Chemical Potential Diagrams for La-M-Zr-O (M=V, Cr, Mn, Fe, Co, Ni) Systems: Reactivity of Perovskites with Zirconia as a Function of Oxygen Potential

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The chemical potential diagrams for the La-M-Zr-O (M=transition metals) systems at 1273 K have been constructed as a log P(O2) vs. log \( \frac{a(M)}{a(La)} \) plot under a condition of \( a(ZrO_2) = 1 \). Since only a La\(_2\)Zr\(_2\)O\(_7\) phase is known as double oxides in the La-Zr-O system, the thermodynamic features of reactions of perovskites, La\(_M\)O\(_3\), with ZrO\(_2\) can be judged in terms of whether or not La\(_2\)Zr\(_2\)O\(_7\) is formed. To simultaneously present stability of perovskites against decompositions as well as their compatibility with ZrO\(_2\), the chemical potential diagrams for the La-M-O systems have been superimposed on those for the La-Zr-M-O systems drawn using the same coordinates; in the combined diagram, areas of those compounds which react with ZrO\(_2\) to form La\(_2\)Zr\(_2\)O\(_7\) are completely covered by the stability polygon of La\(_2\)Zr\(_2\)O\(_7\).

1. INTRODUCTION

There has been a growing interest in applying sophisticated thermodynamic analyses to practical materials problems.\(^1\)-\(^3\) While chemical equilibria calculations\(^4\)-\(^6\) and phase diagram calculations\(^7\),\(^8\) have been successfully extended to multicomponent systems, few attempts have been made so far to construct chemical potential diagrams for multicomponent systems except for the geochemical fields.\(^9\),\(^10\)

We have engaged in making chemical thermodynamic considerations on materials problems in energy-related fields. In due course, we established a thermodynamic database for inorganic compounds and combined it with the SOLGAS-

**MIX** program for calculating chemical equilibria.\(^4\),\(^6\) To facilitate further applications of such a database, we wrote a computer program, CHD,\(^11\),\(^12\) for constructing chemical potential diagrams. Since a simple but generalized algorithm was adopted, it is quite easy to construct chemical potential diagrams for multicomponent systems. In particular, the multicomponent systems having two metallic elements (M\(_1\) and M\(_2\)) can be treated without any difficulty so that chemical potential diagrams for M\(_1\)-M\(_2\)-O\(_3\), M\(_1\)-M\(_2\)-C-0\(_14\), M\(_1\)-M\(_2\)-H-0-e\(_-15\) and M\(_1\)-M\(_2\)-H\(_16\) systems have been successfully constructed and analyzed from the materials chemistry viewpoint. In the present study, this attempt has been further extended to construct diagrams for the multicomponent systems having more than two metallic elements; as an example, we selected the La-M-Zr-O (M=transition metal) systems of technological importance in developing a solid oxide fuel cell.
2. PEROVSKITE MATERIALS IN A SOLID OXIDE FUEL CELL.

A solid oxide fuel cell consists mainly of ceramic materials such as YSZ (Yttria Stabilized Zirconia) electrolyte, LaMnO₃-based air electrode, Ni/YSZ cermet fuel electrode and LaCrO₃-based separator.¹⁷-¹⁹ The chemical compatibility among these materials becomes quite important during a high-temperature (>1500 K) fabricating process and also during a long-term operation around 1300 K. In our previous investigations,²⁰-²² the general chemical features of reactions between perovskites and ZrO₂ have been derived as follows: Although unusually high valence states of transition metal ions such as Fe⁴⁺ and Cu³⁺ may be stabilized in the perovskite-type crystal structure, those perovskites tend to react with ZrO₂ to form a transition metal compound containing lower valence states.²⁰)

In the present study, the thermodynamic features of reactions between transition metal perovskites and ZrO₂ are reexamined as a function of oxygen partial pressure with an emphasis on interrelationship between the chemical and the geometrical features in chemical potential diagrams.

