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LATENT HEAT STUDY OF PHASE TRANSITION IN $Ba_{0.73}Sr_{0.27}TiO_3$ INDUCED BY ELECTRIC FIELD

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We have developed a modified power-compensation DSC to evaluate the electrocaloric properties of ferroelectrics. With this apparatus, latent heat of electric-field-induced phase transition in $Ba_{0.73}Sr_{0.27}TiO_3$ (BST) ferroelectric ceramics has been investigated in detail. It varies with temperature and reaches its climax at 25°C, close to the ferroelectric-paraelectric phase transition temperature, when induced by the same electric field of 15 kV cm^{-1}. The theoretical saturated endothermicity induced by enough high electric field at 25°C is expected to 0.59 J g^{-1}, which is 84% of the total phase transition latent heat of BST. At last the origins of difference between exothermicity and endothermicity are discussed.

Keywords: *$Ba_{1-x}Sr_xTiO_3$, DSC, electric-field-induced phase transition, ferroelectrics, latent heat, power-compensation DSC*

Introduction

Ferroelectric refrigeration is one of the new environment friendly refrigeration techniques receiving intensive attentions. It makes use of the exothermicity and endothermicity during the first-order phase transition in ferroelectrics induced by electric fields [1]. Most investigations devoted to ferroelectric refrigeration measure the temperature change of specimens rather than the energy exchange [1–3]. The results vary depending on the measurement conditions. Although high-energy X-ray diffraction, Raman scattering spectroscopy, and so on are widely applied to investigate the electric-field-induced phase transition in ferroelectrics [4–6], they cannot evaluate the electrocaloric properties of ferroelectrics directly. So developing a method suitable for evaluating the electrocaloric properties of ferroelectrics directly, such as measuring the latent heat of electric-field-induced phase transition in ferroelectrics is necessary. Investigating from the viewpoint of energy, DSC is a very good technique for phase transition study [7, 8].

In this paper, we present an apparatus modified from a power-compensation DSC. A lead-free material, $Ba_{0.73}Sr_{0.27}TiO_3$ (BST) ferroelectric ceramics, is chosen because its ferroelectric-paraelectric transition temperature is near room temperature, which makes it a potential material for ferroelectric refrigeration. With above apparatus, the latent heat of electric-field-induced phase transition in BST is investigated in detail and compared with that of phase transition at cooling and heating.

Experimental

Our apparatus is developed from the modification of power-compensation DSC (Model CDR-1, Shanghai, China), which is shown in Fig. 1. Zero line of high voltage amplifier was welded to Ni cup, on which one side of specimen was welded. High voltage line was welded to the other side of specimen directly, and insulated from every part of DSC. At certain temperature, when an electric field is applied to and then withdrawn from the specimen, the temperature of specimen will change due to the electric-field-induced transition. The heaters located beneath reference or specimen will work to equalize both temperatures of reference and specimen. For most ferroelectric materials, the leakage

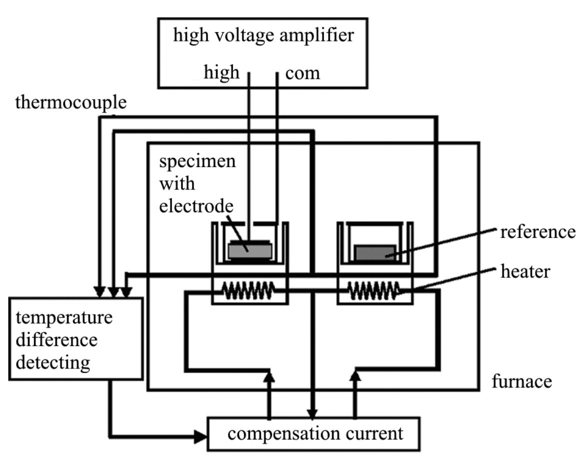

Fig. 1 Scheme of the modified measuring cell of power-compensation DSC

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current is so small (<10^{-7} A cm^{-2}) that its Joule heat can be neglected. So by integrating the compensation power, we are able to obtain the exothermicity and endothermicity during phase transition induced by electric fields at certain temperatures.

