

## Chemical Preparation of Barium-Strontium Titanate

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The precursors of  $Ba_{1-x}Sr_xTiO_3$  ( $x=0.0-0.3$ ) were prepared by the rapid addition of aqueous solution of titanyl oxalate to the mixed aqueous solution of barium and strontium at room temperature. The optimum pH was theoretically calculated from the equilibrium constants and solubility products. The chemical formula of the precursors obtained corresponded to  $Ba_{1-x}Sr_xTiO(C_2O_4)_2 \cdot 4H_2O$  ( $x=0.0-0.3$ ) as determined by thermal gravimetric analysis. The precursors were converted to stoichiometric  $Ba_{1-x}Sr_xTiO_3$  ( $x=0.0-0.3$ ) with a particle size of 0.01-0.04  $\mu m$ . As increasing the amount of strontium substituted to barium sites, the structure of crystal changed from the tetragonal phase to the cubic and the unit cell volume was decreased.

### Introduction

Ever since Clabaugh *et al.*<sup>1</sup> reported that high-purity barium titanate of nearly perfect stoichiometry could be prepared by precipitating barium titanyl oxalate and subsequently converting this material to barium titanate by calcination, a variety of barium-strontium titanates has been prepared by oxalate coprecipitation and calcination.<sup>2,3</sup> These materials, when sintered as ceramic disks after doping with such rare earth metals like La and Sm, give a substantial positive temperature coefficient (PTC) of electrical resistance in the region of the tetragonal to cubic phase transition. The lowering of the transition temperature is achieved by increasing the extent of partial substitution of strontium for barium.

In chemical coprecipitation, strontium gives a problem in that it is quite soluble in aqueous oxalic acid and an excess of strontium must be added to achieve stoichiometry.<sup>2</sup> Schrey modified the coprecipitation method and reported that the precipitation at pH greater than 5 gives a near stoichiometric titanate from the hot (85 °C) oxalic acid solution having no excess strontium.<sup>3</sup> However, this report did not specify a pH range. And the precipitate obtained at pH greater than 5 is a mixture of oxalates of alkaline earth metals and  $TiO(OH)_2$ . The formation of the mixture could be a cause of the high temperature for calcination in the formation of titanates of alkaline earth metals.<sup>4</sup> Moreover, the resulting precipitate is very gelatinous and difficult to filter.

It is desirable to develop a method for the preparation of stoichiometric oxalates by precipitating quantitatively the constituting ions in the starting solution. Additionally, the particle size of the barium titanate prepared by the Clabaugh's method is very large because of the high reaction temperature and slow titration of the mixed solution of barium and titanium solution to the oxalate solution. A further modification is therefore desirable to obtain a stoichiometric and high density ceramics.

In the present study, the Clabaugh's method was revised by noticing that stable titanyl oxalate anion  $TiO(C_2O_4)_2^{2-}$  with an excess of oxalate anions and an aqueous solution of alkaline earth metals formed oxalate precipitates in the range of pH 4 to 5 at room temperature. The range of pH was

calculated from the equilibrium constants and solubility products. The aqueous titanyl oxalate was instantaneously added to an aqueous solution with stoichiometric quantities of barium and strontium. The precipitates thus prepared were easily filterable. The oxalate precipitates obtained were converted by thermal decomposition to titanates which were found to be homogeneous, stoichiometric and very fine powder. The particle size of powder was measured by x-ray peak broadening effect, and changes of a lattice constant ratio  $c/a$  and a unit cell volume along with increasing the amount of strontium substituted to barium sites were also studied.

### Experimental

Weighed quantities of reagent-grade barium and strontium nitrate were each dissolved in distilled water and diluted to 0.25 M solution for Ba and Sr. The metal content in each solution was determined by gravimetric analysis.<sup>5</sup> The  $TiO(NO_3)_2$  solution was prepared following the processes proposed by Yamamura *et al.*<sup>6</sup> and stored in a refrigerator. Ti content in the solution was determined by gravimetric analysis as titanium oxide. The oxalic acid solution (0.12 M) was prepared by dissolving an appropriate quantity of oxalic acid dihydrate in distilled water.

