

## An oxygen sensor based on copper(I)-conducting $\text{CuTi}_2(\text{PO}_4)_3$ glass ceramics

Kousuke Yamamoto,<sup>a)</sup> Toshihiro Kasuga, and Masayuki Nogami<sup>b)</sup>

*Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

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An electrochemical device for sensing oxygen at low temperature, e.g., 100 °C, was developed by using fast  $\text{Cu}^+$ -conducting ceramics. As the solid electrolyte, a dense glass ceramic consisting of crystalline  $\text{CuTi}_2(\text{PO}_4)_3$  and  $\text{Cu}_3(\text{PO}_4)_2$  phases, which three-dimensionally interlock with each other, has been successfully prepared by the controlled crystallization of the glass in the Cu–Ti–P–O system. The electromotive force generated between the electrodes showed a good Nernstian response to the partial pressure of oxygen even at a relatively low temperature such as 100 °C. The mechanism for oxygen sensing was discussed with regard to the fast  $\text{Cu}^+$  ion conductivity and the redox reaction between  $\text{Cu}^+$  ion in the dense glass ceramic and oxygen gas.

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Zirconia ceramics stabilized with  $\text{Y}_2\text{O}_3$  and CaO show high oxygen ion conductivities and are widely used as oxygen gas sensors in the field of automobiles, environments, securities, and chemical plants.<sup>1</sup> When gases with different partial oxygen pressures are introduced into each electrode compartment of the zirconia electrolyte, an oxygen concentration cell is constructed and gives rise to an electromotive force (EMF) between the electrodes of the cell.<sup>2</sup> Taking into account the temperature dependence of the conductivity, in practice, these zirconia sensors should be operated at temperatures above 700 °C. Sensors operating at low temperatures with durability against oxygen attack, if developed, could possibly have their practical extended application beyond the limitations of stabilized zirconia. Here, we demonstrate a new type of oxygen sensor based on a  $\text{Cu}^+$  conductor at low temperatures, viz. 100 °C. Our ideas are based on the utilization of copper ions with high conductivities and high redox activities for oxygen gas. As charge carriers, it is important to choose cations which react with oxygen gas at electrodes to form oxides with an activated barrier as low as possible. Among some cations exhibiting higher conductivities in solids such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cu}^+$ , and  $\text{Ag}^+$ ,<sup>3,4</sup> copper ions are promising because of their low Gibbs free energy for the formations of  $\text{CuO}$  (−130 kJ/mol) and  $\text{Cu}_2\text{O}$  (−146 kJ/mol).<sup>5</sup> For the application of the  $\text{Cu}^+$  ion conductors as the solid electrolyte, conductivities higher than  $10^{-7} \text{ S cm}^{-1}$  at operating temperature are required. To date, however, there is no report on  $\text{Cu}^+$  ion conductors except for a NASICON- ( $\text{Na}^+$  superionic conducting structure) type copper phosphate. The NASICON-type  $\text{CuTi}_2(\text{PO}_4)_3$  crystal exhibits a high conductivity of  $9.0 \times 10^{-4} \text{ S cm}^{-1}$  at 300 °C<sup>3</sup> and an excellent durability against oxygen gas attack,<sup>6</sup> which is ideal for the copper conductors. However, no one has succeeded in the preparation of the dense  $\text{CuTi}_2(\text{PO}_4)_3$  ceramics because of the inefficiency in the sinterability of the powders. We have been conducting numerous studies on the

preparation of glass ceramics and porous materials containing NASICON-type crystals using the glass-to-crystallization method, and recently succeeded in preparing porous glass ceramics with a skeleton of NASICON-type crystals.<sup>7,8</sup> In this letter, we report the  $\text{Cu}^+$  ions conductivities of the NASICON-type  $\text{CuTi}_2(\text{PO}_4)_3$  crystal-precipitated glass ceramics and the oxygen gas sensing properties of the obtained glass ceramics.

A nominal composition of  $50\text{CuO} \cdot 20\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5$  (mol %) was prepared by melting reagent grade  $\text{CuO}$ ,  $\text{TiO}_2$ , and  $\text{H}_3\text{PO}_4$  (liquid; 85%) at 1250 °C for 1 h in an alumina crucible in air. The melt was poured onto a stainless steel plate and quickly quenched by pressing with an iron plate in a  $\text{N}_2$  atmosphere. In order to facilitate the crystallization of the glass, the resultant glass was heated at 520 °C for phase separation and nucleation of the crystal. Subsequently, the sample was heated in air at 590 °C and successively at 800 °C for the crystal growth of  $\text{CuTi}_2(\text{PO}_4)_3$ . The resulting dense glass ceramic had no serious cracking or deformation.

