The effect of point defects on ferroelastic phase transition of lanthanum-doped calcium titanate ceramics

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1. Introduction

CaTiO₃, “the founding father” of the pervoskite family, displays ferroelastic phase transition (also known as the martensitic transition) [1]. A multitude of fundamental studies have been done on ferroelastic phase transition of CaTiO₃ for several decades. It is now generally believed that CaTiO₃ displays two structure transitions. With increasing temperature, a phase transition from the orthorhombic phase to the tetragonal phase occurs at about 1500 K, and then another transition from the tetragonal phase to the cubic phase occurs at a higher temperature of near 1600 K [2–13].

An increasing number of studies reveal that ferroelastic phase transitions in both metal and ceramic are greatly influenced by point defects. Taking the Ti–Ni alloys as an example, it is reported that the phase transition temperature of Ti₀.₅Ni₀.₅ gradually decreases with increasing concentration of Ni (substitutional point defects) [14]. Interestingly, a “glassy-like” transition termed as the “strain glass” transition, has been recently discovered to replace the ferroelastic phase transition of pure Ti₀.₅Ni₀.₅ alloys, when the doped Ni content is sufficient (x ≥ 1.5) in Ti₀.₅Ni₀.₅ system. The strain glass transition in Ni-doped Ti₀.₅Ni₀.₅ is different from the ferroelastic phase transition in pure Ti₀.₅Ni₀.₅. During strain glass transition, excess Ni serving as point defects gives rise to invariability of the average structure and frequency dependence of storage modulus [15–17].

Previous studies reported that doping different kinds of elements such as La [18,19] affects the dielectric properties and transition temperature of CaTiO₃ ceramic systems. However, the role of point defects on the ferroelastic transforming behaviors in CaTiO₃ ceramic systems is unclear so far. In the present paper, we focused on the role of point defects on the tetragonal to orthorhombic phase transition in La-doped CaTiO₃ systems. Our results indicate that, in CaTiO₃ ceramic systems, point defects can also suppress the ferroelastic phase transition, and induce a “glassy-like” behavior similar to the strain glass transition in Ni-doped Ti₀.₅Ni₀.₅ alloys.

2. Experimental

The Ca₁₋ₓLaₓTiO₃ samples at different La-doping levels x = 0.45, and 0.7 were prepared by solid-state reactions with powders of calcium carbonate, lanthanum oxide, titanium dioxide. All the chemicals were of analytical reagent grade quality with purity of 99.9%. Stoichiometric quantities of chemicals were mixed homogeneously by agate ball milling in water for 6 h. The mixture was then dried and calcined first time in the air at 1473 K for 6 h in alumina crucibles; then, cooled in the furnace for 12 h. And after milling for 12 h, the mixture was calcined the second time at 1573 K for 6 h to ensure the homogeneity of lanthanum and the formation of pervoskite structure. Subsequently, the mixture was made into pellets using PVA glue and pressed into small disks with the diameter of 15 mm. Finally, these disks were sintered at 1673 K for 6 h.

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To monitor the structure change during the transition process of Ca$_{1-x}$La$_{2x/3}$TiO$_3$ ($x=0.45$, 0.7) samples, in situ X-ray diffraction was performed in the X-ray diffractometer of SHIMADZU XRD-7000 with Cu Kα radiation. The dynamic mechanical properties, i.e., the storage modulus and internal friction, of Ca$_{1-x}$La$_{2x/3}$TiO$_3$ ($x=0.45$, 0.7) samples during their transition processes were tested by DMA-Q800 from the TA Instrument in the frequency range of 0.2–10 Hz.

3. Results

In this part, we will show X-ray diffraction (XRD) and DMA results of Ca$_{1-x}$La$_{2x/3}$TiO$_3$ with $x=0.45$ and 0.7, abbreviated as CLT45 and CLT70. These results show different transition characteristics of the samples at low and high La-doping levels.

