circumvent the requirement for high temperatures required by conventional methods. In a sol–gel process the first step is the formation of the "sol"—a highly concentrated, often viscous, solution of the reactants. The sol is dried, often under vacuum, to form the gel in the second stage of the process. A modified sol–gel process has been reported by other workers as a method for formation of macroporous $BaTiO_3$.[3] Despite numerous attempts to reproduce the synthesis procedure described by these workers we failed to reproducibly form compositionally homgeneous $BaTiO_3$. Careful TEM characterisation revealed that while $BaTiO_3$ was always the major phase present in the product other impurity phases such as TiO_2 and $BaTi_5O_{11}$ were also present. We believe the reason for this is that while the "sol" contains two molecular species in the correct ratio it is essentially impossible to ensure that the correct ratio between these molecules is maintained within the interstices of the template.

An elegant solution to the problem is to synthesise a well-defined hetero-metallic precursor and to infiltrate the polymer template using this molecule. This ensures that the metal ratio is correct throughout the template and that subsequent calcination results in a single-phase material of the correct stoichiometry. The precursor molecule selected was barium titanium glycolate (BTG), $BaTi(C_2H_4O_2)_3 \cdot 4C_2H_6O_2 \cdot H_2O$, which has been fully characterised by other workers.[4] This precursor was synthesised using the procedure described previously by Day *et al.*[4] Barium oxide (97%, Prolabo) was dissolved in ethylene glycol (99%, BDH) with vigorous stirring. The solution was cooled to ambient temperature, diluted with 2-propanol (99.7%, BDH) and titanium(IV) ethoxide (97%, Aldrich) was added with stirring. After about 30 minutes barium titanium glycolate (BTG) precipitated from the reaction mixture. The BTG was isolated by filtration, washed with 2-propanol and dried under vacuum to produce a fine white powder. The powder exhibited an IR spectrum identical to previously published data.† The solution for infiltration of the latex template was prepared by dissolving BTG in ethylene glycol with stirring and gentle heating to aid dissolution.

The template for the synthesis was formed from a suspension of latex spheres in water. A small amount of the suspension was poured into a PTFE evaporating dish which was placed in a low temperature oven (~60 °C) overnight to allow the water to evaporate. This resulted in a well-ordered, opalescent colloidal crystal, which was extremely fragile. The crystal was divided into a number of small pieces, which were subsequently used for the preparation of the 3-DOM materials.

The latex crystals were placed in a Buchner funnel and a few drops of the hot glycolate solution were placed on top of each crystal using a pipette. A vacuum pump was used to pull the BTG solution through the crystals. This can take several minutes as the solution is viscous and does not pass readily through the filter paper. The filtration cycle was repeated 5 times before the crystals were carefully removed from the filter paper. Any solid BTG particles adhering to the outside of the latex crystals were removed by gentle washing with 2-propanol. Finally, the infiltrated crystals were then placed in an alumina crucible and calcined at 650 °C in flowing air for 6 hours. The samples formed were characterised using powder XRD, scanning electron microscopy and transmission electron microscopy.

Powder XRD of the final product shows that the material is highly crystalline and can be indexed as the cubic form of $BaTiO_3$ (Fig. 1). Calcination of the BTG/latex composite results in a highly periodic macroporous structure as demonstrated by the images shown in Fig. 2.

Fig. 2(a) shows a low magnification SEM image of the

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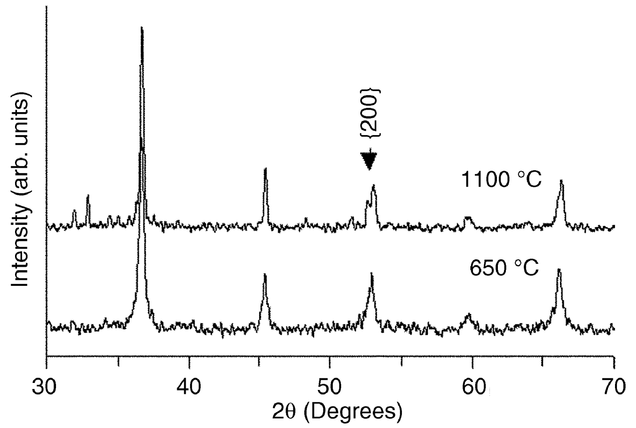

Fig. 1 Powder XRD patterns after calcination at 650 °C and 1100 °C.

structure formed after calcination. In the central part of the image the periodic arrangement of pores is clearly observed. In addition there is evidence of a less porous coating over parts of the 3-DOM structure. This is shown more clearly in a side-view of a cleaved crystal where the coating is thicker (Fig. 2(b)). This film or "crust" probably results from excess BTG on the surface of the template, which on calcination converts to $BaTiO_3$. Corrugations, macroscopic steps and irregularities on the template surface cause significant variation in the thickness and the presence/absence of partial porosity in the coating. The higher magnification SEM image shown in Fig. 2(c) provides clear evidence that the solid is ordered in three dimensions. The defective regions in the centre allow the structure to be projected in the z-direction, demonstrating that the structure clearly consists of a cubic close packed arrangement of voids.

