Perovskite-Like Strontium Titanium Zirconium Oxide Solid Solutions Prepared at Atmospheric Pressure

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Perovskite type oxides of $SrTiO_3$, $SrZrO_3$, and $SrTi_{1-x}Zr_xO_3$ have been systematically synthesized at 1250°C and 1550°C with specimens containing additions of up to x = 0.9 of zirconium by solid state reactions and characterized by X-ray diffraction. X-ray diffraction studies showed that the compound $SrTi_{1-x}Zr_xO_3$ has cubic structure. The lattice paramters of $SrTi_{1-x}Zr_xO_3$ solid solutions obey the Vegard's law and fairly large increase in volume can acompany the formation of this solution with increasing Zr content (x). Assuming the lattice constants of perovskite type compounds $A(B_{1-x}B'_x)O_3$, where $B_{1-x}B'_x$ is $Ti_{1-x}Zr_x$, to be a linear function of the ionic radii of B and B′ ions, the disordered ion pair of Ti^{4+} and Zr^{4+} was verified from the lattice constants of a series compounds varying x = 0, 0.05, 0.25, 0.5, 0.75, 0.9, and 1.0 with known isovalent pairs.

Introduction

The work reported here was carried out as part of the Research Project (ED-84) from Ministry of Education on the development of the semiconducting electrodes as catalysts for photoelectrolysis of water by sun light. Direct photoelectrolysis of water into its components, oxygen and hydrogen, requires photon energy greater than 6.6 eV[1], which is not reached with sun light. However, in 1972, Fujishima and Honda[2] demonstrated that photoelectrolysis of water by sun light was possible by the use of semiconducting electrodes as catalyst, n-type TiO_2 anode. After their work, lots of researches on the finding for anode materials for the photoelectrolysis were performed. TiO_2 itself has produced a profusion of literature. Other compounds also have been investigated; $SrTiO_3$, $CaTiO_3$, $BaTiO_3$, $KTaO_3$, WO_3, SnO_2, $YFeO_3$, $FeTiO_3$, $KTa_{1-x}Nb_xO_3$, $CdFe_2O_3$, $PbFe_{12}O_{19}$, $Hg_2Ta_2O_3$, $Pb_2Ti_{0.5}W_{0.5}O_{6.5}$, *etc.*, and other oxides and nonoxides have also been studied. A number of reviews published summarize the state of the art[3-7].

The restriction for a suitable anode material described above were taken into consideration on designing the oxide electrodes for the photoelectrolysis of water. However, it was not possible to predict the type of band-to-band transitions before the eletrodes were actually tested. Among them the oxides, $SrTiO_3$ and $SrTi_{1-x}Zr_xO_3$, were chosen because it was anticipated that they would be more stable to the conditions of oxygen evolution at their surfaces, and that isovalent substitution of the more electropositive ions[8] Zr^{4+} for Ti^{4+} in $SrTiO_3$ was intended to reduce the electron affinity of $SrTiO_3$ *i.e.* to raise its conduction band edge. In this case the band bending at the electrode-electrolyte interface at a given potential would be increased to give better efficiency of separation of the photogenerated electron-hole pairs. Butler and Ginley[9] proposed the relation $\chi = EN - 0.5\,Eg$, where EN is the geometric mean of the electronegativities of the constituent elements in a compound and Eg is its band gap. From the above relation, it follows that the introduction of a more electropositive ion into a compound would reduce its electron affinity, χ. $SrTi_{1-x}Zr_xO_3$ would require much higher temperature for reduction compared with $SrTiO_3$, which itself might give an initial indication of reduced χ.

In the present work, we have at first focused only on the structural properties of them systematically because none has addressed seriously on the structural features of $SrTiO_3$-$SrZrO_3$ solid solution electrodes. And in a forthcoming paper[10] we will discuss in detail on our investigations of photoelectrochemical behaviors of them.

Experimental

The starting materials used for the preparation of the compounds are as follows with the purities given in parenthesis; $SrCO_3$ (Rare Metallic Co. 99.99%), TiO_2 (purified samples were obtained from Prof. Q.W. Choi: 99.99%) ZrO_2 (Rare Metallic Co. 99.99%).

$SrTiO_3$ was prepared by reacting a stoichiometric mixture of $SrCO_3$ and TiO_2.

$$SrCO_3 + TiO_2 \rightarrow SrTiO_3 + CO_2$$

Initial heating was performed at 1150°C for 12 hours and then the product was reheated at 1250°C for 20 hours in air. A single phase product of cubic perovskite was obtained. A series of stoichiometric compounds of the following proportions was prepared.

$$SrCO_3 + (1-x)\,TiO_2 + x\,ZrO_2 \rightarrow SrTi_{1-x}Zr_xO_3 + CO_2$$

where x = 0, 0.05, 0.25, 0.5, 0.75, 0.9, and 1.0.

