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Giant anelastic responses in ($BaZrO_3$-ZnO)-$BaTiO_3$ composite materials

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Abstract – Composite materials containing particulate $BaTiO_3$ inclusion have been fabricated with $BaZrO_3$-ZnO as the matrix. Giant anelastic responses (abrupt increase in modulus and damping *vs.* temperature) have been observed after 75 °C aging 24 h in these composites in the temperature region far below the Curie point of $BaTiO_3$. Anomalies disappeared after 185 °C aging 4 h. Such responses are attributed to the constraining negative-stiffness effect of the inclusion. An oxygen vacancy mechanism has been discussed which is considered to be responsible for the negative-stiffness effect. The present work is novel in terms of the idea of manipulation of negative stiffness in ferroelastic inclusions to achieve the desired composite properties.

Classical composite theory predicts that composite properties, such as stiffness, damping, thermal expansion, etc., cannot surpass those of the constituents. Such theory tacitly assumes that stiffness is always positive. However, such bounds can be exceeded if the composite has a negative-stiffness phase [1]. Negative stiffness entails a reaction force in the same direction as imposed deformation, and has been used in the design of composites with extremely high physical properties [2,3]. To achieve superior composite responses requires good interfacial conditions, including perfect wetting and sufficient strength. It is easy to achieve these in metal matrix composites prepared via casting techniques with well-selected metal matrix, yet much more difficult in the case of ceramic matrix composites which are usually synthesized via the solid-state reaction method. Porous interface and its brittleness nature are inevitable drawbacks for ceramic matrix composites unfavorable for attaining sufficient negative stiffness for the inclusion in order to achieve the desired composite properties. In view of the typical synthesis temperature (usually > 1000 °C) and time being used for ceramics, inter-diffusion is another unavoidable disadvantage (this will be discussed later). Up to now, no experimental report is available on ceramic matrix composites with negative-stiffness phase which attained the desired composite properties. The present work has filled this gap by studying the anelastic properties of ceramic matrix ($BaZrO_3$-ZnO) composites containing inclusions of $BaTiO_3$. In particular, aging-process–activated giant anelastic responses were observed far below 130 °C. Such an effect is neither due to matrix behavior, as $BaZrO_3$-ZnO has no transformation in the temperature range considered (20 °C to 180 °C), nor can be explained via known transformations of the $BaTiO_3$ inclusion as the classical Landau theory predicts a negative bulk stiffness in constrained $BaTiO_3$ only near its three ferroelastic transformation temperatures (cubic-to-tetragonal: 130 °C; tetragonal-to-orthorhombic: 5 °C; and orthorhombic-to-rhombohedral: -75 °C). A similar phenomenon (extreme responses near 60 °C but only small sigmoid anomalies near 130 °C) was also observed in metal matrix composites (Sn-$BaTiO_3$) [3]. In view of its aging process dependence, we explained such phenomena in the context of negative-stiffness effect [4] in $BaTiO_3$ caused by an oxygen vacancy (OV) mechanism [5,6]. To the best of our knowledge, this is the first experimental report of a manipulation (activation and deactivation) of negative stiffness in ferroelastic inclusion via specific aging processes to attain giant anelastic composite responses. Theory [7] also predicts that giant piezoelectric properties

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can be entailed if the inclusion has a negative stiffness. Ceramic matrix but not metal matrix composites can serve as piezoelectric materials, the present work could also shed a light on fabricating novel piezoelectric materials via the philosophy of composites with negative-stiffness phase.

