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The Growth and Crystallography of Bismuth Tri-iodide Crystals Grown by Vapor Transport

D. Nason
EG&G Energy Measurements, Inc.
Santa Barbara Area Operations
5520-B Ekwill Street
Santa Barbara, California 93111

Ludwig Keller
Camet Research, Inc.
6409-F Camino Vista
Goleta, California 93117

ABSTRACT

A single crystal of bismuth tri-iodide (BiI_3) of dimensions 1.2 X 1.2 X 0.4 cm^3 has been grown by physical vapor transport. The lattice parameters of the hexagonal crystal and its polycrystalline powder precursor were measured by X-ray diffraction (XRD) and were in agreement, indicating that the vapor phase growth and sublimation purification processing at temperatures below 330°C did not significantly affect the stoichiometry. X-ray rocking measurements of the single crystal showed low angle boundaries of the order of 0.05°. In tests as gamma radiation detectors, neither melt grown nor vapor grown crystals were satisfactory, but the vapor grown crystals were promising. Several observations suggest that better performance may be achievable with purer bismuth tri-iodide.

INTRODUCTION

Bismuth tri-iodide (BiI_3) is a wide bandgap semiconductor with a bandgap energy variously reported as 2.18 eV [1] and 1.73 eV [2], and a large average atomic number. At ambient temperatures BiI_3 has a hexagonal crystal lattice [3], black color, large anisotropy, and weak (van der Waal) bonding between adjacent planes of iodine atoms normal to the [0001] axis. In these properties BiI_3 is similar to (tetragonal) α-mercuric iodide (HgI_2), from which nuclear radiation detectors that can operate at room temperature are fabricated [4]. Thus, BiI_3 has attracted attention for its potential in similar applications. To evaluate this potential, single crystals of a sufficiently large size must be obtained.

Phase diagram studies in the B-I system [5] show that the hexagonal polymorph of BiI_3 is stable from the melting point, 408°C, down to ambient temperatures. At temperatures of 250°C to 300°C the vapor pressure is in the general range, $0.1 \rightarrow 1.0$ torr [6]. This is the vapor pressure range in which mercuric iodide crystals having dimensions useful for detectors have been grown by the technique of physical vapor transport. One study [7] has concluded that BiI_3 vapor, $BiI_3(g)$, does not dissociate significantly below about 600°C. An extrapolation of the measurements of another study [8] 2indicates that the dissociation is a few percent at 250°C - 300°C. The substantial vapor pressure and the minimal vapor dissociation of BiI_3 at comparatively low temperatures suggest that purification may be possible by evaporation/recrystallization and that growth of single crystals of usable size may be possible by physical vapor transport.

Single crystal platelets of BiI_3 of thickness 1 - 10μm, and face area of a few mm^2 were grown by open flow sublimation and recrystallization [9]. Platelets of thickness, 10μm, were grown by sublimation in a sealed tube [10]. Thin films of 0.01→0.1μm thickness were grown on a lead iodide substrate by vapor phase epitaxy [11]. Bulk BiI_3 was also grown by a sublimation process in quartz boules [12], from which single crystal slices of approximately 10 mm diameter and 1 mm thickness were cleaved. Such small crystal platelets, cleaved or as-grown, have been useful for the measurement of optical properties [1] [9-12]. The goal of the present study is to grow single crystals of BiI_3 large enough to be tested as gamma radiation detectors, with dimensions of the order of 1 cm, and to grow the crystals free standing, so that the defect inducing process of extracting the crystals from a polycrystalline mass is avoided. The process of growing such a crystal by the physical vapor transport method and its crystallographic characterization are described below.

CRYSTAL GROWTH

Bismuth tri-iodide powder of claimed purity of 99.999% (with respect to Ag, Ba, Ca, Cu, Mg) was obtained from Aldrich Chemical Company. X-ray diffraction powder analysis confirmed that the material was essentially hexagonal BiI_3, and any other phases were below the detection limit of about 1%. The powder was sealed into a quartz tube, evacuated to 10^{-6} torr, and processed by two successive stages of evaporation and recrystallization between zones at $330 \pm 10°C$ and $280 \pm 10°C$. The recrystallized material was loaded into a quartz growth ampoule (shown in Figure 1). A single crystal seed (obtained as described below) was implanted in the ampoule, which was evacuated to 10^{-6} torr, sealed, and placed in the growth furnace.

