

Microstructure Parameters of a Super-Ionic Sample (CsAg_2I_3)

Samir Osman M., Mohammed Hassan S.

Abstract—Sample of CsAg_2I_3 was prepared by solid state reaction. Then, microstructure parameters of this sample have been determined using wide angle X-ray scattering WAXS method. As well as, Cell parameters of crystal structure have been refined using CHEKCELL program. This analysis states that the lattice intrinsic strain of the sample is so small and the crystal size is on the order of 559Å.

Keywords—WAXS, Microstructure parameters, super-ionic conductor.

I. INTRODUCTION

SEVERAL and intensive studies have been devoted on structural research of super-ionic conductors because of their unusually high ionic conductivity at temperatures rather than close to room temperature. The most popular group of this class is silver ion conductors in which silver ion Ag^+ is the fast mobile species. The best representative of this group is silver iodide AgI which has high ionic conductivity in its α -polymorph stable above 420 K. Different series of fast ion conductors were derived from this compound by doping it with either iso or aliovalent cations in an attempt to improve its transport properties by stabilizing the superionic phase at lower temperatures [1-3]. AgI-CsI is one such system which was investigated for this purpose. The phase diagram of the system was suggested by Bradley and Greene contains two stable compounds at room temperature namely, CsAg_2I_3 and Cs_2AgI_3 [4]. The structures of the two compounds were resolved by Brink and his co-workers [5, 6] and by Pettigrosso et al. [7]. Both the compounds were found to adopt orthorhombic unit cell with space groups Pbnm and Pnma respectively. Ionic conductivity of CsAg_2I_3 was found to be an order of magnitude higher than that of Cs_2AgI_3 and that both of them are low ionic conductors [3]. This work is The present study constitutes an attempt to interpret the observed electrical properties of CsAg_2I_3 [8] with microstructural parameters, which were evaluated from X-ray profiles by using Exponential model, asymmetric column length distribution functions.

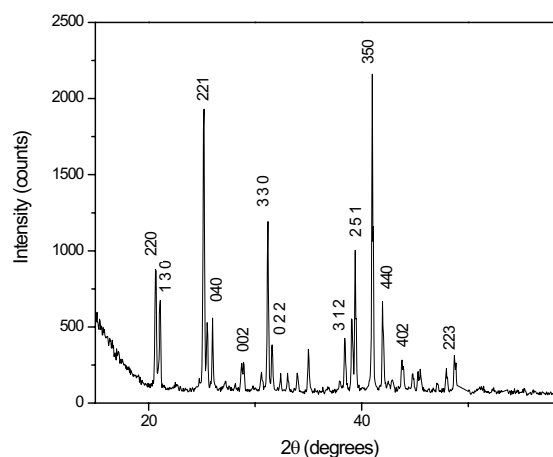
II. EXPERIMENTAL PART

A. Sample preparation

Silver iodide was prepared by precipitation from ammoniacal silver nitrate solution using ammonium iodide. Cesium iodide is from Sigma Aldrich USA with stated purity of 99.9%. The required amounts were mixed thoroughly using agate mortar to produce the CsAg_2I_3 . The mixtures were then heated in an electrical furnace at 470 K for three days with intermittent grinding. The final materials were crushed to fine powders which were of white colour.

B. X-ray diffraction pattern

The X-ray diffraction pattern of the sample was recorded using RIGAKU /MAX-B diffractometer employing X-ray radiation (λ for $\text{CuK}\alpha = 1.54059\text{\AA}$) provided with copper anode. The recorded data of X-ray diffraction lines were performed by step scanning method in 2θ in the range $5^\circ - 100^\circ$ in steps of 0.05° . Figure (1) shows the scan of X-ray diffraction profile obtained from the sample and this profile was used for estimating the microcrystalline parameters of the super-ionic conductors CsAg_2I_3 sample.