Polycrystalline $BaTiO_3$ (Alfa Aesar, 99.9%, 3–12 mm pieces as received) was fragmented and sieved to achieve a particle size range of 150 and 210 μm. Particles were baked dry at 350 °C for 2 h. Optical microscopy observation revealed a grain size in such materials of about 25 μm, and a domain size as small as 1 μm. The ceramic matrix composite was synthesized by the conventional solid-state reaction method. $BaZrO_3$ (Alfa Aesar, 99% metal basis) and ZnO (Alfa Aesar, 99.99% metal basis) powders were mixed in 1 : 1.25 molar ratio and ball milled in a silicon nitride vial for 3 h with a high-energy milling machine (SPEX SamplePrep 8000-series Mill/Mixer). ZnO was used for the purposes of densification and lowering sintering temperature [8]. Powders were then transferred into a polyethylene vial, together with the $BaTiO_3$ particles (15% by volume), and mixed for 5 min with the same milling machine. The mixture was compressed into a pellet without binder under a uniaxial pressure of 110 MPa. Sintering was performed in air at atmospheric pressure. A ramp-up rate of 4.5 °C min was used to achieve a final sintering temperature of 1325 °C, after which the temperature was held for 1 min. Extended soaking time was not applied (sintering may begin when $T > 1000\,°C$ in the presence of a high concentration of ZnO [8]) in order to minimize the diffusion doping effect for the inclusion. The ramp-down rate was 4.5 °C/min. Samples were kept inside an alumina crucible with an alumina lid on top so as to avoid possible contamination from any residue left inside the furnace. To avoid reaction between sample and the crucible, samples were buried inside pure $BaZrO_3$ powders. The final density of the matrix is about 72% of the theoretical value[1]. Two composite specimens of size $2 \times 2 \times 20\,mm^3$ were sectioned with a diamond saw. Anelastic properties (damping and Young's modulus) were studied in bending via broadband viscoelastic spectroscopy [9] at subresonant frequencies (the bending resonant frequency is about 1200 Hz). Deformation of the specimens was induced by an electromagnetic torque exerted on a permanent magnet attached at the end of the specimen and measured by a laser light method. Data were captured by a lock-in amplifier. Aging was performed at i) 75 °C for 24 h and ii) 185 °C for 4 h prior to testing. The maximum surface strain applied was about 8×10^{-6}. A thermal rate of 0.05 °C/s was used. Temperature was monitored by a thermocouple (OMEGA L-0044 K type) directly in contact with the specimen surface.

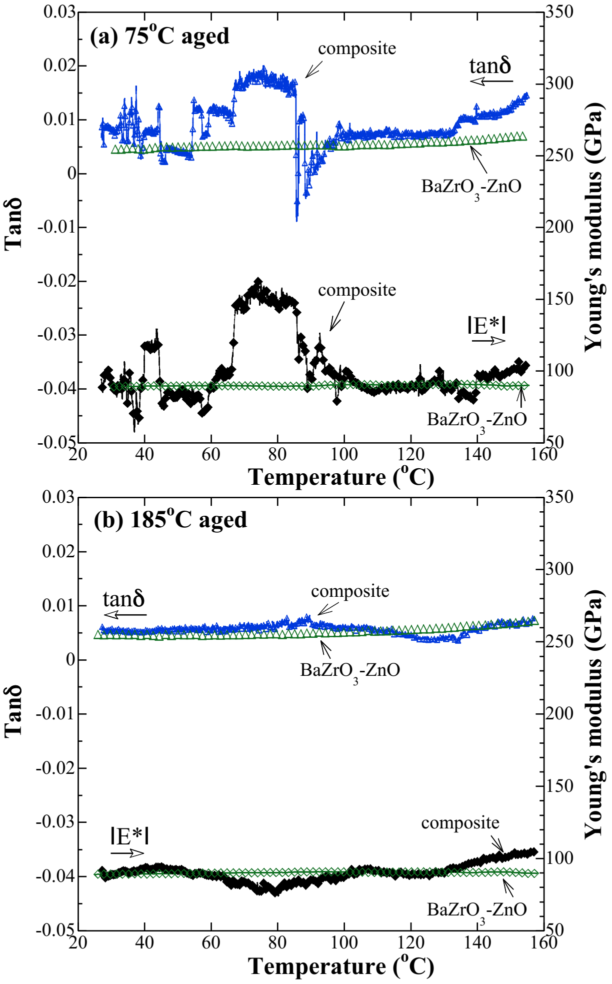

Fig. 1: (Colour on-line) Anelastic responses (Young's modulus $|E^*|$ and damping tan δ) of specimen I after (a) 75 °C aging and (b) 185 °C aging. Responses of $BaZrO_3$-ZnO (molar ratio 1 : 1.25) after 75 °C (a) and 185 °C (b) aging have been given for comparison. 100 Hz excitation frequency was used. A thermal rate of 0.05 °C/s was applied (heating).