$Ba_{0.73}Sr_{0.27}TiO_3$ ferroelectric ceramics are synthesized through solid-state reactions. $BaTiO_3$ is prepared from the mixture of $BaCO_3$ and TiO_2, while $SrTiO_3$ from the mixture of $SrCO_3$ and TiO_2. After that, $Ba_{0.73}Sr_{0.27}TiO_3$ (BST) is prepared by ball milling stoichiometric amount of $BaTiO_3$ and $SrTiO_3$ for 20 h, followed by being pressed to ∅11.7×1.5 mm pellets and sintered at 1350°C for 2 h. Obtained with a Rigaku D/max-IIIA diffractometer with CuK_α radiation, X-ray diffraction pattern of BST ceramics indicates the existence of single perovskite-type phase BST. Heat flux DSC (Netzsch DSC 204) is used to measure its heating and cooling DSC curves. The specimens with dimensions of ∅4.2×1.0 mm are cut out of the sintered pellets and are baked silver pastes for the electrical measurement. Under an electric field of 20 kV cm^{-1}, the leakage current of BST is found to be so small (<10^{-7} A cm^{-2}) that its Joule heat is reasonable to be neglected. Prior to each measurement, an electric field of 15 kV cm^{-1} was repetitively applied to and then withdrawn from the specimen for 20 times to stabilize its electrocaloric effects.

Results and discussion

DSC curves of BST ferroelectric ceramics are shown in Fig. 2. Heating rate and cooling rate are 10 and –10°C min^{-1}, respectively. Its peak temperature corresponding to heating and cooling are 24 and 20°C, respectively. There is a thermal hysteresis of about 4 K between heating and cooling, indicating the transition is a first-order phase transition. Transition latent heat

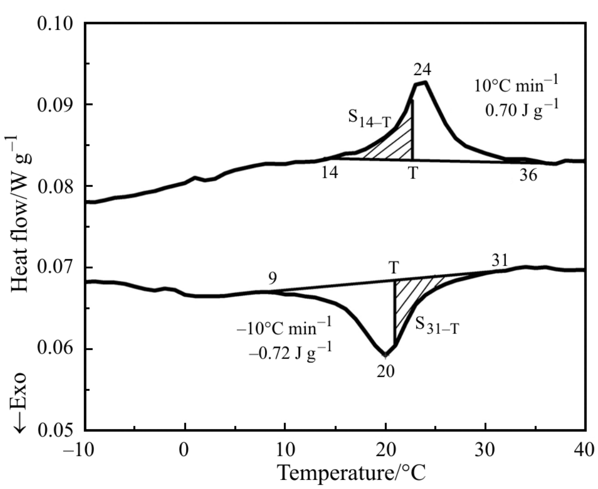

Fig. 2 DSC curves of BST

of heating and cooling are 0.70 and –0.72 J g^{-1}, respectively. The difference may be due to the measurement error, which is popular in the measurement of latent heat of phase transition.

Figure 3 shows the latent heat of BST induced by an electric field of ±20 kV cm^{-1} at 25°C. The electric field of 20 or –20 kV cm^{-1} was applied to the specimen linearly in one second, held constant for 50 s, and then withdrawn from the specimen linearly in one second. Electrocaloric effects induced by positive and negative electric fields are almost the same. Hence, the results are not the interferential signals corresponding to electric field change. They reveal the intrinsic property of electric-field-induced transition.

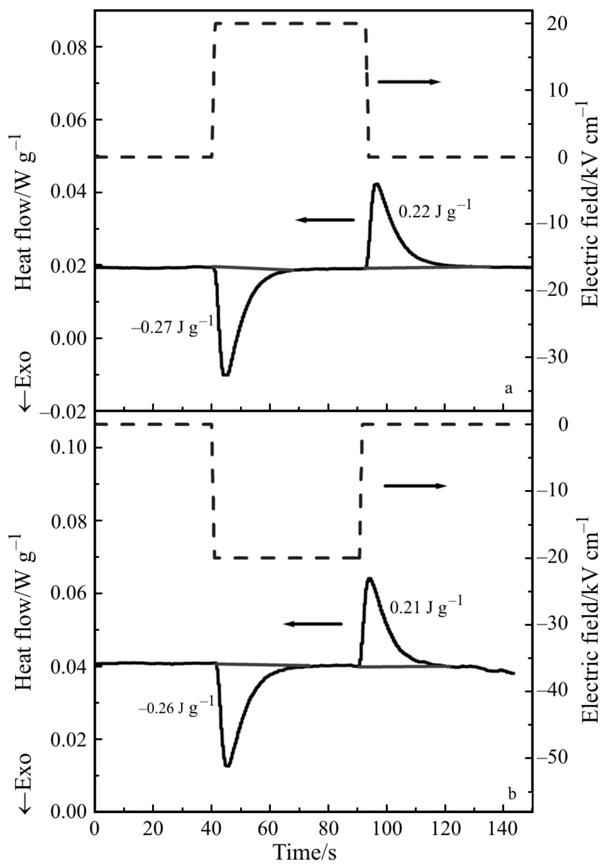

Fig. 3 Latent heat of BST induced by an electric field of ±20 kV cm^{-1} at 25°C

Figure 4a plots temperature dependence of the latent heat of BST induced by an electric field of 15 kV cm^{-1}. Figure 4b shows temperature dependence of the dielectric constant ε_r of BST. The electric-field-induced latent heat of BST reaches its climax at 25°C, close to the paraelectric-ferroelectric phase transition temperature (23.8°C). This indicates that the latent heat of BST induced by an electric field stems from an electric-field-induced paraelectric–ferroelectric phase transition.

