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Effects of doping with La and Mn on the crystallite growth and phase transition of $BaTiO_3$ powders

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The effects of La and Mn dopants on the crystallite growth and the phase transformation of $BaTiO_3$ powders were studied. The barium titanate powders were obtained by calcining barium titanyl oxalate tetrahydrate in the temperature range 800 to 1200 °C. Crystallite growth of $BaTiO_3$ powders was promoted by the use of Mn dopant due to the increase of oxygen vacancies. The dissolution of La dopant into $BaTiO_3$ structure may decrease the oxygen vacancies so that the growth of $BaTiO_3$ crystallites is inhibited at high temperature ($\geqslant 900$ °C). When the crystallite size is small, the barium titanate can exist as a cubic phase due to the manifestation of the surface energy. Undoped cubic $BaTiO_3$ powders can be stable at a size < 30 nm. Doping with La and Mn would bring the crystallite size for the cubic-to-tetragonal phase transformation to ~ 100 nm, resulting from the presence of cation or oxygen vacancies.

1. Introduction

Studies involving barium titanate ceramics with aliovalent cation dopants have been undertaken to improve electric properties [1, 2]. The semiconducting and the dielectric properties of $BaTiO_3$ ceramics are well known to be highly dependent upon the grain size, phase contents of the ceramic body and also the types of dopants used. However, the use of a dopant to improve dielectric properties may also affect the grain growth and mineral phase contents, which can result in unexpected effects. It is therefore important to find the effects of using the dopants. La and Mn have been two of the commonly used dopants for $BaTiO_3$ series ceramics. Studies on how to attain expected grain growth and phase transformation have been reported [3, 4]. However, data on the effects of using the two dopants on the crystallite growth and the phase transition of ultrafine $BaTiO_3$ powders are not available.

It is well known that $BaTiO_3$, when cooled through the transition temperature (120 °C), transforms from a cubic paraelectric to a tetragonal ferroelectric state, i.e. the tetragonal phase is thermodynamically stable at room temperature. Additions of La and Mn dopants may stabilize the cubic phase at room temperature [4]. However, Arlt and de With [5] reported that, as the grain size of $BaTiO_3$ ceramics is below 1.5 μm, $BaTiO_3$ phases of tetragonal and pseudocubic can coexist. Furthermore, when below 0.5 μm, only the pseudocubic phase (defined as C) is available. Recently, the effect of crystallite size on the phase transformation of pure barium titanate powders prepared by coprecipitation processes has been studied by Yen *et al.* [6]. Similar phenomena were also found in which the crystallite size plays a crucial role in the formation of the crystalline phase of barium titanate particles. Cubic $BaTiO_3$ crystallites can be stable at room temperature once the crystallite size is less than 30 nm. Thus, the cubic-to-tetragonal (c → t) phase transition of $BaTiO_3$ powder can notably be influenced by both the crystallite size and doping with La and Mn.

Moreover, Swilam and Gadalla [7] pointed out that an activation energy of 88 $kJ\,mol^{-1}$ is required for the growth of $BaTiO_3$ crystallites during the calcination of barium titanyl oxalate. Because the value is close to that observed for the activation energy of the diffusion of oxygen vacancies, 59.9 $kJ\,mol^{-1}$ (for barium and titanium vacancies, they are 333 and 1459 $kJ\,mol^{-1}$, respectively [8]). Moreover, the rate controlling mechanism for the growth of $BaTiO_3$ crystallites is believed to be determined by the diffusion of oxygen vacancies. In this study, XRD and TEM methods are employed to examine the effects of La and Mn dopants on the crystallite growth and phase transformation of ultrafine $BaTiO_3$ powders. Emphases are placed upon the phase transition of $BaTiO_3$ powders.

2. Experimental procedure

2.1. Specimen preparation

$BaTiO_3$ powders were prepared using coprecipitation methods. The general procedure followed was that of Clabaugh *et al.* [9] with some modifications [10, 11]. Analytical grade chemicals (E. Merck, Darmstadt, FRG) were used without further purification. The composition of precipitates was analysed by an inductively coupled plasma to ensure that the dopant molar ratio of precipitates was 0.02.