3.1. Ca$_{1-x}$La$_{2x/3}$TiO$_3$ with $x=0.45$ (CLT45): normal ferroelastic phase transition

The ferroelastic phase transition of CLT45 monitored by the DMA and XRD are shown in Fig. 1. An obvious peak of internal friction and a corresponding dip on storage modulus appear at 710 K ($T_c$) in Fig. 1(c). Moreover, it can be found that the peak/dip temperature of internal friction and storage modulus is independent on the frequency. Thus, the DMA results suggest that a normal ferroelastic phase transition happened in CLT45.

The ferroelastic phase transition of CLT45 is further verified directly by XRD results in Fig. 1(a) and (b), which demonstrates the average structure change before and after the transition. The profile of (1 1 1)$_c$ peak in the cubic structure of pure CaTiO$_3$ can be used as a reference for the diffraction spectrum of different phase structures for CLT45 sample, which was examined by monitoring the characteristic peaks in the 2θ range of 36° to 42° as a function of temperature. Compared with pure CaTiO$_3$ [10], CLT45 shows two diffraction peaks in the 2θ range of 36° to 42° at 720 K [Fig. 1(b)], which can be indexed as (2 0 2)$_T$ and (2 1 1)$_T$ planes of the tetragonal phase. When cooling to 298 K, CLT45 shows superlattice reflections in the diffraction pattern, which can be indexed as (2 1 1)$_O$, (1 0 3)$_O$, and (1 2 1)$_O$ peaks of the orthorhombic phase as shown in Fig. 1(a). Therefore, based on the DMA and XRD results, it can be concluded that a tetragonal to orthorhombic ferroelastic phase transition happens at 710 K in CLT45.

3.2. Ca$_{1-x}$La$_{2x/3}$TiO$_3$ with $x=0.7$ (CLT70): “glassy-like” frozen process

Transition properties of CLT70 are shown in Fig. 2. With further increase of the defect concentration $x$ of Ca$_{1-x}$La$_{2x/3}$TiO$_3$ to 0.7, the XRD diffraction patterns of CLT70 [Fig. 2(a), (b) and (c)] show quite different features from those of CLT45 [Fig. 1(a) and (b)]. Moreover, great differences can also be observed in DMA results of CLT70 [Fig. 2(d)] compared with those of CLT45 [Fig. 1(c)].

The structure evolution of CLT70 at three temperatures of 450 K [Fig. 2(c)], 298 K [Fig. 2(b)], and 173 K [Fig. 2(a)], shows that the XRD patterns in three different temperatures keep the same, spanning the whole temperature range of DMA results [Fig. 2(d)]. And all peaks of XRD results can be indexed by the tetragonal phase [10]. This indicates that the average crystal structure of this sample does not change from 450 K to 173 K. Therefore, the XRD results indicate that CLT70 is a “nontransforming” system. However, it exhibits obvious frequency dependence of storage modulus dips from 319.5 K to 334.6 K shown in Fig. 2(d), which are followed by lower peaks associating with internal friction. Temperatures of the storage modulus minimum of CLT70 are much lower than those of CLT45 shown in Fig. 1(c). More interestingly, these modulus dips show a frequency-dependent property; that is, the dip temperature $T_d(\omega)$ shifts to a higher temperature from 319.5 K to 334.6 K with the frequency increasing from 0.2 Hz to 10 Hz. The peaks of internal friction (tan $\delta$) in Fig. 2(d) also exhibit the same tendency.

All above experimental results of CLT70 give a clue that normal ferroelastic phase transition in CaTiO$_3$ is suppressed; instead, a “glassy-like” frozen process appears, which will be further discussed in Section 4.2.