Figure 1 presents the behaviors of specimen I. Giant anelastic anomalies occurred below T_c after 75 °C aging 24 h (fig. 1a). In particular, Young's modulus has increased by a factor of two over a wide range of temperature (∼ 20 °C). The baseline damping tan δ for the matrix $BaZrO_3$-ZnO ranged from 0.0048 at 40 °C to 0.005 at 100 °C. The composite aged at 75 °C exhibited excursions in tan δ from -0.008 to $+0.018$ in the region between 60 °C and 90 °C. Positive values of tan δ indicate energy dissipation and negative values indicate energy release. Anomalies largely disappeared after 185 °C aging 4 h (fig. 1b). Anelastic responses of specimen II are shown in fig. 2 (note the difference in scale with respect to fig. 1). The anomalies do not shift in temperature with frequency, suggesting a non-relaxation process (such phenomenon also applies to specimen I). Apart from the anomaly

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[1] Densification of a $BaZrO_3$-based ceramic is difficult (ref. [8]), it requires a much longer sintering time, which is not favorable in the present study for the purpose of minimizing the interdiffusion effect. Density can be improved via the hot isostatic pressing sintering method. However, according to composite theory, pores will only lower the modulus magnitude rather than having any effect on the temperature- or frequency-dependent properties.

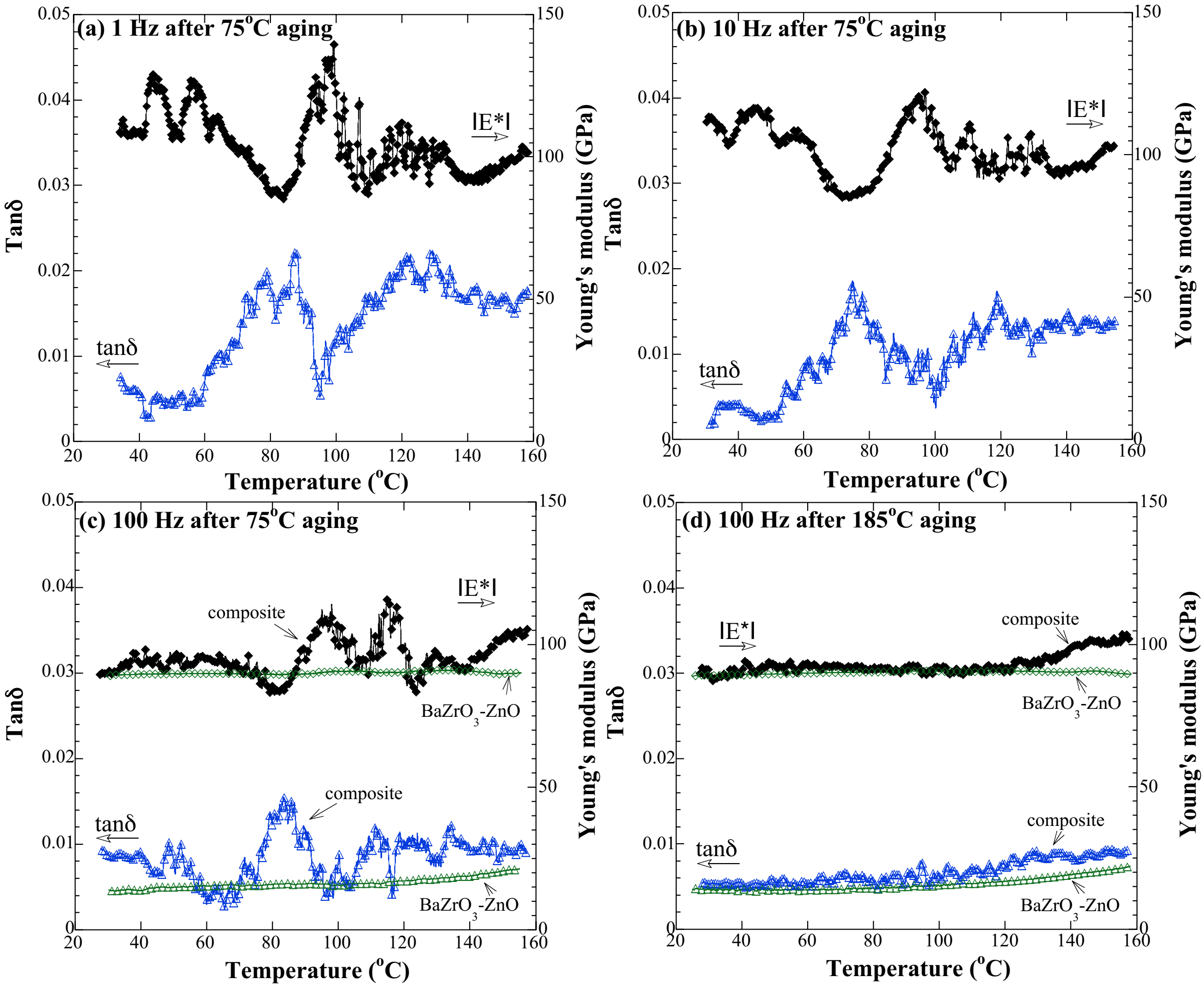

Fig. 2: (Colour on-line) Anelastic responses (Young's modulus $|E^*|$ and damping $\tan\delta$) of specimen II at (a) 1 Hz, (b) 10 Hz, and (c) 100 Hz after 75 °C aging and at (d) 100 Hz after 185 °C aging. Responses of BaZrO$_3$-ZnO (molar ratio 1 : 1.25) after 75 °C (c) and 185 °C (d) aging have been given for comparison. A thermal rate of 0.05 °C/s was applied (heating).

