LOW TEMPERATURE HYDROTHERMAL PROCESSING (<100°C) OF STOICHIOMETRIC $Ba_xSr_{1-x}TiO_3$ THIN FILMS AND POWDERS

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ABSTRACT

$Ba_xSr_{1-x}TiO_3$ (BST) thin films and powders were processed below 100°C by hydrolyzing Ti metal-organic precursors and TiO_2 powder in alkaline Ba/Sr containing aqueous solutions. Film and powder stoichiometries were examined by x-ray diffraction (XRD), and powder stoichiometries were measured by wavelength dispersive spectroscopy (WDS). Both XRD and WDS results showed that Sr cations were more readily incorporated in BST than Ba cations. A thermodynamic model is introduced to predict BST stoichiometry for pH and solution composition. The model is demonstrated for carbonates that also form hydrothermally with Ba and Sr in solid solution, showing good agreement with experimentally measured stoichiometries and confirming a higher reactivity of the Sr cation.

INTRODUCTION

Hydrothermal processing, while used routinely for crystal growth and powder production, has only recently been used to fabricate thin films [1-4]. In order to produce useful films, the stoichiometry of films with more than one cationic species must be controllable and predictable. Processing variables -including pH, cation and anion concentrations in solution, time, precursor structure, and impurities- are expected to affect film stoichiometry.

Previous work has considered the relationship between the concentration of Ba and Sr cations put into solution and the stoichiometry of the resulting BST film or powder. Lin and Yan [5] showed little deviation of BST powder stoichiometry from that of the cations in the solution. Others have also suggested that BST powder and film stoichiometries are the same as that of the cations in the solution [6,7]. On the other hand, Kajiyoshi et al.[8] have shown an appreciable favorability for the incorporation of Sr in BST. In all of these studies, BST stoichiometries were either estimated from lattice parameter measurements, or measured by energy dispersive x-ray spectroscopy (EDS) where overlapping Ba and Ti peaks must be deconvoluted.

In this study, $Ba_xSr_{1-x}TiO_3$ thin films were processed below 100°C by hydrolyzing Ti metal-organic precursors in alkaline Ba/Sr containing aqueous solutions. To facilitate quantitative x-ray analysis, BST powders were processed from a mixture of anatase and rutile TiO_2 powder. A thermodynamic model is introduced to predict BST stoichiometry for pH and solution composition. The model is demonstrated for $Ba_xSr_{1-x}CO_3$ solid solutions that also form hydrothermally.

EXPERIMENTAL PROCEDURE

BST thin films were processed by a reacting films of titanium metal-organic precursors in alkaline, aqueous solutions containing Ba and Sr. Titanium dimethoxy dineodecanoate (TDD) diluted with 70 vol% xylene was spun on glass substrates (9 x 9 x 0.2 mm) attached on one side to acrylic slides (15 x 15 x 1.5 mm). Spin coating was carried out at 5000 rpm for 15 s for each of two coatings per substrate. TDD films were dried and placed on a teflon ballast for reactions. $BaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 6H_2O$, and NaOH were dissolved in HPLC-grade water that had been boiled for at least 20 min to remove dissolved CO_2. After dissolution, solutions were filtered to remove any carbonates that had precipitated during mixing, and placed in a polyethylene bottle which was purged with Ar, sealed and stored in an oven at 80°C. The teflon ballast and substrates were placed in the bottles, backfilling with Ar, and reacted at 80°C for 30 min. The substrates were then removed, washed with warm CO_2-free de-ionized water, and dried.

BST powders were processed by reacting a mixture of anatase and rutile TiO_2 powder (P25, Degussa Corp. Ridgefield, NJ) in alkaline, aqueous solutions containing Ba and Sr,

prepared the same as above. TiO_2 powder was added to solutions and reacted at 80°C for 48 h. Following the reactions, powders were washed thrice in pH=10 HPLC-grade water and dried.

Carbonate powders were produced by allowing alkaline Ba and Sr containing solutions to react with atmospheric CO_2. Solutions were again prepared as above, excluding carbonate filtration, and placed in open beakers in an oven at 80°C. Due to evaporation, water was periodically added to solutions to maintain concentrations. After reacting for 9 h, the carbonate powders were filtered from the solutions and dried.