The weighed mixtures were ground, pressed, and then initially heated at 1150°C, 1250°C, 1400°C, and 1460°C in air several times. At temperature below 1460°C under oxidizing conditions, a solid solution of $SrTiO_3$-$SrZrO_3$ was sometimes formed with a small portion of $SrTiO_3$, ZrO_2, $ZrTiO_4$, $SrZrO_3$, and not identified phases. The samples reground and repelletized were finally reheated at 1550°C, then anealed at 1400°C and quenched in ice water. Single phases of solid solutions of whole series were obtained. The conditions of the final heat treatments of the compounds which we attempted to prepare in the present work are described in Table 1.

The identification of the resultant phases and the determination of the lattice constants were accomplished by powder X-ray diffraction method (Philips Norelco diffractometer) with nickel-filtered Cu-K_α radiation (wavelength = 1.54178 Å), using silcon powder (99.99%) as a standard. Lattice constants were refined using the observed 2θ values by least-square method. The diffraction intensity of every line was conventionally measured by cutting and weighing its profile.

Results and Discussion

Despite the heat treatment of 1460°C for 5 hrs., samples expected to form perovskite-type compounds of $AB_{1-x}B'_xO_3$ type ($SrTi_{1-x}Zr_xO_3$) were obtained as multiphase mixture as mentioned already. Phases other than desired one were often found to be concentrated near the surface of the fired pellet and could be removed simply by surface grinding. Final products were obtained by quenching the batches from 1520°C and 1550°C, respectively. (Table 1)

$SrTiO_3$ was synthesized as single phase perovskite structure from heat treatment below 1250°C as shown in Tables 1 & 2. The observed d-values were compared with d_{ASTM} and it was found that the calculated lattice parameter (3.905(1)Å) agrees very well with literature value of 3.9051Å. In compounds with the formula $AB_{1-x}B'_xO_3$ having the cubic perovskite-type structures, the larger A cations are distributed among the cation sites surrounded by twelve oxygen ions and smaller B and B′ cations are regularly (orderly) or randomly (disorderly) arranged in the octahedral cation sites surrounded by six oxygen ions.

TABLE 1: Synthetic Conditions of $SrTi_{1-x}Zr_xO_3$

Compounds (x=0)	Reaction Temp. (°C)	Reaction Time (hrs.)	Cell Parameter (Å)
$SrTiO_3$ (x = 0)	1250	20	3.905
$SrTi_{0.95}Zr_{0.05}O_3$(x = .05)	1520	> 10	3.921
$SrTi_{0.75}Zr_{0.25}O_3$(x = .25)	1550	4	3.955
$SrTi_{0.50}Zr_{0.50}O_3$(x = .50)	1520	> 10	4.016
$SrTi_{0.25}Zr_{0.75}O_3$(x = .75)	1550	4	4.062
$SrTi_{0.10}Zr_{0.90}O_3$(x = .90)	1550	4	4.087
$SrZrO_3$ (x = 1)	1550	4	4.097

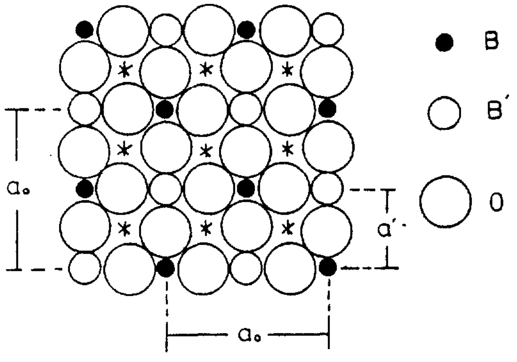

Figure 1. Rock salt arrangement of B and B′ cations in the (100) plane of the cubic perovskite structure for $A(B_{0.5}\ B'_{0.5})O_3$. Lattice constant a′ and dimension of superlattice a_0 are shown. Asterisks stand for the A-sites.