below T_c, small undulations were also observed near T_c after 75 °C aging. Such undulations were not observed after 185 °C aging. Anelastic properties of BaZrO$_3$-ZnO (molar ratio 1 : 1.25) after 75 °C aging are shown in fig. 1a for comparison. Variations in responses in the different samples are considered to be attributed to the differences in domain textures and defect concentration in the inclusions or the interfacial morphology, or the extent of oxidation or strain level near the interface during preparation.

The anelastic anomalies observed below T_c after 75 °C aging are attributed to the negative stiffness of the inclusions. Negative stiffness can occur in systems with stored elastic energy [1]. Such systems include, via Landau theory, materials that undergo phase transformations under full constraints. Such effects have been predicted to appear naturally on a fine scale [10] down to the nanoscale. In our earlier work [5], we found that in well-aged tetragonal BaTiO$_3$, negative stiffness can be entailed via the electromagnetic interaction of defects with spontaneous polarization. In view of its aging-dependent effect, the anomaly observed in the present (BaZrO$_3$-ZnO)-BaTiO$_3$ composite below T_c is considered to be associated with this defect mechanism. The broadening effect is due to negative-stiffness heterogeneity [11].

This mechanism is understood in the context of the symmetry-conforming property of point defects (SCP-PD) [6]. Spontaneous polarization $\mathbf{P}_s$ exists in BaTiO$_3$ below T_c but not above it. Impurities, such as Al^{3+}, $Fe^{3+,2+}$, etc., in BaTiO$_3$ will preferably locate at the Ti^{4+} site, and can form defect dipoles polarization $\mathbf{P}_d$ with OV. OV can occupy either of A (B) sites or C sites of the oxygen octahedron with identical conditional probabilities above T_c as these sites have identical distances to the center of the oxygen octahedron (fig. 3). Below T_c, OV tends to migrate to and accumulate at C sites, which are closer to the center of the octahedron, from A (B) sites during aging, and forms defect dipole polarization $\mathbf{P}_d$ with impurities, which will generate a restoring stress on $\mathbf{P}_s$ forcing $\mathbf{P}_s$ and $\mathbf{P}_d$ to align along the same direction in order to minimize the local free energy provided an

