



Basicity and hydroxyl capacity of proton-conducting perovskites

Shu Yamaguchi^{a,*}, Kenji Nakamura^a, Toru Higuchi^b, Shik Shin^c, Yoshiaki Iguchi^a

^aDepartment of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

^bFaculty of Science, Science University of Tokyo, Kagurasaka 1-3, Shinjuku, Tokyo 162-0825, Japan

^cInstitute of Solid State Physics, University of Tokyo, Tanashi 188-8501, Japan

Abstract

In order to understand the large solubility of protons in perovskite proton conductors, a new approach employing the hydroxyl capacity, termed $C'_{\text{OH}} \equiv [\text{OH}'_{\text{O}}] \cdot [\text{V}''_{\text{O}}]^{-1} \cdot p_{\text{H}_2\text{O}}^{-1/2}$, is proposed and examined for 5 mol% $\text{YbO}_{1.5}$ -doped BaCeO_3 . Prior to the solubility experiments, the phase relation in an isothermal section of the phase diagram for $\text{BaO}-\text{CeO}_2-\text{YbO}_{1.5}$ was determined and activity measurements for BaO were carried out. The values of C'_{OH} were evaluated by measuring the solubility of water using the thermogravimetric method under a controlled BaO activity by employing the reaction $\text{BaO}_{(\text{in BaCeO}_3)} + \text{CO}_2(\text{g}) = \text{BaCO}_3$. C'_{OH} did not exhibit a strong dependency on the BaO activity, indicating that the basicity of BaCeO_3 , defined as the activity of O^{2-} ions, is almost constant across the homogeneity region. It has been estimated that the A-site vacancy in ABO_3 mainly contributes to the steep change in BaO activity. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Proton; Perovskite; Basicity; Capacity; Solubility; Activity; Thermodynamics

1. Introduction

One of the most important characteristics of proton-conducting oxides is the extent of solubility of the protons. The dissolution reaction of protons has been well described by defect chemical reactions in earlier investigations. On the other hand, the activity of the basic oxide (AO) in an ABO_3 perovskite oxide is expected to show a steep change across its narrow homogeneous range. Because of the strong affinity of AO for H_2O , one can expect enhanced solubility in the AO-rich composition. As the thermochemical activity of AO is closely related

to the basicity of the oxide at a given composition, a strong correlation between the solubility of water or protons and basicity is expected. No discussion, however, has been given on the relation between basicity and the solubility of protons, since the basicity of complex oxides has never been taken into account in the defect chemical treatment. It is also known that the solubility of protons varies with the concentration of dopant cations in perovskite-type oxides. However, the relation between the dopant concentration and the solubility has never been discussed in terms of the basicity. In the present study, a new approach employing the hydroxyl capacity, proposed by Wagner [1], is applied to the defect chemistry in order to discuss the solubility of protons in perovskite-type oxides.

*Corresponding author. Fax: +81-52-735-5318.

E-mail address: yamagchi@mse.nitech.ac.jp (S. Yamaguchi).

2. Theoretical background

The basicity of a complex oxide system is defined as the chemical potential of the oxide ion ($\mu_{O^{2-}}$) or the thermochemical activity of the oxide ion ($a_{O^{2-}}$) in an ionic solution, since O^{2-} is the common anion in oxide systems. However, it is not measurable without approximation because complex oxides are concentrated ionic solutions, in contrast to ionic aqueous solutions which may be regarded as ideal dilute (Henrian) solutions. Many kinds of measurable measures of basicity using thermochemical and physical methods have been proposed. Among them, the thermochemical activity of basic oxide and the solubility of gaseous components, termed capacity, have been widely accepted as a thermochemical measure of the basicity in liquid oxides [1].

