Field-induced structural transition in mesocrystallites

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Abstract

We have fabricated multiply-coated microspheres that exhibit appreciable electro-magneto-rheological responses. Under crossed electric and magnetic fields, the microspheres form columnar crystallites with an internal structure that transforms from body-centered tetragonal to face-centered cubic as the ratio between the magnetic and the electric fields exceeded a minimum value. The observed transition scenarios are in excellent agreement with calculations. © 2000 Elsevier Science B.V. All rights reserved.

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Crystals with lattice constants ranging from a few thousand Angstroms to tens of microns are called mesocrystals. The ER or MR fluids are generally particle suspensions where the particles have large electric polarizability or magnetic permeability/magnetic moments. The ER or MR effect can order suspended particles into body-centered-tetragonal (BCT) mesocrystallites [1–7]. Here, we demonstrate that crossed electric and magnetic fields can induce a transition from the BCT to the face-centered-cubic (FCC) structure. Uniform glass spheres with diameters of 34 ± 2 µm were chosen as the core onto which we coat nickel (approximately 2 µm) using electroless plating technique [8]. A layer of PZT was coated on top of the Ni layer by using the sol–gel method [9]. We have further coated another layer of Ni, followed by a layer of TiO₂. The outer coatings were intended to give a large ER response [10]. The cross-sectional scanning electron microscope (SEM) pictures of the EMR spheres are shown in Fig. 1.

We mix the EMR spheres with silicon oil, and put the sample in a cell with four electrodes. The high electric field, at 50 Hz and up to 2 kV/mm, was applied across the top and bottom electrodes, separated by 3 mm. Another two parallel plates were mounted on two sides, 6 mm apart, and connected to a HP4282A LCR meter. The whole cell was placed in the central region of an electromagnet (GNW Magnet System, model 3470) with a pole surface diameter of 40 mm and a gap of 20 mm.

At fixed electric field, the structural changes induced by the magnetic field inside the mesocrystallites were monitored by measuring the small dielectric constant changes in a direction perpendicular to both the electric and magnetic fields. The results are summarized in Fig. 2 for a sample with 20% solid volume fraction, at four values of the electric field. The dielectric constant at the small magnetic field region was at and reversible. For the curve with 2 kV/mm, this region occurred for magnetic fields less than 30 G. Irreversibility sets in at magnetic fields greater than this value. The associated structural changes inside the columns were monitored by taking many cross-sectional micrograph pictures at various magnetic field values (by freezing the configurations in solid epoxy, and cutting the resulting samples). Four such micrograph pictures are shown in Fig. 3, with an applied electric field of 2 kV/mm. Figs. 3(a) and (b) are for the configuration under zero magnetic field, and Figs. 3(c) and (d) are for the configuration at 54 G of applied magnetic field. Other cuttings were taken at 20,

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30, 35, 38, 40, and 50 G. Together with the dielectric constant measurements, they gave the following picture of the BCT-FCC transition. At magnetic fields less than 30 G, only the BCT structure was seen. From 30 to 50 G, there was a coexistence of local BCT structures with locally non-BCT structures. This coincides approximately with the onset of irreversibility in the dielectric constant measurement. At 54 G, where Figs. (c) and (d) were taken, only the FCC structure was seen. The structural transformation occurred via a cooperative movement of the spheres without any long-range diffusion of the spheres. As such, it can be regarded as a Martensitic transition driven by competing external fields.

In our calculations, we assume that the spheres form columns. We consider the free energy density of the EMR fluid, \( F = F_E + F_H \), where \( F_E \) and \( F_H \) are the electrostatic and magnetostatic part of the free energy respectively. The electrostatic free energy density is given by \( F_E = -\varepsilon_{zz} E^2/8\pi \). Here, \( z \) is the direction of the electric field \( E \), and \( \varepsilon_{zz} \) is the \( zz \) component of the effective dielectric tensor for the anisotropic composite system. The effective dielectric constant \( \varepsilon_{zz} \) of the mesocrystal inside the columns is calculated through the Bergman-Milton representation [7,11–14]. The overall \( \varepsilon_{zz} \) can then
be found from $\tilde{e}_{zz} = f_c e_{zz} + (1-f_c)e_2$. The magnetic free energy density is given by

$$F_H = F_m - M \cdot H + 2\pi \eta_{ab} M_s M_p.$$  \hspace{1cm} (1)

The first term

$$F_m = -\frac{1}{2\Omega_i} \sum_i \mathbf{m}_i \cdot \sum_j \frac{1}{\sqrt{\Omega_j}} [3\mathbf{\hat{n}} \cdot \mathbf{m}_j - \mathbf{m}_j]$$  \hspace{1cm} (2)

is the dipole–dipole interaction due to the permanent moments of the EMR spheres. The second term is the interaction between the applied magnetic field $H$ and the magnetization of the entire system $M$. The third term takes care of the depolarization effects, where $\eta_{ab}$ are the demagnetization factors. A spin dynamics simulation is used to determine the orientation of $\mathbf{m}_i$ (magnitude fixed at $1.0 \times 10^{-6}$ emu) and hence $F_m$ and $M$. We describe our system by a body-centered-orthorhombic unit cell. We align the $c$-axis with the $E$ field and the $a$ axis with the $H$ field. We found that up to $H = 60$ G, the minimum energy state is associated with $c = 2R$. In addition, the spheres must be in physical contact with each other. At $H = 0$, the ground state is the BCT structure, with $a/c = \sqrt{b/2}$ (and $b = a$), as seen experimentally. The closed-packed (1 1 0) plane is invariant under the BCT $\rightarrow$ FCC transformation. Together with the constraint of $c = 2R$, the transformation path can be described by the equation $b^2 = 12R^2 - a^2$. The hard sphere condition ($a \geq 2R$, $b \geq 2R$) requires $1 \leq a/c \leq \sqrt{2}$, with the limits corre-

sponding to FCC structures oriented differently with respect to the magnetic field. We performed energy calculations along this path, and the results are shown in Fig. 4 for different values of magnetic field strengths with a fixed applied electric field of 2 kV/mm. From Fig. 4, we see that for $H$ below $\sim 30$ G, BCT remains the optimal structure. For magnetic fields above 30 G, the minimum free energy state rapidly moves to the FCC structure. This coincides with the observation of non-BCT structures at these magnetic fields. We note that a increases under the action of the $H$ fields implies a decrease of $\tilde{e}_{yy}$. This is observed in Fig. 2.

In short, we observed external field-induced Martensitic transition in mesocrystallites of multiply-coated spheres. The agreement among theory, experiment and characterization is excellent.

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