Figure 1 shows the arrangement of ions in the (100) plane of the cubic perovskite structure for $AB_{1-x}B'_xO_3$ type compounds, where B and B′ cations could be alternately or randomly arranged between oxygen ions. The site preference type "regular" or "random" can be determined by measuring the composition dependence of lattice parameters. As can be seen in Figure 1, it appears that the lattice constant a for an $AB_{1-x}B'_xO_3$-type compound is a linear function of ionic radii of the B and B′ cations. If B-site cations, B and B′, are distributed orderly, all the diffraction lines in the powder X-ray pattern might be indexed by a face centered unit cell with the double edge of the perovskite unit, which is an integral multiple of the unit cell parameter of simple perovskite of AB(or

TABLE 2: X-ray Dffraction Data of $SrTiO_3$

2θ	I/I(obs.)	I/I(ASTM)	do(Å)	d_{ASTM}(Å)	dc(Å)	hkl
22.76	1.3	12	3.907	3.900	3.905	100
32.40	100	100	2.763	2.759	2.761	110
39.96	26.3	30	2.256	2.253	2.255	111
46.50	55.3	50	1.953	1.952	1.953	200
52.38	2.4	3	1.747	1.746	1.746	210
57.82	57.2	40	1.595	1.594	1.594	211
67.87	33.6	25	1.381	1.381	1.381	220
72.625	1.3	1	1.302	1.302	1.302	300
77.265	23.7	15	1.235	1.235	1.235	310
81.80	8.2	5	1.177	1.177	1.177	311
86.28	9.5	8	1.127	1.127	1.127	222
95.225	31.6	16	1.044	1.044	1.044	321

a = 3.905(1) Å, a = 3.9051 Å (from ASTM).

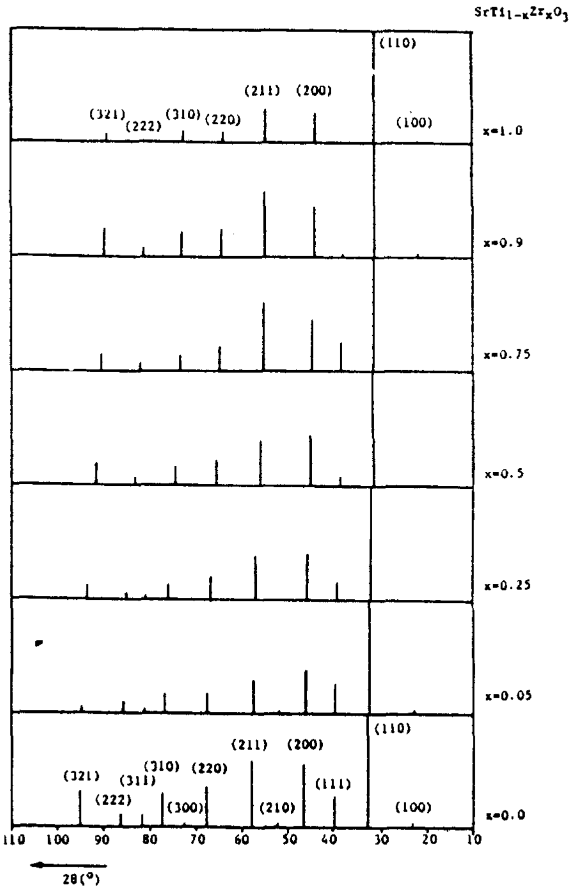

Figure 2. X-ray diffraction patterns for $SrTi_{1-x}\ Zr_xO_3$.

B')O_3. But in the disordered system, all the diffraction lines can be indexed by a simple unit cell with no abrupt change in unit cell parameter. Therefore, in case of "regular" an anomalous change in the composition vs. lattice parameter curves must be seen due to the structural phase transition from higher symmetric structure to lower one around a certain x-value. But in case of "random", there would be no such anomalous change in the curves but gradual change.

As shown in Figure 2, powder X-ray diffraction patterns of $SrTi_{1-x}Zr_xO_3$ shows that diffraction patterns of all the compounds from x = 0 to 1.0 are very similar in intensities and diffracting angles to one another.

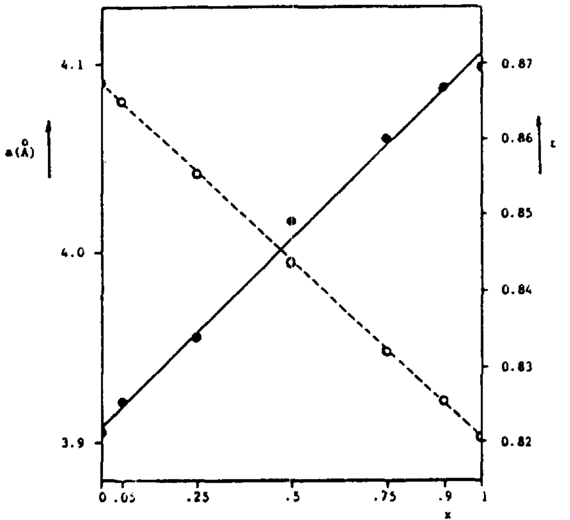

Figure 3. Plot of lattice parameter (solid line) and tolerance factor (dotted line) vs. zirconium content in $SrTi_{1-x}Zr_xO_3$.