The titanyl oxalate solution was prepared by adding slowly the  $TiO(NO_3)_2$  solution to the oxalic acid solution. The concentration of hydrogen ion was adjusted to pH 4.5 by an aqueous ammonium hydroxide solution.<sup>7</sup> The advantage of this method is that a stable solution of titanyl oxalate anions is formed at room temperature and is not as subject to hydrolysis. A first series of mixed solution were prepared in which the strontium to barium ratio was maintained at a range of 0.0 to 0.3. The solution of titanyl oxalate anion was instantaneously added to the mixed solution. The final mixed solution was readjusted to pH 4.5 by adding aqueous ammonium hydroxide solution and stirred at 1,200 rpm for 3 hours. It should be noted that the quantity of oxalic acid was 20% in excess over the stoichiometric amount required to produce oxalate precipitates, and that the volume of aqueous solution of oxalic acid (0.12 M) was three times

greater than the summed one of original aqueous solution of  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{TiO}^{2+}$ .

The oxalate precipitates were filtered and washed with chilled water and finally with acetone. The precipitates were dried at  $100^\circ\text{C}$  for 12 hours and then calcined at  $900^\circ\text{C}$  for 2 hours to produce  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ( $x=0.0-0.3$ ). The barium-strontium-titanium ratio was measured by the wet analysis and inductively coupled plasma. In wet analysis, the calcined powders were dissolved in concentrated sulfuric acid by heating. After cooling, dropwise titration of distilled water brought about the precipitation of  $\text{BaSO}_4$  and  $\text{SrSO}_4$ . Weighing the precipitates were used for the determination of the sum of barium and strontium. The amount of titanium presented in the filtrate, was analyzed by UV spectrophotometer (Kontron, Uvikon 860) using hydrogen peroxide as a coloring reagent.

In analysis by inductively coupled plasma spectroscopy, the titanate powder was dissolved in concentrated hydrochloric acid in high strength acid digestion bomb (Parr, 4746) by heating at  $170^\circ\text{C}$  for 3 hours. The dissolved solution was transferred to a 100 mL volumetric flask. The contents of barium, strontium and titanium were analyzed by the inductively coupled plasma spectroscopy (TJA, ICAP 61E) and compared with the results of the wet analysis.

The thermal analysis of the oxalate precipitates was carried out by thermal gravimetric analysis (Du Pont, 951). The morphology of particle was measured using a scanning electron microscopy (JEOL, JAX-840). The crystal structures were determined with x-ray diffractometer (Rigaku, D/MAS-3C) by using Ni-filtered Cu  $K\alpha$  radiation.

The particle size was calculated by x-ray peak broadening effect, which is known as Scherrer formula<sup>8</sup> given by following equation,

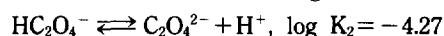
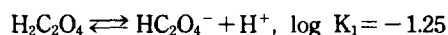
$$t = \frac{0.9\lambda}{B \cos\theta_B}$$

where  $t$  is the particle size,  $\lambda$  the x-ray wavelength,  $B$  the half-width of maximum intensity (radian) and  $\theta_B$  the Bragg diffraction angle.

## Results and Discussion

It is desirable to establish a method for completely precipitating the constituting ions and for giving a finely divided, but readily filterable precipitates. The controlling to an optimum pH appears to be practical. According to the following considerations, all conditions for obtaining the desired precipitates are seem to be satisfied in the pH 4 to 5 range.

In the aqueous oxalate system, the following equilibria are considered,<sup>9</sup>



Considering the  $\text{C}_2\text{O}_4^{2-}$  ion as the main precipitant, it can be shown that the fraction of  $\text{C}_2\text{O}_4^{2-}$  takes the following form

$$\begin{aligned} \alpha_0 &= \frac{[\text{C}_2\text{O}_4^{2-}]}{A_7} = \frac{[\text{C}_2\text{O}_4^{2-}]}{[\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]} \\ &= \frac{K_1 K_2 [\text{H}^+]^{-2}}{1 + K_1 [\text{H}^+]^{-1} + K_1 K_2 [\text{H}^+]^{-2}}, \end{aligned}$$