In liquid oxides, two types of dissolution mechanisms for water have been proposed, indicating that H_2O acts as either an acid or a base depending on the basicity of the solution. Typical results for liquid silicates are shown in Fig. 1:

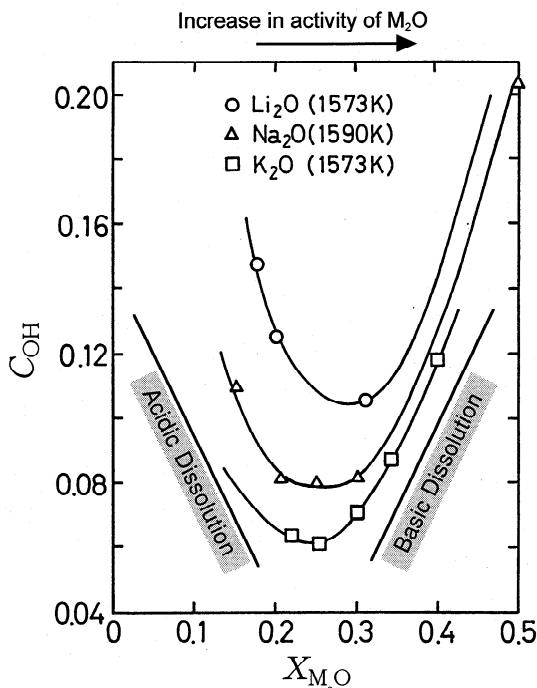
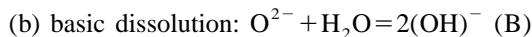


Fig. 1. Relation between hydroxyl capacity and composition of alkaline silicates [2].



$$K_A = [H^+]^2 \cdot a_{O^{2-}} / p_{H_2O}; \quad (1)$$

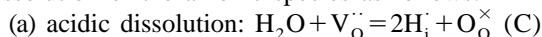


$$K_B = [OH^-]^2 / a_{O^{2-}} \cdot p_{H_2O}. \quad (2)$$

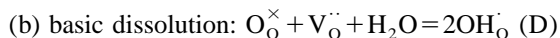
Both reactions are considered as buffering reactions to neutralize the basicity or acidity. The hydroxyl capacity (C_{OH}) is defined for liquid oxide systems such as oxide slags as

$$C_{OH} = [\%HO_{0.5}] \cdot p_{H_2O}^{-1/2} (= [H^+, OH^-] \cdot p_{H_2O}^{-1/2}) \\ = (K_B \cdot a_{O^{2-}})^{1/2}, \text{ or } (K_A \cdot a_{O^{2-}}^{-1})^{1/2}. \quad (3)$$

For the sake of application of the hydroxyl capacity to solid complex oxides, it is necessary to make a small modification on the available site for the dissolution of the anionic species as follows:



$$K_A = [H_i^+]^2 \cdot [O_O^{\times}] / [V_O^{\cdot\cdot}] \cdot p_{H_2O}; \quad (4)$$



$$K_B = [OH_O^{\cdot}]^2 / [O_O^{\times}] \cdot [V_O^{\cdot\cdot}] \cdot p_{H_2O}. \quad (5)$$

The Kröger and Vink notation is used for the description of defect species in solids. Since H_2O is believed to dissolve by the basic dissolution mechanism in ABO_3 perovskite [3], the apparent hydroxyl capacity of a solid complex oxide can be written by the following equation:

$$C_{OH} \equiv [OH_O^{\cdot}] \cdot [V_O^{\cdot\cdot}]^{-1/2} \cdot p_{H_2O}^{-1/2} \\ = (K_B \cdot a_{O_O^{\times}})^{1/2}. \quad (6)$$

The activity of O_O^{\times} is further related to $a_{O^{2-}}$ in equilibrium with the crystal through the following relation: $O^{2-} + V_O^{\cdot\cdot} = O_O^{\times}$ (E):

$$K_O = [O_O^{\times}] / a_{O^{2-}} \cdot [V_O^{\cdot\cdot}]. \quad (7)$$

Then, the overall reaction for the water dissolution may be written as $O^{2-} + 2V_O^{\cdot\cdot} + H_2O = 2OH_O^{\cdot}$ (F)

$$K_O K_B = [OH_O^{\cdot}]^2 / a_{O^{2-}} \cdot [V_O^{\cdot\cdot}]^2 \cdot p_{H_2O}. \quad (8)$$