Film microstructures were examined in a scanning electron microscope (SEM) (JSM-35CF, JEOL Ltd., Tokyo, Japan). BST and carbonates were identified in both films and powders by XRD (Siemens D500, Madison, WI) using Cu Kα radiation. The stoichiometry of carbonates was determined by EDS (model 5502, Tracor Northern, Middleton, WI) using phase pure $BaCO_3$ and $SrCO_3$ standards. The overlap of Ba and Ti peaks in EDS necessitated the use of WDS (Cameca SX-50, Cameca Instruments Co., Stamford, CT) for determining BST stoichiometry. WDS analysis was performed at 15 kV accelerating voltage with 20 nA beam current and a 10 μm diameter spot size.
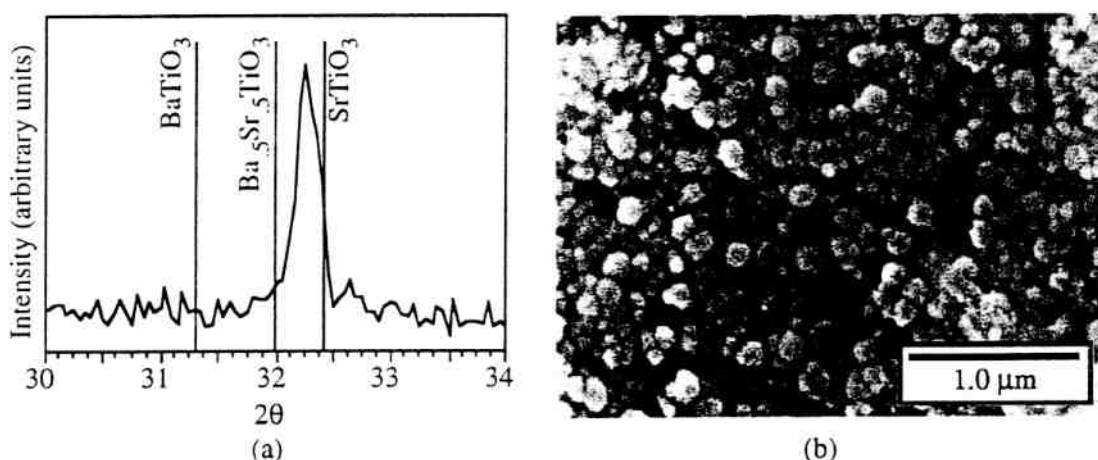

Figure 1. a) XRD pattern of a BST thin film processed in an alkaline, aqueous solution containing a 1:1 atomic ratio of Ba and Sr cations. Vertical lines correspond to x-ray standards. b) SEM micrograph of the film surface.

RESULTS AND DISCUSSION

Experiments

BST thin films were processed from solutions containing 1:1 atomic ratios of Ba and Sr cations. Figure 1 shows an XRD pattern and the microstructure of a BST film processed in a solution containing 0.05M $BaCl_2$, 0.05M $SrCl_2$, and 1.0M NaOH. The peak position shown indicates that the atomic ratio of Ba to Sr atoms in the BST was considerably less than 1:1. The exact stoichiometry was not determined because of the small amount of material present.

