

The Phase Diagram of CaTiO_3 - SrTiO_3

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Phase equilibria in the binary system CaTiO_3 - SrTiO_3 were studied above 1300°C. This system is characterized by a complete series of solid solutions, with a minimum in the solidus at 23 mol% SrTiO_3 and 1940°C. The volume change of the unit cell of CaTiO_3 as a function of composition shows very little deviation from Vegard's law for solid solutions. No immiscibility gap was found. © 1987 Academic Press, Inc.

Introduction and Previous Investigations

Because of the interest in the ferroelectric and dielectric properties of (Ba, Ca, Sr) TiO_3 solid solutions, considerable work has been done in this ternary system and subsequent binary systems. An X-ray study of compositions in this ternary system has been made by Durst *et al.* (1). The barium titanate-calcium titanate binary system has been studied by DeVries and Roy (2) and others (3, 4). The barium titanate-strontium titanate binary system has also been studied extensively (5-7). It has been found that there is complete solid solubility between barium titanate and strontium titanate, and between strontium titanate and calcium titanate. McQuarrie (8) also studied transitions from orthorhombic calcium titanate structure to the cubic strontium titanate structure along that binary. The transition between the barium titanate structure and that of strontium titanate has also been

thoroughly explored (2, 3). However, the previous studies of the ternary system did not include, to our knowledge, any experimental work regarding the solidus and the extent of liquid solubility in the calcium titanate-strontium titanate binary system probably due to experimental difficulties.

Experimental Procedure

The starting materials for CaTiO_3 synthesis were TiO_2 (p.a. Ventron) and CaCO_3 (p.a. Merck). TiO_2 was ball-milled for 1 hr in a zirconia mill to obtain particles with a mean diameter of approximately 2 μm . A mixture of CaCO_3 and TiO_2 was wet-milled. After drying, the material was pressed into a pellet and fired for 24 hr at 1100°C. After firing the pellet was crushed and the CaTiO_3 was used as starting material for experiments in the CaTiO_3 - SrTiO_3 system.

Samples containing 5, 10, 15, 20, 25, 30, 40, 50, 70, and 90 mol% SrTiO_3 (Transelco) were prepared. The materials were mixed in a dry state and were homogenized by

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ball-milling with ethyl alcohol. The slurries were dried at 110°C and pressed pellets were fired three times for 20 hr at 1000°C and once for 15 hr at 1300°C . After each firing the process of homogenization was repeated.

All experiments were carried out in a W-strip furnace, designed especially for work with high-temperature materials. Experiments were carried out in a protective helium atmosphere. A sample, positioned on a tungsten bed, was placed in the middle of the heating element. The temperature was measured with an optical pyrometer and a W3Re-W25Re thermocouple with a cold junction. The optical pyrometer was calibrated against the melting points of Pt and Al_2O_3 . The thermocouple was calibrated against the melting points of Pt, Rh, and Al_2O_3 . The estimated precision of the temperature measurements was $\pm 10^\circ\text{C}$ for the optical pyrometer and $\pm 5^\circ\text{C}$ for the W3Re-W25Re thermocouple.

Solidus and liquidus data were obtained by using several techniques. Previous studies have shown that this can be helpful in evaluating data taken at high temperatures in systems where there is difficulty distinguishing the primary phase from the secondary phase.

For determining solidus, small sintered pellets with a diameter of 3 mm were used. A sample was placed on a tungsten bed and heated to 1900°C at a heating rate of $20^\circ\text{C}/\text{min}$. Thereafter, a heating rate of $5^\circ\text{C}/\text{min}$ was applied. The sample was observed through the optical pyrometer. The temperature at which the first appearance of liquid (i.e., the first change in shape of the pellet) was observed was taken to be the solidus temperature. At this point, heating was stopped and the sample was quenched after being held at the temperature for some minutes.

Liquidus data were obtained in two ways. Pellets with the same composition were quenched at different temperatures

above the solidus temperature. Microstructural investigation provided the necessary data for construction of the liquidus line. The second technique was to mount a pellet in a loop made from tungsten wire. The end of melting resulted in the formation of a meniscus.