3. CONSTRUCTION OF CHEMICAL POTENTIAL DIAGRAMS

The pyrochlore phase, La₂Zr₂O₇, is known as one of reaction products.²³-²⁵) In the absence of other zirconium compounds in the La-Zr-M-O system, the thermodynamic features of reactions of LaM₀₃ with ZrO₂ can be examined in terms of whether or not La₂Zr₂O₇ is formed. This is common to almost all LaM₀₃ (M=V,Cr,Mn,Fe,Co,Ni); only one exception is the formation of La₅NiZrO₈ phase in a reaction between La₂NiO₄ and ZrO₂.²⁶) Thus, the present chemical potential diagrams for the La-M-Zr-O systems have been constructed in the following way:

1) First, one diagram is constructed for the La-M-O system in a log P(O₂) vs. log \( \frac{a(M)}{a(La)} \) plot. In this plot, compounds are represented as polygons; their horizontal width shows the stability of the compound as a function of oxygen potentials, whereas the vertical width represents the stability of the double oxide from their constituent oxides. The slope of borderlines depends on stoichiometry or valence number of two phases.¹³)

2) Another diagram for the La-Zr-M-O \( \{a(ZrO₂)=1\} \) system is constructed using the same coordinates and then superimposed on the chemical potential diagram obtained above.

In such combined diagrams, those compounds which can stably coexist with ZrO₂ appear without change, whereas the stability areas of those compounds which should react with ZrO₂ are completely covered by that of La₂Zr₂O₇; these are presented as dashed lines in the present diagrams.

The thermodynamic data used to construct the present diagrams were already reported elsewhere.²⁰-²²)

3.1 La-Zr-V-O system

In the La-V-O system, five double oxides are known; that is, LaVO₃, LaVO₄, and \( nLa₂O₃•mV₂O₅ \) \( (n/m = 1.62/0.38, 3/1, 1.42/0.58) \). The last four double oxides have the pentavalent vanadium ions; in the chemical potential diagram shown in Fig. 1, these four compounds appear sequentially between V₂O₅ and La₂O₃. LaVO₃ appears between V₂O₃ and La₂O₃. The difference in slope between V₂O₃/LaVO₃/La₂O₃ borderlines and V₂O₅/LaVO₄/La₂O₃ borderlines is due to the difference of the valence state of vanadium ions.

When zirconium is added and the activity of ZrO₂ is fixed at unity, the lower part of the chemical potential diagram is changed; that is, instead of La₂O₃, La₂Zr₂O₇ appears. Its area is larger than that of La₂O₃. Correspondingly, some polygons disappear and some lose partially their own area. These changes
in the diagram can be related with chemical reactions as follows.

The stability areas of nLa$_2$O$_3$$\cdot$mV$_2$O$_5$ are completely covered by that of La$_2$Zr$_2$O$_7$. This means that nLa$_2$O$_3$$\cdot$mV$_2$O$_5$ tend to react with ZrO$_2$. These chemical reactions can be written as follows:

$$n\text{La}_2\text{O}_3$$\cdot$$m\text{V}_2\text{O}_5 + 2(n-m)\text{ZrO}_2 = 2m\text{LaVO}_4 + (n-m)\text{La}_2\text{Zr}_2\text{O}_7, \quad (1)$$

in which the valence state of vanadium ions does not change. Thus, these reactions can be characterized as the recombination of constituent oxides which may be caused by the difference in the stabilization energy from constituent oxides among La$_2$Zr$_2$O$_7$, LaVO$_4$ and nLa$_2$O$_3$$\cdot$mV$_2$O$_5$.

Note that the polygon of La$_2$Zr$_2$O$_7$ partially covers those of LaVO$_3$ and LaVO$_4$, indicating that LaVO$_4$ and LaVO$_3$ can coexist with both ZrO$_2$ and La$_2$Zr$_2$O$_7$. The equilibrium oxygen partial pressure between LaVO$_3$ and LaVO$_4$ is derived from the following reaction:

$$\text{LaVO}_4 = \text{LaVO}_3 + 1/2\text{O}_2(g). \quad (2)$$

which is not affected by the presence of ZrO$_2$ nor of La$_2$Zr$_2$O$_7$. On the other hand, the decomposition oxygen partial pressure of LaVO$_3$ is affected by the presence of ZrO$_2$. In the absence of ZrO$_2$, LaVO$_3$ decomposes as follows:

$$\text{LaVO}_3 = 1/2\text{La}_2\text{O}_3 + \text{V} + 3/4\text{O}_2(g). \quad (3)$$

In the presence of ZrO$_2$, LaVO$_3$ decomposes as follows:

$$\text{LaVO}_3 + \text{ZrO}_2 = 1/2\text{La}_2\text{Zr}_2\text{O}_7 + \text{VO} + 1/4\text{O}_2(g). \quad (4)$$

Since the main reaction product changes from La$_2$O$_3$ to La$_2$Zr$_2$O$_7$, the decomposition oxygen partial pressure increases, and the decomposition product of the vanadium component changes from V metal in eq. (3) to VO(s) in eq. (4). The present diagram clearly shows why reaction products as well as the decomposition pressure change in the presence of ZrO$_2$.