![Fig. 1. Evidence of normal long-range ordered ferroelastic phase transition for Ca$_{1-x}$La$_{2x/3}$TiO$_3$ ($x=0.45$) (CLT45). (a) and (b) XRD results at angles 2θ from 36° to 42° at 298 K and 720 K, respectively. The peaks between 38° and 39° are related to (2 1 1)$_O$, (1 0 3)$_O$, and (1 2 1)$_O$ peaks in orthorhombic phase splitting from (2 1 1)$_T$ peak of tetragonal phase. (c) DMA results of CLT45, which shows a dip in storage modulus and a corresponding peak in internal friction (tan $\delta$) at 710 K.](image1)

![Fig. 2. Evidence of “glassy-like” frozen process in Ca$_{1-x}$La$_{2x/3}$TiO$_3$ ($x=0.7$). (a), (b), and (c) XRD results of 2θ from 36° to 42° at 173 K, 298 K and 450 K respectively. Two peaks at 2θ = 40.3° and 39° corresponds to (2 0 2)$_T$ and (2 1 1)$_T$ planes of tetragonal phase. (d) DMA result, which shows both the temperature of storage modulus dip and corresponding internal friction peak shift to higher temperature with increasing frequency.](image2)
Fig. 3. In situ XRD results of (a) Ti_{48.5}Ni_{51.5} (cited from [22]) and (b) CLT70. (a) shows there is no average structure change from 373 K to 108 K in 2θ from 40 to 80° in Ti_{48.5}Ni_{51.5}. (b) shows no difference of diffraction pattern in CLT70 from 450 K to 173 K in the angle of 2θ from 36° to 42°, indicating there is no average structure change in CLT70.

4. Discussion

In this part, we explore the role of point defects on the transition behaviors of the La-doped CaTiO₃ systems. We will first compare the ferroelastic phase transition between pure CaTiO₃ and low defect concentration sample CLT45. Then, we shall compare the transition of the high defect concentration sample CLT70 with the strain glass transition of Ni-doped Ti_{50−x}Ni_{50+x} (x = 1.5). Finally, we discuss why La-doped CaTiO₃ and Ni-doped Ti_{50−x}Ni_{50+x} show similar transition behaviors by doping point defects.

4.1. The effect of point defects on ferroelastic phase transition with low defect concentration in Ca_{1−x}La_{2x/3}TiO₃

In Ca_{1−x}La_{2x/3}TiO₃ (x = 0.45) the transition temperature is 710 K, as shown in Fig. 1(c). However, previous studies suggested that the tetragonal to orthorhombic transition temperature of pure CaTiO₃ is 1498 ± 25 K [2]. Thus, it can be found that the transition temperature dramatically decreased by nearly 800 K when doping 45% La in Ca_{1−x}La_{2x/3}TiO₃. Therefore, the first role of point defects (La atoms) in CaTiO₃ is that it can destroy the thermal stability of long-range ordered ferroelastic phase and lower the thermodynamic driving force for ferroelastic phase transition, which is similar to previous studies of Ni-doped Ti–Ni alloys [16,20].

4.2. The effect of point defects on ferroelastic phase transition with high defect concentration in Ca_{1−x}La_{2x/3}TiO₃

It is reported that point defects have induced the crossover from long-range ordered ferroelastic phase transition to the “stain glass” transition in Ti_{48.5}Ni_{51.5} [15]. Considering that both CLT70 and Ti_{48.5}Ni_{51.5} are highly doped ferroelastic systems, we compare the mechanical properties and XRD results of these two systems to demonstrate the similarity between them. From such a comparison, the effects of point defects on transition at high defect concentration in Ca_{1−x}La_{2x/3}TiO₃ will be revealed.

In Fig. 3, XRD results indicate that both Ti_{48.5}Ni_{51.5} and CLT70 are absence of change in average crystal structure and keep the original high-temperature crystal structure down to the low temperature. This is one substantial evidence that long-range ordered ferroelastic phase transition from the tetragonal to orthorhombic phase has been ceased, which consists with the previous research of synchrotron X-ray diffraction measurements [18].

