X-RAY DIFFRACTION STUDIES OF $\alpha$-AGI SUPERIONIC CONDUCTOR BY RIETVELD PROFILE ANALYSIS METHOD

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ABSTRACT

X-RAY DIFFRACTION STUDIES OF $\alpha$-AGI SUPERIONIC CONDUCTOR BY RIETVELD PROFILE ANALYSIS METHOD. Silver iodide (AgI) has three solid phases, $\alpha$, $\beta$, and $\gamma$. Above the transition temperature $T_c = 147 \degree C$ it shows superionic conducting properties and forms an $\alpha$-phase. Powder X-ray diffraction data at $180 \degree C - 450 \degree C$ have been obtained and analysed by Rietveld profile analysis method. The results showed that the iodine ions formed a body centered cubic lattice and the two Ag ions were distributed among 24 crystallographic sites at 24g(x,0,1/2) of Im3m space group which were pairs of sites, displaced about 12d(1/4,0,1/2) tetrahedral sites. The diffraction pattern also showed a comparatively strong diffuse background due to the Ag ions liquid-like distribution, which qualitatively explained the high ionic conductivity in the $\alpha$-phase.

INTRODUCTION

Superionic conductor, also known as the fast ionic conductor, is a type of material which has a very high ionic conductivity ($\sigma \approx 10^{-1} \Omega^{-1} \text{cm}^{-1}$), which is almost equal to the molten salt conductivity. The transition from isolator properties to superionic conductor takes place above critical temperatures, and may proceed sharply as in the case of $\alpha$-AgI at $T_c = 147 \degree C$, or gradually as in the case of PbF$_2$. Crystal structure of $\alpha$-AgI was derived from powder diffraction measurements and at first was assumed that it has the cation distributed randomly. Strock [1] was the first who studied the material and purposed an average structure, where two Ag cations are distributed randomly at 42 sites 6b, 12d, and 24h in Im3m space group among the bcc lattice points filled by iodine ions. The cation distribution then was reinvestigated by X-ray diffraction and extended with the observation of diffuse scattering [3,8]. From these data, analysis of the anharmonicity effects and thermal vibrations of the cations were evaluated. The validity of the analysis was reported for the case of CuCl [3] and CuBr [8], which were known as superionic conductor materials. Previous researchers however, assumed that, since 12d sites were the center of iodine distorted tetrahedral having 42m symmetry, hence the analysis should be based on a model in which the Ag ions were distributed randomly at 12d sites in an anharmonic potential. Recent reports on structural refinements
by neutron diffraction suggested different model in which the Ag ions were
distributed around 24g (x,0,1/2) sites [1,8]. The main purpose of this
experiment is to reinvestigate another possible structure than that of the
previous investigations by the former researcher [1,2,5].

EXPERIMENTAL METHOD

Sample preparation of $\beta$-AgI was carried out according to the
procedure written in the Handbook of Preparative Inorganic Chemistry [4].
The diffraction experiments were carried out at the temperatures of, 180°C,
255°C, 350°C, and 450°C using Shimadzu X-ray Diffractometer type XD-
5A, having Cu target. The detector’s angular range was 12° to 51° with steps
of 0.04° and counting time of each steps was 20 seconds. Continuous
counting were carried out for several temperatures between 150 °C to 450 °C ,
which were varied at 50°C intervals. It is due to that the AgI sample well
known has the following properties: between room temperature to 147 °C,
AgI is in $\beta$-phase, whereas about 147 °C AgI transform to $\alpha$-phase or
superionic phase. The data results from the experiment analyzed by
Rietveld analysis method [9]. All of these works were carried out in the
Material Science Research Center, Indonesian National Atomic Energy
Agency (BATAN), Serpong.

RESULTS

Table-1 shows refined parameters at different temperatures obtained
by means of the Rietveld profile analysis method.

Fig. 1a (in appendix-1) shows refinement of $\alpha$-AgI profile at 180 °C.
It is shown that diffraction peaks appeared at the scattering angles around
24.77°, 35.3°, 43.6°, and 50.8°, related to the reflection planes of (110),
(200), (211), and (220). Fig.1b shows refinement of $\alpha$-AgI at 255°C; it is
shown that the diffraction peaks appear around the same angles, with a little
decrease of intensity and a little shift from that of Fig. 1a; due to the
increase of the thermal vibrations effect which increased the thermal diffuse
scattering. Fig.1c shows refinement of $\alpha$-AgI at 450°C; diffraction pattern
at this temperature was similar to that of Fig. 1a and Fig. 1b.

From the patterns of Fig. 1a to Fig. 1c the following cases can be
derived: first, there are peak shifts leading to lower scattering angles as the
temperature increase that especially can be observed from the ends of the
pattern around 51° ; an exception is for 180 °C to 255 °C where the peaks
shift to the higher scattering angles; the reason is due to the lattice
parameters dilatation, whereas from 180 °C to 255 °C the lattice parameters
shrunk due to the anomalous property of the AgI during the transition to
the superionic material. Second, there is a tendency of having higher diffuse scattering as the temperature increases. The oscillation in the background is remarkable indicating liquid-like behaviour of the silver atoms, and high Debye-Waller factor reducing the (220) peak tremendously and this is due to the increasing lattice vibration which tends to be anharmonic. The temperature variation of the lattice parameters and the linear thermal expansion coefficients have been deduced from the experiments, in order to observe anomalies around the transition temperature. Unfortunately, the paucity of data around the transition temperature rules out the observation of the anomaly.