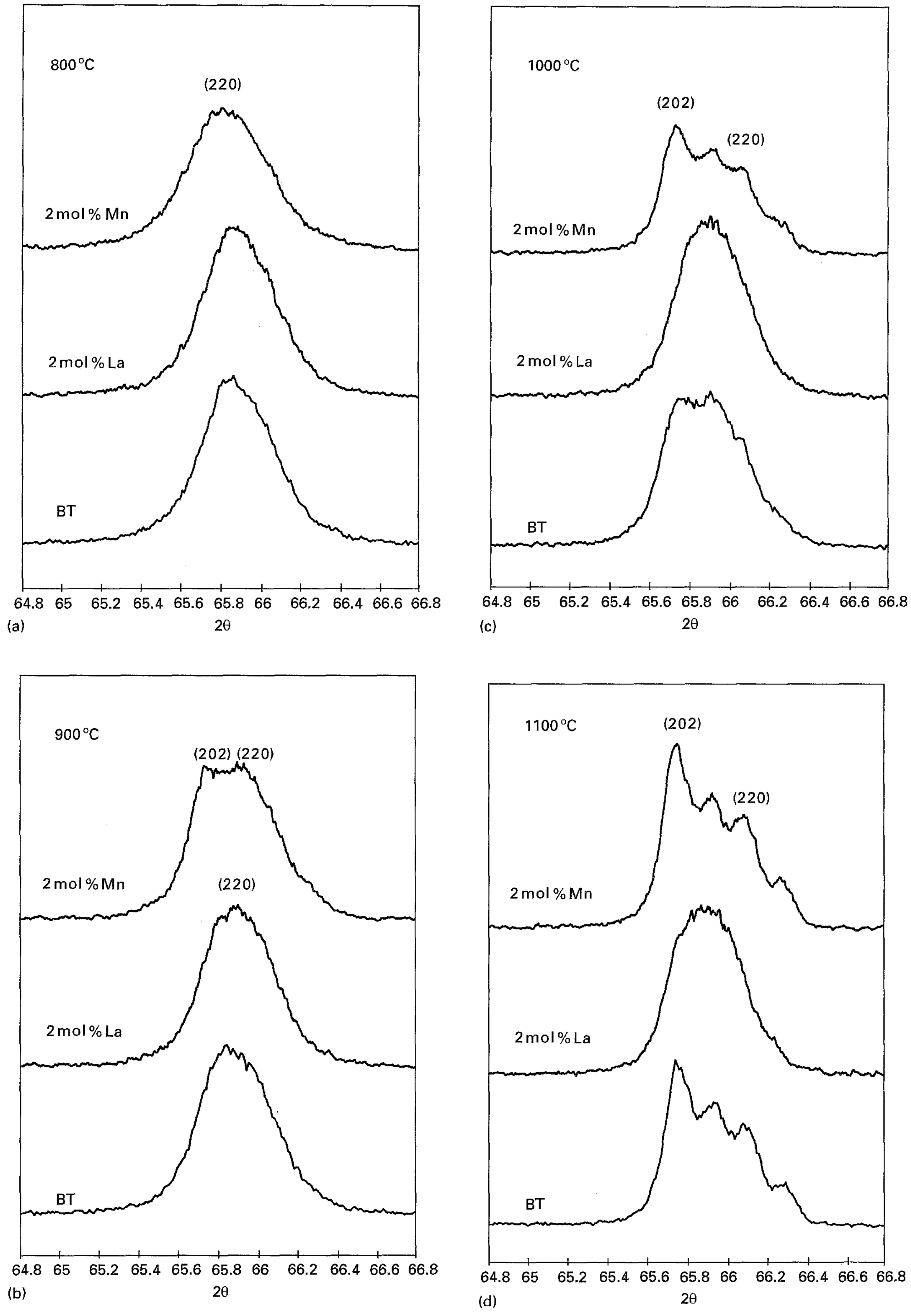


Figure 1 X-ray diffraction patterns of pure and doped $BaTiO_3$ powders calcined at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C and (e) 1200 °C, respectively.

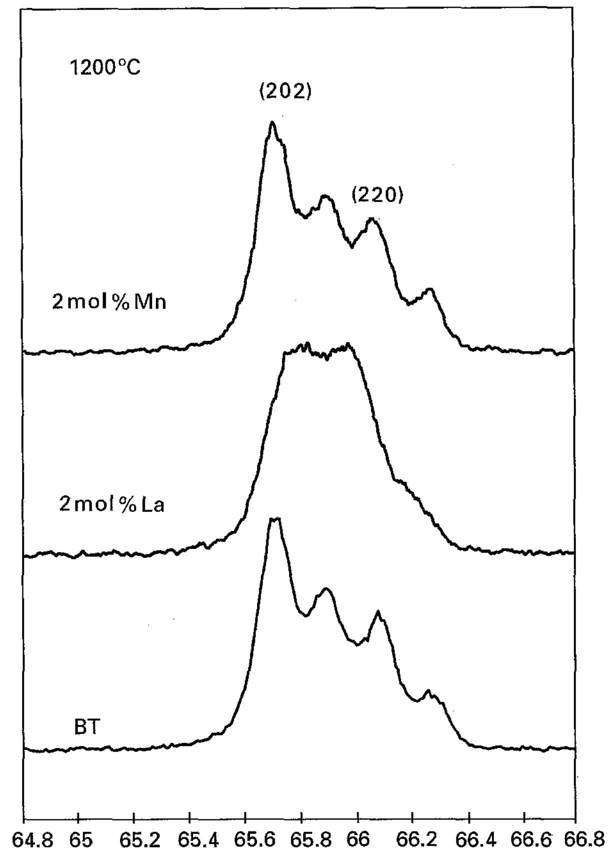


Figure 1 Continued.

