

## Observation of Two Kinds of Structural Phase Transitions of $\text{Ba}_2\text{In}_2\text{O}_5$ System

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$\text{Ba}_2\text{In}_2\text{O}_5$  exhibits structural phase transition at  $\sim 900^\circ\text{C}$  involving the abrupt increase of oxide ion conductivity.[1] Stabilization of the high temperature phase of  $\text{Ba}_2\text{In}_2\text{O}_5$  has been attempted in order to develop new oxide ion conductor. [2, 3] It was reported that the crystal structure of  $\text{Ba}_2\text{In}_2\text{O}_5$  below and above  $\sim 900^\circ\text{C}$  was brownmillerite-type with ordered oxide ion vacancy and perovskite-type with disordered one. The abrupt increase of oxide ion conductivity at  $\sim 900^\circ\text{C}$  was ascribed to this order-disorder structural phase transition. However, there are few reliable reports on the crystal structure of  $\text{Ba}_2\text{In}_2\text{O}_5$  at high temperatures and the structural phase transition. In this study, we have analyzed structural phase transition of  $\text{Ba}_2\text{In}_2\text{O}_5$  by using TG-DTA, dilatometry, quantitative DTA and high temperature X-ray diffraction.

$\text{Ba}_2\text{In}_2\text{O}_5$  ceramic specimen was prepared with solid-state reaction of  $\text{BaCO}_3$  and  $\text{In}_2\text{O}_3$ . Nominal amounts of dry  $\text{BaCO}_3$  (99.9%) powder and dry  $\text{In}_2\text{O}_3$  (99.9%) one were mixed in ethanol. The mixture was calcined at  $800^\circ\text{C}$  for more than 24 h in air. The calcined powder was pressed into pellet with 10 mm  $\Phi$  diameter and sintered at  $1400^\circ\text{C}$  for 17 h in air. The powder X-ray diffraction measurement revealed that the sample was single phase with brownmillerite structure. TG-DTA measurement (Rigaku Co., Ltd.: TG8120) was performed on powder specimen under static air in temperature range of room temperature  $\sim 1400^\circ\text{C}$  to determine the phase transition temperature.  $\text{Al}_2\text{O}_3$  and Pt were used as reference and material for pan, respectively. The heating rate was  $10^\circ\text{C}/\text{min}$ . The quantitative DTA (Rigaku Co., Ltd.: DSC8270) on the powder was also carried out to confirm the phase transition observed by TG-DTA and to estimate the variation of enthalpy,  $\Delta H$ , of the structural phase transition. The reference, pan and heating rate was the same as TG-DTA measurement. The behavior of thermal expansion of  $\text{Ba}_2\text{In}_2\text{O}_5$  sintered body was analyzed with dilatometry (Rigaku Co., Ltd. TMA8310). The rectangular specimen with 12.40 mm x 4.90 mm x 2.25 mm size and 87 % of the ideal density was cut from the pellet. The measurement was performed under static air at heating rate of  $10^\circ\text{C}/\text{min}$  using  $\text{Al}_2\text{O}_3$  rod as a reference. The X-ray diffraction patterns of  $\text{Ba}_2\text{In}_2\text{O}_5$  at temperature range  $30\sim 1200^\circ\text{C}$  were obtained by using Rigaku RINT-2500 ( $\text{CuK}\alpha$ : 50 kV-250 mA) All the measurements were carried out under static air at intervals of 1 h after temperature was reached to the measurement one.

Fig. 1 shows quantitative DTA curve of  $\text{Ba}_2\text{In}_2\text{O}_5$ . The endothermic peak was observed at  $\sim 900^\circ\text{C}$ . Since the TG-DTA curve indicated no weight variation at the temperature and the abrupt increase of oxide ion conductivity was reported at around  $900^\circ\text{C}$ , the endothermic peak could be attributed to the first order structural phase transition of  $\text{Ba}_2\text{In}_2\text{O}_5$ . The  $\Delta H$  of the phase transition was estimated to be  $\sim 10.5$  kJ/mol from the area of the endothermic peak. Fig. 2 shows

temperature dependence of thermal expansion and thermal expansion coefficient of  $\text{Ba}_2\text{In}_2\text{O}_5$  sintered specimen. The abrupt decrease of the thermal expansion was observed at  $\sim 900^\circ\text{C}$ , showing agreement with the first order structural phase transition observed both with TG-DTA and quantitative DTA. Besides the first order structural phase transition, discrete increase of the thermal expansion coefficient was observed at  $\sim 1070^\circ\text{C}$ , indicating the second order structural phase transition. In quantitative DTA curve depicted in Fig. 1, slight base-line shift was observed around  $1070^\circ\text{C}$ , showing agreement with the result of dilatometry. X-ray diffraction patterns at  $900^\circ\text{C}$ ,  $1000^\circ\text{C}$  and  $1100^\circ\text{C}$  indicated variation of the crystal structure at each temperature, which agreed well with the results of TG-DTA, quantitative DTA and dilatometry.

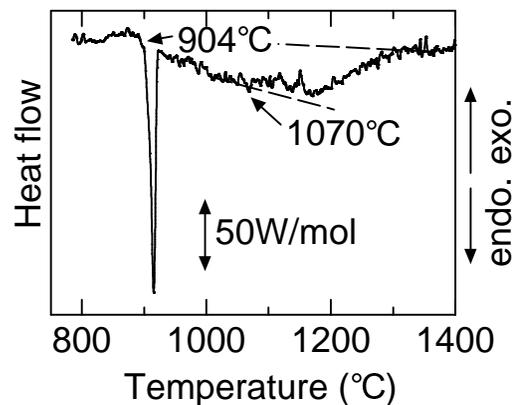


Fig. 1 quantitative DTA curve of  $\text{Ba}_2\text{In}_2\text{O}_5$ . The endothermic peak and base-line shift were observed at  $\sim 900^\circ\text{C}$  and  $\sim 1070^\circ\text{C}$ , respectively.

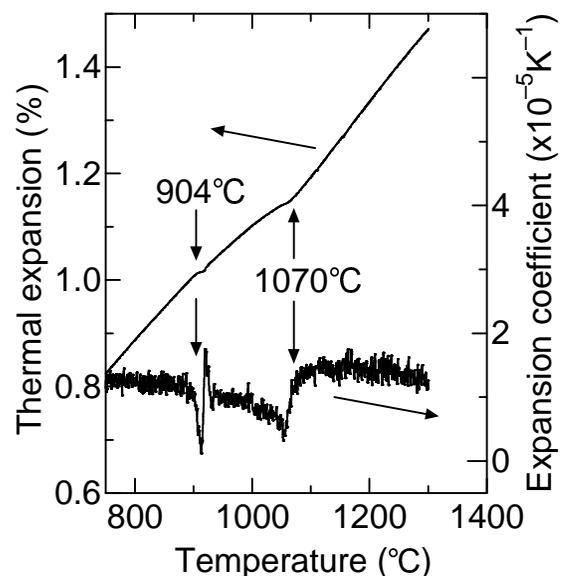


Fig. 2 Thermal expansion and expansion coefficient of  $\text{Ba}_2\text{In}_2\text{O}_5$ . The first order structural phase transition and the second order one were observed at  $\sim 900^\circ\text{C}$  and  $\sim 1070^\circ\text{C}$ , respectively.

[1] J. B. Goodenough et al., *Solid State Ionics*, 44 (1990) 21.

[2] H. Yamamura et al., *Solid State Ionics*, 108 (1998) 377.

[3] T. Yao et al., *Solid State Ionics*, 132 (2000) 189.

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