Lawrence Berkeley National Laboratory
Recent Work

Title
SMALL ANGLE X-RAY SCATTERING BY DIFFUSE INTERFACES

Permalink
https://escholarship.org/uc/item/21k668dm

Author
Bose, S.

Publication Date
1977-09-01

eScholarship.org Powered by the California Digital Library
University of California

UC-25
LBL-6656
Preprint

Submitted to Metallurgical Transactions

RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAR 23 1978

LIBRARY AND
DOCUMENTS SECTION

SMALL ANGLE X-RAY SCATTERING BY DIFFUSE INTERFACES

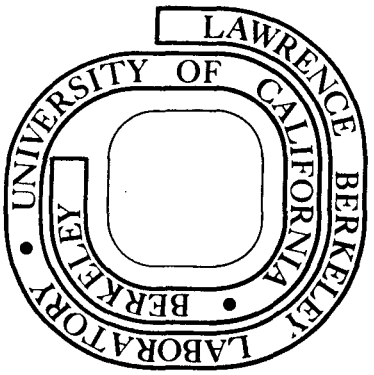
S. Bose and R. H. Bragg

September 1977

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-6656

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 4 8 0 5 5 8 2

LBL-6656

SMALL ANGLE X-RAY SCATTERING BY DIFFUSE INTERFACES

S. Bose and R. H. Bragg

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Materials Science and Minerals Engineering, University of California, Berkeley, CA 94720

ABSTRACT

The small angle x-ray scattering method to characterize the diffuse interface between the inhomogeneity such as precipitates, particles, or other second phases and the matrix is analyzed. The theory, which is generally applicable to spinodally decomposed systems, predicts that in the Porod region a plot of $h^3\tilde{I}(h)$ versus h^2 should be a straight line with a negative slope. ($\tilde{I}(h)$ is the intensity and $h = 4\pi \mathrm{Sin}\theta/\lambda$). The ratio of the slope to the intercept at $h = 0$ gives a measure of the width of the interface. Experimental data from a spinodally decomposed system (Al-20 a/o Ag) and a Li_2O-SiO_2 glass are used to test the theory.

1. INTRODUCTION

Small angle x-ray scattering (SAXS) has been used extensively in the field of materials science to study GP zones, to determine size and surface area of dispersed particles and voids, and more recently to follow the early stages of kinetics of spinodal decomposition. However, the power of the SAXS technique in characterizing diffuse precipitate-matrix interfaces has remained unused. The aim of this paper is to provide a semi-quantitative theory supported by experimental data in this direction.

2. THEORY

If $\rho(\bar{u})$ is the electron density (with respect to the surrounding matrix) at a point $\bar{u}$ in a particle, then the amplitude of the scattered x-rays from the particle, in electron units, is given by the Fourier transform of the electron density. The intensity, therefore, becomes[1]

$$I(h) = \iiint_V \left\{ \rho(\bar{u}) \rho(\bar{u} + \bar{r}) \, dV_{\bar{u}} \right\} e^{i\bar{h}\cdot\bar{r}} dV_{\bar{r}}$$

where $h = 4\pi \sin\theta/\lambda$

2θ = angle of scattering

λ = wavelength of x-rays

$\bar{r}$ = dummy variable covering the same space as $\bar{u}$

V = volume of sample

0 0 3 0 4 8 0 5 5 8 3

The quantity in brackets is related to Debye's correlation function defined by

$$C(r) = \int_V \frac{\rho(\bar{u})\rho(\bar{u} + \bar{r})dV_{\bar{u}}}{V\langle\rho^2\rangle}$$

Thus we can write

$$I(h) = V\langle\rho^2\rangle \int_V C(r)\, e^{i\bar{h}.\bar{r}}\, dV_{\bar{r}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where $\langle\rho^2\rangle$ is the volume average of the square of the electron density. The integration extends over the volume of the irradiated sample.