TABLE 3: X-ray Dffraction Data of $SrTiO_{0.5}Zr_{0.5}O_3$

2θ	I/I(obs.)	do(Å)	dc(Å)	hkl
31.48	100	2.842	2.840	110
38.82	8.3	2.320	2.819	111
45.15	43.8	2.008	2.008	200
56.08	39.5	1.640	1.640	211
65.765	20.8	1.420	1.420	220
74.78	15.63	1.270	1.270	310
83.34	5.7	1.160	1.159	222
91.88	18.8	1.073	1.073	321
100.42	4.0	1.003	1.004	400

a = 4.016(2) Å

Table 3 listed the $d_{obs.}$, $d_{calc.}$, and I/I_o of $SrTi_{0.5}Zr_{0.5}O_3$ as an example, together with the (hkl) indices for cubic structure.

Cell parameters can be represented by a linear equation of the zirconium content as follows (Figure 3):

$$a = 0.1959x + 3.9094 \quad (r = 0.9976)$$

where a stands for the cell parameter of synthesized perovskites and x for the zirconium content in the B-site. This good linearity indicates that the solid solution $SrTi_{1-x}Zr_xO_3$ follows the Vegard's law[11] well with no significant difference between the binding energies of Ti^{4+} and Zr^{4+} with surroundings and that Ti^{4+} and Zr^{4+} are randomly distributed to the B-sites.

To certificate the indexing for the cubic structure, tolerance factor, which determines the possibility of a perovskite to have the cubic structure, was applied to our system. Originally, tolerance factor, t, is defined as $R_A + R_O = t\sqrt{2}(R_B + R_O)$ where R_A, R_B, and R_O represent the radii of A-, B-site cations and oxygen in the ABO_3 perovskite type structure, respectively, and only in the range of $0.8 < t < 0.9$, perovskites are permitted to have the cubic structure.

In order to consider the effect of isovalent substitution of Zr^{4+} for Ti^{4+}, a modified formula, $R_A + R_O = t\sqrt{2}((1-x)R_B + xR_{B'} + R_O)$, where B- and B' represent the B-site cations and x stands for the mole fraction of Zr ion in the B-site, was used. Ahrens' radii were adopted for the calculation[12]. Calculated tolerance factors vary from 0.8675 (for $SrTiO_3$) to 0.8209 (for $SrZrO_3$) which validate our indexing for pseudocubic or cubic structure. (Figure 3)

The X-ray diffraction patterns and the structure of synthesized $SrTiO_3$ showed a good agreement with those of literature, but for $SrZrO_3$, no such agreement was observed. (Table 4) There are two X-ray diffraction data[13]. One of them is reported as orthorhombic (a = 5.814 Å b = 8.916 Å and c = 5.972 Å) and the other as cubic (d = 4.182 Å) at high temperature of 2000°C. But our result is different from both, a cubic structure with slightly smaller unit cell parameter (a = 4.087 Å) than that of cubic phase at high temperature was obtained. It might be due to the fact that the high temperature cubic phase might

TABLE 4: X-ray Dffraction Data of $SrZrO_3$ with Cubic Phases (a) and Orthorhombic one (b)

Cubic phase (a) at 25°C					at 2000°C		Orthorhombic (b)		
2θ	I/I(obs.)	do(Å)	dc(Å)	hkl	I/I_0(ASTM)	d_{ASTM}(Å)	I/I_0	d(Å)	hkl
21.67	0.1	4.101	4.098	100	6	4.16	5	4.096	020
30.88	100	2.896	2.898	110	100	2.955	5	3.666	111
38.12	0.1	2.361	2.366	111	6	2.414	65	2.900	121
44.22	27.9	2.048	2.049	200	45	2.090	100	2.895	002
—	—	—	—	210	6	1.868	3	2.598	201
54.88	29.0	1.673	1.673	211	45	1.707	3	2.590	102
64.32	10.0	1.448	1.449	220	16	1.478	5	2.469	112,031
72.995	9.0	1.296	1.296	310	20	1.323	5	2.369	220
81.35	0.2	1.183	1.183	222	4	1.2075	40	2.050	202,040
89.4	7.6	1.096	1.095	321	14	1.1185	3	1.986	212,230
		at 25°C a = 4.097(4) Å			at 2000°C a = 4.182 Å			at 25°C a = 5.792 Å b = 8.189 Å c = 5.818 Å	