Figure 1(a) shows the powder x-ray diffraction (XRD) pattern of the sample after heat treatment. Although the XRD pattern shows a slight amount of  $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$  and an unidentified crystal, the main phases identified were  $\text{CuTi}_2(\text{PO}_4)_3$  and  $\text{Cu}_3(\text{PO}_4)_2$ . In general, when the glass is melted at a high temperature (e.g., >1000 °C), the copper ions are incorporated as monovalent ions, since  $\text{Cu}^+$  ions are thermodynamically more stable than  $\text{Cu}^{2+}$  at high temperature.<sup>9,10</sup> Therefore,  $\text{CuTi}_2(\text{PO}_4)_3$ , in which the copper ion is monovalent, can be directly crystallized from the base glass. The microscopic observation of the obtained sample showed a completely dense body without pores. The microscopic observation of the obtained sample showed a completely dense body without press. The morphology of the crystallized phases was examined using a scanning electron microscope (SEM). Prior to the SEM observations, the sample was immersed in 0.5 N  $\text{H}_2\text{SO}_4$  for 3 days at room temperature. By this treatment, the  $\text{Cu}_3(\text{PO}_4)_2$  crystal was completely dissolved, leaving behind the main  $\text{CuTi}_2(\text{PO}_4)_3$  phase, as is evident from Figs. 1(b) and 1(c). From these studies, we concluded that both phases of  $\text{CuTi}_2(\text{PO}_4)_3$  and  $\text{Cu}_3(\text{PO}_4)_2$

<sup>a)</sup>Electronic mail: kyamamot@mse.nitech.ac.jp

<sup>b)</sup>Electronic mail: nogami@mse.nitech.ac.jp

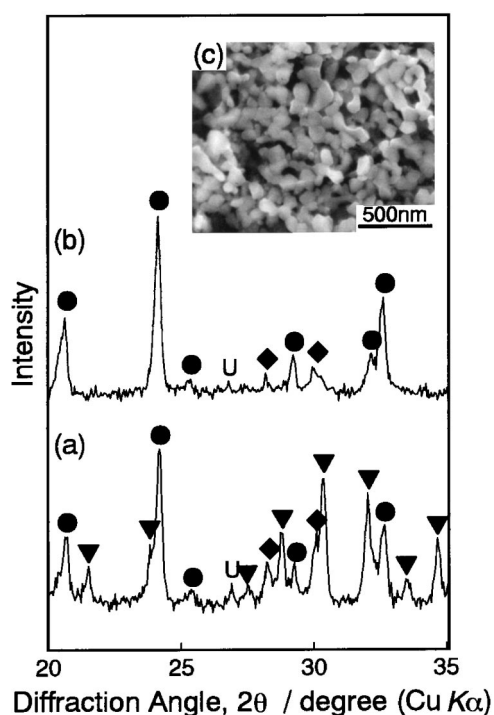


FIG. 1. (a) Powder x-ray diffraction pattern of the glass ceramic obtained by heating by 800 °C. (b) and (c) XRD pattern and SEM photograph of the glass ceramic, respectively, after immersing in 0.5 N H<sub>2</sub>SO<sub>4</sub> at room temperature for 3 days. (●); CuTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, (▼); Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, (◆); α-Cu<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, and (u); unknown phase.

were crystallized into an interconnecting three-dimensional network, in which the volume fraction of the Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> crystal was about 38%.

The alternating current (ac) conductivity was determined from the Cole–Cole plot of the complex impedance using platinum electrodes in the temperature range of 25–300 °C in an argon atmosphere. The Cole–Cole plots of the frequency-dependent complex impedance show a single semicircle, and the electrical conductivity can be determined from the intersecting point of the semicircle with the real axis. Figure 2 shows the relation between the conductivity and temperature.

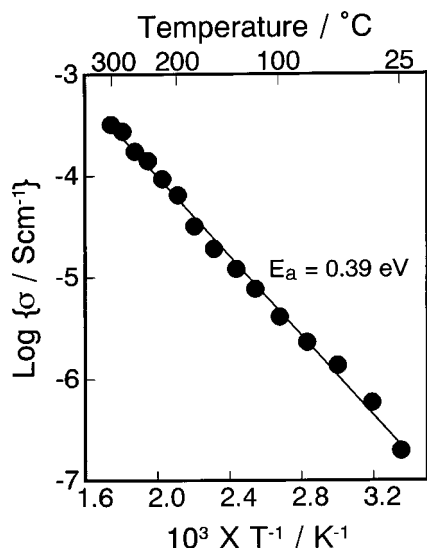


FIG. 2. Temperature dependence of electrical conductivity of glass ceramic obtained by heating at 800 °C.

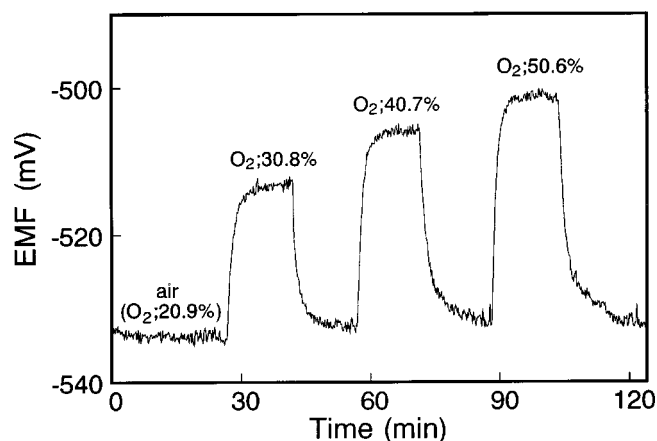


FIG. 3. EMF response upon changing oxygen partial pressure ( $P'_{O_2}$ ) to the reference ( $P''_{O_2} = 20.9\%$ ), measured at 100 °C, for the NASICON-type CuTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>-precipitated glass ceramic obtained by heating at 800 °C.