Barium chloride monohydrate ($BaCl_2{\cdot}H_2O$) (purity: 99%), titanium tetrachloride ($TiCl_4$) (purity: 99%), manganese chloride dihydrate ($MnCl_2 \cdot 2H_2O$) (purity: 99%) and lanthanum chloride ($LaCl_3{\cdot}7H_2O$) (purity: 99%) were used as the starting materials. Desired amounts of $BaCl_2$, $TiCl_4$ and dopant solutions were mixed and then dripped slowly into a hot (80 to 82 °C) solution of oxalic acid (purity: 99.5%) which was stirred vigorously. The precipitate was obtained and filtered in a Bruchner funnel without cooling, thereby preventing the possibility of a deviation from the anticipated composition on cooling [11]. Next, the filtered cake was washed with a 2% hot solution of oxalic acid, and refiltered three more times. After being air-dried, the precipate was calcined at temperatures ranging between 800 and 1200 °C for 2 h.

2.2. Characterization

Crystalline phases present in the calcined powders were identified using a X-ray powder diffractometer (Rigaku), and Ni-filtered CuK_α radiation. Lattice parameters of $BaTiO_3$ were determined using its (3 1 1) and (2 2 2) CuK_α reflections. The Feret diameter of as-calcined powders was determined using TEM micrographs.

3. Results

3.1. Phase identification

Fig. 1a–e illustrate the changes of X-ray profiles (2 2 0) for the samples subjected to various heat treatments from 800 to 1200 °C. Obviously, pure and doped $BaTiO_3$ powders calcined at 800 °C were all cubic phase (c-$BaTiO_3$). With increasing calcination temperature, the (2 2 0) reflection split into (2 2 0) and (2 0 2) reflections of tetragonal (t-) $BaTiO_3$. Two mol% Mn dopant enhanced the splitting at a lower

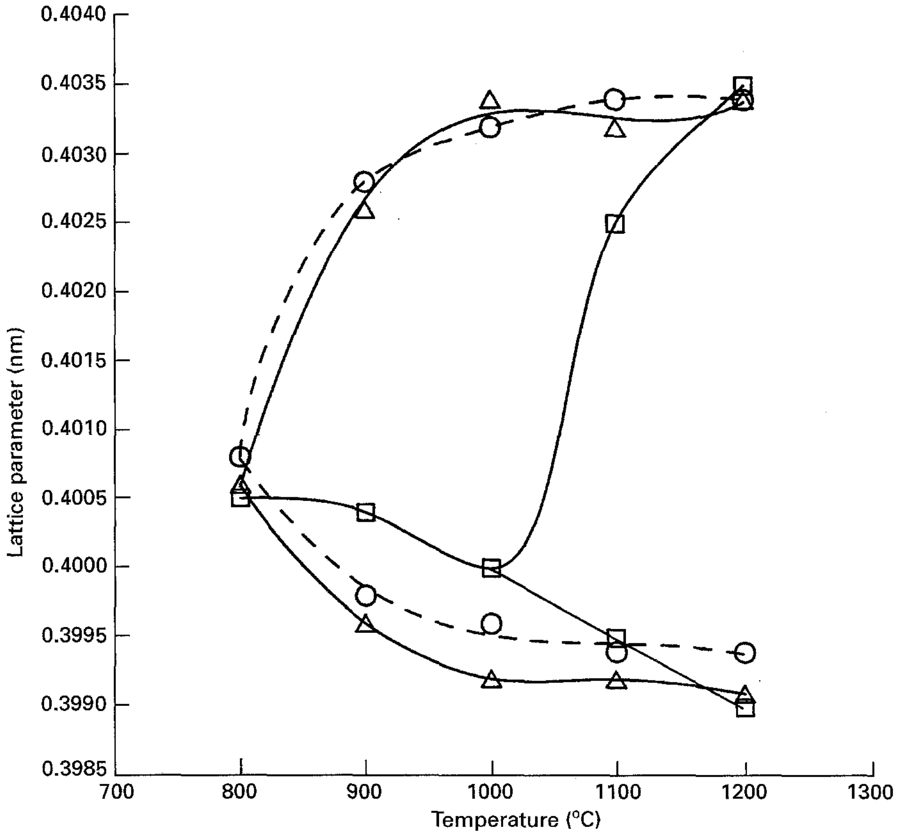


Figure 2 Variations of lattice parameter, *a* and *c*, of pure and doped $BaTiO_3$ powders with various calcination temperatures. Key: ○ BT; □ La 2 mol%; △ Mn 2 mol%.