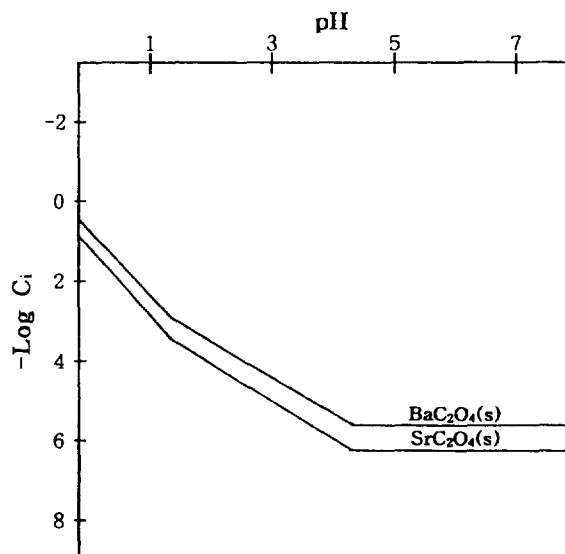
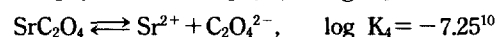
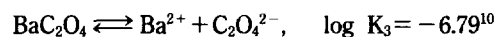


Figure 1.  $-\text{Log } C_i$  vs. pH diagram for  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  oxalate systems.

where  $A_7$  is total oxalate concentration (0.12 M). By applying logarithm the following reduced forms approximately result at given pH ranges.

$$\begin{aligned} \log \alpha_0 &= -(\text{p}K_1 + \text{p}K_2) + 2\text{pH}, & \text{pH} < \text{p}K_1 \\ &= -\text{p}K_2 + \text{pH}, & \text{p}K_1 < \text{pH} < \text{p}K_2 \\ &= 0, & \text{p}K_2 < \text{pH} \end{aligned}$$

For the calculation of relative concentration of Ba and Sr species versus pH, the following equilibria are considered.

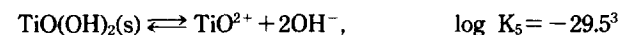


By applying logarithm to above equations and substituting estimated values or above equations for  $A_7$ ,  $\alpha_0$ ,  $K_3$  and  $K_4$ , the following forms approximately result at given pH ranges.

$$\begin{aligned} \log [\text{Ba}^{2+}] &= \log K_3 - \log A_7 - \log \alpha_0 \\ &= -0.35 - 2\text{pH}, & \text{pH} < \text{p}K_1 \\ &= -1.60 - \text{pH}, & \text{p}K_1 < \text{pH} < \text{p}K_2 \\ &= -5.87, & \text{p}K_2 < \text{pH} \\ \log [\text{Sr}^{2+}] &= -0.81 - 2\text{pH}, & \text{pH} < \text{p}K_1 \\ &= -2.06 - \text{pH}, & \text{p}K_1 < \text{pH} < \text{p}K_2 \\ &= -6.33, & \text{p}K_2 < \text{pH} \end{aligned}$$

The calculated results are given in Figure 1, which shows  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  are quantitatively precipitated as oxalates at pH greater than 4 whenever the initial concentrations are greater than  $4 \times 10^{-2}$  and  $2 \times 10^{-2}$  M, respectively. The precipitation of both metals with  $\text{OH}^-$  or  $\text{CO}_3^{2-}$  should also be considered. However, the formation of the precipitates can occur at pH greater than 7 and not considered at present studies.

For the Ti species in aqueous solution, the following equilibria are given,



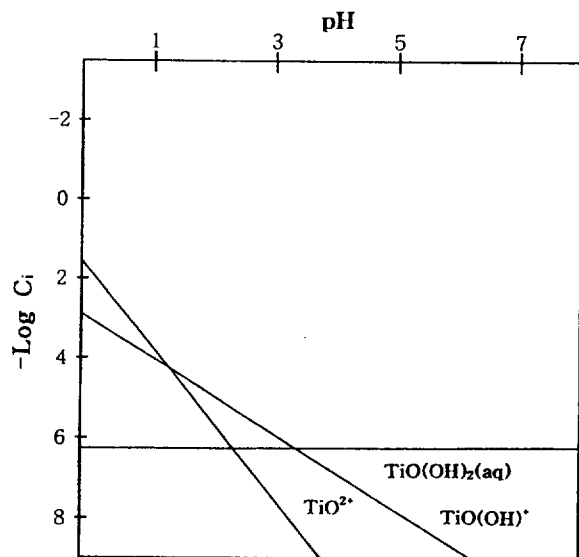
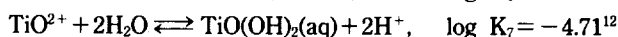
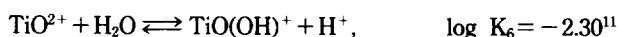