III. THEORY

The crystal size $D(=N \cdot d_{hkl})$ and lattice distortion g are related through the Fourier coefficients $A(n)$ of the X-ray profile intensity $I(s)$ which is given by [9,10,11]

$$I_{cal}(s) = \sum_{n=-\infty}^{\infty} A(n) \cos\{2\pi nd(s - s_o)\} \quad (1)$$

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where $A(n)$ are the harmonic coefficients. $A(n)$ is a function of crystal size and lattice distortion. Here, d is the interplanar spacing, s is the value of $(\sin \theta)/\lambda$, s_o is the value of s at peak position of the reflection, θ is Bragg's angle, λ is the wavelength of the radiation and n is the harmonic number. The Fourier coefficients $A(n)$ of the profile are convolution of crystal size $A_s(n)$ and lattice strain $A_d(n)$ coefficients and are given by

$$A(n) = A_s(n) \cdot A_d(n) \quad (2)$$

The lattice disorder component of the Fourier coefficient is:

$$A_d(n) = \exp(-2\pi^2 m^2 n g^2) \quad (3)$$

Here m is the order of reflection and $g (= \Delta d/d)$ is the lattice strain.

In order to interpret some symbols, which are essential for the analysis, we have considered the crystalline region in the material to be made up of columns of unit cells, along the direction of the scattering vector. Let i be the number of unit cells in a column. The number of cells N_n having n neighbours is,

$$N_n = i - n \quad (4)$$

If $P(i)$ is the probability distribution function of column lengths, then the average number of cells having n neighbours is,

$$N_n = \int_{i=n}^{\infty} (i - n) P(i) di \quad (5)$$

Simplifying this we have,

$$N_n = \int_0^{\infty} [iP(i)di - nP(i)]di - \left[\int_0^n iP(i)di - n \int_0^n P(i)di \right] \quad (6)$$

$$\text{Defining } \langle N \rangle = \int_0^{\infty} iP(i)di,$$

we have,

$$\frac{\langle N_n \rangle}{\langle N \rangle} = 1 - \frac{nd}{D} - \frac{d}{D} \left[\int_0^n iP(i)di - n \int_0^n P(i)di \right] \quad (7)$$

For a probability distribution of column lengths $P(i)$, the crystal size contribution to the Fourier coefficient is,

$$A_s(n) = \frac{\langle N_n \rangle}{\langle N \rangle} = 1 - \frac{nd}{D} - \frac{d}{D} \left[\int_0^n iP(i)di - n \int_0^n P(i)di \right] \quad (8)$$

where, D is the crystallite size. The second derivative of the Fourier coefficient $A_s(n)$ is proportional to the surface-weighted column-length distribution $P_s(L)$, and is given by

$$P_s(L) \propto \left(\frac{d^2 A_s(L)}{dL^2} \right); \quad L = nd \quad (9)$$

The volume-weighted column-length distribution function $P_v(L)$ is,

$$P_v(L) \propto L \left(\frac{d^2 A_s(L)}{dL^2} \right); \quad L = nd \quad (10)$$

we have used the developed single order method wherein it is assumed that an exponential function is the probability function $P(i)$ [12]. In fact, various other types of symmetric and asymmetric functions have been examined by us and it has been suggested that a symmetric exponential function gives good results [13,14]. This distribution depends on the fact that there are no columns containing fewer than p unit cells and

those with more than p will decay exponentially. Hence $P(i)$ can be expressed as,

$$P(i) = \begin{cases} 0 & \text{if } p < i \\ \alpha \exp \{-\alpha(n-p)\} & \text{if } p \geq i \end{cases} \quad (11)$$

Where $\alpha = 1/(N-p)$ is the width of the distribution. Then the simplified expression for size Fourier coefficient is given by,

$$A_s(n) = \begin{cases} A(0) \left(1 - \frac{n}{N} \right) & \text{if } n \leq p \\ A(0) \exp \{-\alpha(n-p)\} / (\alpha N) & \text{if } n > p \end{cases} \quad (12)$$

The surface- and volume-weighted values are computed using equations 9 and 10.

The reliability of this approach is verified by Round Robin method [15,16]. The experimental profiles between s_o the scattering vector at the peak and $s_o + s_o/2$ is matched with the simulated profiles using equations 1,2,3,4 and 6 for various values of $\langle N \rangle$, g , α and a background correction parameter (BG) to minimize the difference between the observed and the simulated data. For this purpose we have used a multidimensional minimization program SIMPLEX [17]. The goodness of the fit between experimental and simulated intensity profiles is less than 10% of the mean value. Essential, we have minimised the standard deviation Δ , where Δ is given by

$$\Delta^2 = \left[I_{cal} - (I_{exp} + BG) \right]^2 / NPT \quad (13)$$

With NPT giving the number of experimental points in a profile. Here I_{cal} , I_{exp} and BG represent calculated intensity, experimental intensity and background correction factor. The cell parameters have been refined using "CHEKCELL" program. We have used the standard cell parameters for CsAg_2I_3 [18, 19] as starting values for "CHEKCELL" program to identify the Bragg reflections. CHEKCELL program is a powder Indexing software.