By gently crushing the crystals, dispersing in propanol then placing a droplet of the suspension on a carbon coated copper grid it is possible to find isolated regions that can be imaged in the transmission electron microscope (TEM). The TEM image shown in Fig. 2(d) provides useful insights into the nature of this structure. The "walls" of $BaTiO_3$ that encapsulate the "air" spheres are observed to be polycrystalline agglomerates and this was confirmed by electron diffraction (Fig. 2(d) inset). This is entirely consistent with our previous observations on macroporous TiO_2.[5] The wall thickness varies around the macropores but at the thinnest point is approximately equal to the size of the crystallites which is in the range 35-55 nm (Fig. 2(d) -inset). The average diameter of the "air" spheres is ~230 nm compared with an original diameter of the latex spheres of 380 nm. This equates to a shrinkage of ~40% which is somewhat larger than our previous observations in 3-DOM TiO_2.[5]

According to the equilibrium phase diagram for $BaTiO_3$ the tetragonal phase is stable at room temperature, transforming to the cubic phase at ~130 °C.[6] However, the powder XRD pattern shown in Fig. 1 does not exhibit the characteristic splitting of the {200} reflection expected of the tetragonal phase suggesting that the material is cubic. Extensive investigations by other workers have shown that the global structure of polycrystalline $BaTiO_3$, as measured by XRD, is dependent on the grain size and some researchers have suggested that a minimum grain size (~120 nm) is necessary to stabilise the tetragonal phase.[7] Since the grain size in the 3-DOM structure is significantly less than this value (~35–55nm) it might be concluded that the material formed is cubic and hence, paraelectric.

The effect of grain size on the structure and properties of $BaTiO_3$ has been extensively examined by Frey and Payne.[8] These workers demonstrated that the global (XRD) structure can appear to be inconsistent with the local symmetry. Analysis of XRD patterns revealed samples with grain sizes of 35, 100 and >400 nm to be cubic, tetragonal (c/a = 1.006) and tetragonal (c/a = 1.011), respectively. However, Raman spectra recorded for the same specimens all show essentially the same features, which are associated with the presence of the acentric local structure that would normally be associated with tetragonal or orthorhombic materials. In fact, one small feature in the spectrum of the first sample suggests that the