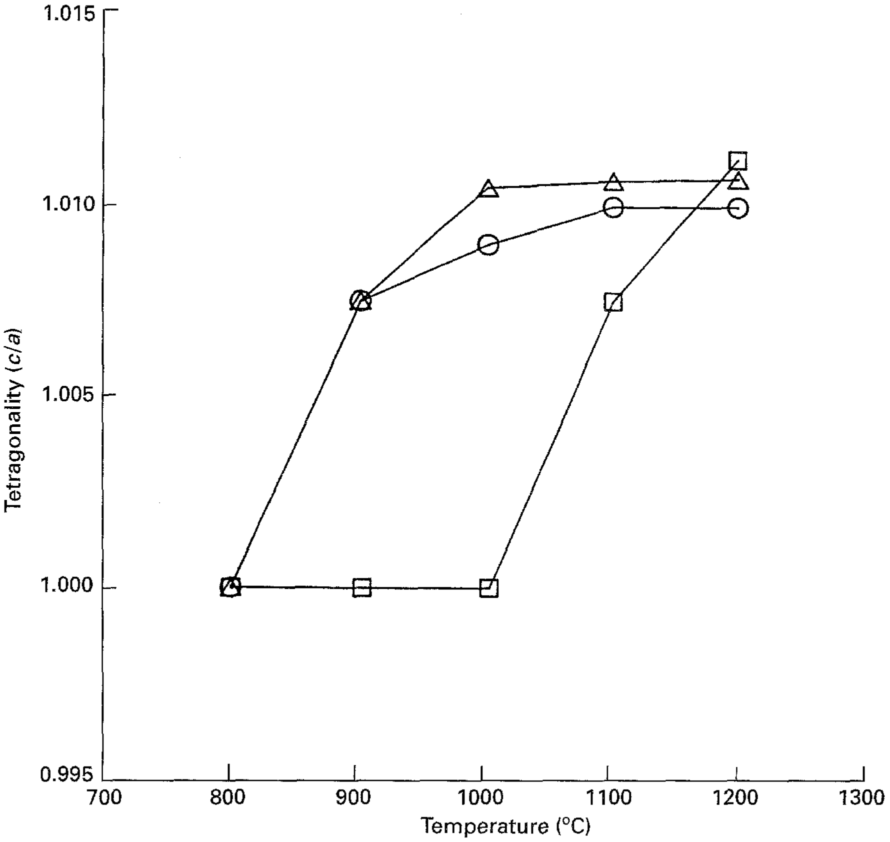


Figure 3 Changes in tetragonality of pure and doped $BaTiO_3$ powders with calcination temperatures. Key: ○ BT; □ La 2 mol %; △ Mn 2 mol %.

calcination temperature (900 °C), followed by the pure $BaTiO_3$ at 900 °C. However, doping with the same amount of La suppressed splitting until the temperature was increased to 1100 °C. Therefore, the La-doped $BaTiO_3$ powders could remain as a cubic perovskite phase when calcined at up to 1000 °C for 2 h.

3.2. Lattice parameters

Results for the lattice parameter measurements of the calcined $BaTiO_3$ powders are shown in Fig. 2. This figure indicated that ionic substitutions of the larger Ba^{+2} and Ti^{+4} by the smaller La and Mn would slightly shrink the lattice volume. The tetragonal phase was obtained by calcining at around 900 °C for the pure and Mn-doped $BaTiO_3$ powders. While for the La-doped powders, the calcination temperature increased to about 1100 °C. Tetragonality (*c*/*a*) for the Mn-doped $BaTiO_3$ is larger than that for the pure $BaTiO_3$ obtained at the same calcination temperature ($\geqslant$ 900 °C) (Fig. 3); whereas, that for the La-doped one is significantly smaller.

3.3. Crystallite size

The mean crystallite size of $BaTiO_3$ powders and La- or Mn-doped $BaTiO_3$ powders calcined at various temperatures are shown in Fig. 4 using TEM micrograph techniques (Fig. 5a–c). Although the three sizes were different from each other, the difference was small, i.e. around 30, 40, 65 nm for pure, La and Mn doped powders calcined at 800 °C, respectively.

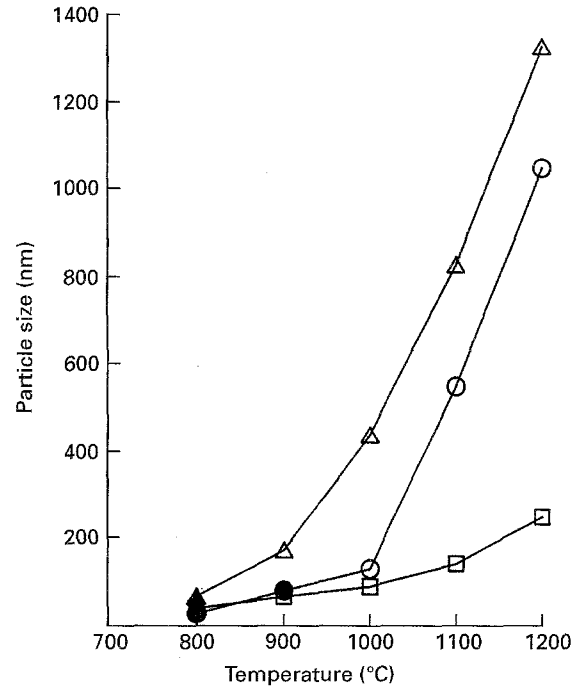


Figure 4 Crystallite sizes of pure and doped $BaTiO_3$ powders after calcination at different temperatures. Key: cubic — ● BT; ■ La 2 mol %; ▲ 2 mol %; tetragonal — ○ BT; □ La 2 mol %; △ Mn 2 mol %.

