Electrorheological behavior of rare earth-doped barium titanate suspensions*

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Abstract   Doping Y, La, Ce into barium titanate is found to be able to improve its electrorheological (ER) effect in DC electrical field. The yield stress of a typical doped barium titanate/silicone oil suspension is approximately 3.2 kPa at 3.5 kV/mm, which is 10 times larger than that of pure barium titanate/silicone oil suspensions. The ER effect increases with the decrease of ionic radius of rare earth (RE) dopant when RE concentration remains constant, and the suspensions exhibit a relatively high shear stress when Y, La, Ce mole fractions are 15%, 10%~15%, and 5%, respectively. Dielectric measurements show that the suitable doping with RE element increases dielectric loss of barium titanate and causes very marked dielectric relaxation at low frequency. By measuring X-ray diffraction patterns of doped barium titanate, it is considered that the occurrence of lattice distortion or defects may be responsible for the change of dielectric properties which results in the improvement of ER effect of barium titanate in DC electrical field.

Keywords: electrorheological materials, barium titanate, rare earth, dielectric properties.

Electrorheological (ER) materials are attractive to engineers because their rheological behavior can be rapidly and continuously controlled by an external electrical signal. ER materials have potential uses in vibration damping, pressing, optical and force transfer devices[1,2]. However, the industrial production of ER materials is limited by their poor properties, such as low yield stress, temperature instability and sedimentation[3,4]. The use of barium titanate or other ferroelectric materials as ER active substrates has been known for some time[3]. In terms of dielectric polarization mechanism and permitivity mismatch between dispersal particles and continuous medium, the ER effects of barium titanate are presumed to be large because of the high dielectric constant of the ferroelectric state. However, some investigations show that pure barium titanate is fairly weak in ER effect, even suffering from electrophoretic effects in high DC field when it is dry[5,6]. Some studies have been carried out to understand the intrinsically polarizable properties of weak ER effect of barium titanate. Low dielectric loss or conductivity, arising from intrinsic fast polarization process of barium titanate in DC or low frequency AC field, has been regarded as responsible for its poor ER effect in DC or low frequency AC field[7~9]. Ostub[10] reported that barium titanate was water activated which was related to the increase of conduction of barium titanate. Unfortunately, up to now no high-performance barium titanate-based ER materials have ever been produced. Thus it is of great interest to design and prepare barium titanate ER materials so as to make clear the ER mechanisms and explore new ways to prepare high-performance ferroelectric substrate based ER materials[3,5,7].

It has been accepted that the dielectric and polarization properties of particles are responsible for ER effect[11~14]. As is well known, the dielectric and polarization properties are closely related to the molecular or crystal structure of the materials. So it is possible to modify the dielectric and polarization properties to increase ER effect by designing the molecular or crystal structures of the ER materials. Block[15] reported that doping with acid or alkali to control the conductivity could modify the ER activation of semiconductor polymer. Bloodworth[16] reported that adding lithium ion to polyurethane could enhance the ER activity. The doping of inorganic materials has not received sufficient attention in the field of ER materials, although its optical and electric property have been widely investigated. Zhang et al.[17] have ever reported the ER behavior of complex strontium ti-

tanate suspensions, but they did not deal with the effect of doping on the ER behavior of strontium titanate because the rheological properties might be strongly influenced by the porous and surfactant in ER materials. In previous studies[18,19], we presented a new class of ER materials consisting of water-free RE-doped titanium dioxide particles, which exhibited a higher ER activity than that of pure titanium dioxide without additives. In this paper, we will describe a new class of RE-doped barium titanate based ER materials and focus on the effect of RE doping on ER behavior of barium titanate. Based upon the results of preliminary measurement of rheological and dielectric properties, we try to propose a novel way to prepare high-performance ferroelectric-based ER materials.

