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Development of optical high-temperature furnace and its application to the analysis of optoelectronic property of the ionic conductor AgI

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ABSTRACT

The temperature dependence of the electrical conductivity of polycrystalline silver iodide and photoirradiation effect on it are studied by using a compact high temperature furnace that is developed for the analysis of photoirradiation effects on electrical properties of solid materials. With this apparatus, experiments at different temperatures under various environments, *i.e.*, under any gaseous condition or under vacuum condition are possible. The sample composed of the γ-phase AgI shows a hump at ~70 °C in the resistance as a function of temperature. This result suggests the transformation from the γ-phase at this temperature. In the aged sample composed of the mixture of the β-phase and γ-phase, a monotonic decrease of the resistance with the increase of temperature is observed below 147 °C, at which the phase transition to the superionic conducting α-phase takes place. In the polarized α-phase sample at 155 °C, the conductivity change is induced by the photoirradiation of the visible light of 450 nm.

KEYWORDS

Solid state ionic conductor;
Photoirradiation effects;
Optical furnace;
Silver halides.

INTRODUCTION

Electrical properties including electrical conductivity and dielectric response are the most fundamental among a variety of material properties, and these properties have been frequently investigated. Analysis of photoresponse of electrical properties of materials as a function of temperature also yields fundamental information for the understanding of their optoelectronic functions. For such studies, analytical instruments that are equipped with transparent windows, temperature controller, and signal wires for electrical connections are prerequisite. The analytical instruments with which variable sample conditions can be prepared are commercially available, but most products are designed for cryogenic experiments and they are usually quite expensive. On the instruments applicable for spectroscopy at high temperatures, a few papers are reported for Raman spectroscopy and transmission spectroscopy.[1,2] However, a handy furnace which can be used for the study of optoelectronic properties of solid materials at temperatures much higher than room temperature has been scarce.

A class of solid materials in which ionic conductivity is exceptionally high is known as superionic or fast ionic conductors.[3] In particular, superionic conductivity in solids has attracted a great deal of interest for the understanding of the microscopic mechanism underly-

ing the ion transportation. In addition, superionic conductors can be potentially used as solid electrolytes for solid-state devices such as battery or fuel cell. For example, α-phase of silver iodide, *i.e.*, the high-temperature phase of silver iodide (α-AgI) has been extensively studied since it shows a high ionic conductivity (> 10 Scm^{-1}), which is comparable to that of the liquid electrolytes.[4] AgI is also known to show polymorphism. β–AgI with hexagonal wurtzite type structure and γ–AgI with cubic zincblende type structure coexist at room temperature, and phase transition occurs to α–phase at T_c = 147 °C.[3,5] Recently, we have reported the ultraviolet-visible photoirradiation effects on ionic conductivity in AgI at room temperature.[6,7] In this article, we report the experiments at temperatures near or above the T_c. We will show the design of the compact high-temperature furnace that was developed for an analysis of the optoelectronic property of ionic conductors. The study of temperature dependence as well as photoirradiation effects on the conductivity of polycrystalline AgI will be also shown.

The high temperature furnace for electrical measurements with photoirradiation

The first priority in the design of our high temperature optical furnace was the stability of temperature and the selectivity of sample environment. A schematic diagram of the furnace constructed in the present study is shown in Figure 1. The main components of the furnace are a couple of concentric tubes having optical windows.

The outer shroud is a stainless steel tube. Heatproof resin is used to seal the quartz optical windows. The inner chamber composed of a stainless steel tube of a one-inch diameter is connected to a copper block having the same inner diameter as the tube. A hole is prepared at one side of the faces of the copper block to put a quartz window for the optical measurements. The quartz window is sealed using a silicone o-ring. The inner chamber is connected to a one-inch vacuum connector (Swagelok, Ultra-Torr series). This connector and the outer shroud are welded to stainless steel vacuum flanges of the same size. An o-ring is used to seal these flanges. In order to keep the stability of the sample temperature, it is essential to minimize the heat conduction from the inner chamber to laboratory ambience. In our furnace, the space between the outer shroud and the inner chamber serves as a vacuum guard. The air in this space can be evacuated using a vacuum pump through an evacuation port.

