Lattice Parameters of Sol-Gel Derived Metastable ZrO_2-CaO Solid Solutions

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Metastable cubic and tetragonal phases in $(1-x)ZrO_2$–xCaO solid solutions (x=0—0.155) were prepared by the sol-gel method. A sequential phase transition from amorphous to cubic, tetragonal, tetragonal+monoclinic with a rise in treatment temperature was observed for specimens of x=0.044. The lattice parameter of the metastable cubic phases changed linearly with the composition, indicating that the Vegard's law can be extended to the metastable phase. The validity of the Vegard's law and the stability of metastable phases are discussed.

Control of crystal structures and lattice parameters by compositional changes is widely used in ceramic materials design. It is well known as the Vegard's law that lattice parameters of thermal equilibrium solid solutions between compounds with the same crystal structure change linearly with the composition. Recently, not only equilibrium stable phases but also non-equilibrium and metastable phases have been examined in an attempt to find new functional materials. Preparation of metastable phases by low temperature processing techniques such as sol-gel methods, chemical vapor deposition, and rapid quenching has been extensively studied. In these studies, the crystal structure of metastable phases was found to depend strongly on the preparation methods and conditions. For this reason, the basic principle to control the crystal structure of metastable phases has not been unraveled. The purpose of our work is to find out such a principle and to apply it to ceramic materials design. In this paper, we investigate cubic and tetragonal metastable phases of ZrO_2–CaO solid solutions which have been studied as a tough engineering material and a good ionic conductor.

The stable crystal form of pure ZrO_2 at room temperature is monoclinic. However, it was reported that cubic or tetragonal phases were formed when prepared at low temperatures by sol-gel methods,[1—3] precipitation from aqueous solutions,[4,5] chemical vapor deposition,[6—9] and thermal decomposition of zirconium salts.[4,10—12] The origin of the metastable phase formation has been discussed by many researchers mainly in terms of two aspects: (1) crystallite size effect due to the difference in surface energy between the monoclinic and metastable phases;[4,13] and (2) stabilization based on a martensitic transformation.[14] Little work has been done, however, on the details of crystal structures including lattice parameters of the metastable phases. One of the reasons for this is that the reproducibility of specimens is supposed to be poor because a slight change in the preparation methods and conditions led to significant changes in crystal structures. Another factor is that metastable phases are intermediate ones and considered to have no definite structure. In this study, metastable cubic and tetragonal ZrO_2–CaO solid solutions were prepared by the sol-gel method and the relationship among the compositions, the heating conditions, and the crystal structures was examined by means of powder X-ray diffraction. We also investigate the applicability of the Vegard's law for metastable solid solutions on the basis of the lattice parameter measurements.

Experimental

Sample Preparation. Zirconium tetraisopropoxide (ZIP) and calcium nitrate tetrahydrate were used as starting materials for the sol-gel synthesis. ZIP was dissolved in ethanol which had been dried with molecular sieves. Calcium nitrate was dehydrated by heating to constant weight at 393 K and added to the alkoxide solution. The amount of Zr+Ca was 0.01 mol per 20 ml of ethanol. After 0.5 ml of diethylene glycol (DEG) was added to avoid precipitation,[2] hydrolysis was carried out with a 1 : 1 mixture of water and ethanol added dropwise under stirring. The molar ratio of water to ZIP ranged from 2 to 10. The solution became viscous and cloudy with the progress of hydrolysis.

The solution thus obtained was poured into a glass container with a lid, followed by gelation in a few minutes. The resultant gels were dried at 333 K for 10 d and subsequently heat-treated in air at a temperature ranging from 573 to 1073 K for 16 h. The effect of heating time was evaluated for selected compositions by heating the specimens for 8—40 h. The evaporation of water, solvents, and resultant organic compounds contained in the gels changed the bulk gel into pieces of a few millimeters in diameter during heat treatments. Specimens treated below 773 K turned brown due to a small amount of residual carbon originating from organic compounds.

Preparation by a conventional mixed powder method was also carried out for comparison. Mixing in an agate mortar and firing at 1573 K for 4 h were repeated 3 times using zirconium oxide and calcium carbonate as starting materials.

Elemental Analysis. A scanning electron microscope equipped with an energy dispersion analyzer was used to determine the Zr and Ca contents in specimens. Peak areas of Zr $L\alpha$ and Ca $K\alpha$ spectra were measured with an accelerating voltage of 20 kV, analyzing area of 0.2×0.3 mm, and measuring time of 5 min. Compositions of the sol-gel derived specimens were determined using a calibration curve obtained from measurements on the specimens prepared by the mixed powder method.