Note that the conductivity ( $\sigma$ ) exponentially varies with reciprocal temperature ( $T$ ) over the measured temperature range;  $\sigma = \sigma_0 \exp(-E_a/RT)$ , where  $\sigma_0$  and  $E_a$  denote the pre-exponential term and activation energy of the conduction, respectively. The conductivity and the calculated activation energy are  $4 \times 10^{-6} \text{ Scm}^{-1}$  at 100 °C and 0.39 eV, respectively. These values are compared to those of the CuTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> crystal,<sup>6</sup> indicating that the precipitated CuTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> crystal has conduction channels for the Cu<sup>+</sup> ions.<sup>11</sup> Thus, the glass-to-crystallization process is appropriate for the preparation of fast Cu<sup>+</sup>-ion conductors of the NASICON-type CuTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> crystal.

The oxygen concentration cell was constructed using the polished sample with a 9 mm diameter and 0.25 mm thickness. Both faces of the disk were covered with Pt black electrodes. The electrode with the higher oxygen gas pressure was the positive pole and the EMF generated between the electrodes was measured as a function of oxygen gas partial pressure and time. The electrode for sensing oxygen gas was exposed to different O<sub>2</sub>–N<sub>2</sub> gas mixtures, in which the oxygen partial pressure was changed from 20.9 to 80.2 vol % at a flow rate of 200 mL/min. Dried air was used as the reference. Figure 3 shows a typical EMF response, measured at 100 °C, upon changing the oxygen partial pressure. Note that the EMF quickly changes and reaches a steady level within 3 min. Similar EMF responses were observed at different temperatures, and the response speed increased with increasing temperature. The observation of oxygen gas sensing at 100 °C, to our knowledge, is the first time for the Cu<sup>+</sup> ion-containing NASICON-type CuTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> glass ceramic. In Fig. 4 is shown the EMF response versus the logarithm of the oxygen partial pressure at 100 °C, thus satisfying the linear relation with a slope of 170 mV/decade.

The oxygen concentration cell gives rise to an EMF corresponding to the oxygen partial pressure and the EMF is given as follows:

$$E = (RT/nF) \ln(P'_{O_2}/P''_{O_2}),$$

where  $n$  is the number of electrons transferred in the reaction,  $P_{O_2}$  is the partial pressure of oxygen in each electrode compartment, and  $F$  is Faraday's constant. From the slope of

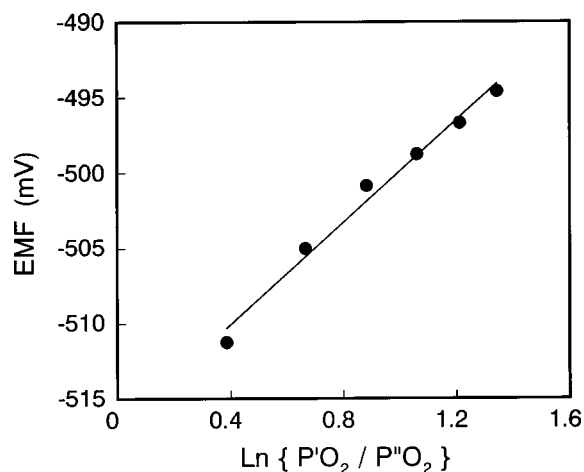


FIG. 4. Relation between EMF and the ratio of oxygen partial pressure ( $P'_{O_2}$ ) to the reference ( $P''_{O_2}=20.9\%$ ), measured at 100 °C, for NASICON-type  $\text{CuTi}_2(\text{PO}_4)_3$ -precipitated glass ceramic obtained by heating at 800 °C.

the line in Fig. 4, the number of electrons ( $n$ ) is estimated to be 1.9. The experimental value  $n=1.9$  is close to  $n=2$ , indicating that the EMF originated from the two-electron reaction for oxygen. Thus, we can conclude that for our glass-ceramic electrolyte, the redox reaction on the electrodes is  $2\text{Cu}^+ + \text{O}_2 + 2e^- = 2\text{CuO}$ , and the high conductivity is attributed to the fast transfer of the ionized  $\text{Cu}^+$  ions through the solid electrolyte.

The glass ceramics investigated here exhibited good stability under a high oxygen concentration at high temperature,

which is further advantageous for practical applications. The preparation of the sensing device working at room temperature is now under investigation, together with the sensing of oxygen gas over a wide range of oxygen pressures.

In conclusion, we have successfully prepared fast  $\text{Cu}^+$ -conducting NASICON-type  $\text{CuTi}_2(\text{PO}_4)_3$  glass ceramics exhibiting excellent oxygen gas sensing even at 100 °C. It is concluded that the EMF is attributed to the redox reaction of the  $\text{Cu}^+$  ions through the electrolyte. These electrochemical cells could show great potential for use in oxygen sensors.

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