BST powders were also processed from solutions containing containing 1:1 atomic ratios of Ba and Sr cations. Figure 2a shows an XRD pattern of a BST powder processed from a solution containing 0.5M $BaCl_2$, 0.5M $SrCl_2$, 1.0M NaOH, and 0.9M TiO_2. Notice that after 48 h unreacted TiO_2 remained mixed with BST. Complete dissolution of Ti in water requires ≈6M NaOH [9]. However, when Ba and Sr was in excess to Ti, negligible amounts of unreacted TiO_2 remained after 48 h. The peak position shown Figure 2b indicates that, as was the case in the film, the atomic ratio of Ba to Sr atoms in the BST was considerably less than 1:1. The exact powder stoichiometry was determined to be $Ba_{.21}Sr_{.79}TiO_3(\pm.02)$ using WDS. Powders produced from other solutions with different Ba:Sr atomic ratios all revealed a consistent favorability for the incorporation of Sr cations in the BST.
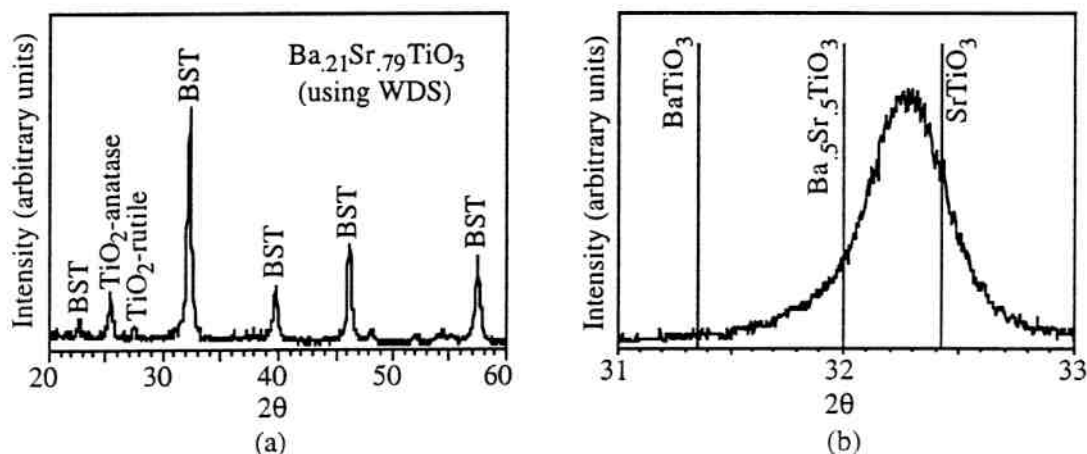
Figure 2. XRD patterns of a BST powder reacted 48 h at 80°C in an alkaline, aqueous solution with a 1:1 atomic ratio of Ba and Sr cations (0.5M $BaCl_2$, 0.5M $SrCl_2$, 1.0M NaOH, and 0.9M TiO_2), showing a) phase identification and b) powder stoichiometry.