X-Ray Diffraction. Crystalline phases in the specimens were determined from powder X-ray diffraction (XRD) patterns. Tetragonal and cubic phases were identified from the separation of (4 0 0) and (0 0 4) diffraction peaks. It should be noted, however, that exact determination of metastable cubic and tetragonal phases in the low temperature treated specimens by XRD is difficult, as mentioned by Mitsuhashi et al.,[14] due to a small separation of (4 0 0) and (0 0 4) diffraction peaks and the broad line widths.

The (1 1 1), (2 2 0), (3 1 1), and (4 0 0) peaks in the cubic-phase specimens were measured by the step scanning method to calculate lattice parameters. Step scanning measurements were performed with a 0.01 degree step using Cu $K\alpha$ radiation (40 kV, 200 mA). Lattice parameters were calculated from peak positions which had been corrected with powdery Si as an external standard.

Results

Composition, Heating Condition, and Phases. The relation between the composition and crystal phase in specimens prepared by the mixed powder method by heating at 1573 K are shown in Table 1. MP00 consisted of a monoclinic single phase and MP15—MP20 consisted of single cubic phases. Both monoclinic and cubic phases are present at intermediate compositions (MP02—MP14). According to an equilibrium phase diagram at 1573 K determined by Hellmann and Stubican,[15] the compositions for MP05—MP14 are in the two-phase field of cubic and tetragonal phases. This coincides with the present results because the tetragonal phase at 1573 K transforms into the monoclinic phase on cooling to room temperature, resulting in a mixture of monoclinic and cubic phases.

The compositions of the sol-gel derived specimens are given in Table 2. The compositions found by analysis are in good agreement with the expected values. Figure 1 shows the variation of phases in the sol-gel derived specimens with composition, x for $(1-x)ZrO_2$-xCaO,

Table 1. Compositions and Phases of ZrO_2–CaO Prepared by the Mixed Powder Method

Specimen	Ca/(Zr+Ca)	Phase[a)]
MP00	0	M
MP02	0.02	M+C
MP05	0.05	M+C
MP10	0.10	M+C
MP14	0.14	C+M (traces)
MP15	0.15	C
MP16	0.16	C
MP17	0.17	C
MP20	0.20	C

a) M, monoclinic; C, cubic.

Table 2. Compositions of ZrO_2–CaO Prepared by the Sol-Gel Method

Specimen	Ca/(Zr+Ca) Expected	Ca/(Zr+Ca) Found
SG00	0	0
SG02	0.02	0.019
SG05	0.05	0.044
SG07	0.07	0.061
SG10	0.10	0.102
SG13	0.13	0.133
SG15	0.15	0.155

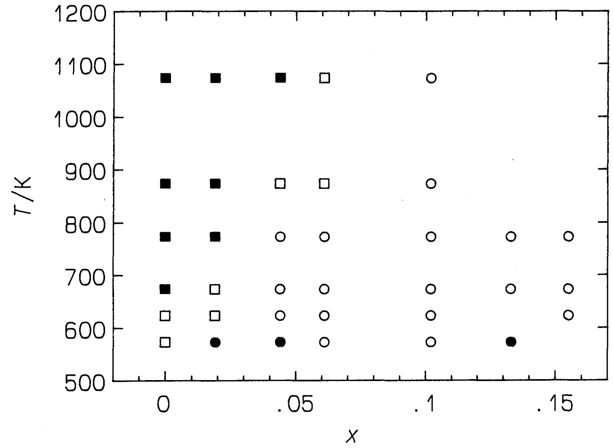

Fig. 1. Variation of phases with composition and heat treatment temperature in the sol-gel derived specimens.
●: amorphous, ○: cubic, □: tetragonal, ■: tetragonal +monoclinic.

