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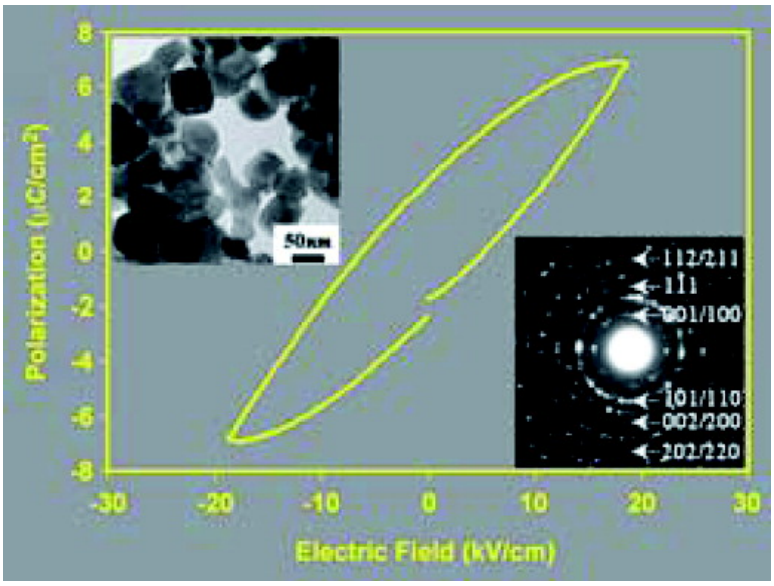

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Rapid Bioenabled Formation of Ferroelectric $BaTiO_3$ at Room Temperature from an Aqueous Salt Solution at Near Neutral pH

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Nature provides spectacular examples of organisms that form intricate inorganic (bioclastic) assemblies under ambient conditions with precise control of structure at multiple length scales and over three dimensions.[1] While mechanistic analyses of these biological processes may lead to new insights in the ambient syntheses of hierarchical 3D structures, the known range of biomineral chemistries is rather limited, with the majority of bioclastic structures composed of $CaCO_3$ or SiO_2.[2] Several authors have used combinatorial cell surface display or phage display ("biopanning") methods to identify peptides that bind strongly to,[3] and in some cases induce the precipitation of,[4] synthetic inorganic materials.

Here we demonstrate that peptides identified by phage display biopanning are capable of inducing the rapid, room-temperature formation of tetragonal barium metatitanate, $BaTiO_3$, from an aqueous precursor solution at near neutral pH. $BaTiO_3$-based ceramics can exhibit attractive dielectric, ferroelectric, pyroelectric, optical, and electrochemical properties for capacitors, displays, thermistors, sensors, and other devices.[5] A variety of chemical approaches (mixed salt, sol−gel, vapor-diffusion sol−gel, microemulsion, co-precipitation, polymeric precursor, etc.) have been used to synthesize $BaTiO_3$ powder.[5,6] However, the formation of ferroelectric (tetragonal) $BaTiO_3$ by such processes has required heat treatment at ≥500 °C for ≥1 h. Tetragonal $BaTiO_3$ has been produced via hydrothermal synthesis at 240 °C, but only after prolonged annealing (≥9 h) under highly alkaline conditions.[7]

Nuraje et al.[8] have recently demonstrated that a synthetic peptide-like bolaamphiphile, bis(*N*-α-amidoglycylglycine)-1,7-heptane dicarboxylate, can induce the room-temperature precipitation of ferroelectric $BaTiO_3$. While an important result, such precipitation occurred after exposure for 1−4 days to an alcohol-based alkoxide solution. The rapid room-temperature synthesis of ferroelectric $BaTiO_3$ from a stable aqueous precursor solution at near neutral pH has yet to be accomplished.