Thermodyamic Modeling

Lencka and Riman [10] have developed electrochemical stability diagrams for hydrothermal systems based upon the equilibrium reaction constants for various species present. These diagrams are essentially a manipulation of a Pourbaix diagram, showing the effects varying cation concentrations at zero applied voltage [11]. Both types of diagrams show phase stability only. A more complete description is given by calculating a "cross-section" of a stability diagram, holding the concentration of the reaction determining cation species constant, and calculating the amounts of each species present for varying pH. Figure 3 schematically demonstrates this approach and its relation to stability diagrams. Note that an electrochemical stability diagram has not been developed for BST, only for $BaTiO_3$ and $SrTiO_3$ separately.
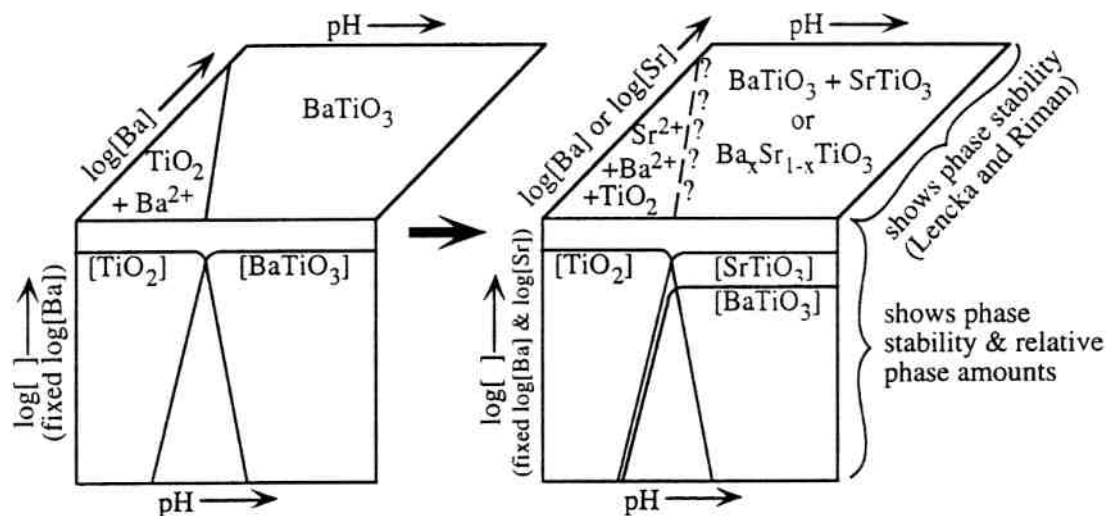
Figure 3. Interpretation with respect to electrochemical stability diagrams of the thermodynamic model for determining relative phase amounts. Note that only the upper half of the stability diagram [10] is shown.
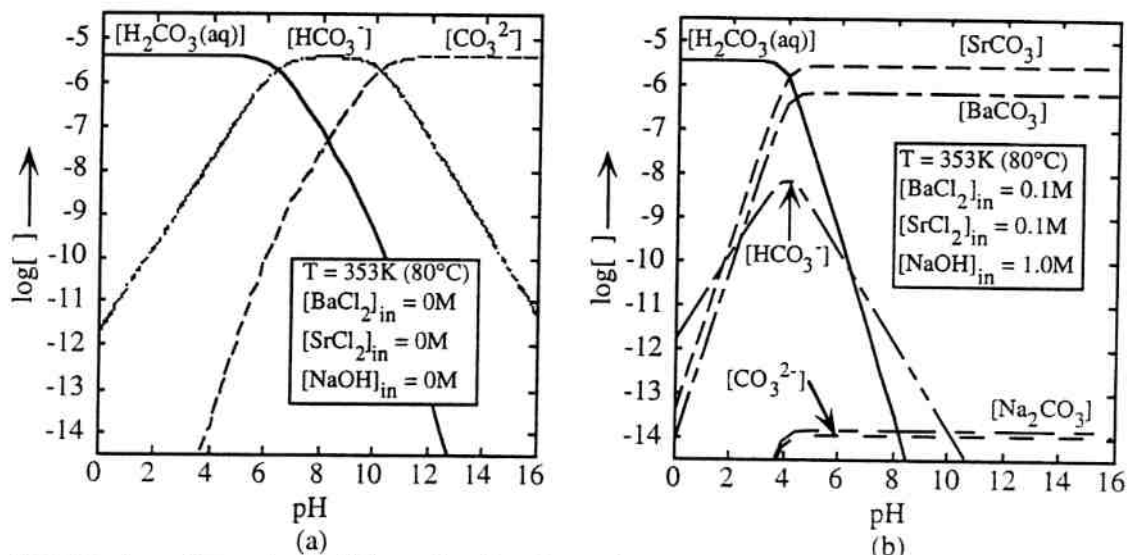
Figure 4. Example model results for the carbonate system showing a) carbonic acid dissociation and b) the formation of solid carbonates when Ba and Sr cations are present in the solution.

Most thermodynamic and electrochemical data for aqueous Ti ions is purely theoretical. Experimental measurements are lacking due to the inherent surface oxide on Ti metal in water. While a complete model for titanate equilibria is currently being developed [16], an example of the model is demonstrated here for carbonate equilibria. The carbonate system is computationally similar to the titanate system, and thermodynamic and electrochemical data sets are well developed for carbonate species.

Thermodynamic data as a function of temperature was obtained for all aqueous, ionic and solid chemical species from references 10-15. The Gibbs free energy of formation (ΔG) for carbonate ions was calculated from well known reaction constants for the carbonic acid dissocation reactions [17,18], making the model self-consistent. Carbonic acid dissociation occurs as H_2CO_3 goes to HCO_3^- and CO_3^{2-} with increasing pH (Fig. 4a). Thus, the following chemical equilibria were considered:

1) $H_2CO_3 = H^+ + HCO_3^-$
2) $HCO_3^- = H^+ + CO_3^{2-}$
3) $Ba^{2+} + HCO_3^- = H^+ + BaCO_3$
4) $Sr^{2+} + HCO_3^- = H^+ + SrCO_3$
5) $Na^{2+} + HCO_3^- = H^+ + Na_2CO_3$