Following Hoseman & Bagchi[2] and Ruland[3] one can represent an electron density with a diffuse boundary as a convolution between an electron density with a sharp interface and a smoothing function such as a Gaussian[3]. Thus

$$\rho_{diff}(\bar{u}) = \int g(\bar{w})\rho(\bar{w} + \bar{u})dV_w = g(\bar{w}) * \rho(\bar{u}) \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where g is the smoothing function. The new correlation function, when the interface is diffuse, is

$$C_{diff}(r) = \frac{\int \rho_{diff}(\bar{u})\rho_{diff}(\bar{u} + \bar{r})dV_{\bar{u}}}{V\langle\rho^2\rangle} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Upon inserting (2) into (3), we obtain the relation

$$C_{diff}(r) = C(r) * g^{*2}(r) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Here the subscript 'diff' means "for the particle with diffuse boundary" and *2 is a self convolution. The intensity equation for the particle

with diffuse interface is obtained by taking the Fourier transform of (4) to obtain C(r), and inserting the result into (1). We obtain

$$I_{diff}(h) = I(h)\ [G(h)]^2$$

where G(h) is the Fourier transform of the smoothing function.

Thus $G(h) = \left[\frac{I_{diff}(h)}{I\quad(h)}\right]^{1/2}$

This is equivalent to

$$\int_V g(\bar{w}) w^{i\bar{h}.\bar{w}}\ dV_{\bar{w}} = \left[\frac{I_{diff}(h)}{I\quad(h)}\right]^{1/2}$$

By inverse Fourier transform we get

$$g(\bar{w}) = \left(\frac{1}{2\pi}\right)^3 \int_h \left[\frac{I_{diff}(h)}{I\quad(h)}\right]^{1/2} e^{-i\bar{h}.\bar{w}}\ dV_{\bar{h}}$$

Thus, in general the form of the smoothing function may be determined by Fourier inversion provided intensity data are recorded upto sufficiently large values of h. However a problem arises when interparticle interference effect is present. Equation (1) is then no longer valid at smaller angles. It is, therefore, safer to use the Porod region which is little affected by interparticle interference.

A simple approximation will be to assume g(w) to be a Gaussian $\frac{1}{K} \exp\left(\frac{-\pi w^2}{K^2}\right)$. Its transform is also Gaussian, $G(h) = \exp(-K^2h^2/4\pi)$.

$\frac{K}{\sqrt{2\pi}}$ is a measure of the width of the diffuse boundary. Thus

0 0 0 0 4 8 0 5 5 8 4

$$I_{diff}(h) = I(h) \exp(-k^2h^2/2\pi)$$

In the "Porod region"[4] h is large. If $k^2h^2/2\pi < 1$, we can expand the exponential. Replacing I(h) by Porod's expression[4] we have

$$I_{diff}(h) = \frac{2\pi\langle\rho^2\rangle S}{h^4} - \frac{\langle\rho^2\rangle K^2 S}{2h^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

This is an expression for point collimation where S is the surface area of the particle per unit volume. For the usual experimental set up using an infinitely long and narrow slit the smeared intensity[4] is

$$\gamma(h) = \int_{-\infty}^{+\infty} I\left(\sqrt{h^2+y^2}\right) dy$$

which gives

$$\tilde{I}_{diff}(h) = \frac{\pi\langle\rho^2\rangle S}{h^3} - K^2 \frac{\pi\langle\rho^2\rangle S}{2h} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Thus when the interface between the particle and the matrix is diffuse

$$h^3\tilde{I}_{diff}(h) = \pi\langle\rho^2\rangle S - K^{2\pi}\frac{\langle\rho^2\rangle S}{2} h^2 \quad \ldots\ldots\ldots\ldots (7)$$

while for sharp interface

$$h^3\gamma(h) = \pi\langle\rho^2\rangle S = \text{constant}$$

A plot of $h^3\tilde{I}(h)$ vs h^2 should, therefore, be a horizontal straight line if the interface is sharp, while it should be a straight line with a negative slope if the interface is diffuse. The ratio of the slope to intercept at h = 0 gives $K^2/2$, an estimate of the width of the interface.