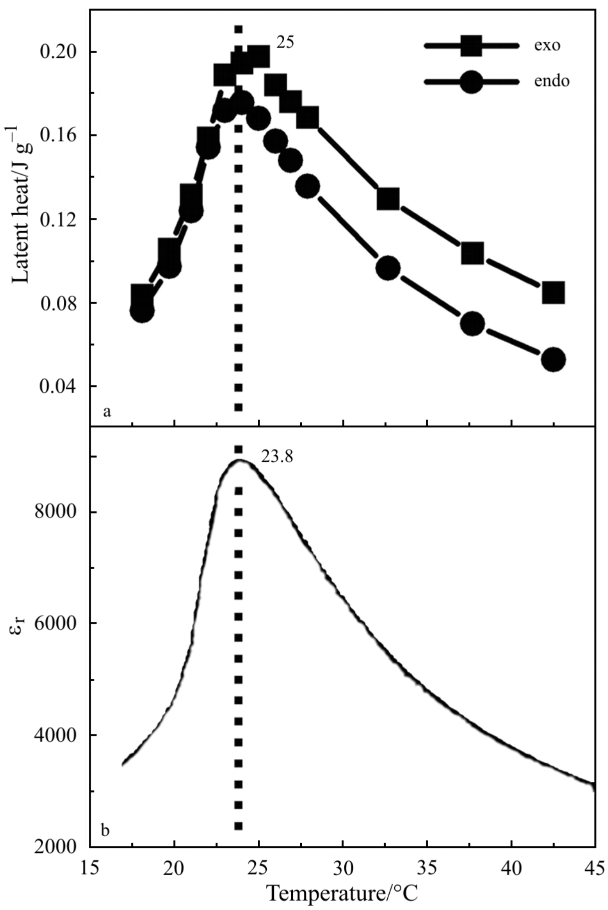

Fig. 4 a – Temperature dependence of the latent heat of BST induced by an electric field of 15 kV cm^{-1}, b – temperature dependence of the dielectric constant ε_r of BST

Figure 5 shows the values of electric-field-induced latent heat of BST as a function of the electric field. When the electric field increased from 10 to 24 kV cm^{-1} at 25°C, the exothermicity increased from 0.12 to 0.32 J g^{-1} linearly, and the endothermicity increased from 0.11 to 0.28 J g^{-1} linearly. Because the electric-field-induced latent heat increased linearly as the electric field increased to 24 kV cm^{-1}, the phase transition induced by an electric field of 24 kV cm^{-1} at 25°C may be not saturated. How much is the latent heat of saturated phase transition induced by enough high electric field?

From DSC curves of Fig. 2, ferroelectric phase transited to paraelectric phase in temperature range of 14 to 36°C at heating rate of 10°C min^{-1}, while paraelectric phase transited to ferroelectric phase in temperature range of 31 to 9°C at cooling rate of –10°C min^{-1}. Therefore, ferroelectric phase fraction of heating $f_{ferr-H}(T)$ equals to $1-(S_{14-T}/S_{14-36})$, where S_{14-T} is defined as an area in Fig. 2 and S_{14-36} is S_{14-T} with T=36°C. Ferroelectric phase fraction of cooling $f_{ferr-C}(T)$ equals to (S_{31-T}/S_{31-9}), where S_{31-T} is defined as an area in Fig. 2

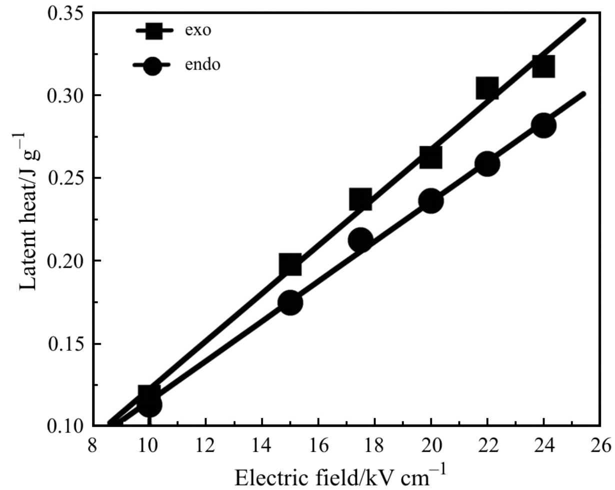

Fig. 5 Electric field dependence of the electric-field-induced latent heat of BST at 25°C

and S_{31-9} is S_{31-T} with T=9°C. We define equilibrium ferroelectric phase fraction as $f_{ferr}(T)=(f_{ferr-H}(T)+f_{ferr-C}(T))/2$. Temperature dependence of ferroelectric phase fraction $f_{ferr}(T)$ at zero field is plotted in Fig. 6.