Accurate intensity measurements of the (110), (200), (211), and (220) peaks at 180 °C, 255 °C, 350 °C, and 450 °C, respectively were made as shown in Fig. 2 (appendix-2). Experiments at temperatures beyond 450 °C have not been performed because of a strong decrease in the peak intensities at high scattering angles due to the increasing Debye Waller factors. The intensity was calculated by Covell Method. Error bars are not constructed as experiment errors are not propagated by the method.

Fig. 3 (in appendix-2) shows the variation of the temperature factors (B) for Ag and I ions. $B_{Ag}$ is remarkable high and has a slight increment as the temperature raises whereas $B_I$ has a steep increment. This suggests that the decrease in intensities may be caused not only by the thermal vibrations but also by the disorder structure. The Ag ionic displacements were deduced from the harmonic approximation [10], $B_{Ag} = 8\pi\langle u^2 \rangle$ and were found approximately to be 0.4 Å as shown in Table-2.

DISCUSSION

The fast ionic theory shows that the superionic condition is obtained if a large number of sublattice positions are available to conduct - in the case of $\alpha$-AgI, the Ag cations. Hence it requires low occupation number, due to the silver cations movement. Furthermore, for jump as well as molten sublattice conductions, a large number of Frenkel defects are required and the defect positions should fulfill the space group of the crystal. Several models have been tried giving the most suitable one. With Ag ions distributed around 24g(x,0,1/2) sites, the result is in accordance with the purposed model by Bührer and Hälg [1].

According to the proposed model, the silver ions were located in the 24g sites which are pairs of sites, namely (x,0,1/2) and (1/2-x,0,1/2) displaced about 12d (1/4,0,1/2) tetrahedral sites in the <100> direction. It is
in accordance with the neutron quasielastic scattering study by Eckold et. al [2] revealed that <100> directions were indeed the direction of cations diffusion. Although the best refinements are obtained if Ag ions are assigned to 24g sites, the remarkable large thermal motions of 0.4 Å which is much larger than the 24g pairs distance of 0.07 Å causes doubtfull that the displaced pairs represent genuine discrete sites in the structure. Therefore, it is suggests that the thermal motion of the silver ions are confined in ellipses in the <100> direction due to the anharmonic and anisotropic thermal motion.

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REFERENCE


Table 1: Several Refinement Parameters

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Rwp (%)</th>
<th>Re (%)</th>
<th>R(%)</th>
<th>x (Å)</th>
<th>B(Å^2)</th>
<th>BAg(Å^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>20.92(2)</td>
<td>15.55(1)</td>
<td>28.62(2)</td>
<td>0.321(1)</td>
<td>0.41(1)</td>
<td>13.41(1)</td>
</tr>
<tr>
<td>255</td>
<td>17.70(1)</td>
<td>13.70(1)</td>
<td>15.71(1)</td>
<td>0.316(1)</td>
<td>6.41(1)</td>
<td>13.23(2)</td>
</tr>
<tr>
<td>350</td>
<td>17.79(1)</td>
<td>14.00(1)</td>
<td>16.65(1)</td>
<td>0.308(2)</td>
<td>8.31(1)</td>
<td>15.11(1)</td>
</tr>
<tr>
<td>450</td>
<td>17.01(1)</td>
<td>13.82(1)</td>
<td>16.73(1)</td>
<td>0.329(1)</td>
<td>9.51(1)</td>
<td>13.62(1)</td>
</tr>
</tbody>
</table>

Rwp = Profile error by taking into account the weight factor; RE = Error expected; RI = Integrated profile error; x = one of the estimated coordinates of the purposed site 24g(x,0,1/2); B_I = iodine temperature factor; B_Ag = silver temperature factor. Number in parentheses are estimated standard deviations of the last significant digit.

Table 2: Temperature factors (B_Ag) and displacements of silver ions (u) vs. temperature

<table>
<thead>
<tr>
<th>No.</th>
<th>T(°C)</th>
<th>B_Ag(Å^2)</th>
<th>&lt;u^2&gt;^{1/2}(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
<td>13.39(1)</td>
<td>0.411(1)</td>
</tr>
<tr>
<td>2</td>
<td>255</td>
<td>13.23(1)</td>
<td>0.409(1)</td>
</tr>
<tr>
<td>3</td>
<td>350</td>
<td>15.10(1)</td>
<td>0.437(1)</td>
</tr>
<tr>
<td>4</td>
<td>450</td>
<td>13.62(1)</td>
<td>0.415(1)</td>
</tr>
</tbody>
</table>

Number in parentheses are estimated standard deviations of the last significant digit.
Appendix -1

Fig.-1a : Diffraction Pattern of $\alpha$-AgI at temperature 180 °C. The curve under the diffraction pattern is error bar, presented difference between observed data and the calculated result from the Rietan program.

Fig.-1b : Diffraction Pattern of $\alpha$-AgI at temperature 255°C. The curve under the diffraction pattern is an error bar, presented difference between observed data and the calculated result from the Rietan program.
Fig. 1c Diffraction Pattern of $\alpha$-AgI at temperature 350$^\circ$C. The curve under the diffraction pattern is error bar, presented difference between observed data and the calculated result from the Rietan program.

Fig. 1d Diffraction Pattern of $\alpha$-AgI at temperature 450$^\circ$C. The curve under the diffraction pattern is error bar, presented difference between observed data and the calculated result from the Rietan program.
Appendix -2

Fig. 2: Integrated Intensity vs. Temperature; the intensity was calculated by Covell Method. Error bars are not constructed as the experiment errors are not propagated by the method.

Fig. 3: Temperature Factor (B) vs. Temperature. Error bars are not constructed as experiment errors are not propagated by the method.