TABLE 5: Lattice Constants and Parameters of Perovskite-type Compounds used in the Present Work

Compound	a	b (Å)	c	Z	$\sqrt[3]{V/Z}$ (Å)	r_B (Å)	Symmetry
$SrMnO_3$	3.8060			1	3.8060	0.54	cubic
$SrTiO_3$	3.9051			1	3.9051	0.605	cubic
$SrRuO_3$	5.56	5.55	7.86	4	3.929	0.62	orthorhombic
$SrMoO_3$	3.9751			1	3.9751	0.65	cubic
$SrSnO_3$	8.0682			8	4.0341	0.69	cubic
$SrHFO_3$	8.138			8	4.069	0.71	cubic
$SrZrO_3$	5.792	8.189	5.818	4	4.101	0.72	orthorhombic
$SrZrO_3$	4.182			1	4.182	0.72	cubic
(high temp. phase (2000°C))							
$SrPbO_3$	5.864	5.947	8.336	4	4.173	0.775	orthorhombic
$SrCeO_3$	5.986	8.531	6.125	4	4.276	0.80	orthorhombic
$SrPuO_3$	5.980	4.276	6.114	2	4.276	0.80	orthorhombic
$SrThO_3$	8.84	($\beta \sim 90°C$)		8	4.42	1.00	monoclinic (Pseudocubic)

$\sqrt[3]{V/Z} = 3.048 + 1.4456\, r_B$ $r = 0.9746$ ($r^2 = 0.9498$).

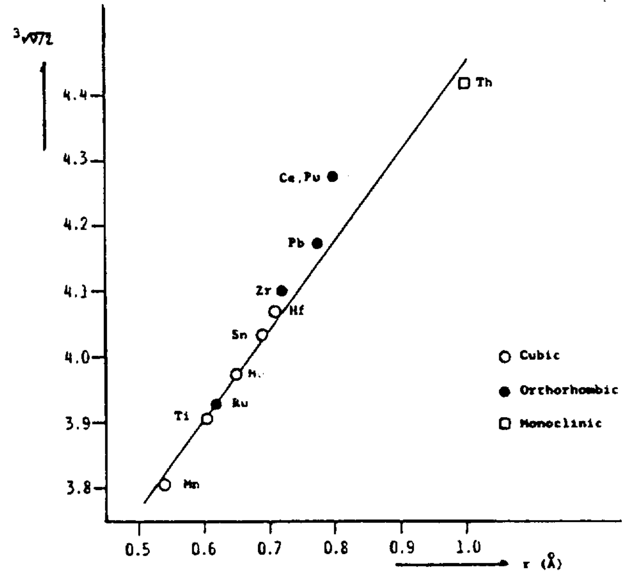

Figure 4. The linear relation between cube root of cell volume for formula unit ($\sqrt[3]{V/Z}$) vs. ionic radius of M^{4+} ion for perovskites $SrM^{4+}O_3$.

be frozen out by quenching the sample from 1550°C to ice water, And also the cell volume might be contracted as the result of temperature decrease. Table 5 listed the lattice constants, the number of formula in unit cell, cube root of cell volume per formula unit (perovskite parameter), Shannon's ionic radii and the symmetry of the compounds synthesized in the present work, together with those of other related compounds used in discussion.

In Figure 4 the cube roots of unit cell volume of many other perovskite type compounds of the formula $SrMO_3$, where M is any tetravalent cation, were plotted as a function of the ionic radius of M (Shannon's data[14]). This plot shows a good linearity with correlation coefficient $r = 0.9746$ and supports our assumption that the cell parameter of $SrTi_{1-x}Zr_xO_3$ depends linearly on the weighted mean radius of B-site cations, namely on the zirconium content x.

The composition dependence of lattice paramters in $SrTi_{1-x}Zr_xO_3$ systems with $SrTiO_3$-type cubic perovskite structures gives us the information about the substitution modes from which we can guess "regular" or "random" distribution of B- and B'-site cations for compounds $AB_{1-x}B'_xO_3$ and ABO_3.

Studies on the preparation and structural properties of all possible ABO_{3-x} and $AB_{0.5}B'_{0.5}O_{3-x}$ systems with perovskite-type structure are now in progress, together with complementary studies using electrical conductivity and photoelectrochemical measurements.

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