We take the ratio of $endo_{field}/endo_{All}$ as the additional fraction of ferroelectric phase induced by an electric field, where $endo_{field}$ is the electric-field-induced endothermicity and $endo_{All}$ is the total endothermicity of BST, which is 0.70 J g^{-1} (Fig. 2). Then we can get the temperature dependence of ferroelectric phase fraction $f_{ferr}(T)$ under an electric field of 15 kV cm^{-1} (Fig. 6). It can be seen that ferroelectric phase fraction at the same temperature increases when induced by an electric field.

It can be seen from Fig. 6 that f_{ferr} (25°C) at zero field is 16%. The endothermicity induced by an electric field of 24 kV cm^{-1} is 0.28 J g^{-1} (Fig. 5). The additional fraction of ferroelectric phase is $endo_{field}/endo_{All}=$

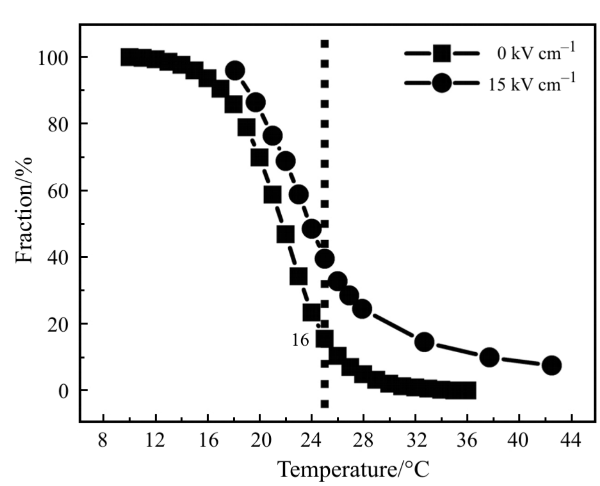

Fig. 6 Temperature dependence of ferroelectric phase fraction $f_{ferr}(T)$

0.28/0.70=40%. So the ferroelectric phase fraction under an electric field of 24 kV cm^{-1} at 25°C is 56%. It is not saturated. The latent heat of saturated transition induced by enough high electric field at 25°C is expected to 100–16%=84% of the total phase transition latent heat of BST, namely 0.70·84%=0.59 J g^{-1}.

It is appreciated that enough high electric field would induce saturated phase transition. Unfortunately, silicon oil was found to disturb our heat measurements and gas in air would be ionized under ultrahigh electric field, so the electric field in our measurements has to be lower than 24 kV cm^{-1}.

At last, we discuss the origins of difference between exothermicity and endothermicity. The exothermicity is larger than the endothermicity when the same electric field is applied to and then withdrawn from BST at the same temperature (Fig. 4a). Likewise, the exothermicity increased faster than the endothermicity when the electric field increased (Fig. 5). These phenomena result from the leakage current under high electric field. Although the leakage current of BST ferroelectric ceramics is very small ($<10^{-7}$ A cm^{-2} at 20 kV cm^{-1}), it still generates detectable Joule heat for our modified DSC. Hence, compared with the endothermicity, the exothermicity is larger when induced by the same electric field, and increases faster when the electric field increases. On the other hand, the structure of ferroelectric phase differs from that of paraelectric phase, so the leakage current of ferroelectric phase differs from that of paraelectric phase. The majority of BST is ferroelectric phase at temperature lower than 23.8°C, while paraelectric phase is the major part at temperature higher than 23.8°C. Therefore, the gap between the exothermicity and endothermicity induced by the same electric field at temperature lower than 23.8°C differs from that at temperature higher than 23.8°C, which can be seen in Fig. 4a.

Conclusions

In summary, we have demonstrated herein a new method to evaluate the electrocaloric properties of ferroelectrics. Investigated with our modified DSC, latent heat of electric-field-induced phase transition in BST varies with temperature and reaches its climax at 25°C, close to the ferroelectric-paraelectric phase transition temperature, when induced by the same electric field of 15 kV cm^{-1}. This indicates that the latent heat stems from paraelectric-ferroelectric phase transition induced by electric field. When the electric field increased from 10 to 24 kV cm^{-1} at 25°C, the exothermicity and endothermicity of BST increased linearly and are not saturated. The theoretical endothermicity of saturated transition induced by enough high electric field at 25°C is expected to 0.59 J g^{-1}, which is 84% of the total phase transition latent heat of BST. There is difference between exothermicity and endothermicity, which mainly results from the leakage current under high electric field.

Acknowledgements

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