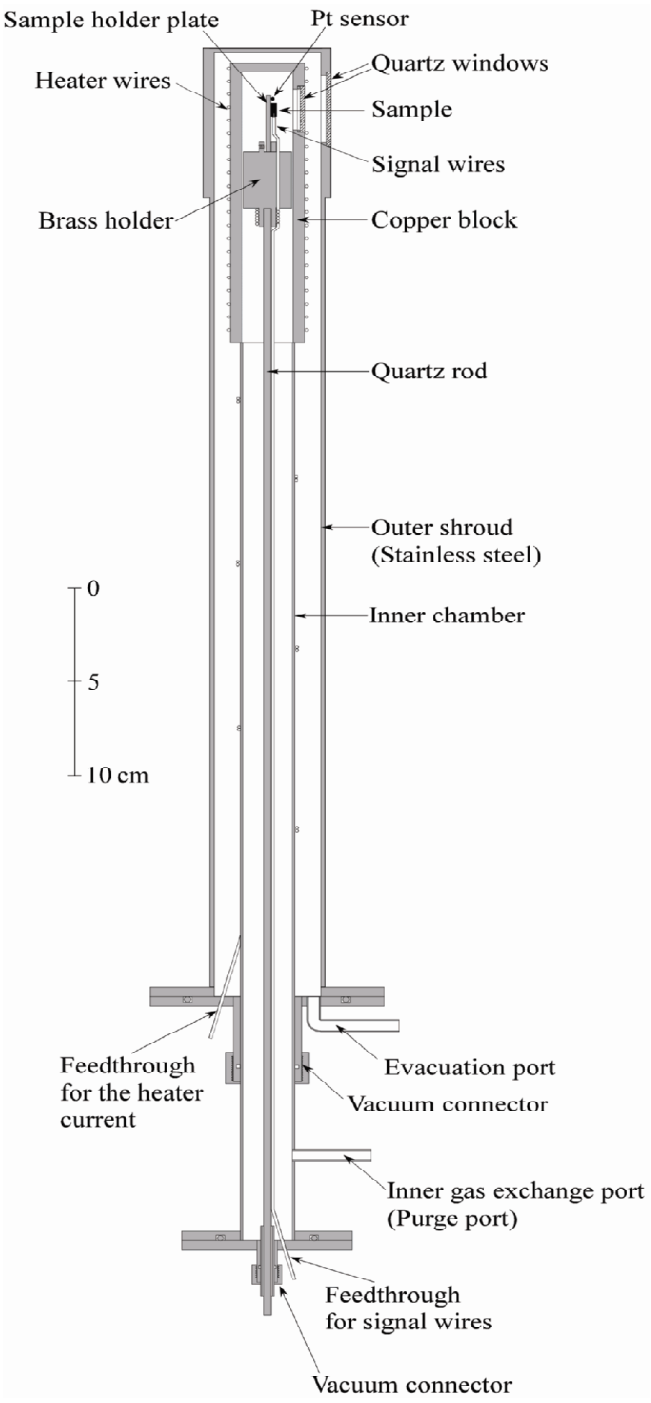

Figure 1 : Schematic diagram of the furnace.

Sample and signal wires for electrical measurements are placed inside the inner chamber. Sample and small platinum sensor (Lakeshore, DT series) which monitors the temperature of the sample are installed on a sample