IV. RESULTS AND DISCUSSION

Using the equations mentioned in the text, we have simulated the intensity profile and compared it with experimental profile in Figures(2,3,4,5 and 6). The micro-structural parameters are given in Table(1). From Table1, the results show isotropically intrinsic strains, which are small but different along different directions for the sample. Whereas, the crystal size values are also showing different values in different directions and the crystal size in the order 559Å (mean value). There is a high value of crystal size in the direction (1 3 0) whereas the minimum value in the direction (2 2 3). It is noticed from the Table that the mean standard deviation of this micro-structural study is around 0.07, this value in our decision is acceptable for this work. The cell parameters for CsAg_2I_3 are $a=0.783$ nm, $b=0.821$ nm, c (fiber axis) = 1.032 nm, $\alpha = 90^\circ$, $\beta = 96.03^\circ$ and $\gamma = 90^\circ$. The crystal system is orthorhombic unit cell with space group Pbnm for CsAg_2I_3 . The cell parameters have been refined with mean standard deviation of 0.001. The small intrinsic strain obtained from this study may result from site disorder that is related to the size of the atoms, vacancies, and interstitials. The presence of the small strain explains that the sample shows low ionic

conductivity, which can be enhanced by doping with other iso- or aliovalent cations^[8, 19]. The ionic conductivity is expected to be higher in the 002 direction due to the high lattice strain in this direction.

V. CONCLUSION

As it is noticed from the results that we can say there must be a strong link between crystal size and electrical conductivity in that associated direction. The different values of crystal size and lattice strain also confirm our conclusion about the isotropic property of electrical conductivity in this sample.

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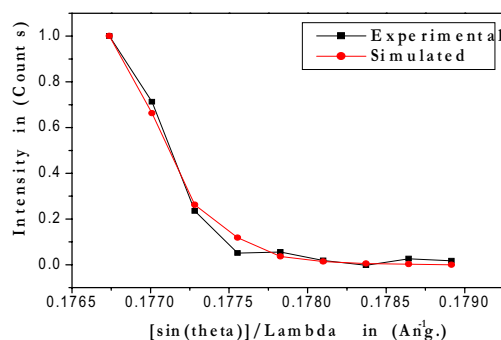


Fig. 2 Experimental and simulated X-ray profiles for (0 2 2) reflection using Exponential distribution function

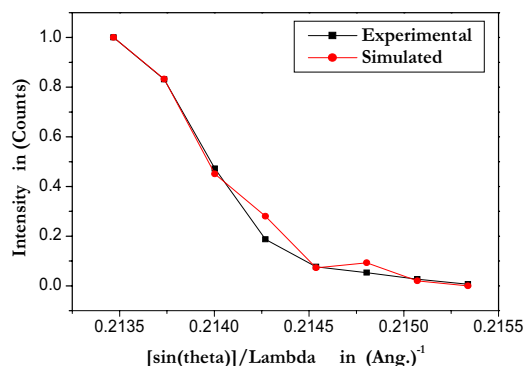


Fig.3 Experimental and simulated X-ray profiles for (3 1 2) reflection using Exponential distribution function

TABLE I

(A AND B) MICROSTRUCTURE PARAMETERS OF CSAG_2I_3 , USING EXPONENTIAL DISTRIBUTION FUNCTION. (HKL) BRAGG'S PLANE, 2θ IS SCATTERING ANGLE, G IS LATTICE STRAIN, D_{HKL} IS THE INTERPLANAR SPACING, D_s IS SURFACE-WEIGHTED OF CRYSTALLITE SIZE, Δ IS THE STANDARD DEVIATION)