The growth furnace (Figure 1) is based on the design used to grow free standing mercuric iodide crystals by physical vapor transport [13]. The temperature profile, as shown schematically, is controlled by the upper and lower heaters, the position adjustable cold finger, and the transparent, double bell jar isolation containers. The temperatures were measured by type K thermocouples in contact with the upper and lower ampoule walls, and were controlled to ± 0.1°C by a Eurotherm 906D controller which has 0.01°C set point resolution. The process of initiating the growth of the seed and controlling the vapor transport so as to grow a single crystal has been described elsewhere [13].

The BiI_3 seeds for initiating growth can be obtained in two ways. Some platelets which recrystallized during the purification process by sublimation in sealed tubes had face areas of a few square millimeters and thicknesses of approximately 1 mm, which made them suitable as seeds. Also, similar platelets were found during material redistribution of the source material in course of crystal growth and could be extracted for seeding subsequent ampoules. These platelets have their c axis normal to their large face, and those selected for seeds grew with only one edge attached to the glass vessel or to adjacent crystals.

A single crystal of BiI_3, grown by the above method from a seed with its c axis vertical, is shown in Figure 2a. It has approximate dimensions of $1.2 \times 1.2 \times 0.4$ cm^3 and a mass of 2.6 g. The morphology displays a hexagonal crystal system which was confirmed by x-ray diffraction (see below) and is shown in Figure 2b. The growth rate was around 1 mm/day, measured from the point where the stabilized seed began to grow. Small platelets of approximate size $3 \times 3 \times 1$ mm^3 also grew incidentally in the ampoule by redistribution of the source material.

Growth trials were also attempted under other conditions. Using BiI_3 which had been sublimed from the melt at 420°C and then recrystallized, the growth ampoule showed the distinctive color of iodine vapor, indicating some decomposition. The iodide vapor pressure was 1.0 torr at 225°C and 1.3 torr at 275°C, as measured by optical absorption [14]. The iodine vapor color was also evident during a zone refining process, where the molten zone temperature exceeded the BiI_3 melting point, 410°C. These results indicate that, in order to minimize complications from decomposition, sublimation treatments to purify the material should be done at temperatures as low as is consistent with maintaining useful rates of vapor transport. Attempts to self-nucleate a single crystal, avoiding the use of an implanted seed, were unsuccessful. Amorphous, dark residues often occurred at locations in the ampoule where polycrystalline material had been sublimed away. Presumably, these are impurities and this may account for the difficulties in achieving smooth crystal growth without spurious nucleation, in comparison to growing HgI_2 crystals by the same general method.

X-RAY DIFFRACTION ANALYSIS

BiI_3 in the forms of commercial material, sublimed material, and vapor-grown single crystals was subjected to X-ray diffraction analysis. X-ray powder diffraction was used to determine the BiI_3 phase purity, the lattice symmetry and the lattice parameters. Single crystal platelets were ground to powder in an agate mortar prior to probing. To minimize preferred orientation effects, powder samples were prepared by dusting ground particles onto a background-free quartz plate. The powder diffraction measurements were carried out on a Bragg-Brentano diffractometer employing Ni-filtered CuKα radiation.

The crystalline perfection of the hexagonal single crystal was assessed by X-ray rocking curve analysis. Rocking curves of basal (0001) planes were produced with a monochromatic X-ray beam ($CuK_{\alpha 1}$) which had been conditioned by a four channel cut Ge 220 monochromator. The individual faces of the crystal (Figure 2b) were determined using a quarter circle goniometer.

The diffraction results showed that all polycrystalline materials, whether commercial, recrystallized, or sublimation purified, were single phase BiI_3. The major peak intensities in the BiI_3 powder pattern, as shown in Figure 3, agree well with those published by the Joint Committee for Powder Diffraction Standards - International Center for Diffraction Data (JCPDS) (#7-269). However, unexplained weak peaks were also observed (* in Figure 3). Bismuth tri-iodide has a hexagonal unit cell which contains six formula units, and its space group is R3. Using the positional atomic parameters of Trotter [15], powder patterns were calculated using Rietveld least square analysis, and the (*) peaks could only be identified as BiI_3 lines [15].

The lattice parameters of the starting material were determined from a mixture of BiI_3 powder (Aldrich Chemical Company) and Si-powder (NBS Reference material 640b) which acted as an internal standard. By least square analysis the following parameters were derived from an XRD scan ranging between 8° and 100°2Θ: a=7.520(1)Å and c=20.72(1)Å. Within the error of measurement the values are close to those of JCPDS (#7-269) (a=7.522Å and c=20.730Å).