All samples that were used to obtain solidus and liquidus data were polished by established metallographic techniques and their microstructures were analyzed by optical and electron microscopy. EDX microanalysis of the samples was performed with a PGT 4 EDX microanalyzer attached to Leitz AMR 1600 T electron microscope.

The room temperature X-ray patterns of CaTiO_3 , SrTiO_3 , and solid solutions were taken on a Phillips Pw 17-10 diffractometer using Cu radiation. Lines with 2θ values up to 150° were recorded. The resulting patterns were indexed by comparison with standard X-ray patterns. From a knowledge of the *hkl* values and the Bragg angle of each line in the pattern, the lattice spacing was calculated.

Results and Discussion

The phase diagram for the CaTiO_3 - SrTiO_3 system constructed on the basis of experimental data (Fig. 1) shows a complete series of solid solutions with a minimum in the solidus at 1940°C and 23 mol% SrTiO_3 . The melting point of CaTiO_3 and SrTiO_3 were determined to be 1968°C and 2080°C , respectively, which is in good agreement with literature data (9). Temperatures measured with the optical pyrometer were on average 5°C lower than values obtained using the W3Re-W25Re thermocouple. A phase diagram was constructed using temperature readings that were measured with the thermocouple, since the conditions of a "black body," necessary for accurate pyrometer data, could not be obtained.

Microstructural examination showed that the liquid and solid phase are distinguish-

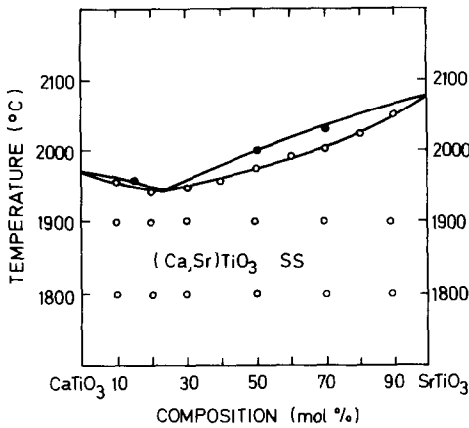


FIG. 1. Phase diagram of CaTiO_3 - SrTiO_3 constructed on the basis of experimental data.

able by optical microscopy, as well as by electron microscopy, in contrast to literature data concerning the BaTiO_3 - SrTiO_3 system (3) (Fig. 2).

EDX microanalysis of liquid and solid phases in the two-phase region showed results which were in agreement with the phase diagram of CaTiO_3 - SrTiO_3 (Fig. 1).

Liquid phase that formed within samples

containing 30 mol% SrTiO_3 or more contained less strontium than the solid phase. Liquid phase that formed within samples containing less than 20 mol% SrTiO_3 contained more strontium than the solid phase. The results thus confirm the existence of a minimum in solidus between 20 and 30 mol% SrTiO_3 . However, quantitative evaluation of the liquid phase composition by EDX technique does not give reliable data because of the semiquantitative nature of the measurements. Besides this, the liquid phase was not uniform in composition, as was proved by line analysis. It seems that the process of liquid phase formation is greatly affected by the heating and cooling treatment.

From the X-ray data, the lattice parameters of CaTiO_3 - SrTiO_3 solid solutions were calculated. The unit cell of SrTiO_3 is cubic, whereas CaTiO_3 has an orthorhombic unit cell in which the two cell parameters a and c differ very little (Table I) (10). X-ray data of sintered samples containing both starting materials showed a single phase over the entire range of composition. According to