The solution was assumed ideal, such that equations could be written for each equilibria according to $\Delta G_{rxn} = -RT\ln(K_{rxn})$. The initial concentrations of Ba, Sr, and Na cations were entered as fixed input variables. The initial concentration of H_2CO_3 present is determined by the rate-limiting solubility of CO_2 in water at the given temperature [19]. Therefore, a sixth equation could be written as a carbon balance: $[CO_2]_{in} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [BaCO_3] + [SrCO_3] + [Na_2CO_3]$. Thus, the six equations were solved as a funtion of pH for a specified temperature and solution composition, resulting in the equilibrium amounts of the six chemical species considered over the entire pH range.

Figure 4a is calculated at 80°C for a solution with no added cations, showing the carbonic acid dissociation. The maximum concentrations of ions present correspond to the solubility of CO_2 in H_2O at 80°C. Figure 4b shows the precipitation of carbonates when Ba and Sr are added to the initial solution in equal atomic fractions, predicting a preferred precipitation of $SrCO_3$.

The stoichiometries predicted by the model were compared against those measured in $Ba_xSr_{1-x}CO_3$ (confirmed by XRD) powders using EDS. Table 1 lists the results for the specific solution compositions used, and figure 5 displays the comparison graphically. The predicted stoichiometries are a close match to those determined experimentally, thereby demonstrating the utility of the thermodynamic model. Application of the model to the titanate system is in progress.

Table 1. Thermodynamic model vs. experimental results for the stoichiometry of $Ba_xSr_{1-x}CO_3$

solution composition		model		experiment (EDS)	
		atom% Ba	atom% Sr	atom% Ba	atom% Sr
1.0M Ba	0.01M Sr	95.7	4.3	86.7	13.3
0.9M Ba	0.1M Sr	66.9	33.1	73.6	26.4
0.7M Ba	0.3M Sr	34.4	65.6	35.8	64.2
0.5M Ba	0.5M Sr	18.3	81.7	17.2	82.9
0.1M Ba	0.1M Sr	18.3	81.7	21.2	78.8
0.3M Ba	0.7M Sr	8.8	91.2	15.6	84.4
0.01M Ba	1.0M Sr	0.2	99.8	0.2	99.8

Figure 5. Comparison of the thermodynamic model to experimental results for stoichiometries in the carbonate system. The axes show the atom fraction of Ba cations, considering only Ba and Sr cations, in starting solution (horizontal) vs. the precipitated carbonate (vertical). Error bars show one standard deviation.
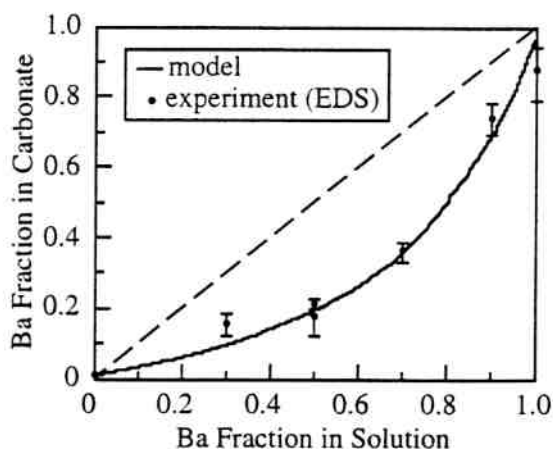
SUMMARY

$Ba_xSr_{1-x}TiO_3$ (BST) thin films and powders were processed below 100°C by hydrolyzing Ti metal-organic precursors and TiO_2 powder in alkaline Ba/Sr containing aqueous solutions. XRD and WDS results show that Sr cations are more readily incorporated in BST than Ba cations. A thermodynamic model was introduced to predict BST stoichiometry for pH and solution composition. The model was demonstrated for carbonates that also form hydrothermally with Ba and Sr in solid solution, showing good agreement with experimentally measured stoichiometries and confirming a higher reactivity of the Sr cation.

ACKNOWLEDGMENTS

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