### 3.2 La-Zr-Cr-O system

In the present treatment, lanthanum chromates, namely, La$_2$CrO$_6$ and its decomposition derivatives$^{27}$, are neglected; this is partly because no experimental value nor estimate is available at present for their thermodynamic properties. Since behavior of these compounds may become important in preparing LaCrO$_3$-based interconnectors in a planar solid oxide fuel cell, it is hoped to construct diagrams including these compounds.

The present chemical potential diagram without lanthanum chromates is simple (see Fig. 2). The stability polygon of LaCrO$_3$ is wide and it decomposes only in an extremely reductive atmosphere:

$$\text{LaCrO}_3 = 1/2\text{La}_2\text{O}_3 + \text{Cr} + 3/4\text{O}_2(g). \quad (5)$$

LaCrO$_3$ does not react with ZrO$_2$ except for an extremely reductive condition as follows:

$$\text{LaCrO}_3 + \text{ZrO}_2 = 1/2\text{La}_2\text{Zr}_2\text{O}_7 + \text{Cr} + 3/4\text{O}_2(g). \quad (6)$$

In a practical sense, it can be concluded that LaCrO$_3$ and ZrO$_2$ is chemically compatible. This is apparently due to the fact that the stabilization energy of LaCrO$_3$ from La$_2$O$_3$ and Cr$_2$O$_3$ (estimated as $-34 \times 2 \text{kJ/mol}$) is much larger than that of La$_2$Zr$_2$O$_7$ (evaluated as $-22 \times 4 \text{kJ/mol}$).

Although chromates are excluded in the present treatment, their possible effects can be qualitatively predicted from comparison with the La-Zr-V-O system; that is, La$_2$CrO$_6$ will appear at the lower and right-hand side of the polygon of LaCrO$_3$ and will be covered partly by the polygon of La$_2$Zr$_2$O$_7$.

### 3.3 La-Zr-Mn-O system

LaMnO$_3$ decomposes as follows:

$$\text{LaMnO}_3 = 1/2\text{La}_2\text{O}_3 + \text{MnO} + 1/4\text{O}_2(g). \quad (7)$$

whereas LaMnO$_3$ reacts with ZrO$_2$ in a reductive atmosphere as follows:

$$\text{LaMnO}_3 + \text{ZrO}_2 = 1/2\text{La}_2\text{Zr}_2\text{O}_7 + \text{MnO} + 1/4\text{O}_2(g). \quad (8)$$
Fig. 1 Chemical potential diagram for La-Zr-V-0 system at 1273 K under a condition of a(ZrO2)=1; dotted lines show the stability polygons of double oxides in La-V-0 system. Superimposed area of La2Zr2O7 indicates that nLa2O3•mV2O5 phases react with ZrO2 to decompose into La2Zr2O7 and LaVO4.

Fig. 2 Chemical potential diagram for La-Zr-Cr-0 system at 1273 K under a condition of a(ZrO2)=1.

Fig. 3 Chemical potential diagram for La-Zr-Mn-0 system at 1273 K under a condition of a(ZrO2)=1.

Fig. 4 Chemical potential diagram for La-Zr-Fe-0 system at 1273 K under a condition of a(ZrO2)=1.

Fig. 5 Chemical potential diagram for La-Zr-Co-0 system at 1273 K under a condition of a(ZrO2)=1. La4Co3O10 and La2CoO4 react with ZrO2.