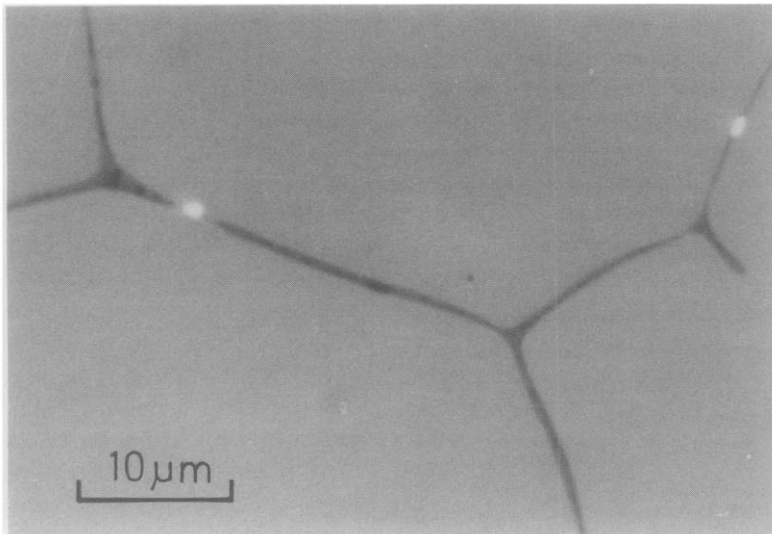


FIG. 2. Formation of liquid phase at the grain boundary at solidus temperature for a sample containing 10 mol% SrTiO_3 . Small particles of tungsten from the tungsten bed can be seen in the liquid phase.

TABLE I
EXPERIMENTALLY DETERMINED LATTICE
PARAMETERS OF CaTiO₃ AND SrTiO₃

Lattice parameter	CaTiO ₃ (10 ⁻¹⁰ m)	SrTiO ₃ (10 ⁻¹⁰ m)
<i>a</i>	5.383(1)	3.9075(3)
<i>b</i>	7.642(2)	
<i>c</i>	5.439(1)	

the work of McQuarrie (8), there is a structural transition from an orthorhombic unit cell to a tetragonal at ~55 mol% SrTiO₃, and a transition of a tetragonal unit cell to a cubic unit cell at 80 mol% SrTiO₃. However, no ferroelectric properties of solid solutions in this compositional range were discovered despite the obvious structural analogy with tetragonal BaTiO₃. Dielectric constants decreased steadily from a value of 200 for strontium titanate to a value of 100 for calcium titanate. Since it is very difficult to distinguish these structural transitions due to very slight changes in characteristic line patterns, the existence of tetragonal phase might be questionable, especially since there even appears to be a possibility that there is no tetragonal phase at all in pure calcium titanate (8). The

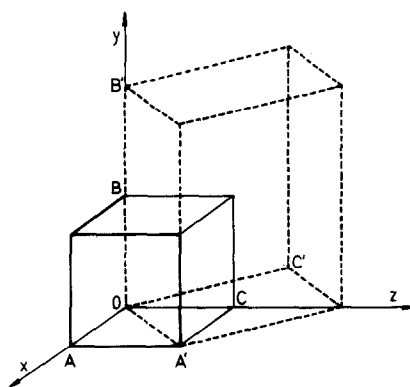


FIG. 3. Transformation of the cubic SrTiO₃ unit cell by a transformation matrix (101, 020 101). ABC, cubic SrTiO₃ cell; A'B'C', orthorhombic CaTiO₃ cell.

results of our experimental work cannot confirm the existence of tetragonal phase. X-ray patterns of solid solutions at room temperature showed no splitting of characteristic lines that could indicate an orthorhombic-tetragonal transition. The characteristic orthorhombic lines of CaTiO₃ are gradually transformed into the characteristic lines of the cubic structure of strontium titanate. At ~60 mol% strontium titanate, only displaced diffraction lines characteristic of a cubic structure are present. To demonstrate the continuous change from orthorhombic CaTiO₃ struc-