Figure 2.  $-\text{Log } C_i$  vs. pH diagram for  $\text{TiO}^{2+}$ - $\text{OH}^-$  system.



Using the above equilibrium constants, the relative concentrations of  $\text{TiO}^{2+}$ ,  $\text{TiO(OH)}^+$  and  $\text{TiO(OH)}_2(\text{aq})$  ions are given as follows

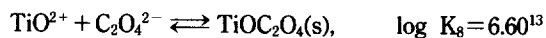
$$\log [\text{TiO}^{2+}] = -1.50 - 2\text{pH}$$

$$\log [\text{TiO(OH)}^+] = -3.80 - \text{pH}$$

$$\log [\text{TiO(OH)}_2(\text{aq})] = -6.21$$

The approximately calculated results are given in Figure 2, which shows that  $\text{TiO(OH)}_2$  is precipitated at the pH greater than 3.

But for the Ti species in aqueous oxalate solution, the  $\text{OH}^-$  ions are competing with  $\text{C}_2\text{O}_4^{2-}$  ions. The equilibria between  $\text{TiO}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  ions and the relative concentrations of  $\text{TiO}^{2+}$  and  $\text{TiO(C}_2\text{O}_4)_2^{2-}$  ions are given.



$$\begin{aligned} \log [\text{TiO}^{2+}] &= -0.16 - 2\text{pH}, & \text{pH} < \text{p}K_1 \\ &= -1.42 - \text{pH}, & \text{p}K_1 < \text{pH} < \text{p}K_2 \\ &= -5.68, & \text{p}K_2 < \text{pH} \end{aligned}$$

$$\begin{aligned} \log [\text{TiO(C}_2\text{O}_4)_2^{2-}] &= -4.48 + 2\text{pH}, & \text{pH} < \text{p}K_1 \\ &= -1.97, & \text{p}K_1 < \text{pH} < \text{p}K_2 \\ &= 6.56 - 2\text{pH}, & \text{p}K_2 < \text{pH} \end{aligned}$$

The relative concentrations of  $\text{TiO}^{2+}$  and  $\text{TiO(C}_2\text{O}_4)_2^{2-}$  calculated by using the  $K_8$  and  $K_9$  are given in Figure 3. The precipitate  $\text{TiOC}_2\text{O}_4$  is formed at the pH lower than 1. As the pH increased, the  $\text{TiO(C}_2\text{O}_4)_2^{2-}$  anion is formed predominantly.

Figure 2 and 3 show that the formation of  $\text{TiO(C}_2\text{O}_4)_2^{2-}$  anions is predominant in the pH 1 to 5 range when the concentration of  $\text{TiO}^{2+}$  ions are approximately less than  $10^{-3}$  M. The results agree with the studies described by Babko

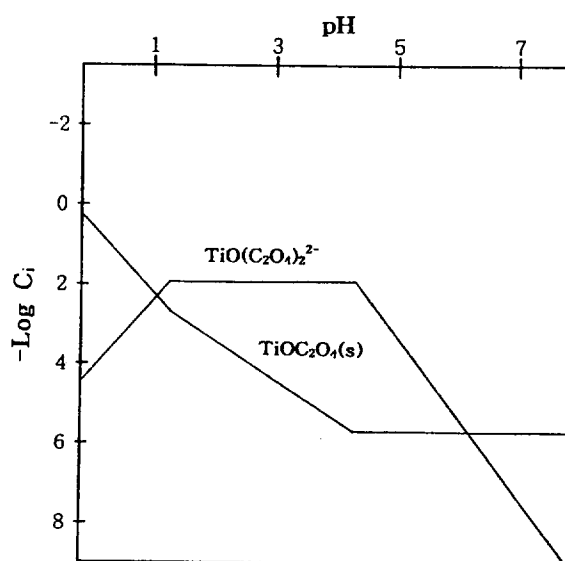


Figure 3.  $-\text{Log } C_i$  vs. pH diagram for  $\text{TiO}^{2+}$ - $\text{C}_2\text{O}_4^{2-}$  system.