1 Experiments

1.1 Materials preparation

Particles of pure and rare earth (RE)-doped barium titanate were prepared by a modified sol-gel method. Tetrabutyl titanate, barium acetate, RE acetate (La, Ce, Y, etc.) and deionized water were solved in anhydrous mixed solvent composed of alcohol and acetic acid (Here, mixed solvent is used to increase the solubility of inorganic salts, the volume ratio of acetic acid/ alcohol is in the range of 15/13 ~ 15/12). The H_2O/Ti mole ratio was 1.0 ~ 1.5 and Ti concentration was 0.5 ~ 0.8 mol/L. The mole fraction of Y dopant y_Y was 1%, 5%, 10%, 15%, 20% respectively, La dopant y_{La}, 3%, 7%, 10%, 15%, 20% respectively and Ce dopant y_{Ce}, 1%, 5%, 7%, 10% respectively. The resulting clear solution was kept at 50 ℃ for 3 ~ 10 h to form transparent gel. The gels were then dried at 85 ℃ and subjected to the following stepwise calcination programs in air in a furnace: 1 h at 200 ℃, 2 h at 400 ℃, 2 h at 600 ℃ and 2 h at 800 ℃. Thus, the crystalline barium titanate or doped barium titanate particles were produced.

1.2 Material characteristics

The thermal characteristics of xerogel were measured with a DSC-TG technique (SH-500, NET2SCH-Gerateban Gabh Thermal Analysis, Germany) at a heating rate of 10 ℃/min in air. The crystallographic structure of particles after calcination was characterized by X-ray diffraction (D/MAX-γ A, Japan) technique using CuK_α radiation.

1.3 Rheological and dielectric measurements

The particle size, typically 0.5 ~ 1.0 μm, was estimated by an optical microscope (ALPHAPHOT-2, Nikon, Japan). The density of series of pure and doped barium titanate particles was in the range of 4.74 ~ 5.02 g/mL. The particles were dried at 150 ℃ for 4 ~ 8 h to remove any trace water, then mixed quickly with dried silicone oil (ε_f = 2.60 ~ 2.80, $\sigma_f = 10^{-12}$ S/m, ρ_f = 0.997 ~ 1.003 g/mL, and η = 500 mPa·s at 25 ℃) with a volume fraction ϕ of 26%. No additives were added in suspensions. Rheological measurements were made using a coaxial cylinder rotational viscometer (NXS-11A, Chengdu, China) modified to suit for high-voltage DC electric fields. The inner bob and outer cup acted as two electrodes with a (2.00 ± 0.01) mm gap in between. The suspensions were rubbed for about 0.5 h for sufficient dispersion, then the rheological measurement was carried out.

Due to the difficulty of directly measuring the dielectric properties of particles, the suspensions were used in the dielectric measurements. Then the dielectric properties of particles could be gained in terms of the conventional mixture model that was usually used in ER system[20]. Here, the capacitance C and dielectric loss tangent (tan δ) of suspensions were measured by an automatic LCR meter (WK-4225, Germany) at frequencies of 10^2, 10^3 and 10^4 Hz, respectively. The dielectric constant was derived from the measured C according to the relation $\varepsilon = Cd/(\varepsilon_0 S)$, where ε_0 is the dielectric constant of vacuum, i.e. 8.85×10^{-12} F·m^{-1}, and d the thickness of the gap between electrodes and S the contact areas of electrodes.

2 Results and discussion

2.1 Thermal character and crystal structure

We examined the changes in charring barium titanate by heating from room temperature to 900 ℃ in air at a rate of 10 ℃/min using a thermal analyzer. The DSC-TG patterns (not given in the present paper) of the typical doped barium titanate xerogel show that the endothermic effect at 78.1 ℃ and the sample weight loss represent the loss of residual water and solvent. The exothermic peaks at 315 ℃ and 410 ℃ are considered to be attributable to the combustion of a residual alkyl group. The exothermic peaks at 550 ℃ and 600 ℃ are considered to be corresponding to the formation of barium carbonate when barium salt is partly carbonized. However, as shown by the exothermic peak at 741.5 ℃ and continuous

weight loss, barium carbonate disappeared with increasing temperature, and in the meantime, crystalline barium titanate phase was formed. This result is consistent with the XRD results.