holder plate made with fused quartz. We have chosen heat-proof coaxial cables as the signal wires. The platinum sensor leads are connected to a temperature controller using phosphor bronze wires. A brass holder is used to fix the sample holder plate uprightly, and the other end of the holder is fitted with a fused quartz rod having 3 mm diameter. The brass holder is designed such that it can be suited to the wall of the inner chamber snugly. As a heating element, nichrome wire (ϕ0.3 mm) is wound on the copper block. The heater current is supplied through the feedthrough installed on the vacuum flange. As an environment of the sample, we can select either air or inert gas, which also serves as a heat exchange medium. It is also possible to prepare the vacuum environment. The purge of the inner chamber is performed by using a purge port. The end of the inner chamber is connected to a vacuum flange, which has a vacuum connector for the support of the fused silica rod. It is possible to adjust the position of the sample by sliding or rotating the rod at the vacuum connector. The feedthrough for the signal wires is also installed in the same flange. For the replacement of the sample, the flange at the end of the inner chamber is opened, and the fused silica rod is drawn out together with the sample holder plate. A conventional PID-type temperature controller (Nippon Heater, Model TIC) is used to regulate heater current. A vacuum pump is used both for the continuous evacuation of the vacuum shroud and for the purge of the inner chamber. Any standard pump which is used in laboratory will work, and a diaphragm pump (ULVAC, DTC-21, 20 L/min) was used in our experiments. The most important factor which determines the maximum operation temperature of the present furnace may be a tolerance of the o-ring on the window of the inner chamber toward the heating. The upper limit of the usable temperature range of silicone rubber is usually specified to 280 °C, and accordingly we can use the furnace below this temperature in usual experiments. In addition, the furnace should be installed such that the sample holder becomes the top of the furnace, since this layout is expected to minimize a convection of gas in the chamber and to play an important role in the stabilization of the sample temperature.

Application to the measurement of the optoelectronic property of AgI

The performance of the high temperature furnace constructed in the present study was examined as follows: one is the precise measurement of the sample temperature; another is the applicability of this simple furnace for the measurement of the optoelectronic properties of the materials at high temperature. The examination of the stability as well as the precise detection of the sample temperature was carried out by measuring the temperature dependence of the ionic conductivity of polycrystalline AgI, with the ac method, in the temperature range from room temperature to 200 °C.

AgI was used in a pellet form. Commercially available AgI powder (Junsei Chemical, 99%) was grinded in the agate mortar by hand, and pellets having 13 mm diameter and 0.7–0.8 mm thickness were prepared by using a pellet press. The AgI pellet was connected to signal cables by using the carbon paste, which was used for the preparation of electrodes on the same surface of the pellet with distance of 2–4 mm, and the sample was fixed with the sample holder plate. Care was taken to fix the AgI pellet very near to the platinum sensor in order to measure the temperature of the sample precisely. The electrical resistance of the sample as a function of temperature was measured with electrochemical impedance spectroscopy technique.[8] The impedance spectra were recorded by using an LCR meter (HIOKI, 3532-50) in the frequency range from 42 Hz to 5 MHz. The so-called Cole-Cole plots (Nyquist plots) were obtained from the complex plane plots of the observed impedance value.[8] Examples of the data obtained for AgI have already been reported elsewhere.[6,7] The impedance of the electrochemical cells including solid electrolyte or electrode can be often modeled by equivalent *RC* circuits.[8] It is then possible to separate the element corresponding to the bulk resistance from the impedance including other elements such as an electrode polarization.

By using the constructed furnace, Cole-Cole plots of the polycrystal pellet of AgI were measured at various temperatures, and the bulk resistance (*i.e.*, conductance) of AgI was obtained as a function of temperature. Two kinds of samples of polycrystalline AgI have been examined; one is the polycrystalline AgI having the γ-phase just after preparation of the pellet following a grinding, and the other is an admixture of β- and γ-phases prepared by aging of the γ-phase sample. The crystal structures of both samples at room tem-

perature were confirmed by the XRD measurements.[9] Hereafter, these samples are called as γ- and β-AgI, respectively. The microscope images of the surfaces of these samples are shown in Figure 2. The grain size of the β-AgI sample is greater than that of the γ-AgI sample. The bulk resistances for both of the samples are shown in Figures 3 and 4, respectively.

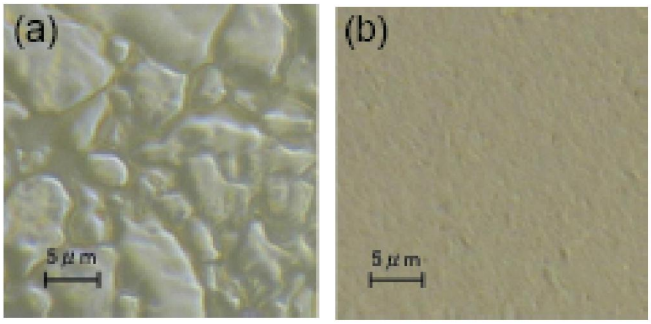

Figure 2 : Microscope images of the surface of (a) β-AgI and (b) γ-AgI.