Table 1. Result of wet analysis for  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$

x	0.0	0.1	0.2	0.3
(Ba+Sr)/Ti	0.991	0.989	0.993	0.989
Mole Ratio				

and Dubovenko,<sup>13</sup> who reported that the  $\text{TiO}^{2+}$  ion will not precipitate in the form of hydroxide in the presence of an excess of oxalic acid at the range of pH less than 5.

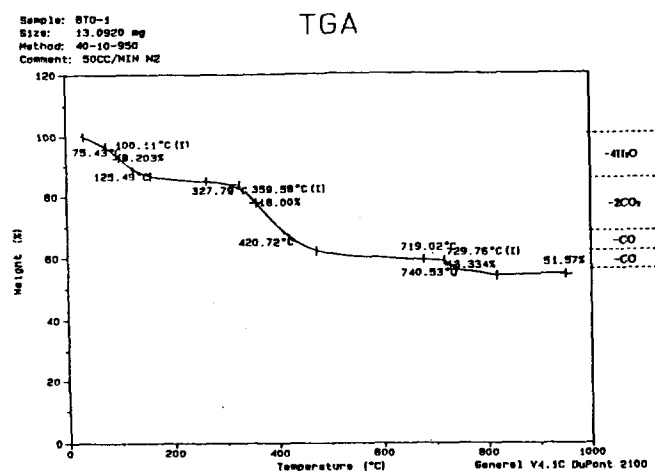
The above considerations about optimum pH indicate that  $\text{TiO}^{2+}$  ions can be stabilized at room temperature by forming  $\text{TiO(C}_2\text{O}_4)_2^{2-}$  ions in the pH 1 to 5 range. And  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions can be stabilized by formation of oxalate precipitates at pH greater than 4. From these results, it can be concluded that a relatively narrow pH range of 4 to 5 as well as the instantaneous addition of aqueous titanyl oxalate solution to the solution with a stoichiometric quantities of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions can be adopted for optimum condition in the preparation of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO(C}_2\text{O}_4)_2 \cdot y\text{H}_2\text{O}$ , which is a precursor of stoichiometric  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  with a very fine particle size.

The present method using an optimum pH range of 4 to 5 and the instantaneous addition of stable solution of titanyl oxalate anion to the solution with stoichiometric amounts of barium and strontium ions has an apparent advantage. The oxalate precipitates were prepared at room temperature and easily filtered. The analytical results of the wet analysis and the inductively coupled plasma spectroscopy for the calcined powders are given in Table 1 and 2. It can be seen that the stoichiometric  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ( $x=0.0-0.3$ ) powder is achieved because of a quantitative precipitation of constituting ions. At pH lower than 4, the stoichiometry could be poor as shown in Figure 1. At pH greater than 5, hydroxide precipitates of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO(OH)}_2 \cdot \text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}$  could be formed, which is very gelatinous and difficult to filter and could be a cause of requiring a higher calcination temperature.<sup>34</sup>

**Table 2.** Analytical result of Ba and Sr in  $Ba_{1-x}Sr_xTiO_3$  by inductively coupled plasma

x	Starting Solution <sup>†</sup>		Calcined Precipitate <sup>†</sup>	
	Ba	Sr	Ba	Sr
0.0	1.000	0.000	0.985	0.000
0.1	0.900	0.100	0.893	0.101
0.2	0.800	0.200	0.771	0.217
0.3	0.700	0.300	0.679	0.319