Fig. 6 Chemical potential diagram for La-Zr-Ni-0 system at 1273 K under a condition of a(ZrO2)=1. LaNiO3 is not stable in air. La4Ni3O10 and La2NiO4 are not stable against reactions with ZrO2.
The decomposition oxygen pressure for eq. (7) is about $10^{-15}$ bar at 1273 K, whereas the equilibrium oxygen pressure for eq. (8) is about $10^{-6}$ bar. This change in oxygen pressure caused by the presence of ZrO$_2$ is larger in the La-Zr-Mn-O system than in the La-Zr-Cr-O system. This is due to the difference in the chemical reaction scheme given in eqs. (5)-(8). In the La-Zr-Cr-O system, one of reaction products is Cr, whereas MnO is formed in the La-Zr-Mn-O system; correspondingly, the mole number of evolved oxygen per one mole of transition metal in eq. (6) is three times larger than that in eq. (8). When the valence change of the transition metal on reaction is large, the effect of the presence of ZrO$_2$ becomes small. Interrelation between these chemical features and the geometrical features in the chemical potential diagram will be discussed later from the thermodynamic point of view.

3.4 La-Zr-Fe-O system

Although LaFeO$_3$ decomposes into La$_2$O$_3$ and Fe,

$$\text{LaFeO}_3 = \frac{1}{2} \text{La}_2\text{O}_3 + \text{Fe} + \frac{3}{4} \text{O}_2(g), \quad (9)$$

the decomposition reaction in the presence of ZrO$_2$ can be written as follows;

$$\text{LaFeO}_3 + \text{ZrO}_2 = \frac{1}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \frac{1}{3} \text{Fe}_3\text{O}_4 + \frac{5}{12} \text{O}_2(g). \quad (10)$$

The decomposition product is Fe$_3$O$_4$ instead of Fe in eq. (9), and the equilibrium oxygen pressure is shifted to the oxidative side as given in Fig. 4. These features are similar to those of LaVO$_3$.

3.5 La-Zr-Co-O system

In the La-Co-O system, LaCoO$_3$, La$_4$Co$_3$O$_{10}$ and La$_2$CoO$_4$ are known. Figure 5 shows that the stability areas of La$_2$CoO$_4$ and of La$_4$Co$_3$O$_{10}$ are located in a limited region of oxygen partial pressure and are both covered by La$_2$Zr$_2$O$_7$; this suggests that these compounds are not compatible with ZrO$_2$ as follows;

$$\text{La}_2\text{CoO}_4 + 2 \text{ZrO}_2 = \text{La}_2\text{Zr}_2\text{O}_7 + \text{CoO} \quad (11)$$

$$\text{La}_4\text{Co}_3\text{O}_{10} + 4 \text{ZrO}_2 = 2 \text{La}_2\text{Zr}_2\text{O}_7 + 3 \text{CoO} + \frac{1}{2} \text{O}_2(g). \quad (12)$$

LaCoO$_3$ reacts with ZrO$_2$ to form La$_2$Zr$_2$O$_7$ even in air at 1273 K.

$$\text{LaCoO}_3 + \text{ZrO}_2 = \frac{1}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \frac{1}{4} \text{CoO} + \frac{1}{4} \text{O}_2(g). \quad (13)$$

Note that the stability area of LaCoO$_3$ is mainly delimited by CoO in the upper side of the diagram; this makes the stability area of LaCoO$_3$ sharpened to the reductive side and also gives rise to a large shift of the equilibrium oxygen partial pressure to the oxidative side in the presence of ZrO$_2$.

3.6 La-Zr-Ni-O system

At 1273 K, LaNiO$_3$ is no more stable in air against decompositions as shown in Fig. 6. LaNiO$_3$ decomposes as follows;

$$\text{LaNiO}_3 = \frac{1}{4} \text{La}_4\text{Ni}_3\text{O}_{10} + \frac{1}{4} \text{NiO} + \frac{1}{8} \text{O}_2(g). \quad (14)$$

La$_4$Ni$_3$O$_{10}$ as well as LaNiO$_3$ react with ZrO$_2$ as follows;

$$\text{LaNiO}_3 + \text{ZrO}_2 = \frac{1}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \frac{1}{4} \text{NiO} + \frac{1}{4} \text{O}_2(g). \quad (15)$$

$$\text{La}_4\text{Ni}_3\text{O}_{10} + 4 \text{ZrO}_2 = 2 \text{La}_2\text{Zr}_2\text{O}_7 + 3 \text{NiO} + \frac{1}{2} \text{O}_2(g). \quad (16)$$

The formation of La$_2$ZrNiO$_6$ will be discussed later.