Therefore, the hydroxyl capacity, C'_{OH} , for solid

oxides in the basic dissolution domain is defined by the equation

$$C'_{\text{OH}} \equiv [\text{OH}^-] \cdot [\text{V}_\text{O}^{\bullet}]^{-1} \cdot P_{\text{H}_2\text{O}}^{-1/2} \\ = (K_\text{O} K_\text{B} \cdot a_{\text{O}^{2-}})^{1/2}. \quad (9)$$

Finally, $a_{\text{O}^{2-}}$ is related to the activity of a basic oxide (AO), a_{AO} , by the equilibrium $\text{AO} = \text{A}^{2+} + \text{O}^{2-}$ (G):

$$K_{\text{AO}} = a_{\text{A}^{2+}} \cdot a_{\text{O}^{2-}} / a_{\text{AO}}, \quad (10)$$

where $\text{A}^{2+} + \text{V}_\text{A}^{\bullet} = \text{A}_\text{A}^\times$ (H):

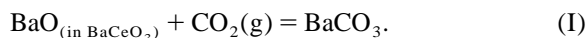
$$K_\text{C} = [\text{A}_\text{A}^\times] / a_{\text{A}^{2+}} \cdot [\text{V}_\text{A}^{\bullet}]. \quad (11)$$

The above discussion suggests a difference between solid and liquid systems: vacant sites ($\text{V}_\text{O}^{\bullet}$) are explicitly necessary for the dissolution of OH^- to proceed in solid systems, while it is implicitly included in the case of liquids. Since a_{AO} changes markedly across the ABO_3 perovskite phase from the AO-rich to the BO_2 -rich side, one may expect a change in C'_{OH} across the ABO_3 phase.

One of the disadvantage of the capacity is that all the activity coefficients of solutes and defects are assumed to be constant, since the Henrian standard state is used for the activity unit. As the activity coefficient changes with variation of the composition even in a system of the same components, as well as in different component systems, it is not possible to make a direct comparison among the capacities of different perovskite systems.

3. Experimental

For the solubility measurements, 5 mol% $\text{YbO}_{1.5}$ -doped BaCeO_3 ($\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.75}$) was chosen, because of its appropriate CO_2 range for controlling BaO activity. The solubility of water at 900°C as a function of BaO activity (a_{BaO}) was examined by thermogravimetric analysis (TGA) in order to estimate C'_{OH} . The value of a_{BaO} was controlled by equilibrating samples with CO_2 in the atmosphere by the reaction



Polycrystalline samples composed of two phases

of $\text{YbO}_{1.5}$ -doped BaCeO_3 and BaCO_3 were prepared by a solid state reaction method. Powdery raw materials weighed to a proportion of 2–5 mol% excess BaCO_3 were mixed and fired initially at 1400°C for 10 h followed by a sintering process at 1500 or 1600°C for 10 h. The samples were annealed at 900°C for about 1 month under a dry atmosphere at $P_{\text{O}_2} = 0.20$ and the same P_{CO_2} for subsequent solubility measurements. Then, a sample piece was installed into a TGA system (Shimadzu TGA-40) and equilibrated under a dry $\text{O}_2 + \text{CO}_2 + \text{Ar}$ atmosphere until the weight of the sample stabilized. Subsequently, a water-saturated gas mixture of $\text{O}_2 + \text{CO}_2 + \text{Ar}$ was introduced and the equilibrium weight change was recorded after the weight increase reached a constant value. The time required for equilibration was several hours to 20 h in most cases.

Prior to the solubility measurements, activity measurements of BaO in the $\text{BaO}-\text{CeO}_2-\text{YbO}_{1.5}$ system were made using the formation reaction of BaCO_3 (reaction (I)) by a TGA method, in addition to the determination of the isothermal phase relation in the $\text{BaO}-\text{CeO}_2-\text{YbO}_{1.5}$ system at 1200°C . Details of the thermochemical stability will be published elsewhere [4].

