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Thermal Expansion Properties of Ag_2O Crystal Structure by Powder Neutron Diffraction

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Thermal expansion property of Silver(I)-Oxide (Ag_2O) was structurally investigated by neutron powder diffraction from 3 K to 400 K, and measured by X-ray powder diffraction from 20 K to 498 K. Temperature dependency of lattice parameter by neutron diffraction indicates the negative thermal expansion (NTE) below room temperature, and it changes to positive thermal expansion (PTE) from 300 K to 400 K. And this result is consistent with X-ray diffraction and TMA measurement. Moreover, the result by X-ray diffraction shows that lattice parameter significantly decreases above 400 K. Since the result by TG measurement shows the mass loss remarkably in this temperature region, it is considered that decreasing lattice parameter above 400 K is caused from thermal decomposition.

KEYWORDS: Ag_2O, negative thermal expansion, powder neutron diffraction

1. Introduction

Silver(I)-Oxide (Ag_2O) is known as one of components in super ionic glass of AgI-Ag_2O-V_2O_5 that is expected practical application for a solid electrolyte of a storage battery cell [1]. The crystal structure of Ag_2O is so called cuprite structure, and it belongs to the space group $Pn\bar{3}m$ (No. 224) [2]. The Ag atoms occupy 4*b* positions at (1/4 1/4 1/4) and the O atoms the 2*a* positions at (0 0 0). Arrangements are constructed two sublattice from fcc (Ag site, $\bar{3}m$) and bcc (O site, $\bar{4}3m$), and there is edge-sharing Ag_4O tetrahedra which is put on bcc oxygen site.

As a viewpoint of thermal properties based on diffraction study, Srivastava and Taylor have reported that it has a positive thermal expansion (PTE) from 100 K to 500 K [3,4]. On the other hand, Kennedy has reported that the Ag_2O shows the negative thermal expansion (NTE), and nonlinear dependency of lattice constants by Synchrotron X-ray diffraction in recent [5]. In addition, Tiano have suggested the negative thermal expansion of Ag_2O above room temperature by using X-ray powder diffraction [6]. Similarly, there have been reported thermal expansion studies of Cu_2O with same cuprite structure. Ivanda displayed that it has a weak negative thermal expansion below 200 K by X-ray powder diffraction [7]. And Schafer pointed out that the thermal expansion of Cu_2O changes from NTE to PTE above 200 K, and displayed increasing lattice parameter

to 600 K by neutron powder diffraction [8].

In this study, thermal properties of Ag_2O were investigated by neutron and X-ray powder diffraction over the entire temperature range from 3 K to 400 K. Moreover, it was discussed thermal expansion of lattice parameter over 400 K compared with Thermo Mechanical Analyzer and Thermo Gravimetric Analyzer measurement.

2. Experimental and Data Analysis

Neutron powder diffraction experiments were carried out using high-resolution neutron powder diffractometer, ECHIDNA, installed at ANSTO [9]. The wavelength was 1.300 Å by using Ge-335 monochromator, and it was calibrated using NIST Standard Silicon (SRM 640d). The Ag_2O sample (99% up, Kojundo Chemical) was contained in Vanadium cylinder of diameter 10ϕ. Sample was mounted in CryoFurnance (Janis Toploading Cryofurnaces) and data collection was conducted at 10 temperature points, 3 K, 25 K, 50 K, 70 K, 100 K, 150 K, 200 K, 300 K, 350 K, 400 K respectively. Fig.1 shows the neutron diffraction pattern of Ag_2O and the temperature dependency of (3 0 1) and (3 1 1) peak shifts by using contour mapping. In Addition, to compare with thermal expansion of Ag_2O, X-ray powder diffraction was measured by two diffractometers for low temperature and high temperature. Data collection from 20 K to 300 K was carried out by Rigaku RINT-2500H, which is equipped with cryostat (Iwatani, CRT 216-45) under vacuum. And high temperature X-ray diffraction measurement was performed by Rigaku Smartlab equipped with furnace (AntonPaar HTK1200) under vacuum, from 300 K to 500 K. In case of horizontal typed Bragg-Brentano geometry such as Smartlab diffractometer, since stage height is changing with increasing temperature, calibration parameters were determined based on measurement of NIST Standard Silicon. Lattice parameter of Si for each temperature was assumed by using quadratic formula of thermal expansion according to reference by Yim [10]. For both measurements X-ray generator was used by Cu-Kα radiation and applied 40 kV and 30 mA, and 2θ region covered from 10° to 90° by 0.02° steps.