The XRD patterns show the formation of pure barium titanate and series of doped barium titanate particles. The patterns are in good agreement with the XRD pattern of tetragonal barium titanate of the *Joint Committee on Powder Diffraction Standards* (JCPDS) file number 5-626. Fig. 1 shows the pattern of typical doped barium titanate with different La content. At the same time, we can find that the lattice distortion becomes larger with increasing rare earth content and decreasing ionic radius. Fig. 2

shows the dependence of the lattice parameters on the content of rare earth. The lattice parameter decreases linearly with RE content, and it decreases faster with Y content than with La or Ce content. It indicates that rare earth ions have substituted for Ba^{2+} because the ionic radius of RE is much smaller than that of Ba^{2+} (the radii of Y^{3+}, La^{3+} and Ce^{3+} are 0.892 Å, 1.061 Å, 1.034 Å respectively, and the radius of Ba^{2+} is 1.340 Å). However, some peaks of low intensity characteristic of La_2O_3, CeO_2, Y_2O_3 phase are noticed for $y_{La} = 20\%$, $y_{Ce} = 5\%$ and $y_Y = 20\%$ compounds.
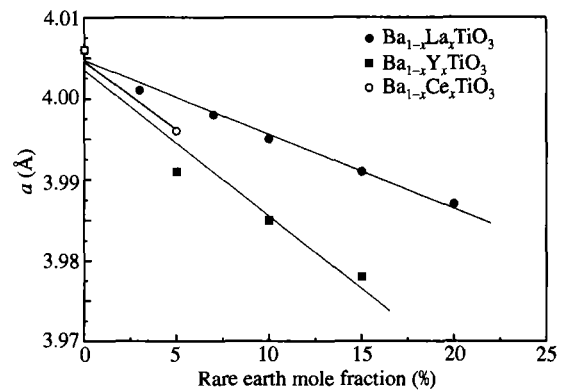
Fig.2.   The dependence of lattice parameter of doped barium titanate on rare earth content.