3.7 Effects of Temperature in La-Zr-Mn-O system

Since a good electrical contact between electrode and electrolyte can be obtained by high temperature heat treatment, it is of technological importance to see whether or not the reaction between two materials proceeds at high temperatures. Figure 7 shows the chemical potential diagrams for the La-Zr-Mn-O system at selected temperatures. Since the reaction between LaMnO$_3$ and ZrO$_2$ given in eq. (8) is accompanied with the reduction of transition metal ions, the equilibrium oxygen partial pressure increases with increasing temperature.

$$\text{La}_2\text{CoO}_4 + 2 \text{ZrO}_2 = \text{La}_2\text{Zr}_2\text{O}_7 + \text{CoO} \quad (11)$$

$$\text{La}_4\text{Co}_3\text{O}_{10} + 4 \text{ZrO}_2 = 2 \text{La}_2\text{Zr}_2\text{O}_7 + 3 \text{CoO} + \frac{1}{2} \text{O}_2(g). \quad (12)$$

LaCoO$_3$ reacts with ZrO$_2$ to form La$_2$Zr$_2$O$_7$ even in air at 1273 K.

$$\text{LaCoO}_3 + \text{ZrO}_2 = \frac{1}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \frac{1}{4} \text{CoO} + \frac{1}{4} \text{O}_2(g). \quad (13)$$

Note that the stability area of LaCoO$_3$ is mainly delimited by CoO in the upper side of the diagram; this makes the stability area of LaCoO$_3$ sharpened to the reductive side and also gives rise to a large shift of the equilibrium oxygen partial pressure to the oxidative side in the presence of ZrO$_2$.

3.6 La-Zr-Ni-O system

At 1273 K, LaNiO$_3$ is no more stable in air against decompositions as shown in Fig. 6. LaNiO$_3$ decomposes as follows;

$$\text{LaNiO}_3 = \frac{1}{4} \text{La}_4\text{Ni}_3\text{O}_{10} + \frac{1}{4} \text{NiO} + \frac{1}{8} \text{O}_2(g). \quad (14)$$

La$_4$Ni$_3$O$_{10}$ as well as LaNiO$_3$ react with ZrO$_2$ as follows;

$$\text{LaNiO}_3 + \text{ZrO}_2 = \frac{1}{2} \text{La}_2\text{Zr}_2\text{O}_7 + \frac{1}{4} \text{NiO} + \frac{1}{4} \text{O}_2(g). \quad (15)$$

$$\text{La}_4\text{Ni}_3\text{O}_{10} + 4 \text{ZrO}_2 = 2 \text{La}_2\text{Zr}_2\text{O}_7 + 3 \text{NiO} + \frac{1}{2} \text{O}_2(g). \quad (16)$$

The formation of La$_2$ZrNiO$_6$ will be discussed later.

3.7 Effects of Temperature in La-Zr-Mn-O system

Since a good electrical contact between electrode and electrolyte can be obtained by high temperature heat treatment, it is of technological importance to see whether or not the reaction between two materials proceeds at high temperatures. Figure 7 shows the chemical potential diagrams for the La-Zr-Mn-O system at selected temperatures. Since the reaction between LaMnO$_3$ and ZrO$_2$ given in eq. (8) is accompanied with the reduction of transition metal ions, the equilibrium oxygen partial pressure increases with increasing temperature.
Correspondingly, the reductive-side corner of the hatched area of LaMnO₃ moves to the oxidative side with increasing temperature.

4. NONSTOICHIOMETRY OF LaMnO₃

LaMnO₃ is the perovskite compound that has the most appreciable A-site nonstoichiometry among the transition metal perovskites.²⁸,²⁹

We have made an attempt¹⁹ to represent the nonstoichiometric LaMnO₃ in terms of an ideal association solution consisting of La₉.₆₆₇MnO₃, La₉.₆₆₇MnO₂.₅, LaMnO₃ and LaMnO₂.₅. After their thermodynamic parameters were determined so as to reproduce the thermogravimetric results, the stable composition region of La₉MnO₃₋δ and its reaction zone with Y₂O₃ stabilized ZrO₂ (YSZ) were calculated as functions of oxygen partial pressure and temperature using the CTC/SOLGASMIX program.⁴,⁶

In Fig. 8, results of chemical equilibria calculations at 1273 K are reproduced at the upper part, whereas at the lower part, the same equilibria are plotted in the present adopted chemical potential diagram; note that in this calculations, YSZ was adopted as one of reactants. For comparison, phase equilibria obtained without consideration on nonstoichiometry are also presented as dashed lines. To directly compare with results for YSZ in which the activity of ZrO₂ is about 0.6, dotted and dashed lines were obtained for the case of a(ZrO₂) = 0.6.