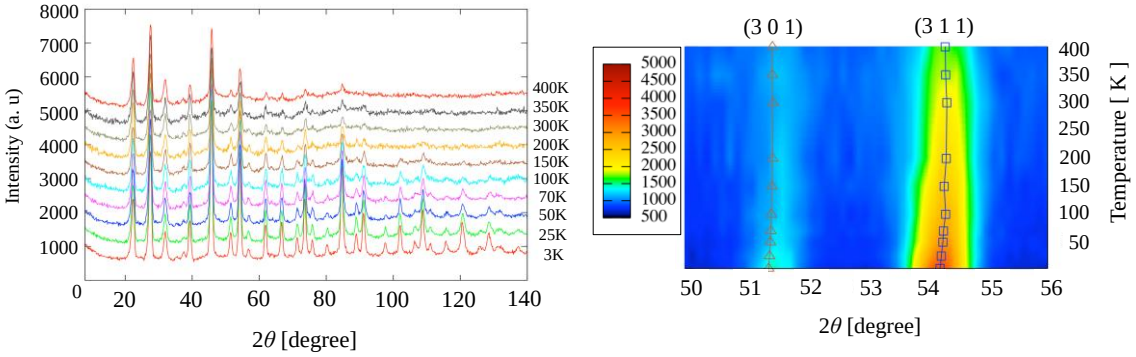

Fig. 1. (Left) Neutron diffraction by ECHIDNA from 3 K to 400 K. (Right) Temperature dependency of peak shift on (3 0 1) and (3 1 1) profiles. Dot points on contour mapping are center position estimated by Gaussian function.

All crystal structure analysis by Rietveld method was performed using *Z-Rietveld*, version 0.9.42.4 [11, 12]. Profile function is setting by Type A-1, and asymmetry parameters are used as the axial divergence model according to Finger-Cox-Jephcoat [13]. The result of Rietveld analysis and crystal structure model on 3 K is shown in Fig. 2. And Table I. shows the result of Rietveld analysis.

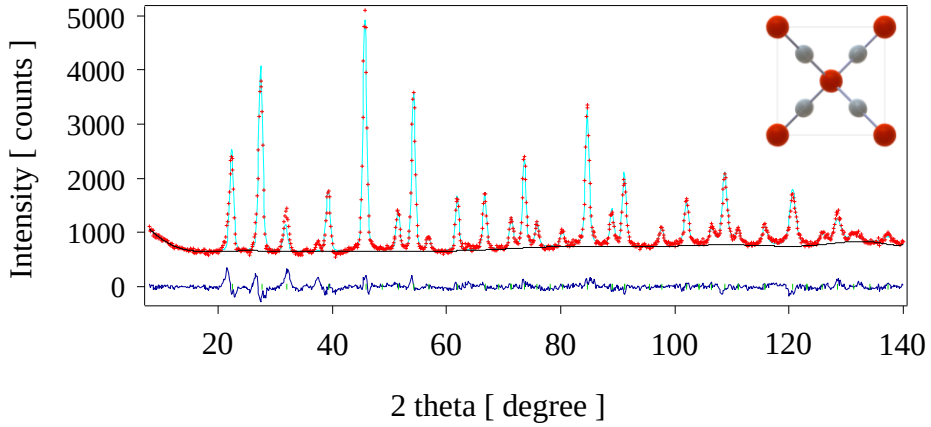

Fig. 2. Result of Rietveld analysis by neutron diffraction at 3 K. Red point, cyan line, and blue line means observed, calculated, and difference respectively. The insert shows the structure of Ag_2O drawn by *Z-3D* [14] along to c-axis. Thermal ellipsoid of oxygen anion is isotropic in *Pn-3m*.

Table I. *Rwp*, *Rp*, and R_F values for each solution

▪	3 K	25 K	50 K	70 K	100 K	150 K	200 K	300 K	350 K	400 K
Rwp (%)	6.01	5.29	5.31	5.02	6.03	4.95	5.42	4.5	5.73	4.88
Rp (%)	4.6	4.11	4.08	3.79	4.73	3.85	4.24	3.42	4.39	3.62
R_F (%)	3.68	2.78	4.35	4.37	5.22	5.8	5.45	7.07	6.25	7.83