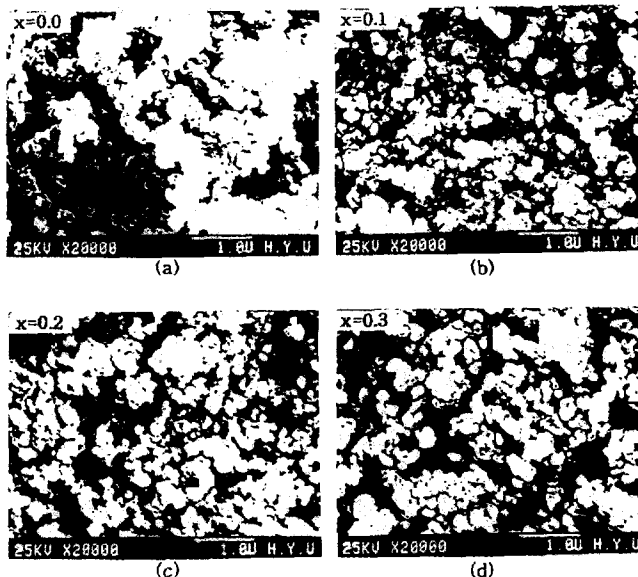
<sup>†</sup>The titanium content was normalized as unity.

**Figure 4.** Thermal gravimetric analysis of  $Ba_{1-x}Sr_xTiO(C_2O_4)_2 \cdot yH_2O$  ( $x=0.0$ ).

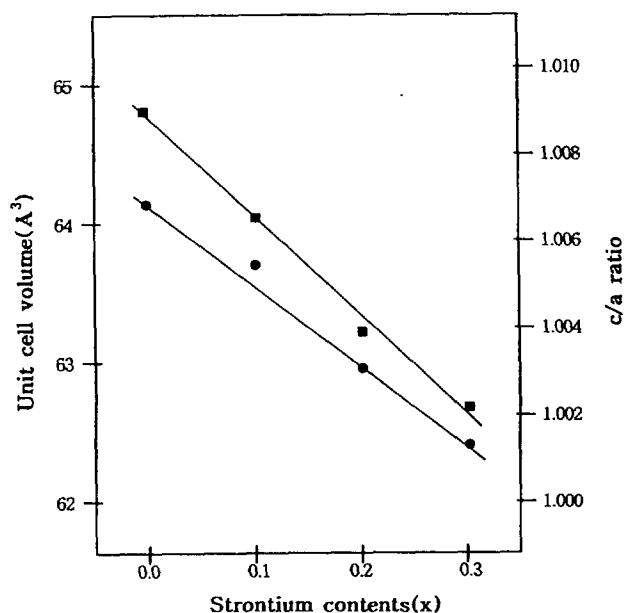
Thermal gravimetric analysis (TGA) was made with oxalate precipitates obtained in the pH 4 to 5 range. Figure 4 shows the TGA curve for the sample in which barium is not substituted by strontium. The weight loss was 48.4 wt%, which was nearly equal to the calculated value of 48.1 wt% for barium titanyl oxalate prepared by the Clabaugh's method.<sup>1</sup> Thus the chemical formula of the oxalate obtained in this study could correspond to  $BaTiO(C_2O_4)_2 \cdot 4H_2O$  when the strontium was not substituted to the barium.

Figure 5 shows the scanning electron microscopic observation of the  $Ba_{1-x}Sr_xTiO_3$  ( $x=0.0-0.3$ ) powder. The powder consists of very fine spherical particles. The particle size was estimated in range of 0.01 to 0.1  $\mu m$ . Table 3 shows the variation of particle size as a function of the strontium addition. The particle size of powder was calculated from the Scherrer formula by x-ray peak broadening effect in the behavior of the (101) plane. As shown in Table 3, the particle size of the  $Ba_{1-x}Sr_xTiO_3$  ( $x=0.0-0.3$ ) series is around 0.01 to 0.04  $\mu m$ . The decreasing of the particle size and the broadening of X-ray peak are due to the radius of strontium ion smaller than that of the barium ion and the increasing of the amount of strontium addition to the barium sites.