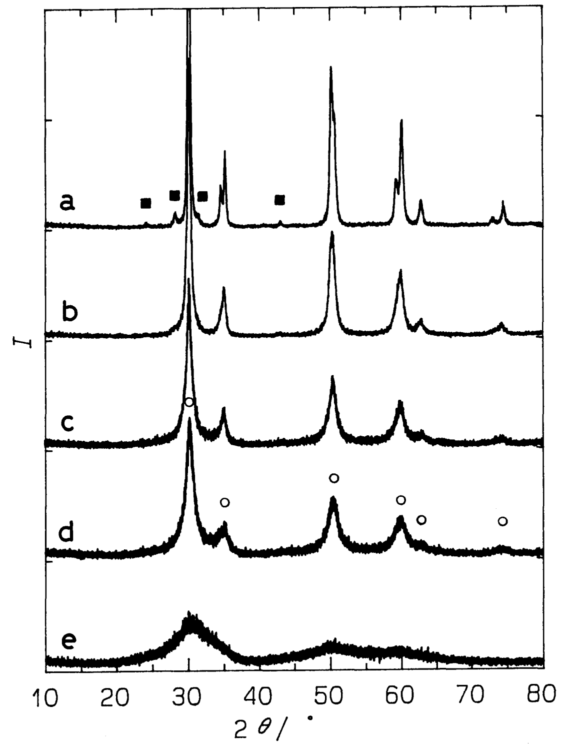

Fig. 2. X-Ray diffraction patterns of SG05 specimens prepared by heating at (a) 1073, (b) 873, (c) 673, (d) 623, and (e) 573 K.
○: cubic or tetragonal, ■: monoclinic.

and temperature of heat treatment. All dried gels showed broad halo patterns of amorphous phases in XRD. After heat treatments at 573 K, SG00 alone clearly crystallized to a tetragonal phase. Amorphous or very broad cubic patterns were obtained for the other specimens. SG00 consisted of two phases, tetragonal and monoclinic, when heated above 673 K. The temperature at which the monoclinic phase appeared is in agreement with the reported value.[6]

Figure 2 displays the variation of XRD patterns with the heat treatment temperature for SG05 specimens. The sequence of transformation is clearly depicted; from amorphous to cubic (623 K) and from tetragonal to tetragonal+monoclinic (1073 K). Figure 3 shows (4 0 0) and (0 0 4) peak profiles of SG05 measured by the step scanning method, indicating that the cubic-tetragonal transformation occurs at about 873 K. It also indicates the difficulty to determine the exact transformation temperature as mentioned above, because the cubic phase transforms continuously into the tetragonal phase.

The transformation sequence was no longer observed for the compositions with a high Ca content such as SG10—SG15. The cubic structure was retained up to 1073 K and only the peak sharpening was observed.

Lattice Parameters. The (4 0 0) and (0 0 4) diffraction peaks of metastable phases in the sol–gel derived specimens with various compositions are shown in Fig. 4. Cubic phases are obtained above x=0.05 as a metastable phase. A shift in the peak position of the cubic phases toward the small angle side with an increase in the Ca content is evident, though the peaks remain broad. The peak positions of (1 1 1), (2 2 0), and (3 1 1) similarly shifted to the small angle side, indicating a change in lattice parameters.

Figure 5 shows lattice parameters of the cubic phases obtained by the sol–gel and the mixed powder methods as a function of the Ca content. The solid line indicates the change in lattice parameters for the specimens prepared by the mixed powder method. The dotted line is the extrapolation of the lattice parameters of the cubic solid solution to x=0. The lattice parameters of the specimens prepared by the mixed powder method are in agreement with those observed by Hellmann and Stubican.[15] The lattice parameters change linearly with composition for $0.15<x<0.20$ due to the formation of single-phase cubic solid solutions. The lattice parameters are constant for $0<x<0.14$ due to the formation of monoclinic and cubic phases.

In contrast, lattice parameters of the cubic phases in

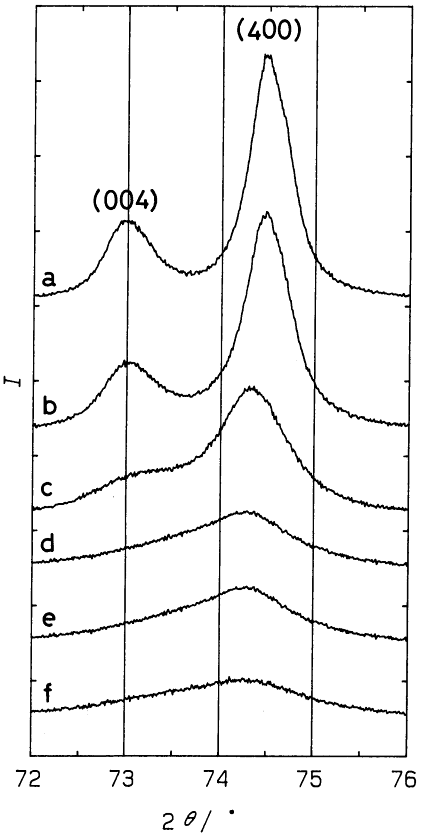

Fig. 3. (4 0 0) and (0 0 4) XRD peak profiles of SG05 specimens prepared by heating at (a) 1073, (b) 973, (c) 873, (d) 773, (e) 673, and (f) 623 K.