Fig. 4. Similarity of DMA results between (a) and (b) Ti_{48.5}Ni_{51.5} (cited from [16]) and (c) and (d) CLT70. (a) and (c) Storage modulus of two systems show that the minimum temperature shifts to higher temperature when the frequency increases, which followed by a maximum in internal friction at lower temperature in (b) and (d). (c) inset shows the dip temperature of storage modulus at different frequencies, which are fitted well with Vogel–Fulcher relation, giving the “idea” freezing temperature T₀ = 316.9 K.

From DMA results in Fig. 4, it is found that CLT70 and Ti48.5Ni51.5 share same characters of ac mechanical properties. First, with decreasing the temperature, storage modulus of CLT70 and Ti48.5Ni51.5 shows a softening behavior. At lower temperature, the ac storage modulus of the two systems becomes hardening with further decreasing temperature. The dip temperature of storage modulus [shown in Fig. 4(a) and (c)] and the corresponding peak temperature of internal friction [shown in Fig. 4(b) and (d)] of both samples move to a higher temperature with increasing frequency.

The “clone” of XRD and DMA results of CLT70 from Ti48.5Ni51.5 implies that the CLT70 sample no longer undergoes a long-range ordered ferroelastic phase transition but a “glassy-like” frozen process similar to Ti48.5Ni51.5. Moreover, as shown in Fig. 4(c) inset, the storage modulus dip temperatures of different frequencies were well fitted with Vogel–Fulcher relation [21] \[ \omega = \omega_0 \exp[-E_a/k_b(T_0 - T)] \], which further demonstrates that the transition process in CLT70 is a frozen process. And through fitting, the “ideal” freezing temperature T0 can be obtained as 316.9 K.

Through the comparison between CLT70 and Ti48.5Ni51.5, we can conclude that the second effect of point defects in Ca(1−x)La2x/3TiO3 is that it is capable to induce a “glassy-like” transition when the dopant concentration beyond a certain level.

4.3. Why Ti50−xNi50+x and Ca(1−x)La2x/3TiO3 show similar transition behaviors?

As discussed in Sections 4.1 and 4.2, it can be found that the behavior of La-doped CaTiO3 compounds and Ni-doped Ti–Ni alloys are quite similar. In the low doping level, the transition temperature of the two systems is intensively suppressed compared to that of their pure systems. In the high doping level, a “glassy-like” behavior appears instead of the normal ferroelastic phase transition in each system. These results suggest that there must be some common factors driving the two different systems into the same final glassy state.

The defect-doped CaTiO3 compounds and Ti–Ni alloys are quite different from an electronic point of view. However, they share the following common features: (1) both the pure CaTiO3 compound and Ti–Ni alloy undergo ferroelastic phase transition intrinsically with long-range ordering of lattice strain; (2) doping point defects reduces the thermodynamic driving force for ferroelastic phase transition in both systems; (3) point defects will introduce local stress fields with similar features in the two different systems, due to the mismatch strain between the matrix and dopants. These local stress fields play a similar role that is dedicating the formation of nano domains and eventually resulting in glassy-like behaviors in both Ti50−xNi50+x and Ca(1−x)La2x/3TiO3 systems upon cooling. That is why Ti50−xNi50+x and Ca(1−x)La2x/3TiO3 share similar transition behaviors.

5. Conclusions

Ca1−xLa2x/3TiO3 (x = 0.45, 0.7) have been studied by DMA and XRD measurements at different temperatures. It is found that the transition properties of these two compositions are of great difference. CLT45 undergoes a normal long-range ordered ferroelastic phase transition. On the contrary, the high defect concentration sample, CLT70, displays a “glassy-like” frozen process. Based on the results and discussion, we conclude that, the dopant La serving as point defects has two effects in Ca1−xLa2x/3TiO3 ferroelastic ceramics: (i) they weaken the thermodynamic stability of long-range ordered ferroelastic phase and lower the driving force of ferroelastic phase transition of CaTiO3; (ii) they induce a “glassy-like” frozen process when the defect concentration beyond a certain level through introducing local stress fields.

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