A M13 phage-displayed 12-mer peptide library (Ph.D.-12 Kit, New England Biolabs, Beverly, MA) was used to search for peptide-bearing phage that bind to tetragonal $BaTiO_3$. After five rounds of selection, two unique phage clones were isolated. The 12-mer peptides carried by these phage are labeled as BT1 and BT2 in Table 1. In order to determine whether the peptides BT1 and BT2 could induce the room-temperature precipitation of $BaTiO_3$, 20 μL of a 20 mg mL^{-1} aqueous solution of the BT1 or BT2 peptide was added to 200 μL of an aqueous precursor solution composed of 1.25 mM barium acetate ($Ba(OOCCH_3)_2$) and 1.25 mM potassium bis(oxalato) oxotitanate(IV) ($K_2[TiO(C_2O_4)_2]\cdot 2H_2O$) at pH 6.8. After incubation for 2 h, the resulting precipitates were washed in water and then methanol and then dried for 0.5 h under vacuum.

Table 1. $BaTiO_3$-Forming Peptides

peptide	amino acid sequence	pI[a]
BT1	HQPANDPSWYTG	5.1
BT2	NTISGLRYAPHM	8.8

[a] Isoelectric point calculated using pI/mass program at http://ca.expasy.org.

Secondary electron (SE) and transmission electron (TE) images indicated that the precipitates generated in the presence of the BT1 and BT2 peptides contained fine (50−100 nm) faceted particles present within 0.3−0.5 μm aggregates (Figures 1 and S1). (Note: some amorphous precipitate material was also detected.) Selected area electron diffraction (SAED) analyses (Figures 1c and S1c) and X-ray diffraction (XRD) analyses (Figures 2 and S2) of these faceted particles yielded patterns consistent with crystalline $BaTiO_3$. The XRD pattern of the BT2-induced precipitate exhibited distinct splitting of the (002) and (200) peaks (see the inset in Figure 2), which was consistent with tetragonal $BaTiO_3$. Rietveld analyses of the XRD patterns from the BT1- and BT2-induced precipitates yielded good fits to tetragonal crystal structures with lattice parameters of $a = 4.0086$ Å and $c = 4.0246$ Å (for BT1 $BaTiO_3$) and $a = 4.0064$ Å and $c = 4.0328$ Å (for BT2 $BaTiO_3$).

While the BT1 and BT2 peptides possessed various types of amino acids (nonpolar, aromatic, hydroxyl-bearing, noncharged polar, charged), 8 of the 12 amino acids were common to both peptides. A variety of control peptides (CON1−CON6 in Table S1) that shared some similarities with the BT1 and BT2 peptides, but were not isolated via specific binding to $BaTiO_3$, were selected for additional precipitation experiments. The pI values of the CON1, CON2, and CON3 peptides spanned the pI range of the BT1 and BT2 peptides. The CON3, CON4, and CON5 peptides possessed 2, 5, and 4 hydroxyl-bearing residues, respectively (note: the BT1 and BT2 peptides both possessed serine, tyrosine, and threonine residues). Replacement of the arginine and histidine residues of the BT2 peptide with glycine residues yielded the CON6 peptide. (Note: Dissolution of the CON6 peptide required the use of a 1:3 solution of *N*,*N*-dimethylformamide in water. Precipitation trials for the CON6 peptide were otherwise conducted under the same conditions as for the BT1, BT2, and other control peptides.) SAED analyses of small amounts of precipitates formed upon exposure to some of these control peptides (Figure S3) did not reveal the presence of crystalline $BaTiO_3$ within such precipitates. These observations suggest that the combination of conserved amino acids (hydroxyl-bearing, amide-bearing, charged, hydrophobic) in the BT1

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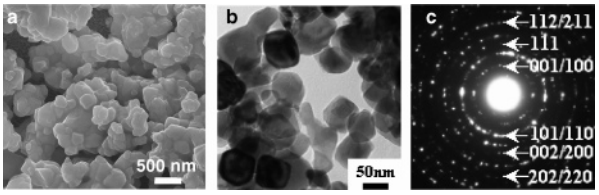

Figure 1. $BaTiO_3$ precipitates formed at room temperature upon exposure of the BT2 peptide to an equimolar (Ba:Ti = 1:1) aqueous precursor solution for 2 h. (a) SE and (b) TE images of the precipitates. (c) SAED pattern, consistent with crystalline $BaTiO_3$, obtained from the faceted particles.