4. Results and discussion

4.1. Thermochemical stability

Fig. 2 shows the isothermal section of the ternary phase diagram for $\text{BaO}-\text{CeO}_2-\text{YbO}_{1.5}$ at 1200°C determined in the present study. The phase relation examined was almost identical to that reported for $\text{BaO}-\text{CeO}_2-\text{NdO}_{1.5}$ [5]. The three-phase regions of [A] $\text{BaCeO}_3 + \text{CeO}_2 + \text{YbO}_{1.5}$ and [B] $\text{BaCeO}_3 + \text{Ba}_3\text{Yb}_4\text{O}_9 + \text{YbO}_{1.5}$ were identified. In addition, [C] $\text{BaCeO}_3 + \text{Ba}_3\text{Yb}_4\text{O}_9 + \text{BaO}$ was estimated as being present, in which the activity of BaO is almost unity.

Fig. 3 shows the equilibrium CO_2 pressure as a function of the absolute reciprocal temperature for the two-phase coexistence of $\text{BaCeO}_3 + \text{CeO}_2$ in the binary system and the three-phase coexistence (TPC) regions of [A] and [B] in the ternary system. The knee at about 900°C observed for the binary system may correspond to the transformation between the rhombohedral and cubic phase, while no indication

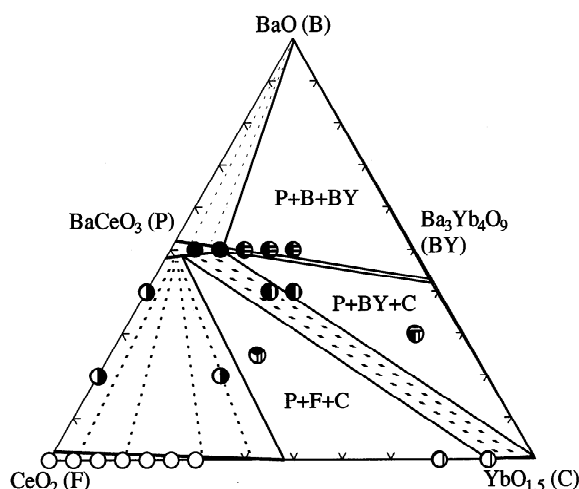


Fig. 2. Isothermal section of the phase diagram for the BaO–CeO₂–YbO_{1.5} quasi-ternary system at 1200°C.

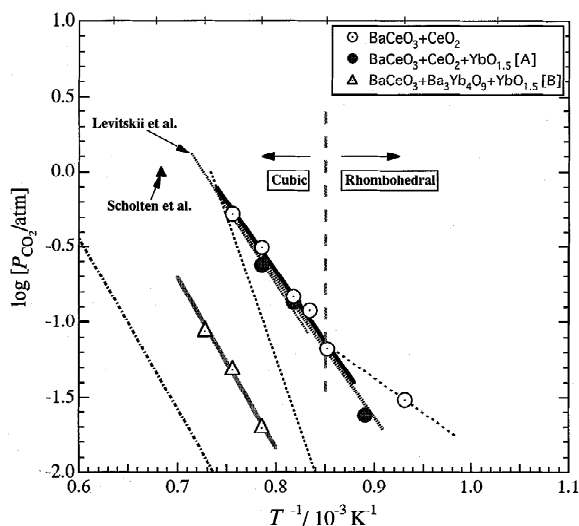


Fig. 3. Relation between $\log(P_{\text{CO}_2}/\text{atm})$ and $1/T$ for the reaction $\text{BaO}_{(\text{in BaCeO}_3)} + \text{CO}_2 = \text{BaCeO}_3$ in the two-phase region of $\text{BaCeO}_3 + \text{CeO}_2$ and the three-phase regions of [A] $\text{BaCeO}_3 + \text{CeO}_2 + \text{YbO}_{1.5}$ and [B] $\text{BaCeO}_3 + \text{Ba}_3\text{Yb}_4\text{O}_9 + \text{YbO}_{1.5}$.

of the transformation was observed for YbO_{1.5}-doped ternary systems. The present results show excellent agreement with those of Levitskii et al. [6], but differ from those of Scholten and Schoonman [7] and Gopalan and Virkar [8]. The results of [A] and [B] TPCs indicate an increase in the BaO activity with the increase of YbO_{1.5} content. It has been reported

that extrapolation of the nose of the BaCeO₃ homogeneity domain deviates towards the CeO₂ side in NdO_{1.5}-doped BaCeO₃ [3], indicating an increase in the extent of the A-site vacancy by NdO_{1.5} substitution. A similar tendency is expected for the YbO_{1.5}-doped system.