2.2   The effect of RE substitution on ER properties of barium titanate

The rheological measurements reveal that no remarkable ER effect is seen in the pure barium titanate suspension and its yield stress is only 140 Pa under DC electrical field of 3.5 kV/mm. The suitable doping with RE is found to obviously improve the ER effect of barium titanate. The typical result of the yield stress as a function of electrical field strength is given in Fig. 3. The yield stress of Y-doped barium titanate suspension is about 3.2 kPa at 3.5 kV/mm, which is one order of magnitude larger than that of pure barium titanate. Under the condition of the same preparation process, particles treatment and volume fraction for all suspensions, we observed that the ER effect is remarkably stronger for Y-doped barium titanate than for La or Ce-doped barium titanate when rare earth concentration remains the same constant. For every kind of doped barium titanate, the ER effect initially increases with RE content, then declines beyond some content. A relatively high yield stress can be obtained when y_Y is close to 20%, y_{La} close to 10%~15%, and y_{Ce} close to 5% (Fig. 4).
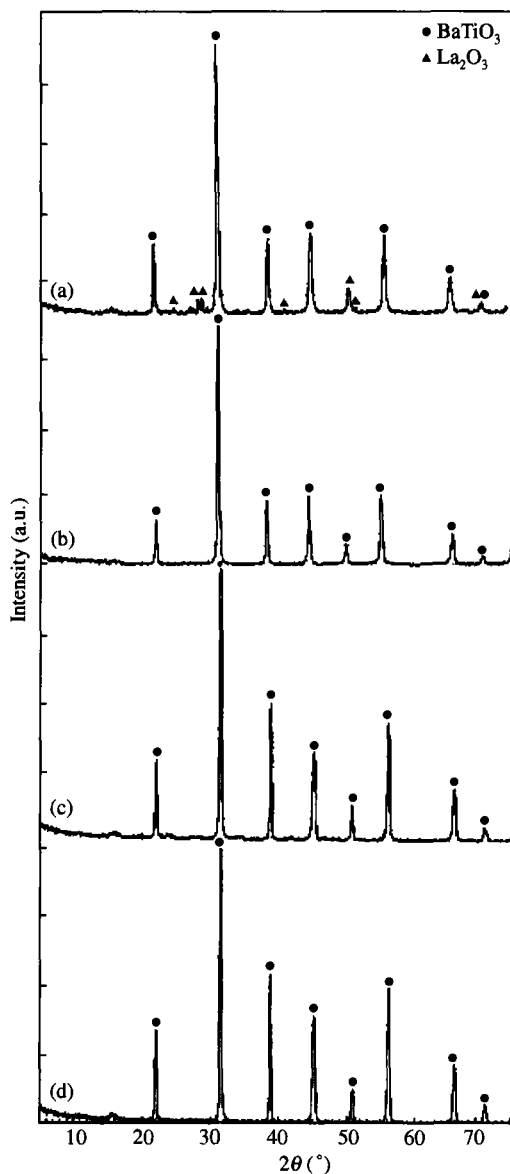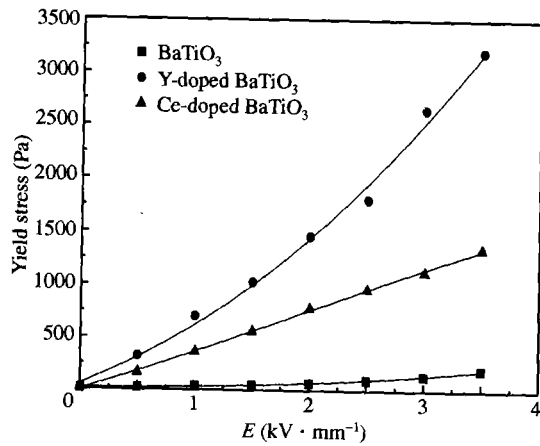

Fig. 1.   The X-ray diffraction patterns of La-doped barium titanate particles. (a) $y_{La} = 20\%$; (b) $y_{La} = 15\%$; (c) $y_{La} = 10\%$; (d) $y_{La} = 0$.

Fig. 3. The yield stress of pure and doped barium titanate suspensions ($\phi = 26\%$) as a function of DC electrical field strength at 20 ℃ ($\dot{\gamma} = 2.110 \, s^{-1}$).

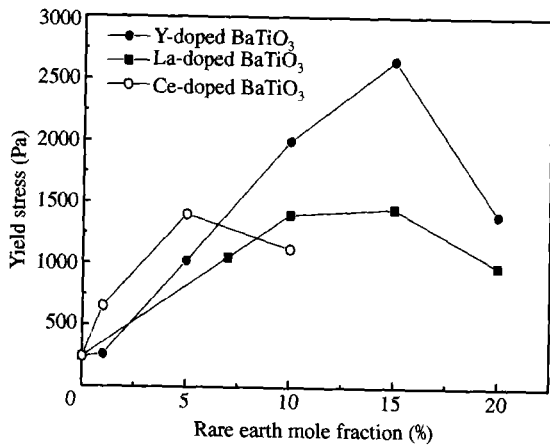Fig. 5. The shear stress of typical Y-doped barium titanate suspensions ($\phi = 26\%$) as a function of shear rate at 20 ℃.

Fig. 4. The dependence of yield stress doped barium titanate suspensions ($\phi = 26\%$) on rare earth content in 3.0 kV/mm DC field and 20 ℃ ($\dot{\gamma} = 2.110 \, s^{-1}$).