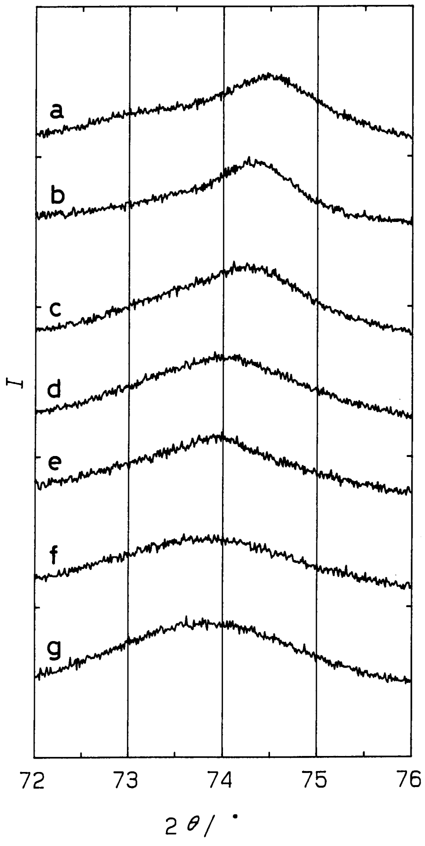

Fig. 4. (4 0 0) and (0 0 4) XRD peak profiles of the sol–gel derived specimens. (a) SG00 prepared by heating at 573 K, (b) SG02 (623 K), (c) SG05 (623 K), (d) SG07 (673 K), (e) SG10 (673 K), (f) SG13 (673 K), (g) SG15 (773 K).

the sol–gel derived specimens change with composition even in the region $x<0.15$. A linear relationship is observed for $0.044<x<0.155$. If the Vegard's law for the stable ZrO_2–CaO solid solutions could be extended to the metastable solid solutions, the lattice parameters should be on the dashed line in Fig. 5. The agreement is not satisfactory: The lattice parameters of the metastable phase are slightly larger. However, it may be that the Vegard's law can be extended or modified for the metastable phases of ZrO_2–CaO solid solution since the linear relationship is evident.

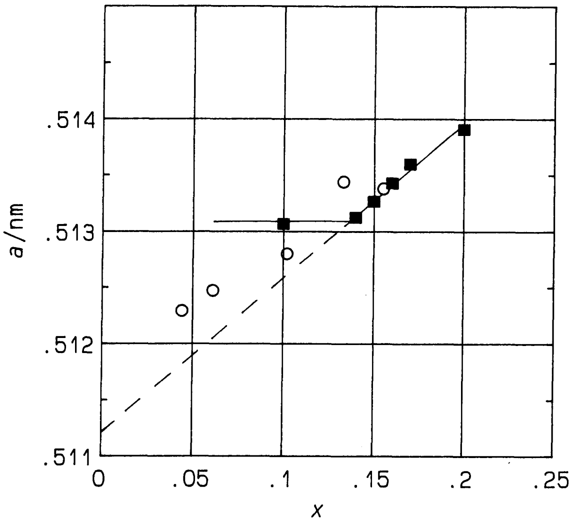

Fig. 5. Lattice parameters of the cubic phase in specimens prepared by the mixed powder method (■) and the sol–gel method (○).