Doping with the ions seemed to cause different growth behaviours toward the crystallites and the size deviations obtained at each calcination temperature between the pure and the ion-doped, and between the two ion-doped titanates became manifest. With increasing calcination temperature, however, the rate of crystallite growth was favoured by the Mn-dopant, while inhibited by the La-dopant.

4. Discussion

4.1. Effects of dopants on crystallite growth

Previous studies have revealed that $BaTiO_3$ crystallite growth is enhanced by the presence of oxygen vacancies [6]. The oxygen diffusion, would be the rate-controlling step for the growth of $BaTiO_3$ crystallites as its capability depends on the concentration of oxygen vacancies. Thus, defects arising from different dopants may individually play a significant role in the growth of $BaTiO_3$ crystallites.

Chan *et al.* [12] have reported that the defect chemistry of $BaTiO_3$ with acceptor is as below:

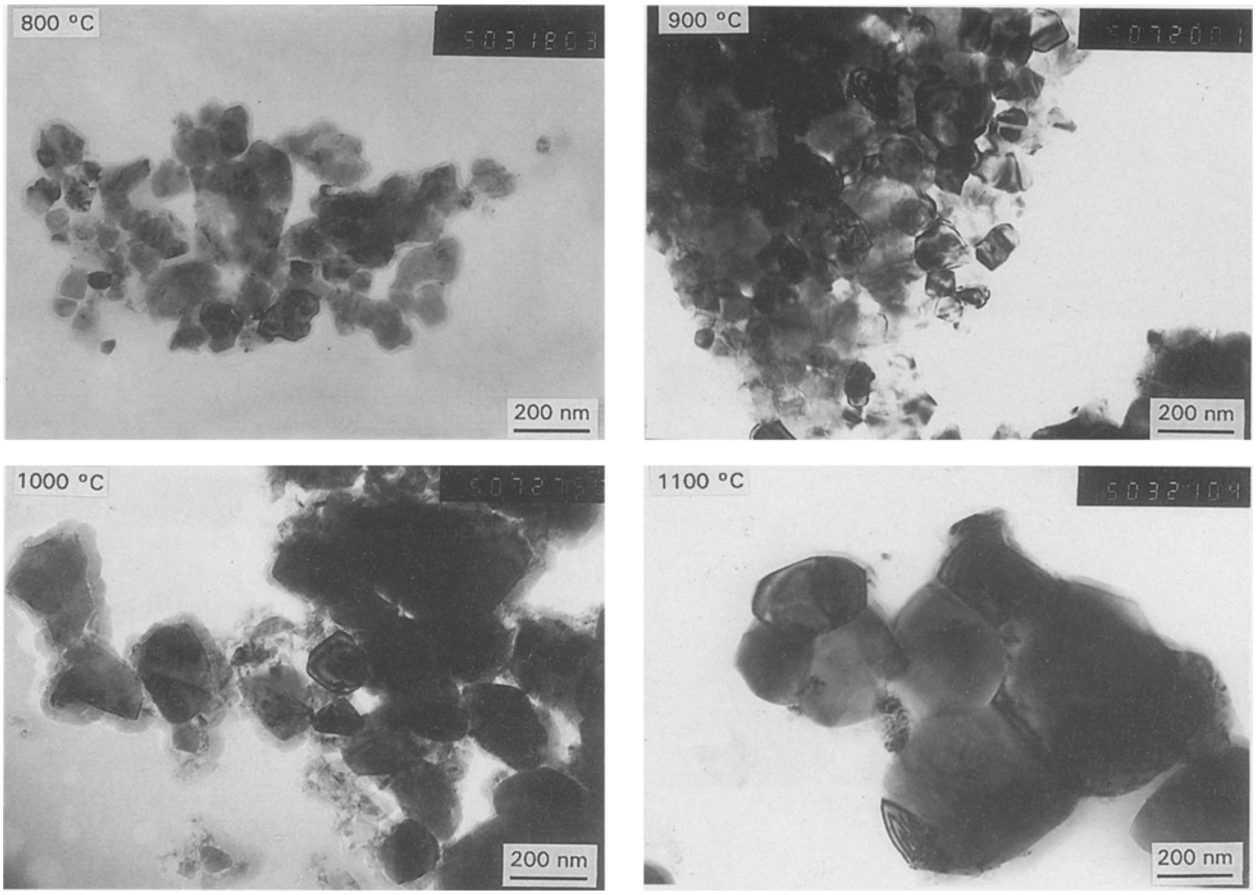
$$MnO \xrightarrow{BaTiO_3} Mn_{Ti} + V_O^{\cdot\cdot} + O_O^x$$

$BaTiO_3$ doped with acceptors will create oxygen vacancies.