3. EXPERIMENTAL SUPPORT

Before loss of coherency, spinodally decomposed systems are likely to have diffuse interfaces between the separated phases[5]. Thus equation (1) can be applied to such systems. However, there is a problem. It was recognized by Erb and Hilliard[6] and Cook[7] that even in the absence of any decomposition there will be SAXS due to thermal fluctuations in concentration. Thus equation (1) should contain an additional term. In the early stages of spinodal decomposition this term is comparable with the two other terms and gives rise to a positive contribution which more than offsets the negative term of equation (2). Thus in the early stages of spinodal decomposition the limiting $h^3\tilde{I}(h)$ should increase with increase of h in the Porod region. But in the later stages the two terms of equation (1) become much larger than the additional term. The effect of the diffuse boundary can, therefore, be detected at later stages of aging, provided the interface does not become sharp by that time.

The data of Bonfiglioli[8] on Al-20 at % Ag are available to test the theory. This alloy, homogeneized in a single phase region, then quenched to $-50^{\circ}C$ was aged at room temperature for 20 days. The composition at room temperature is within the spinodal as evidenced by the work of

0 0 3 0 4 8 0 5 5 8 5

Kallstrom and Hilliard[9] and Roberge and Herman[10]. Bonfiglioli's data when plotted as $\frac{h^3 I(h)}{8\pi^3}$ vs $\frac{h^2}{4\pi^2}$ (Fig. 1) gives a straight line with a negative slope as predicted by equation (7). Assuming a Gaussian smoothing function, the width of the interface is 14A° while the Guinier radius[4] of the minor phase is 80A°.

Tomozawa[11] has used SAXS to study phase separation in Li_2O-SiO_2 glass. For a composition 27.43 mol % Li_2O, his data plotted as $I(2\theta)x(2\theta)^4$ vs $(2\theta)^2$ also shows straight lines with negative slopes for two aging temperatures as shown in Fig. 2. (The $I(2\theta)$ data are corrected for slit geometry). This particular composition is fairly within the missibility gap as determined by Tomozawa and is likely to have decomposed spinodally. In Fig. 2 it can be seen that the curve corresponding to aging at 500°C for two hours has a strong negative slope for which the width of the interface is calculated to be 90A°. At 9 hours aging at the same temperature, the interface seems to have become sharp as indicated by the zero slope of the corresponding curve. Aging at 525°C for 5.5 hours, on the other hand shows a negative slope but with a smaller width of 75A°. The radius of gyration exceeds 500A° for this system. The indication, therefore, is that the interface becomes sharper on aging at higher temperature and for longer times.

4. SUMMARY

Small angle x-ray scattering technique can be used to determine if the interface between inhomogeneity and the matrix is diffuse. An important field of application is the spinodally decomposed system. The tail portion of SAXS known as the Porod region is modified due to the presence of a diffuse interface. A simple analysis of the intensity in

this region as a function of the scattering angle gives the width of the interface.

ACKNOWLEDGEMENT

The continued support of DOE through the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory is gratefully acknowledged.

0 0 0 0 4 8 0 5 5 8 6

REFERENCES

1. A. Guinier, G. Fournet and C. B. Walker: Small Angle Scattering of X-rays, John Wiley & Sons, N. Y., 1955, p. 10.
2. R. Hoseman and S. N. Bagchi: Direct Analysis of Diffraction by Matter, North-Holland Publishing Co., 1962, p. 64 and 605.
3. W. Ruland: J. Appl. Cryst., 1971, Vol. 4, p. 70.
4. Ref. 1, pp. 25, 80, and 115.
5. John W. Cahn: Met. Trans., 1968, vol. 242, p. 166.
6. D. Erb, Ph.D. Thesis, Northwestern Univ., Evanston, Illinois, 1969.
7. H. E. Cook: Acta. Met., 1970, Vol. 18, p. 297.
8. A. F. Bonfiglioli: Metallic Solid Solution, ed. Friedel and Guinier, W. A. Benjamin Inc., 1963, p. XLI-1.
9. K. Kallstrom and J. E. Hilliard: J. Metals, 1968, Vol. 20, p. 69.
10. R. Roberge and H. Herman: J. Mat. Sci., 1974, Vol. 9, p. 1123.
11. M. Tomozawa: Phys. Chem. Glasses, 1972, Vol. 13, p. 161.

FIGURE CAPTIONS

Fig. 1. Small angle x-ray scattering from Al-20 at % Ag showing negative departure from Porod's Law.

Fig. 2. Small angle x-ray scattering from Li_2O glass showing negative departure from Porod's Law.