Figure 6 shows the variations of the lattice constant ratio  $c/a$  and unit cell volume, which are calculated from the x-ray diffraction peaks by the behaviors of the (001), (101), (111), (002), (102), (112) and (202) planes. For  $x=0.0$  in the  $Ba_{1-x}Sr_xTiO_3$ , the crystal structure of  $BaTiO_3$  displays a tet-

**Figure 5.** SEM micrographs of  $Ba_{1-x}Sr_xTiO_3$  powder : (a)  $x=0.0$ , (b)  $x=0.1$ , (c)  $x=0.2$  and (d)  $x=0.3$ .**Table 3.** Particle size calculated from x-ray peak broadening effect for  $Ba_{1-x}Sr_xTiO_3$  powders

x	Diffraction angle( $\theta$ )	Half-Width (radian)	Particle Size ( $\mu m$ )
0.0	15.81	0.0037	0.0390
0.1	15.84	0.0068	0.0212
0.2	15.92	0.0105	0.0137
0.3	15.97	0.0110	0.0131

**Figure 6.** Variations of unit cell volume (●) and  $c/a$  ratio (■) for  $Ba_{1-x}Sr_xTiO_3$  as a function of strontium substitution to barium sites.

agonal phase with a  $c/a$  ratio of 1.009, which are almost agree with the results reported by King and Goo.<sup>14</sup> They reported that  $c/a$  ratio was 1.01 for  $\text{BaTiO}_3$  and was decreased with increasing calcium content in  $\text{Pb}_{1-x}\text{Ca}_x\text{TiO}_3$ . As greater amount of strontium added, the phase moves from the tetragonal phase to the cubic. For  $x=0.3$ , the crystal structure of  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  clearly shows the cubic (or pseudocubic) phase. The unit cell volume was decreased with increasing amount of strontium substitution to barium sites. As reported by Park *et al.*,<sup>15</sup> the unit cell volume was also linearly decreased by increasing the amounts of strontium addition to barium sites in  $\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_{0.995}\text{Ca}_{0.005}\text{O}_{2.995}$ . The radius of strontium ion is smaller than that of the barium ion. The change of the unit cell volume shown in Figure 6 was due to the substitution of strontium to the barium sites. The decrease of  $c/a$  ratio and unit cell volume along with the amount of strontium substitution to the barium sites shows that the strontium ion was completely substituted to the barium sites up to 30 mol% by the revised oxalate coprecipitation method at room temperature.

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## Rapid Quenching Dynamics of F Center Excitation by $\text{OH}^-$ Defects in KCl

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The rapid quenching dynamics of F center excitation by  $\text{OH}^-$  defects in KCl crystals are investigated by monitoring ground state absorption bleach recovery, using a picosecond streak camera absorption spectrometer. F center absorption bleach in  $\text{OH}^-$ -doped crystals shows three distinguishable recovery components with the current temporal resolution, designated as slow, medium and fast components. The slow one is due to the normal relaxation process of  $\text{F}^*$  centers as found in  $\text{OH}^-$ -free crystals. The others are consequent on energy transfer from electronically excited F centers to  $\text{OH}^-$ -vibrational levels. The fast component is a minor energy transfer process and resulting from the relaxation of somewhat distant, not the closest, associated pairs of  $\text{F}^*$  and  $\text{OH}^-$  defects. The energy transfer between widely separated  $\text{F}^*$  and  $\text{OH}^-$  defects opens up a recovery process *via* the medium component which is assisted by  $\text{OH}^-$  librations, lattice vibrations and  $\text{OH}^-$  dipole reorientations. The quenching behaviors of  $\text{F}^*$  luminescence and photoionization by  $\text{OH}^-$  are explained well by the relaxation process of the medium component.

## Introduction

Electronically excited F centers in alkali halides relax lattice-vibrationally within a few picoseconds at cryogenic temperature into the relaxed excited state.<sup>1</sup> The relaxed excited F centers ( $\text{F}^*$  centers) decay *via* radiative and nonradiative

transitions to the ground state and through ionization to the conduction band.<sup>2</sup>  $\text{F}^*$  centers usually emit a highly efficient, spectrally broad, long-lived and largely Stokes-shifted luminescence at cryogenic temperature,<sup>3</sup> although the radiative quantum efficiency depends on host.<sup>4</sup>  $\text{F}^*$  centers in potassium and rubidium halides have good radiation efficiencies close