Hagemann and Hennings [4] concluded that the oxygen concentration in $BaTiO_3$ increased with the amount of manganese dopant added. However, the defects produced at a temperature (lower than 1300 °C) due to the substitution of Ba^{+2} sites by La^{+3} could be barium and/or titanium vacancies [13, 14]. Moreover, Shirasaki and co-workers [15–17] pointed out that oxygen vacancies decreased at similar lower temperatures when the lanthanum ion was added. Therefore, when the substitution of La^{+3} for Ba^{+2} takes place, the charge is compensated for by cation vacancies:

$$La_2O_3 \xrightarrow{BaTiO_3} 2\,La_{Ba}^{\cdot} + 3O_O^x + V_{Ba}'' \text{ (or } V_{Ti}'''' \text{)}$$

The consequence is that, by adding La and Mn dopants, two different types of crystallite growth ultimately resulting in two different crystallite sizes for La- and Mn-doped $BaTiO_3$ would be obtained at the same calcination temperature and duration (as shown



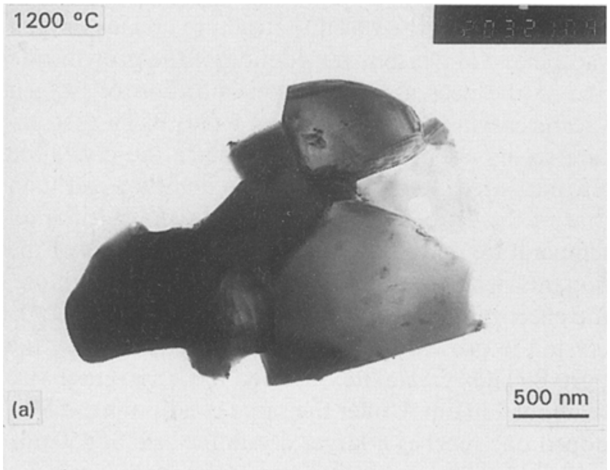


Figure 5 TEM micrographs of (a) pure, (b) La-doped and (c) Mn-doped $BaTiO_3$ powders at different calcination temperatures.

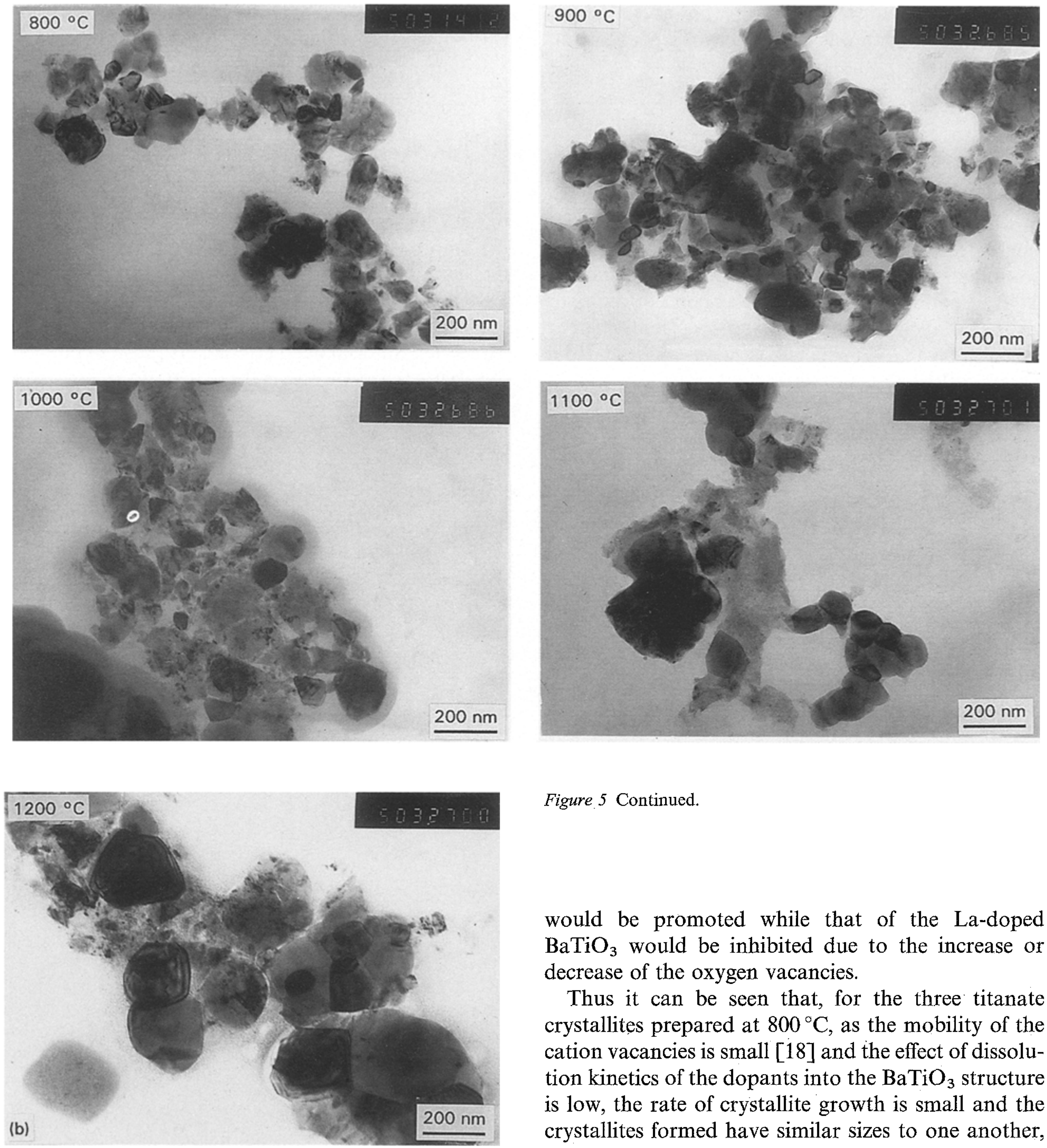


Figure 5 Continued.