Fig. 4 shows the homogeneous domain of BaCeO₃ as functions of $\log a_{\text{BaO}}$ and dopant concentration. The thin solid curves indicate the variation of $\log a_{\text{BaO}}$ under a fixed [A-site]/[B-site] ratio ([Ba]/[Ce+Yb] ratio in this case), estimated from the iso-activity lines of BaO. The present results suggest that Yb substitution increases both a_{BaO} and the vacancy concentration. This may possibly be the reason for the strong dopant concentration dependency of the equilibrium constant of the H₂O dissolution reaction. The activity jump across the BaCeO₃ phase in 5 mol% YbO_{1.5}-doped samples was estimated to be from 1.0 on the BaO-rich side to $10^{-2.2}$ on the CeO₂-rich side.

4.2. Hydroxyl capacity

Fig. 5 shows the relation between $[\text{OH}'_0]/[\text{V}''_0]$ and $P_{\text{H}_2\text{O}}^{1/2}$. From the slope of the plot, the values of C_{H} are calculated, and are shown in Fig. 6, in which the variation of $\log a_{\text{BaO}}$, $2\log C'_{\text{OH}}$, and $\log a_{\text{Ba}^{2+}}$ with $\log P_{\text{CO}_2}$ are also plotted. As the expressions for $a_{\text{Ba}^{2+}}$ and $a_{\text{O}^{2-}}$ (Eqs. (8)–(10)) include the equilibrium constants in which the activity coefficients of the components are involved, the values of $a_{\text{Ba}^{2+}}$ shown in Fig. 4 are relative ones, while those of a_{BaO}

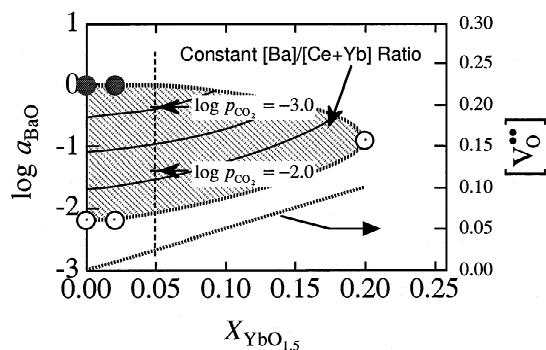


Fig. 4. Variations of BaO activity in the homogeneity domain of the BaCeO₃ phase estimated at 900°C and the concentration of oxygen vacancies with dopant concentration.

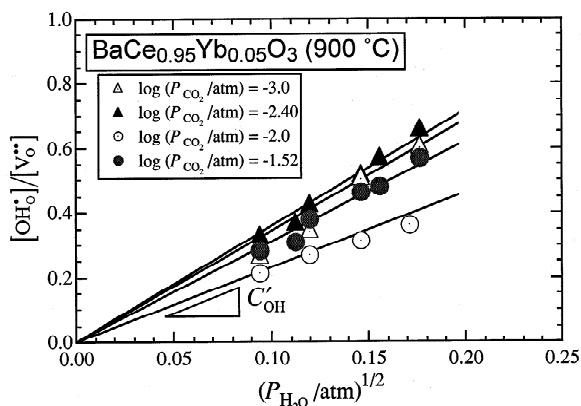


Fig. 5. Relation between $[\text{OH}']/[\text{V}'_{\text{O}}]$ and $(P_{\text{H}_2\text{O}}/\text{atm})^{1/2}$ at 900°C . The slope of each line corresponds to the hydroxyl capacity.