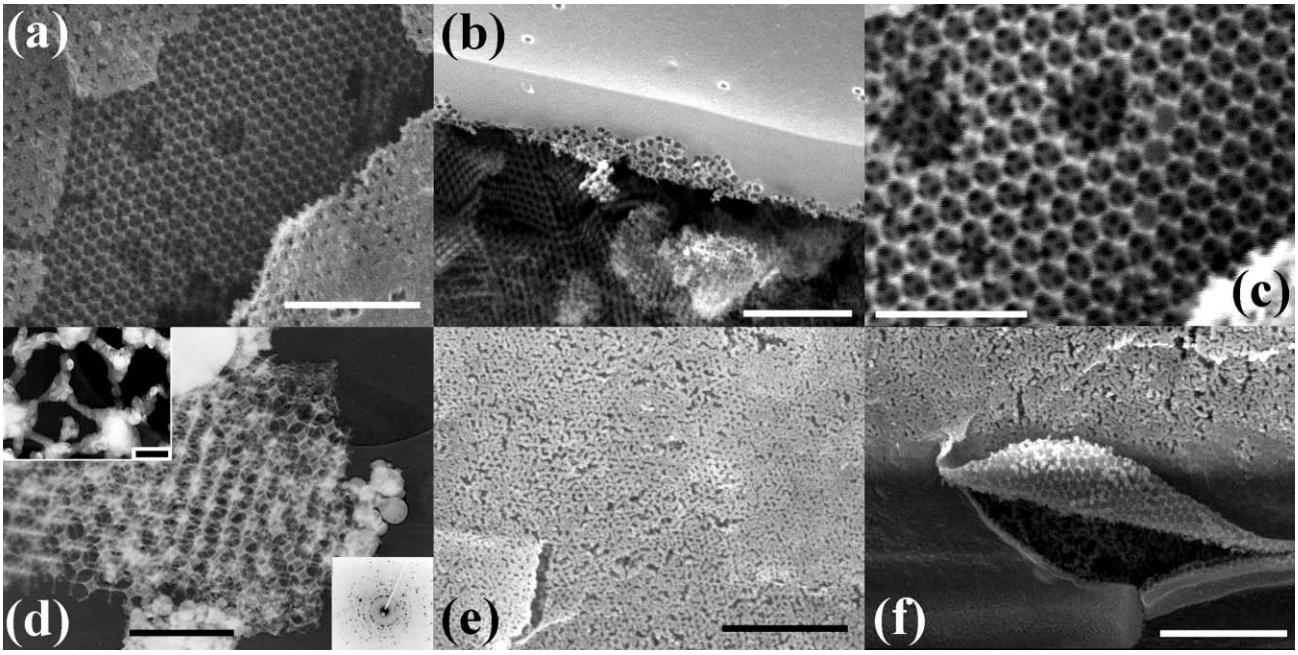

Fig. 2 SEM images of 3-DOM $BaTiO_3$ showing (a) well-ordered arrays of macropores with a thin coating in some areas (scale bar = 2.2 μm), (b) a side view of a cleaved crystal (scale bar = 2.4 μm) and (c) a well-defined ccp array of air spheres (scale bar = 1.2 μm). (d) The TEM image reveals the 3-D arrangement clearly (scale bar = 600 nm). The electron diffraction pattern (inset, bottom right) shows that the walls are polycrystalline and the high magnification image (inset, top left, scale bar = 70 nm) shows that the grains are ~35–55 nm in size (scale bar = 0.4 μm). (e) On heating to 900 °C the macropores retain some regular order but the walls thicken significantly and the pore size decreases (scale bar = 4.4 μm). (f) The increase in density eventually results in delamination of the coating (scale bar = 4.6 μm).

local structure in this sample is orthorhombic. On the basis of the work by Frey and Payne[8] it is likely that the 3-DOM $BaTiO_3$ structure described in the current communication is macroscopically cubic but is microscopically orthorhombic or tetragonal, and consequently is likely to exhibit ferroelectric properties.

To investigate the effect of temperature on the macroscopic crystallography some samples of the 3-DOM structure were prepared at higher calcination temperatures. However, it was discovered that heating at 900 °C for 2 hours results in a dramatic change in the microstructure of the 3-DOM material. Fig. 2(e) shows that the well-defined 3-DOM structure has been lost almost completely. While a regular array of pores is still identifiable the pores are poorly defined and are smaller than those originally present. The walls that separate the pores appear to thicken significantly during the high temperature treatment—a process that is probably due to growth of the nanocrystalline grains that make up the walls of the porous material. In a number of areas of the sample (Fig. 2(f)) the outer film or "crust" has delaminated from the porous structure. This can be rationalised as a consequence of the solid state diffusion that results in thickening of the walls, reduction of the pore size and hence, densification of the 3-DOM structure. Since the outer "crust" lacks the porosity of the 3-DOM structure it is already relatively dense. Hence, the increase in density and decrease in volume of the 3-DOM structure is not matched by a volume change of the "crust" and the mechanical strain that is set up results in delamination. It is somewhat fortuitous that the underside of the delaminated film actually retains an imprint of the original 3-DOM material and provides some confirmation of this hypothesis. TEM measurements show that the grain size of the crystallites in the "walls" of the sample calcined at 900 °C is >120 nm but the powder XRD pattern suggests that the macroscopic structure is still cubic. In fact splitting of the {200} reflection in the XRD pattern was not observed until a calcination temperature of 1100 °C as shown in Fig. 1(b). However, after heating to this temperature for 2 hours all regular porosity in the microstructure has been lost.

In summary, it has been shown that template-directed synthesis of ternary solids with a periodic 3-dimensional arrangement of macropores can be performed using a hetero-metallic precursor. Use of a well-defined hetero-metallic precursor molecule ensures compositional and structural homogeneity in the product that cannot be routinely achieved using a mixture of precursor molecules. The utilisation of a polymer template precludes the use of high temperatures in the synthesis method and in some cases this may limit the "global" structure of the product. However, other studies suggest that an acentric local structure will be present in these materials. This means that the driving force for ferroelectric behaviour has not been lost and investigations to verify this are ongoing. It has been demonstrated that ternary (or quaternary) three-dimensionally ordered macroporous materials can be reliably formed using a precursor method and the results presented open up new opportunities for the formation of multifunctional photonic crystals.

Notes and references

†IR (cm^{-1}, KBr) 3700–3000 s, br; 2937 m; 2874 m; 1648 m; 1455 m; 1302 m, sh; 1085 s; 882 s; 610 m; 526 m.

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