TABLE II
a, b AND c LATTICE PARAMETERS OF (Ca, Sr)TiO₃ SOLID SOLUTIONS AND
VOLUMES OF UNIT CELL

	<i>a</i> (10 ⁻¹⁰ m)	<i>b</i> (10 ⁻¹⁰ m)	<i>c</i> (10 ⁻¹⁰ m)	<i>V</i> (10 ⁻³⁰ m ³)
CaTiO ₃	5.383(1)	7.642(2)	5.439(1)	223.7(1)
(Ca _{0.95} Sr _{0.05})TiO ₃	5.399(3)	7.657(4)	5.441(2)	224.9(3)
(Ca _{0.9} Sr _{0.1})TiO ₃	5.410(2)	7.667(3)	5.442(2)	225.7(3)
(Ca _{0.8} Sr _{0.2})TiO ₃	5.427(2)	7.688(3)	5.453(2)	227.5(3)
(Ca _{0.7} Sr _{0.3})TiO ₃	5.445(1)	7.702(2)	5.455(1)	228.7(1)
(Ca _{0.5} Sr _{0.5})TiO ₃	5.472(2)	7.740(2)	5.476(1)	231.9(2)
(Ca _{0.3} Sr _{0.7})TiO ₃	5.493(2)	7.761(3)	5.499(2)	234.4(3)
(Ca _{0.1} Sr _{0.9})TiO ₃	5.512(5)	7.796(5)	5.522(3)	237.3(5)
SrTiO ₃ ^a	5.5260(3)	7.8150(3)	5.5260(3)	238.64(3)

^a Transformed unit cell, see text.

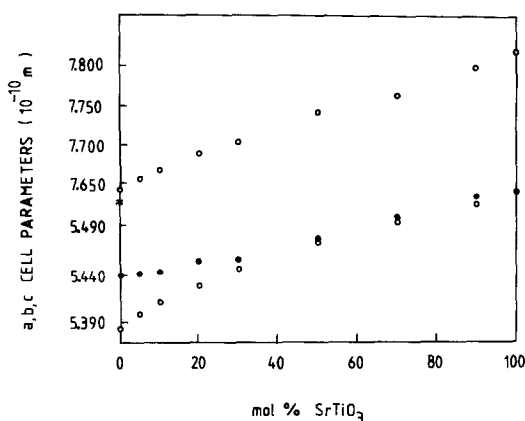


FIG. 4. Change of cell parameters as a function of composition.

ture to cubic SrTiO₃ structure, it is convenient to transform the cubic unit cell of SrTiO₃ by a transformation matrix (101, 020, 101) to a cell with cell parameters $a = c = 5.5260 \times 10^{-10}$ m, $b = 7.8150 \times 10^{-10}$ m (Fig. 3), which could be matched with CaTiO₃ unit cell (Table II). The volume of the cell corresponds to four volumes of the conventional cubic unit cell of the SrTiO₃ structure. The changes of cell parameters as a function of composition are presented in Fig. 4. The volume change of the unit cell was plotted as a function of composition. Displacement from Vegard's law is noticeable (Fig. 5). No separation of phases was

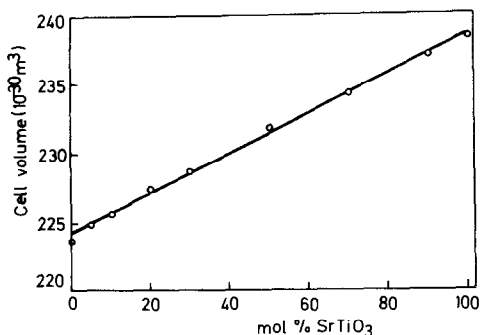


FIG. 5. Volume change of the unit cell as a function of composition.

found in mixtures heated at 1300°C for 2 days. It was concluded that an immiscibility gap goes not exist in the solid state when the temperature is higher than 1300°C.

Summary

Phase equilibria in the CaTiO₃-SrTiO₃ system were investigated by quenching, pellet melting, and X-ray and EDX microanalysis methods. The system is characterized by complete solid solubility, with a minimum in the solidus at 23 mol% strontium titanate at 1940°C. No immiscibility gap was found. It seems that the structural transition from orthorhombic calcium titanate to cubic strontium titanate occurs without an intermediate tetragonal phase. Vegard's law for ideal solid solutions is obeyed with little deviation.

Acknowledgments

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