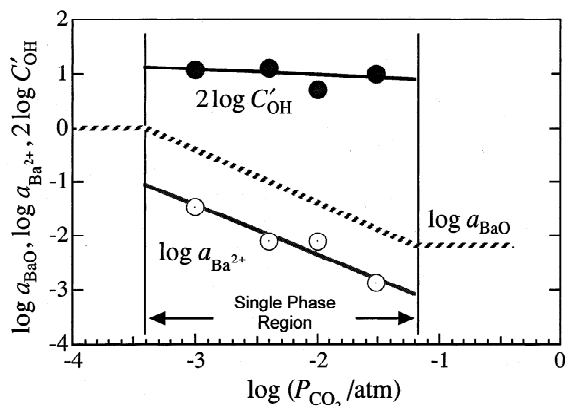


Fig. 6. Variation of $2\log C'_{\text{OH}}$, $\log a_{\text{BaO}}$, and $\log a_{\text{Ba}^{2+}}$ as a function of $\log P_{\text{CO}_2}$.

are based on the Raoultian standard state. The values of $\log a_{\text{Ba}^{2+}}$ were simply calculated from the equation $\log a_{\text{Ba}^{2+}} = \log a_{\text{BaO}} - 2\log C'_{\text{OH}}$ in the present study.

An extremely small dependence of C'_{OH} on $\log P_{\text{CO}_2}$ is observed in contrast to the large activity jump in a_{BaO} across the BaCeO_3 phase. One can carry out further calculations, by combining Eqs. (9) and (10), in order to estimate the variation of $a_{\text{Ba}^{2+}}$.

Results plotted in Fig. 6 show a steep change versus $\log P_{\text{CO}_2}$. As $\log[\text{V}'_{\text{Ba}}]$ is inversely proportional to $\log a_{\text{Ba}^{2+}}$ through reaction (H), the large variation of $\log a_{\text{Ba}^{2+}}$ is estimated to be caused by the extent of the A-site deficiency. As mentioned earlier, an increase in the A-site vacancy in ABO_3 perovskite has been reported for lanthanide oxide substitution. Therefore, the relatively large extent of A-site vacancy dominantly contributes to the change in $\log a_{\text{BaO}}$ across the BaCeO_3 homogeneous domain.

5. Conclusion

A new approach to the understanding of the large solubility of water in ABO_3 perovskite oxides is proposed using the hydroxyl capacity defined as $C'_{\text{OH}} \equiv [\text{OH}'_{\text{O}}] \cdot [\text{V}'_{\text{O}}]^{-1} \cdot p_{\text{H}_2\text{O}}^{-1/2}$, and examined for 5 mol% $\text{YbO}_{1.5}$ -doped BaCeO_3 . Values of C'_{OH} determined under controlled BaO activity indicate that the basicity, defined as the activity of O^{2-} ions, does not show a steep change across the homogeneity domain of BaCeO_3 . It is estimated that the presence of the A-site vacancy in a ABO_3 crystal mainly contributes to the large variation in the BaO activity.

References

- [1] C. Wagner, Metall. Trans. 6B (1975) 405.
- [2] S. Ban-ya, M. Hino (Eds.), Chemical Properties of Molten Slags, The Iron and Steel Institute of Japan, 1991, p. 174.
- [3] T. Norby, Y. Larring, Curr. Opin. Solid State Mater. Sci. 2 (1997) 693.
- [4] S. Yamaguchi, K. Nakamura, unpublished.
- [5] D. Makovec, Z. Samardzija, D. Kolar, J. Am. Ceram. Soc. 80 (1997) 3145.
- [6] V.A. Levitskii, S.L. Solokina, Y.Y. Skolis, M.L. Kovba, Inorg. Mater. 21 (1986) 186.
- [7] M.J. Scholten, J. Schoonman, Solid State Ionics 61 (1993) 183.
- [8] S. Gopalan, A.V. Virkar, J. Electrochem. Soc. 140 (1993) 1060.