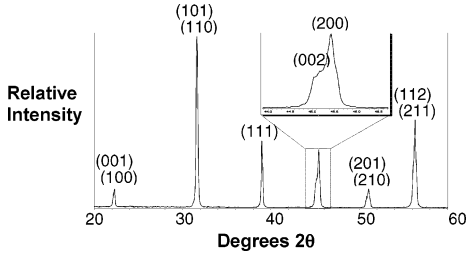

Figure 2. XRD pattern, consistent with crystalline $BaTiO_3$, obtained from precipitates formed at room temperature upon 2 h exposure of the BT2 peptide to an aqueous precursor solution. The inset reveals peak splitting consistent with the (002) and (200) reflections of tetragonal $BaTiO_3$.

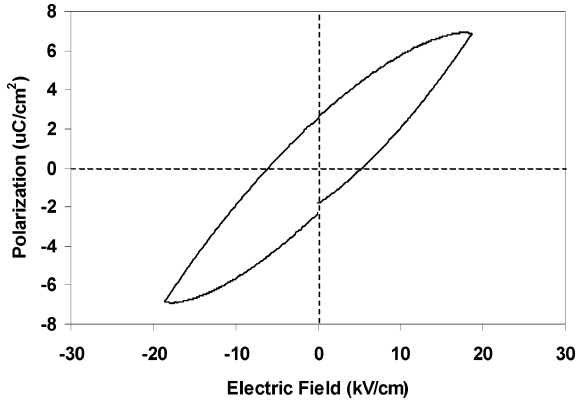

Figure 3. Polarization versus applied electric field at 1 kHz for the BT2 peptide-induced $BaTiO_3$.

and BT2 peptides was important for the formation of crystalline (tetragonal) $BaTiO_3$.

Because the $BaTiO_3$ that formed in the presence of the BT2 peptide exhibited more distinct tetragonal character than the BT1-induced $BaTiO_3$ (compare Figures 2 and S2), additional BT2-induced $BaTiO_3$ was generated for ferroelectric testing. BT2 $BaTiO_3$ particles were dispersed by vortexing in water and then dropcasting with a pipet onto a platinized, high resistivity (>10 kΩ·cm) silicon wafer, so as to obtain a layer with an average thickness of about 16 μm. Gold was then sputter deposited as a top electrode on the $BaTiO_3$ layer. The electric field-induced polarization of the BT2 $BaTiO_3$ was evaluated with a Radiant Technologies' Precision LC tester. As shown in Figure 3, the $BaTiO_3$ particle layer exhibited polarization hysteresis, which is a well-known characteristic of ferroelectric materials. The slope of the $P-E$ curve at low field yielded a relative permittivity value of ~2200, which is comparable to values reported for $BaTiO_3$ of 100−300 nm crystal size.[9]

The present work demonstrates, for the first time, that a phage display isolated peptide can induce the room-temperature formation of ferroelectric (tetragonal) $BaTiO_3$ within 2 h from an aqueous precursor solution at near neutral pH. The ability of peptides to promote the rapid formation of functional crystalline multicomponent ceramics under ambient conditions provides new opportunities for the integration of such functional materials with low-temperature or reactive materials and substrates (e.g., with polymers, bioorganics, or silicon).

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Supporting Information Available: Experimental procedures and control peptide sequences, along with XRD, SAED patterns and SE, TE images of the BT1, CON2, CON3, and CON6 precipitates. This material is available free of charge via the Internet at http://pubs.acs.org.

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