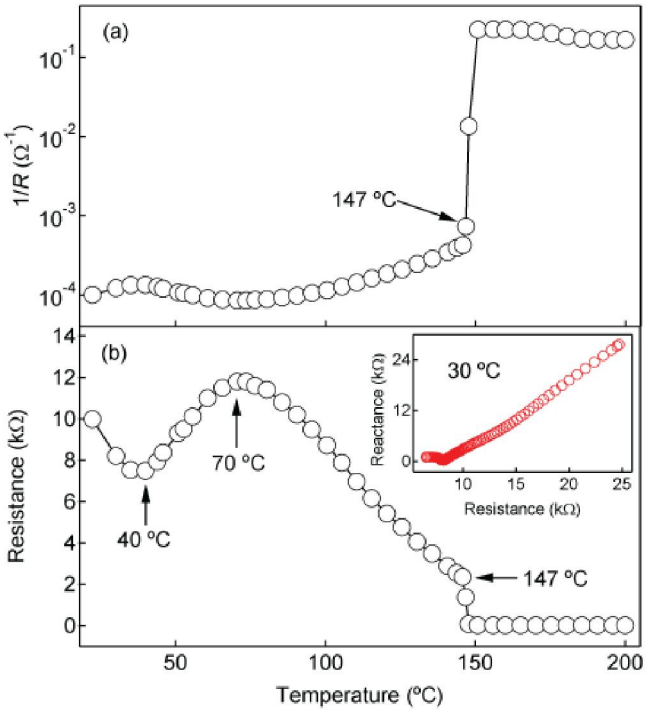

Figure 3 : (a) Inverse of the bulk resistance and (b) the bulk resistance as a function of temperature in the polycrystalline pellet of γ-AgI. (Inset) Cole-Cole plot observed at 30 °C.

In polycrystalline γ-AgI, the bulk resistance, which decreases with an increase of the temperature from room temperature, shows a minimum at ca. 40 °C. With further increase of the temperature, the bulk resistance becomes larger and shows a maximum at ca. 70 °C. At temperatures above 70 °C, the bulk resistance monotonically decreases with an increase of the temperature, *i.e.*, a hump is observed at ~70 °C in the plots of the resistance versus temperature. It is likely that the hump is related to a spontaneous transformation from the γ-phase to the β-phase above this temperature.[10] At a temperature of 147°C, further, the bulk resistance decreases drastically exhibiting the first order phase transition to the α-AgI phase, *i.e.*, the transition to the superionic conducting phase.

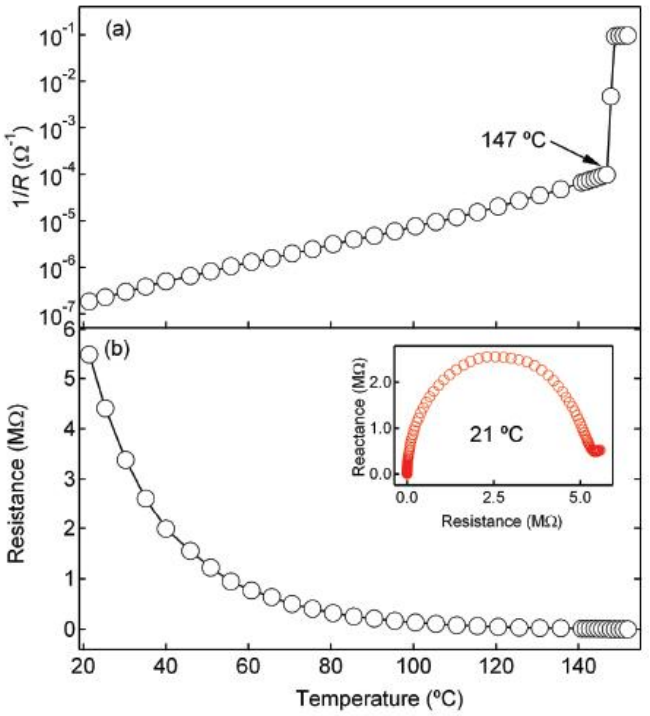

Figure 4 : (a) Inverse of the bulk resistance and (b) the bulk resistance as a function of temperature in the polycrystalline pellet of β-AgI. (Inset) Cole-Cole plot observed at 21 °C.