The shear rate dependence of shear stress for suspensions was determined. Fig. 5 shows the relationship between shear stress and shear rate for typical Y-doped barium titanate suspension. In the range of shear rate measured, a marked yield phenomenon is seen for typical doped barium titanate suspension when an electrical field is applied. The yield stresses of 1.8 and 2.7 kPa are induced at 2.4 and 3.2 kV/mm, respectively. Except that the viscosity of the pure barium titanate suspension is similar to that of doped barium titanate suspension at zero field, no significant increase in shear stress for pure barium titanate suspension can be seen under the applied electrical field.
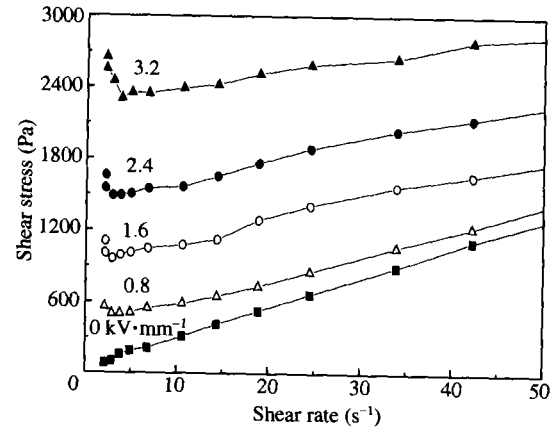
2.3 Dielectric properties of doped barium titanate suspensions

The dielectric properties of ER suspensions depend on the structure induced by the applied electrical field[20]. Hence, to make a reasonable comparison between dielectric values of pure barium titanate and doped barium titanate, we keep the suspensions in randomly dispersed system whose structure is not disturbed by the bias field of only 2 V/mm. The dependence of dielectric constant and dielectric loss tangent of suspensions on rare earth content are presented in Fig.6(a) and (b), respectively. Obviously, the dielectric loss increases by doping with rare earth and the dielectric constant varies with RE substitution. The types and content of RE have been found to affect the dielectric properties of barium titanate. The value of dielectric loss of Y-doped barium titanate is much larger than that of La or Ce-doped barium titanate. However, the dielectric loss and dielectric constant decline when the y_Y and y_{La} go beyond 15% and y_{Ce} beyond 7%. The dielectric properties decline when the other phase appears in XRD patterns, which suggests that the appearance of rare earth oxide prevents the further modification of dielectric properties. In addition, dielectric measurements also show that the dependence of dielectric constant on frequency becomes larger due to doping. A large increment of dielectric constant between low and high frequency, $\Delta\varepsilon = \varepsilon_{100\,Hz} - \varepsilon_{10\,kHz}$, is seen at suitable RE content, which represents a dielectric dispersion. By contrast, the dielectric constant of pure barium titanate remains constant in the frequency range investigated, and dielectric loss is very low. Because the dielectric constant (2.60~2.80) and loss tangent (tan $\delta \sim 0.002$) of silicone oil remain independent of frequency at the
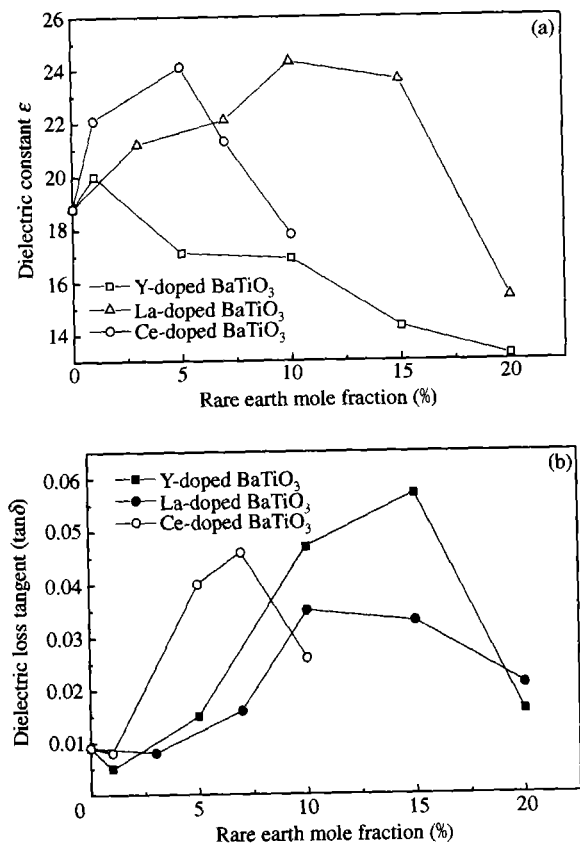
Fig. 6. The dependence of dielectric constant (a) and loss tangent (b) of doped barium titanate suspensions ($\phi = 26\%$) on rare earth content at 10^3 Hz and 20 ℃.