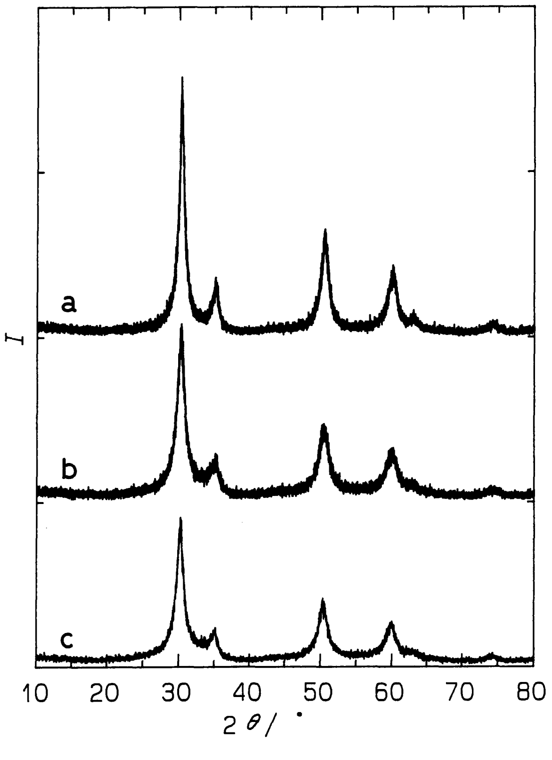

Fig. 6. X-Ray diffraction patterns of SG05 specimens prepared by heating at 623 K for (a) 48, (b) 16, and (c) 8 h.

Effect of Heating Time. The results presented above are for specimens heat-treated for 16 h. It is known that thermal equilibrium is attained very slowly in the system of ZrO_2–CaO. Thus the effect of heating time was studied for SG05, SG07, and SG10 by preparing the specimens at heating times of 8 h, 16 h, and 40 h. Figure 6 shows the results for SG05 heated at 623 K. No significant change was observed in the XRD pattern except for the peak sharpening due to the growth in crystallite size. The local ionic arrangement in the crystallites is most probably close to be equilibrium in heat treatment for 8 h, resulting in the consistency of crystalline phases and lattice parameters.

Discussion

When an amorphous material crystallizes at low temperatures, diffusion of the constituent ions is not fast enough to transform the entire system into the most stable structure. Instead, a locally stable structure appears at first. Considering the symmetry in the local ionic arrangement, amorphous ZrO_2 is closer to a cubic or tetragonal structure than a monoclinic structure. Consequently, cubic or tetragonal ZrO_2 is formed when an amorphous ZrO_2 gel crystallizes at around 573 K.

The most stable structure of ZrO_2 at room temperature is monoclinic. The origin of the transformation to the monoclinic phase is attributed to the ratio of cation–anion radius. In the metastable phases, the lattice distortion arising from the ratio of ionic radii is absorbed by the defects and anti-phase boundaries (APB) which are abundant in the specimens treated at low temperatures. This mechanism for the stability of metastable ZrO_2 is consistent with the surface energy theory and the martensitic theory.

Since metastable phases are stable as a local structure, the distance between individual ions are mainly governed by the ionic potential. Therefore, lattice parameters of metastable phases change with composition unless transformation occurs. The Vegard's law should thus be valid even in the metastable field. In the present study, a linear relationship is noted between lattice parameters and composition in the metastable field ($0.044<x<0.155$) as shown in Fig. 5. It is considered that the Vegard's law can be extended to the metastable ZrO_2–CaO solid solutions. However, the lattice parameters of the metastable cubic phase are slightly larger, indicating that an additional factor must be considered. The additional factor might be the ununiformity in composition or the distortion arising from the ionic radii. The deviations from the Vegard's law increase with a decrease in x, reflecting the occurrence of phase separation and the distortion. Below $x=0.044$, the lattice distortion causes the transformation from cubic to tetragonal and finally to the monoclinic phase. In this field, the ionic distances are not determined by the simple ionic potential, and hence the Vegard's law is not applicable. In contrast, the Vegard's law can be extended to metastable phases which are close to be in equilibrium and maintain the structure of the solid solution as in the case $0.044<x<0.155$. The utilization of the Vegard's law makes it possible to control lattice parameters of metastable phases.

On the other hand, control of the appearance of metastable phases is very difficult since the stability of metastable phases depends strongly on the defects and APB introduced accidentally in the preparation processes. The technique for precisely controlling or evaluating the defects and APB is not available at the present stage. If we prepare, however, the specimens under identical conditions as in the case of the present study, the introduced defects and APB are similar among the specimens and then it is possible to control the formation of metastable phases by composition and heat treatment. Different phases are possibly formed in the specimens prepared by different methods since the nature and amounts of the defects and APB are different. In fact, we have confirmed that pure ZrO_2 films prepared from ZIP by chemical vapor deposition exhibited cubic structure, and their lattice parameter 0.5104 nm is close to the extrapolated value from those for stable cubic phases.[16]

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