3. Results and Discussion

3.1 Thermal expansion properties from neutron powder diffraction

Since Ag_2O is arranged that Ag and O occupy on special position in cubic cuprite structure, parameters as an average structure are determined by lattice parameter and Debye-Waller factor. Shown in Left figure of Fig. 3 is temperature dependence of thermal expansion of Ag_2O from neutron powder diffraction data by ECHIDNA. This result shows the remarkable negative thermal expansion below 200 K. Moreover, the monotonic decreasing of lattice parameter till near room temperature is consistent with the literature data reported by Tiano et al. [6]. The results different from investigation by Srivastava, which is suggested positive thermal expansion at low temperature range [3]. Whereas the previous literature by Tiano et al. has shown that Ag_2O has negative thermal expansion over the whole temperature range till 470 K, which is assumed as thermal

decomposition temperature, this result suggests that thermal expansion changes from negative to positive above room temperature. Meanwhile, such a thermal expansion feature changing from negative to positive is consistent with Cu_2O with same crystal structure reported by Schäfer [8]. In the literature, Cu_2O shows a negative thermal expansion below 225 K, and the derivative of lattice parameter becomes small till room temperature. Furthermore, it shows significant positive thermal expansion above room temperature.

While the atomic form factor of X-ray diffraction is dependent on scattering angle, the coherent scattering length of neutron is constant against 2θ. Accordingly, it is expected that neutron diffraction can determine more accurate temperature factor than X-ray diffraction. Right figure in Fig. 3 shows temperature dependency of isotropic atomic displacement parameters (ADPs) B. Isotropic ADPs increase non-linearly with increasing temperature, and B_O of oxygen is larger than B_{Ag} of silver. Whereas these results of ADPs are different from the reporting by Kennedy et.al [5], it is same feature as Cu_2O by neutron measurement [8].

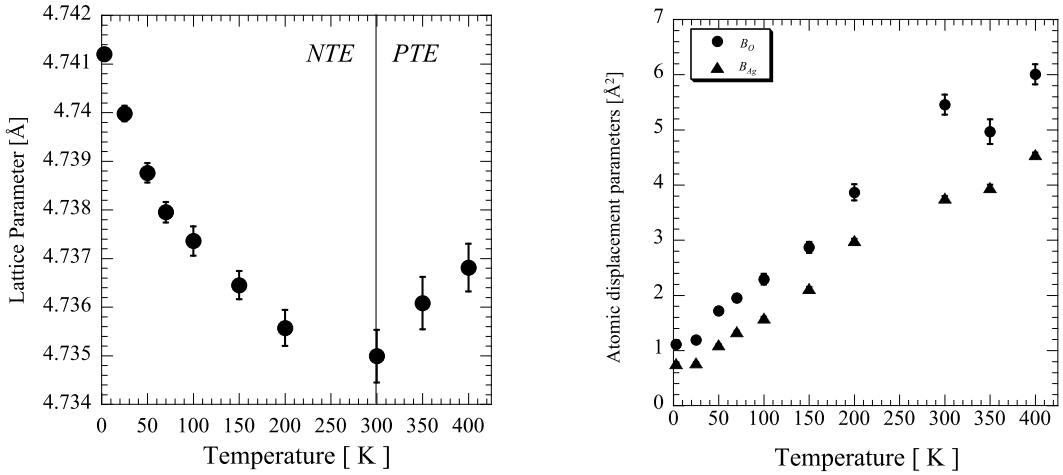

Fig. 3. (Left) Temperature dependency of thermal expansion of lattice parameter by neutron diffraction. (Right) Isotropic atomic displacement parameters of B_{Ag} (circle) and B_O (triangle).

3.2 Comparison with X-ray powder diffraction

Thermal expansion curve of Ag_2O by X-ray powder diffraction from 20 K to 500 K is shown in Fig 4. Compared with the result by neutron powder diffraction, tendency of temperature dependency of lattice parameter is consistent within whole range from low temperature to 400 K. On the other hand, it can point out that the temperature point, which is changing from NTE to PTE, is near 250 K. In case of neutron diffraction in present study, since statistic number of measurement temperature points is not many, it is suggested that determination of accurate temperature point where lattice parameter

changed from NTE to PTE is not easy. Furthermore, it can point out that lattice parameter significantly decreases with increasing temperature above 400 K. It indicates that this remarkable decrease of lattice parameter in high temperature region is same tendency with the data from previous study reported by Tiano et al. [6].