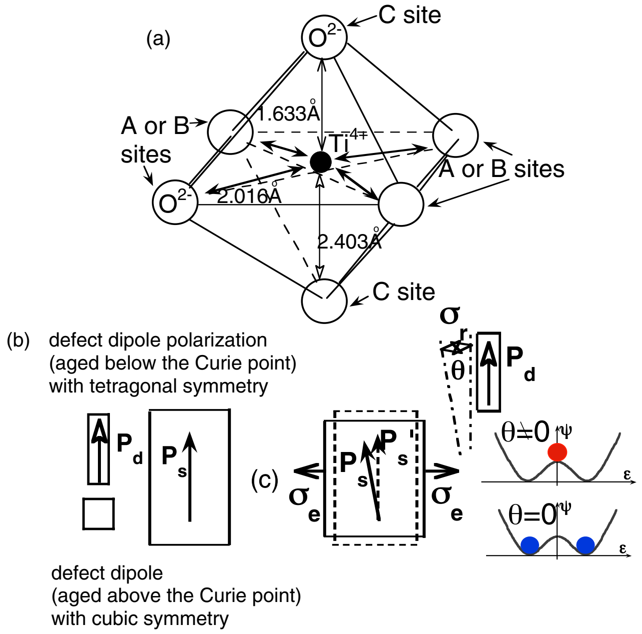

Fig. 3: (Colour on-line) (a) Oxygen octahedron in the tetragonal $BaTiO_3$ unit cell [4]. O^{2-} has two kinds of non-equivalent sites *A* or *B* and *C*. In the cubic phase, the distances from *A* (*B*) and *C* sites to Ti^{4+} are the same; in the tetragonal phase, *C* sites are closer to Ti^{4+} than *A* (*B*) sites. (b) presents spontaneous polarization, defect dipole polarization. (c) shows the deviation (θ) between $\mathbf{P}_s$ and $\mathbf{P}_d$ under external stress. Free energy profiles within unit cell volumes are shown aside. The ball at the top (red) of the potential hill indicates a metastable condition when $\theta \neq 0$; perturbation induces ball (blue) sliding-down to the bottom of the potential wells, causing a negative-stiffness effect during this process.

angular displacement is available between $\mathbf{P}_s$ and $\mathbf{P}_d$. By contrast, sufficient aging above T_c eliminates $\mathbf{P}_d$, interaction between $\mathbf{P}_d$ and $\mathbf{P}_s$ will not be available. $\mathbf{P}_s$ can change direction and magnitude under external stress instantaneously but this is not so for $\mathbf{P}_d$, the changing of which is a diffusion process [6]. Deviation between $\mathbf{P}_s$ and $\mathbf{P}_d$ will thus occur, causing stored elastic energy and a metastable condition for the system. Any perturbation (the external stress or the nonlinear interaction between dipoles) would cause the system to transform into a stable condition [12], and a snap-through effect will be entailed during this process, causing the negative-stiffness phenomenon.

Interdiffusion inevitably occurs near the interface during sintering, the $BaTiO_3$ inclusion is thus in a "core-shell" structure (composition changes from pure $BaTiO_3$ at the core to gradually doped $BaTiO_3$ at the outer shells); transition temperatures of the $BaTiO_3$ unit cells near the interface region will be shifted due to the doping effect. Therefore, in addition to the possible negative-stiffness effect entailed in tetragonal $BaTiO_3$ (*i.e.* the bulk center region of the $BaTiO_3$ inclusion) discussed in last paragraph, it is likely that the anomaly observed below 130 °C is related to the structural transformations of the doped $BaTiO_3$ unit cells at the interfacial region, yet, still activated by an aging process; therefore, we believe the possible negative-stiffness effect in the doped unit cells near the interfacial region is still related to the interaction between $\mathbf{P}_s$ and $\mathbf{P}_d$ under perturbation, but the perturbation comes from the lattice reconstruction at this time.