in Fig. 5). Furthermore, as the mobility of the cation vacancies may be smaller at lower temperatures (800 °C) [18] than that at higher temperatures, the size difference between the pure and the La-doped or the pure and the Mn-doped $BaTiO_3$ crystallites may become larger if the calcination temperature is increased. Additionally, for the three titanates (pure, La-doped and Mn-doped $BaTiO_3$), characteristic growth rates would possibly occur individually. This is because the kinetics of dopant dissolution into the $BaTiO_3$ structure and the oxygen vacancies subsequently formed were distinctive for different ion species. This would eventually be manifested by different rates of crystal growth for the La- or Mn-doped $BaTiO_3$, which presumably deviate from that of the pure $BaTiO_3$. Moreover, the crystallite growth of Mn-doped $BaTiO_3$ would be promoted while that of the La-doped $BaTiO_3$ would be inhibited due to the increase or decrease of the oxygen vacancies.

Thus it can be seen that, for the three titanate crystallites prepared at 800 °C, as the mobility of the cation vacancies is small [18] and the effect of dissolution kinetics of the dopants into the $BaTiO_3$ structure is low, the rate of crystallite growth is small and the crystallites formed have similar sizes to one another, being about 30 nm for pure $BaTiO_3$ and 40 and 65 nm for La- and Mn-doped $BaTiO_3$ (Fig. 4). However, significant effects on the enhancement of growth rate for the Mn-doped $BaTiO_3$ powders seem to be initiated at the 800 °C stage because the dissolution of manganese into the $BaTiO_3$ structure creates oxygen vacancies. Conversely, retardation of the growth rate due to the decrease in the concentration of oxygen vacancies when La^{+3} is dissolved into $BaTiO_3$ structure seems not to occur (Fig. 4) since the crystallite size measured (40 nm) may even be slightly larger than that of the pure $BaTiO_3$ (30 nm). As the calcination temperature increased, the dissolution kinetics of the dopants would increase significantly. Furthermore, the effect of doping with Mn and La on the $BaTiO_3$ crystallite growth became manifest. At 1000 °C, the pure $BaTiO_3$ crystallite obtained has an average size of about 150 nm. Under the same conditions the Mn-doped one reaches a larger crystallite size of 450 nm, and the La-doped one only grows beyond 85 nm.