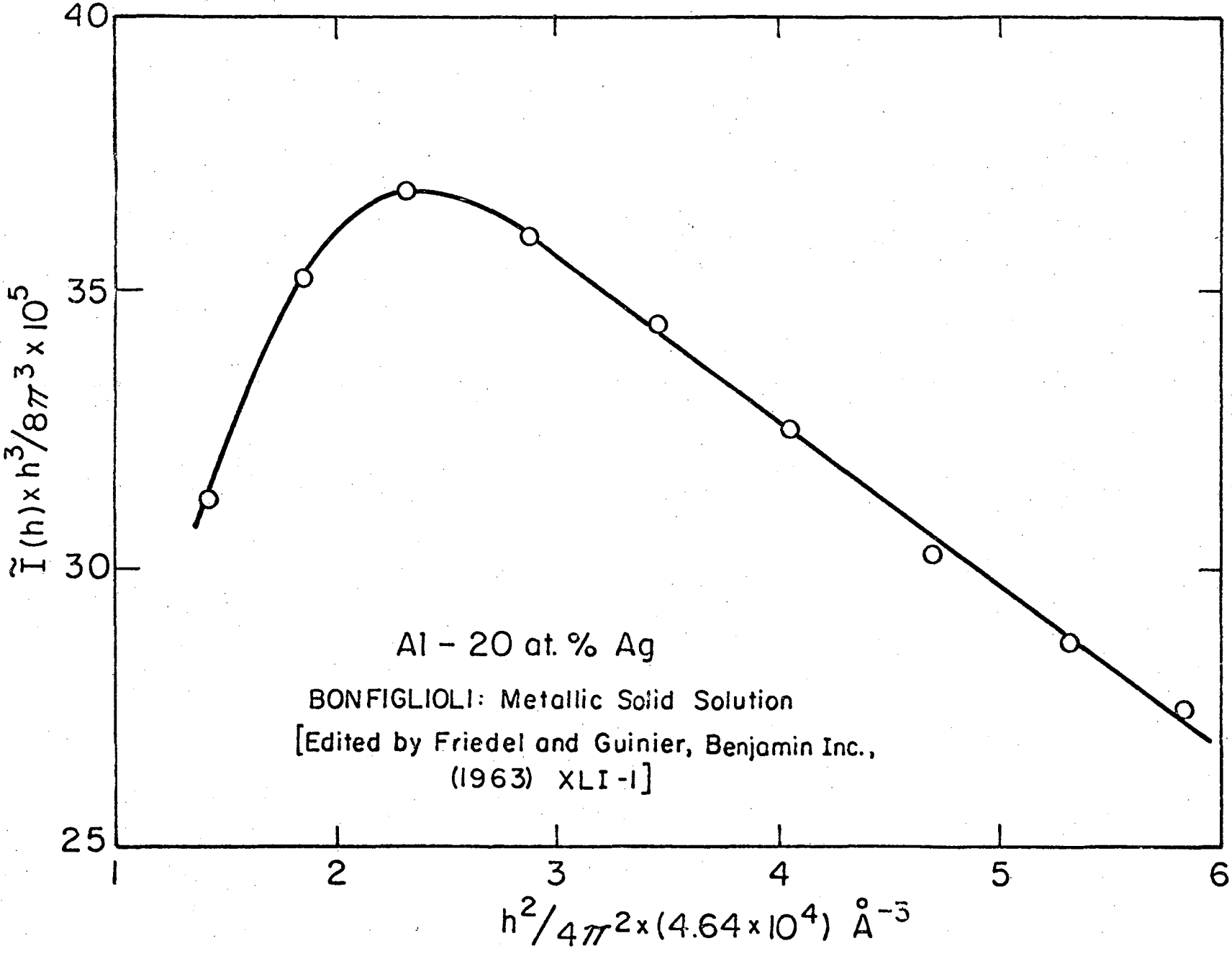


Fig. 1

0 0 0 4 8 0 3 3 8 7

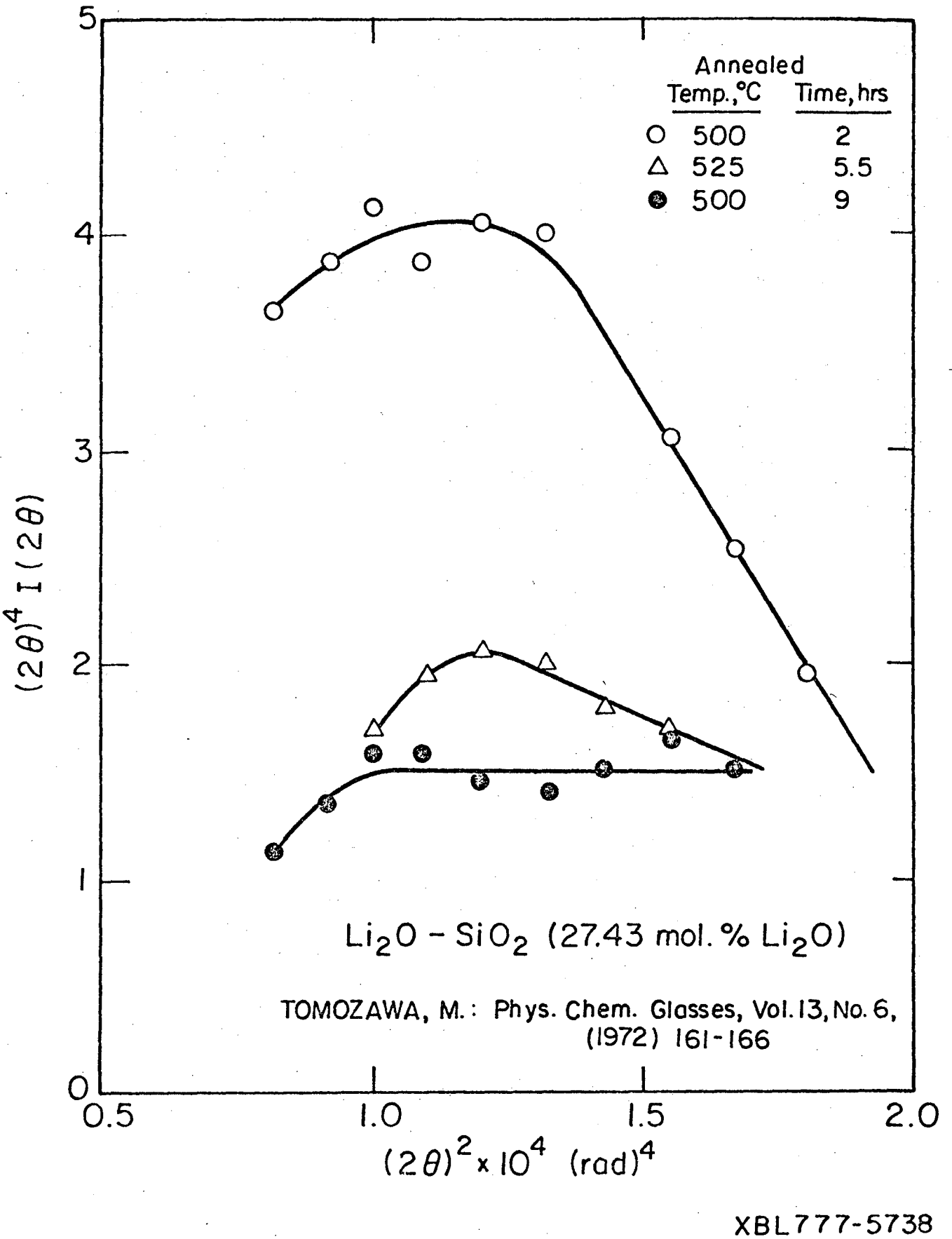

Annealed
Temp.,°C
Time,hrs
500
2
525
5.5
500
9
$(2\theta)^4 I(2\theta)$
$Li_2O - SiO_2$ (27.43 mol. % Li_2O)
TOMOZAWA, M.: Phys. Chem. Glasses, Vol.13, No.6, (1972) 161-166
$(2\theta)^2 \times 10^4$ (rad)^4
XBL777-5738

Fig. 2

0 0 0 0 4 8 0 5 5 8 8

S. Bose is graduate student and research assistant and R. H. Bragg is professor of Materials science, Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Materials science and Mineral engineering,University of California, Berkeley, CA 94720.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720