Figure 8 shows that the stability polygon of LaMnO₃ can be divided into the hatched ZrO₂-compatible area and the La₂Zr₂O₇-compatible area. An important point is that this feature in chemical potentials actually corresponds to the reaction between perovskites and ZrO₂; that is, the manganites in the La₂Zr₂O₇-compatible area can react with ZrO₂ to form La₂Zr₂O₇ and the La-poorer manganites. Note that this reaction can take place even in air; in this sense,
this reaction is different from those represented by eqs. (4) and (8).

Since the stability polygons of perovskites are all divided in terms of the compatibility with ZrO$_2$ as shown in Figs. 1 to 6, this implies that if there would be small La nonstoichiometry in other perovskites (for example, LaCrO$_3$), the perovskites in the La-rich side can react with ZrO$_2$ to form La$_2$Zr$_2$O$_7$ and the La-poorer perovskites.

5. DISCUSSION

The reaction of transition metal perovskites with ZrO$_2$ can be characterized as a combination of the La$_2$Zr$_2$O$_7$ formation and the reduction of transition metal ions.$^{20}$ The former La$_2$Zr$_2$O$_7$ formation is common to all system, whereas the latter reduction depends on system. In this section, interrelationship will be examined between these chemical features and the geometrical features in the chemical potential diagram; a special emphasis will be placed on effects of the valence state of transition metals on the chemical features of the reactions.

The La$_2$Zr$_2$O$_7$ formation as a result of reaction between perovskites and ZrO$_2$ is represented by the point that stability polygons of perovskites are narrowed by the polygon of La$_2$Zr$_2$O$_7$ instead of La$_2$O$_3$. Since two borderlines between LaMO$_3$ and La$_2$O$_3$ and between LaMO$_3$ and La$_2$Zr$_2$O$_7$ are both horizontal, it is easy to compare the extent of shift among Figs. 1 to 6. The same magnitude of shift can be explained thermodynamically as follows:

The borderline between LaMO$_3$ and La$_2$O$_3$ is represented by the following chemical potentials of compounds:

$$\mu (\text{La}) + \mu (\text{M}) + 3\mu (0) = \Delta \mu G (\text{LaMO}_3).$$

Since the vertical axis variable is given as $\log \{a(M)/a(\text{La})\} = (\mu (\text{M}) - \mu (\text{La}))/2.303RT$, it is derived from the difference between eqs. (17) and (18) as:

$$\mu (\text{La}) - \mu (\text{Mo}) = \Delta \mu (\text{LaMO}_3) = \Delta \mu (\text{La}_2\text{Zr}_2\text{O}_7) - \Delta \mu (\text{La}_2\text{O}_3).$$

The borderline between LaMO$_3$ and La$_2$Zr$_2$O$_7$ in the presence of ZrO$_2$ is given as follows:

$$\mu (\text{La}) + \mu (\text{M}) + 3\mu (0) = \Delta \mu G (\text{LaMO}_3) + 2\mu (\text{Zr}) + 7\mu (0) = \Delta \mu G (\text{La}_2\text{Zr}_2\text{O}_7).$$

By rearranging eqs. (20) to (22), the following equation can be obtained:

$$\mu (\text{La}) - \mu (\text{La}) = \Delta \mu (\text{LaMO}_3)$$

$$- \Delta \mu G (\text{La}_2\text{Zr}_2\text{O}_7) - 2\Delta \mu G (\text{ZrO}_2).$$

The difference between eqs. (19) and (23) corresponds to the shift of the polygonal border:

$$\Delta \mu (\text{La}) = \Delta \mu G (\text{La}_2\text{Zr}_2\text{O}_7)$$

$$- \Delta \mu G (\text{LaMO}_3) - 2\Delta \mu G (\text{ZrO}_2).$$

This is the Gibbs energy change for formation of La$_2$Zr$_2$O$_7$ from ZrO$_2$ and La$_2$O$_3$; note that the difference is independent of a kind of transition metal element, M.