h k l	2θ in deg.	d in Å	$\langle N \rangle$	g in %	α	D_s in Å	Δ
2 2 0	20.65	4.29	123.15 \pm 8.6	0.02 \pm 0.001	0.02	528.31 \pm 37	0.07
1 3 0	21.10	4.21	214.01 \pm 15	0.01 \pm 0.001	0.01	900.98 \pm 72	0.08
2 2 1	25.20	3.53	200.09 \pm 16	0.01 \pm 0.001	0.03	706.32 \pm 57	0.08
1 3 1	25.50	3.49	165.93 \pm 13	0.3 \pm 0.024	0.04	579.09 \pm 46	0.08
0 4 0	26.00	3.42	177.68 \pm 14	0.4 \pm 0.032	0.01	607.67 \pm 49	0.08
0 0 2	28.90	3.09	137.29 \pm 10	1.3 \pm 0.091	9.79	424.23 \pm 30	0.07
3 3 0	31.20	2.86	189.65 \pm 13	0.2 \pm 0.014	1.49	542.40 \pm 38	0.07
0 2 2	31.60	2.83	180.62 \pm 13	0.01 \pm 0.001	0.01	511.16 \pm 36	0.07
3 1 2	38.40	2.34	159.98 \pm 13	0.1 \pm 0.008	0.02	374.35 \pm 30	0.08
0 4 2	39.05	2.31	184.08 \pm 15	0.2 \pm 0.016	48.67	425.23 \pm 34	0.08
2 5 1	39.40	2.29	184.95 \pm 11	0.1 \pm 0.006	0.05	423.54 \pm 25	0.06
3 5 0	41.00	2.19	180.01 \pm 5	0.1 \pm 0.003	0.03	394.22 \pm 12	0.03
4 4 0	41.95	2.15	176.10 \pm 7	0.1 \pm 0.004	0.01	378.62 \pm 15	0.04
4 0 2	43.80	2.07	150.67 \pm 12	0.1 \pm 0.008	1.94	311.89 \pm 25	0.08
2 2 3	48.70	1.87	116.23 \pm 9	0.7 \pm 0.056	0.02	217.35 \pm 17	0.08

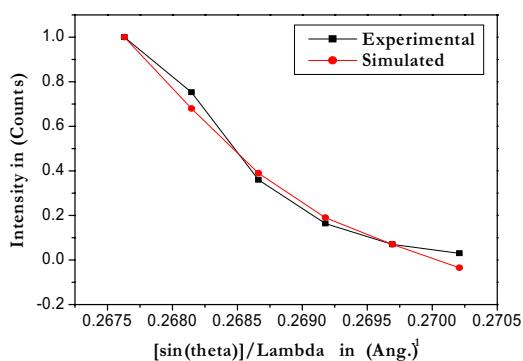


Fig. 4 Experimental and simulated X-ray profiles for (2 2 3) reflection using Exponential distribution function

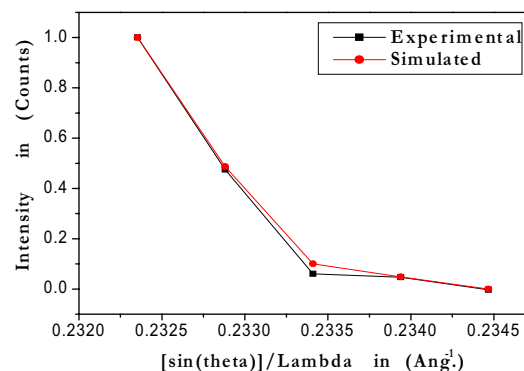


Fig. 6 Experimental and simulated X-ray profiles for (4 4 0) reflection using Exponential distribution function

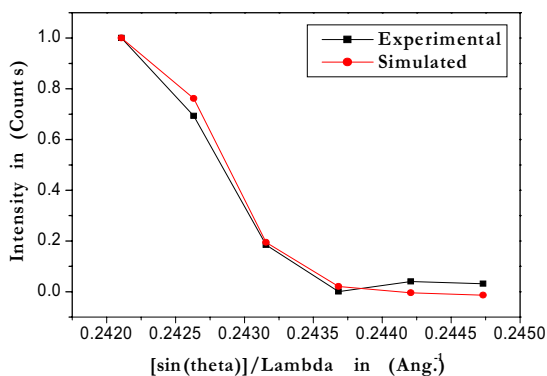


Fig.5 Experimental and simulated X-ray profiles for (4 0 2) reflection using Exponential distribution function