investigated temperature, we believe that the dielectric properties of suspensions are mainly influenced by the dielectric properties of dispersal particles in silicone oil according to the mixture model often used in ER study[20]. Therefore the dielectric results reveal that doping with RE causes changes in polarization of barium titanate. Practically, the dielectric properties are strongly influenced by the presence of the lattice distortion, defects and impurities in crystals[22]. They can improve the defect dipolar orientational or relaxation polarization, even space-charge polarization in low frequency range. These changes will contribute to the dielectric loss of the whole system and dielectric relaxation at low frequency. It is found in the XRD patterns that isovalent substitution for Ba^{2+} with the RE ions of smaller radii causes strong lattice distortion of barium titanate. Especially, the smaller the radii of rare earth ions that substitute for Ba^{2+}, the larger the lattice distortion will be. Based upon the results of dielectric measurement about doped barium titanate, the increasing of the dielectric loss somehow means a large proportion of the defect dipolar orientational po-

larization and the interfacial polarization. Furthermore, the change in the dielectric properties is more significant in Y-doped barium titanate which has a larger lattice distortion accordingly. Unfortunately, the appearance of other phases, which reveals that further substitution of RE ions for Ba^{2+} fails, makes dielectric loss decrease and prevent modifying the dielectric properties.

The widely accepted ER mechanisms[9,12,13,22] suggest that the particle polarization is responsible for the interaction forces between particles that leads to rheological change in ER suspensions. The parameters in connection with particle polarization, such as high dielectric constant (related to strong polarization) and suitable dielectric loss ($\tan\delta \geqslant 0.1$ at 1 kHz) or conductivity (10^{-7} S/m) (related to the polarization response time and stability of interaction between particles), play an important role in raising the performance of ER materials. Comparing the dielectric properties with rheological properties of pure and doped barium titanate suspensions, we find that the poor ER activity of pure barium titanate under DC field is attributed to its low dielectric loss. The reason may lie in the fact that the intrinsic ionic or atomic polarization of pure barium titanate cannot induce large dielectric loss. Therefore, a relative large dielectric loss is necessary for barium titanate to have an optimal ER performance. Our results are in good agreement with the results of other researchers[5,7,9]. More interesting is that we can control the ER activity through a suitable doping.

3 Conclusion

A new class of water-free electrorheological suspension based on nonaqueous rare earth (RE)-doped barium titanate in silicone oil was prepared by means of modified sol-gel technique. It is found that large enhancement of ER activity of barium titanate in DC electrical field can be achieved by doping with RE. We have demonstrated that the different types and content of RE have a marked effect on ER behavior. The yield stress reached 3.2 kPa for y_Y, 15% Y-doped barium titanate suspension and 1.4 kPa for y_{La}, 10% ~15%% or y_{Ce}, 5% Ce-doped barium titanate suspension at 3.5 kV/mm. We attribute the enhancement of ER activity to the increase of dielectric loss that may originate from the lattice distortion defects in barium titanate due to isovalent substitution for Ba^{2+} with small radius RE ions. Therefore, through doping RE to intrinsically modify the dielec-

tric and polarization properties of barium titanate, the ER effect can be greatly enhanced. It may help to open up a novel horizon for preparation of high-performance ferroelectric-based ER materials.

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