In contrast with the γ-phase, the bulk resistance of the β-AgI sample decreases monotonically with an increase of the temperatures from the room temperature (see Figure 4). As in the case of γ-phase, however, the bulk resistance decreases drastically at 147 °C, indicating the first order phase transition to the superionic conducting α-AgI phase. Thus, the phase transition temperature to the α-phase is 147 °C in both β- and γ-phases, though there is a difference in the temperature dependence of the bulk resistance. This phase transition temperature is the same as the reported value for the phase transition to the α-phase.[5] The sharpness of the transition obviously demonstrates an adequate competence for controlling temperature. Thus, the constructed furnace can control and measure the sample

temperature precisely.

The photoirradiation effects on the conductivity of α-AgI at 155 °C were further examined with the dc method. At first, a sample of polycrystalline γ-AgI was subjected to 0.1 V dc voltage at room temperature; the sample was polarized with the so-called Wagner polarization method.[11] After reaching the polarized- and steady-state condition at room temperature, the heater was switched on to increase the sample temperature up to 155 °C, which is higher than the temperature of the phase transition to the α-phase (see Figure 3a). Then, the current was recorded at 155 °C as a function of time with an electrometer (Keithley, Model 617). The dc current was initially measured at the polarized state without photoirradiation, which corresponds to the dark current. Then, the dc current was measured during photoirradiation by 450 nm light, with which the photoinduced change in the bulk resistance of β-AgI shows a maximum at room temperature.[6] The result is shown in Figure 5. The increase of current upon photoirradiation was observed. More detailed study is now in progress for elucidation of the mechanism of the photoinduced change in electrical conductivity of AgI. These results demonstrate that the constructed high-temperature furnace is applicable to the analysis of the optoelectronic properties of materials at high temperatures.

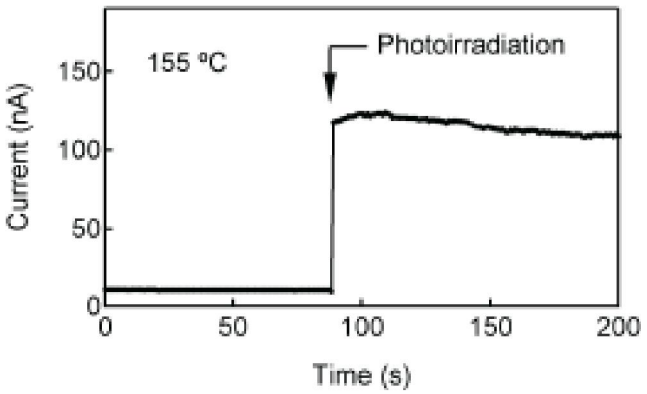

Figure 5 : Current monitored as a function of time with the dc voltage of 0.1 V at 155 °C. The measurement started under dark condition and the photoirradiation was performed after 90 s with the visible light of 450 nm.

In summary, we developed a highly accurate high-temperature furnace for measurements of the photoresponse of the electric properties of solid materials at different temperatures in the range from room temperature to more than 200 °C. The furnace is relatively inexpensive and versatile, and experiments under various environments such as under the air or under vacuum conditions are possible. The temperature dependence of the resistance of AgI with different phase compositions and the photoirradiation effect in the superionic conducting α-phase were investigated. The sample composed of the γ-phase showed a hump at ~70 °C in the resistance as a function of temperature. In the mixture sample of the β-phase and γ-phase, the temperature dependence different from that for the γ-phase sample was observed. The current of the polarized α-phase sample showed the increase upon the photoirradiation at 450 nm.

ACKNOWLEDGEMENTS

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