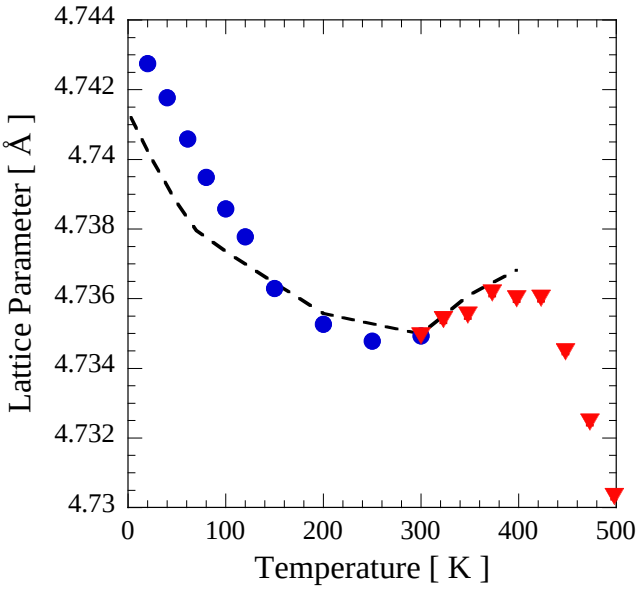

Fig. 4. Thermal expansion properties of Ag_2O by X-ray diffraction from 20 K to 498 K. Blue circle point means by Cryostat, Red triangle point by Furnace. To compare with reasonable consistency for each diffraction method, dashed line draws the result by neutron diffraction from Fig. 3.

3.3 Thermal properties above room temperature by TMA and TG measurement

Fig 5. shows thermal expansion curve by Thermo Mechanical Analyzer (TMA) and Thermo Gravimetric (TG) curve from 320 K to 478 K. These measurements were performed in nitrogen atmosphere.

Result by TMA curve shows the positive thermal expansion from room temperature to 400 K. And it is consistent with neutron and X-ray powder diffraction. Moreover, it indicates the thermal expansion is decreasing above 400 K, which is same feature as the result by X-ray powder diffraction. Then, from the result by TG measurement, it shows that the thermal decomposition of Ag_2O occurs from 400 K, whereas it is assumed that thermal decomposition temperature was 470 K so far. And it can point out that the decreasing of lattice parameter based on neutron and X-ray powder diffraction is synchronized with the result by TG curve. Hence, it is considered that decreasing of lattice parameter in high temperature region above 400 K is occurred from chemical reaction, and its mechanism is different from negative thermal expansion below 250 K that is observed by neutron and X-ray powder diffraction.

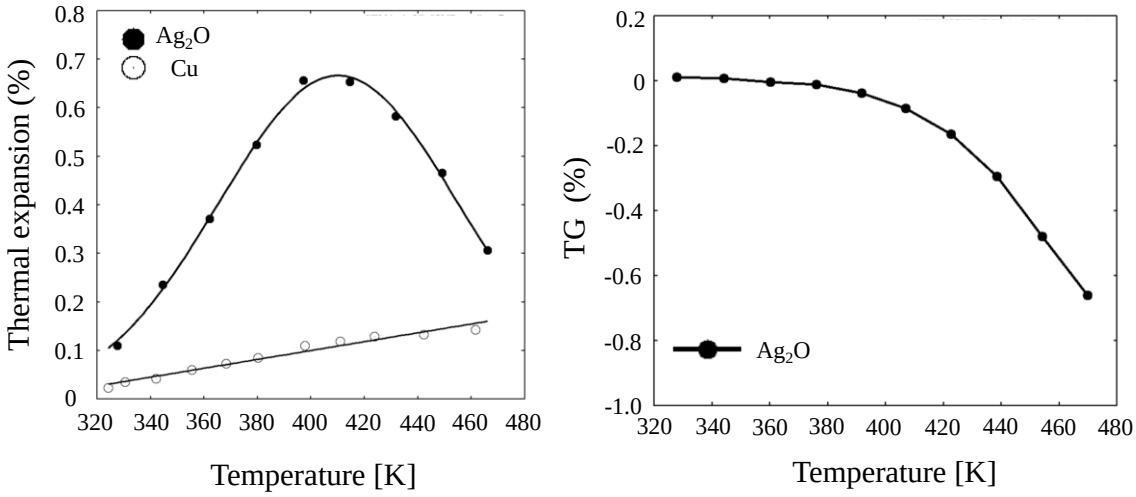

Fig. 5 (Left) Themo Mechanical Analyzer curve of Ag_2O from 320 K to 470 K. (Right) Themo Gravimetric curve of Ag_2O from 320 K to 470 K.

4. Conclusion

Thermal properties of Ag_2O were structurally investigated by neutron and X-ray powder diffraction. Remarkable negative thermal expansion of Ag_2O has observed below 200 K. And the thermal expansion is changing from negative to positive from near 250 K. Since this result is same feature as Cu_2O, it is considered that negative thermal expansion of these cuprite structure, Ag_2O and Cu_2O, occurs from similar mechanism. In addition, it was observed that lattice parameter decreases above 400 K by X-ray powder diffraction. From TMA and TG curve, decreasing of lattice parameter is related on thermal decomposition of Ag_2O, and it is considered that mechanism of its phenomenon is different from negative thermal expansion below 250 K.

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