On the other hand, the vertical width of polygons of LaMO$_3$ (M=V, Cr, Fe) is given in a similar manner as follows:

$$\Delta \mu (\text{La}) - \mu (\text{La}) = 2\Delta \mu G (\text{LaMO}_3) - \Delta \mu G (\text{La}_2\text{O}_3) - 2\Delta \mu G (\text{ZrO}_2).$$

Since the stabilization energy of LaMO$_3$ (M=V, Cr, Fe) given in eq. (25) is much larger than that of La$_2$Zr$_2$O$_7$ in eq. (24), the Gibbs energy change for the following reaction becomes positive:

$$2\text{LaMO}_3 + 2\text{ZrO}_2 = \text{La}_2\text{Zr}_2\text{O}_7 + 2\text{M}_2\text{O}_3.$$
the case of M=V, Fe, and Cr, the M$_2$O$_3$ phase as well as LaM$_2$O$_5$ are relatively stable over a wide range of oxygen partial pressure. In such cases, the compatibility between ZrO$_2$ and LaM$_2$O$_5$ is good over a wide oxygen potential range. On the other hand, for the case of M=Ni and Co, the monoxide phase appears and delimits the stability polygon of perovskites; this gives rise to the high oxygen partial pressure of decomposition of perovskites as well as the high equilibrium oxygen pressure associated with the reaction between perovskites and ZrO$_2$.

This effect of the lower valent oxides is represented as the following geometrical features in the chemical potential diagrams: Although the borderline of LaM$_2$O$_5$ with M$_2$O$_3$ is horizontal, borderlines with the lower valent oxides have slopes. Roughly speaking, the intersect between one of those lines and the horizontal line with La$_2$O$_3$ determines the decomposition point of the perovskite. This means that with increasing stability of the lower valent oxides, the decomposition oxygen partial pressure of perovskite increases.

As described above, the La$_2$Zr$_2$O$_7$ formation gives rise to the shift of the La$_2$O$_3$-side border of the perovskite. Although this shift is in the same magnitude in the vertical direction, the resulting changes of the decomposition oxygen pressure are different; this is due to the deference in the geometrical features among perovskites and transition metal binary oxides. Again, the change in the equilibrium oxygen pressure becomes significant with increasing stability of the lower valent oxides.

When the divalent ions become relatively stable in the end of the transition metal series, another interesting feature appears in the reactions between LaM$_2$O$_5$ and ZrO$_2$, that is, the formation of La$_2$ZrM$_2$O$_7$ (M=NI) observed by Echigoya et al.\textsuperscript{26} This implies that a series of pseudoternary compounds, La$_{n+1}$M$_m$Zrn-m O$_{3n+1}$ (M-divalent transition metal and 2(3n+1)-3(n+1) = 2m+4(n-m)), can be also formed. Appearance of such pseudoternary compounds makes it complicated to graphically show phase relations in the present type of chemical potential diagram. They also found an interesting phenomenon that reaction products between La(Ni,Co)O$_3$ and YSZ formed a multilayered reaction zone. These make it necessary to construct another type of the chemical potential diagram, a log \{a(La)/a(Zr)\} vs. log \{a(M)/a(Zr)\} plot, which was found to be effective in clarifying phase relations including the pseudoternary compounds; this also made clear correlation between the geometrical configuration of compounds in the diagram and the multilayered stacking of reaction products. This will be published elsewhere.

Since the tetravalent ions can exist in the lanthanum manganites, the A-site nonstoichiometry becomes significant. This gives rise to another feature of reaction between LaM$_2$O$_5$ and ZrO$_2$; that is, this reaction which is originated from the A-site nonstoichiometry is not accompanied with reduction of transition metal ions nor with precipitation of other transition metal oxides. As described above, the present chemical potential diagram can account for this feature reasonably from the thermodynamic point of view.

6. CONCLUSION

The present superimposed chemical potential diagrams for the La-Zr-M-O systems are quite convenient to see the stability of double oxides in the La-M-O systems and their compatibility with ZrO$_2$. Since the geometrical features of the chemical potential diagram are not significantly affected by the nonstoichiometric properties, this makes it possible to construct a diagram under a stoichiometric approximation and to use it in making chemical thermodynamic considerations on phase relations with-
out losing the essential points which should be described in terms of chemical potentials.

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