Negative stiffness is predicted near phase transformations under sufficient constraint including that near T_c (∼ 130 °C) of $BaTiO_3$ by the Landau theory. However, giant responses were not observed near 130 °C in the composite specimens tested in the present study; instead, small undulations occurred (figs. 1a, 2a, 2b, 2c) after 75 °C aging. Such undulations were largely eliminated after 185 °C aging (figs. 1b, 2d). In view of the aging process dependence, such small undulations near 130 °C are considered to be entailed by the same mechanism as mentioned above (interaction between $\mathbf{P}_s$ and $\mathbf{P}_d$ under lattice reconstruction). However, the elastic energy due to spontaneous strain ($\sim 2 \times 10^{-4}$) of pure $BaTiO_3$ near T_c would be much greater than the interaction energy between $\mathbf{P}_d$ and $\mathbf{P}_s$ on fine scale [12]; negative-stiffness effect would thus be weakened [4]. As for why the negative stiffness predicted by the Landau theory near T_c of pure $BaTiO_3$ (in the case of without OV effect, *i.e.* after 185 °C aging) does not give rise to the expected anomaly, an adequate negative stiffness to generate the composite behavior depends on the quality of the interface and matrix. The strength of the porous matrix may be insufficient to fully constrain the spontaneous strain of $BaTiO_3$; or the spontaneous strain of $BaTiO_3$ or the amplified applied strain near the inclusion (near T_c) overloaded the strength of the interface. The process associated with the OV configuration in tetragonal $BaTiO_3$ (core of the $BaTiO_3$ inclusion below 130 °C) involves no detectable spontaneous strain and latent heat [5], while the doped $BaTiO_3$ (unit cells near the interface) has smaller spontaneous strain than pure material during phase transformations (this follows composite theory and has been observed in our recent work [13] on $BaZrO_3$-doped $BaTiO_3$ systems); therefore, such processes are less likely to degrade the interface property. However, the dopant smoothed [14] the negative curvature of the Landau free energy curve near phase transformations (under constraint), and a reduced negative stiffness may explain why no extreme anomaly was observed below 130 °C after 185 °C aging due to the phase transformations of doped $BaTiO_3$ unit cells near the interface. Indeed, we found that doped $BaTiO_3$ has much less softening effect but prominent stiffening effect in comparison with pure $BaTiO_3$ [13].

Achievement of giant anelastic composite responses via the manipulation of negative-stiffness behavior of $BaTiO_3$ inclusions is encouraging in the context of fabricating smart materials. Inclusion is not restricted to $BaTiO_3$. For example, VO_2 [15] exhibited similar aging-process–activated phase transformation behaviors (softening in modulus and peak in damping) below T_c associated with OV configurations. Actually, such a defect-mechanism–induced negative-stiffness effect is expected to appear in most ferroelastic materials. In addition, composite properties are not restricted to stiffness and damping; piezoelectricity, thermal expansion, and other coupled field properties can also surpass classical bounds with a negative-stiffness phase. Such properties in composites with ferroelastic inclusions can also be manipulated via specific aging processes.

In conclusion, anelastic anomalies, including stiffness increased by a factor of two and large positive and negative damping, due to the constraining negative-stiffness effect of the inclusions were observed in ($BaZrO_3$-ZnO)-$BaTiO_3$ composites below 130 °C after 75 °C aging 24 h. Anomalies disappeared after 185 °C aging 4 h. In view of the aging process dependence, we believe this phenomenon is associated with an oxygen vacancy mechanism.

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[12] Interaction energy (W) between dipoles can be estimated via the equation $W = (\mu_{\mathrm{defect}} \cdot \mu_{\mathrm{spontaneous}})/4\pi\varepsilon_0 r^3$ (Böttcher C. J. E., *Theory of Electric Polarization* (Elsevier, Amsterdam) 1952). Assume the dipole moment to be $\sim 6.5\times10^{-30}$ C m (a $\mathbf{P}_s = 12\times10^{-6}$ C/cm^2 was used which is an average value of published results 26×10^{-6} C/cm^2: Merz W. J., *Phys. Rev.*, **91** (1953) 513, and 7.5×10^{-6} C/cm^2: Jaffe H., *J. Am. Ceram. Soc.*, **41** (1958) 494), r to be the distance of two or three lattice parameter length (shortest interaction distance between $\mathbf{P}_s$ and $\mathbf{P}_d$), W to be on the order of 10^{-22} J, consistent with the elastic energy induced by the applied stress (given $|E^*| \sim 100$ GPa for $BaTiO_3$, excitation strain of 8×10^{-6}) on this scale. Spontaneous strain $\sim 2\times10^{-4}$ would induce an elastic energy on the order of 10^{-21} J on this scale, overwhelming the interaction energy W, hence weakening the competition between W and U, which, in turn, reduces the negative-stiffness effect.
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