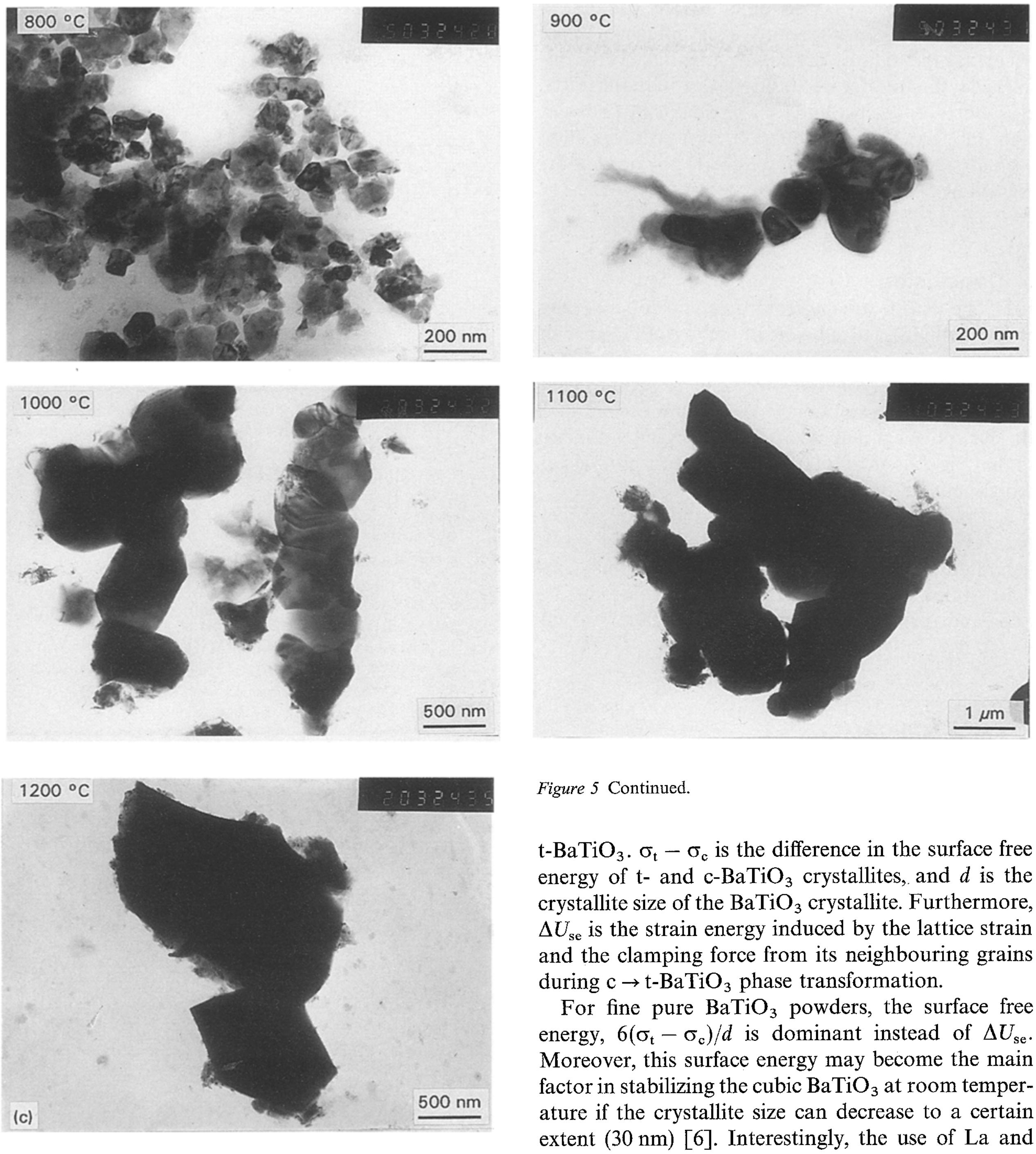


Figure 5 Continued.

4.2. Effects of dopants on c → t-BaTiO$_3$ phase transformation

The c-BaTiO$_3$ crystallite that exists at room temperature eventually is metastable. Considering that the phase stability for BaTiO$_3$ crystallites can exist as the c or t-phase down to submicrometres size, two critical thermodynamical factors should be solved [19]: (a) surface energy difference between the cubic and the tetragonal BaTiO$_3$, and (b) strain energy due to internal lattice distortion, being induced by the occurrence of the defects, along with the clamping force formed from its neighbouring crystallites.

$$\Delta G = -\Delta G_v + 6(\sigma_t - \sigma_c)/d + \Delta U_{se} \quad (1)$$

where ΔG is the free energy of a spherical microcrystal. ΔG_v is the free energy difference between c- and t-BaTiO$_3$. $\sigma_t - \sigma_c$ is the difference in the surface free energy of t- and c-BaTiO$_3$ crystallites, and d is the crystallite size of the BaTiO$_3$ crystallite. Furthermore, ΔU_{se} is the strain energy induced by the lattice strain and the clamping force from its neighbouring grains during c → t-BaTiO$_3$ phase transformation.

For fine pure BaTiO$_3$ powders, the surface free energy, $6(\sigma_t - \sigma_c)/d$ is dominant instead of ΔU_{se}. Moreover, this surface energy may become the main factor in stabilizing the cubic BaTiO$_3$ at room temperature if the crystallite size can decrease to a certain extent (30 nm) [6]. Interestingly, the use of La and Mn dopants seems to bring the critical size for the c → t phase transformation to about 100 nm. This is possibly a result of the substitution of La and Mn for Ba and Ti, which occurs since the addition of La and Mn into BaTiO$_3$ structure will stimulate the problems of electroneutrality which must be compensated for by cation or anion vacancies. The presence of La and Mn cations thus enhances the lattice defects and, meanwhile, may induce microstrains [20], (ΔU_{se} in Equation 1). This eventually can stabilize the cubic phase of the doped BaTiO$_3$ powder at room temperature to a size larger than that of the pure BaTiO$_3$ crystallites. Notably, the as-obtained BaTiO$_3$ using hydrothermal synthesis [21] can exist as a c-phase and has a larger cell parameter. The crystallite size can be stable up to a size of 120 nm. It is believed that the stability mechanism can be resulted from the presence of OH$^-$ and cation vacancies in the structure [20], which is similar to that of the present study.

Conclusively, when the dopants are present in $BaTiO_3$ crystallites or grains, two influences must occur: (a) the rate of crystallite growth may be influenced; (b) an internal strain will be induced in the crystallites (or grains), and for a crystallite in a powder state the term ΔU_{se} in Equation 1 may still be large even though the clamping force exerted by neighbouring grains can be diminished.

5. Conclusion

1. The defects arising from different dopants play an influential significant role in the crystallite growth of $BaTiO_3$ powders. Growth of Mn-doped $BaTiO_3$ crystallites is promoted due to the increase in oxygen vacancies. The dissolution of lanthanum dopant into $BaTiO_3$ powders may decrease the oxygen vacancies so that the growth of $BaTiO_3$ crystallites is retarded at a high temperature ($\geqslant 900\,^\circ C$).

2. Pure $BaTiO_3$ powders with crystallites smaller than about 30 nm would exist as c-phase at room temperature. Doping with La and Mn may induce strain energy due to internal lattice distortion and bring the transition crystallite size to ~ 100 nm.

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