Since the relatively large basal planes yielded a sufficiently flat surface area suitable for powder diffractometry, the single crystal c-parameters could be determined by the extrapolation method to c=20.716(2)Å, as shown in Figure 4. The a-parameter was obtained from the much smaller surface of one of the {hh2h0} type of planes which was mounted to be coplanar with a layer of Si-powder. By recording both the 3360 BiI_3 and 331 Si reflections at $2\Theta=76°$, a=7.517(2)Å was determined. Thus, the single crystal parameters are very close to those determined for a single crystal by Trotter [16] (a=7.516(3)Å and c=20.72(2)Å), and to those of the polycrystalline powder.

X-ray rocking curves were produced at two locations, 2 mm apart, on the as-grown (0001) face of the crystal in Figure 2a, and are shown in Figure 5. These results show a multiple domain structure, with low angle grain boundaries of ~0.05°, or ~200 arc sec. Like HgI_2, BiI_3 is an extremely soft material. Surface and subsurface damage might be expected to occur during growth, due to the crystal's own weight or to thermal stresses, or during handling. The crystalline imperfections displayed in Figure 5 resemble the quality of vapor-grown HgI_2 crystals which have produced passable, though not superior, detectors [17].

RADIATION DETECTOR TESTING

The crystal in Figure 2a was tested as a nuclear radiation detector after applying colloidal graphite electrodes and palladium wire leads to the as-grown, upper (0001) surface and to the underside. DC conductivity measurements showed a resistivity along (0001) of 2-$5 \times 10^9 \Omega$cm which is acceptable. However, there was no photoconductive response to γ (60 keV) or α particle (5 MeV) irradiation. Detector testing of the small platelet crystals showed a small response at 662 keV [18]. These results indicate that the vapor grown single crystals from this BiI_3 material are not yet of a quality suitable for nuclear radiation detectors.

SUMMARY

A single crystal of BiI_3 has been grown by physical vapor transport. X-ray rocking curve analysis of the crystal structure shows low angle grain boundaries of the order of 0.05°. Using XRD, the lattice parameters of the polycrystalline source material and of the single crystal were found to be the same, within the error of measurement, and to agree with earlier values for hexagonal BiI_3. This suggests that the stoichiometry of BiI_3 is not significantly affected by vapor phase processing at temperatures less than 330°C. In tests as a nuclear radiation energy detector, the crystal showed acceptable leakage, but no response to γ- or α-particle radiation. Although vapor growth is shown to be a viable method for producing the (approximate) 1 cm crystals required for γ detectors, ampoule residues and detector shortcomings suggest that further purification of the material is necessary before a full evaluation of the potential of BiI_3 as a nuclear radiation detector can be done.

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FIGURE CAPTIONS

Figure 1. Schematic view of growth ampoule and furnace for growth of BiI_3 single crystals by physical vapor transport.

Figure 2.
- a. Single crystal of BiI_3 grown by physical vapor transport.
- b. Morphology of crystal in a. as determined by XRD.

Figure 3. XRD powder pattern of recrystallized BiI_3 powder (⇒LOT#0783LV (Aldrich)). The (*) indicates the weak lines which are not listed in JCPDS file #7-269 and were subsequently identified as BiI_3 lines by pattern calculation using Rietveld analysis.

Figure 4. Two independent c-axis determinations on different powder diffractometers using $\cos\Theta$-$\cot\Theta$ as an extrapolation function. The 000.15, 000.18, 000.21, and 000.24 reflections from the basal plane (see Figure 2a) are used to determine c with an accuracy of ±0.002Å.

Figure 5. X-ray rocking curves of the basal plane (see Figure 2a) using the 000.12 reflection. Multiple peaks are a result of low angle grain boundaries. The curves in A and B are produced by locations 2 mm apart.

REFERENCES

[1] V.M. Shmandii, V.K. Miloslavskii, and V.V. Mussil, *Sov. Phys. Solid State* 21 (8), 1386 (1979).

[2] V.I. Veshchenko and V.B. Timofeev, *Sov. Phys. Solid State* (9), 1242 (1967).

[3] Powder Diffraction File, published by JCPDS, 7-269 (1993).

[4] V. Gerrish, "Characterization and Quantification of Detector Performance," Chapter Fourteen in "Semiconductors for Room Temperature Nuclear Detector Applications" in Semiconductor and Semimetals, Academic Press, 1995, Ed. T.E. Schlessinger and R.B. James.

[5] S.J. Yosim, L.D. Ransom, R.A. Sallach and L.E. Topol, *J. Phys. Chem.* 66, 28 (1962).

[6] J.H. Kim and S. Blairs, *J. Chem. Thermodynamics,* 22, 803-814 (1990).

[7] V.A. Trifonov, V.A. Dolgikh, B.A. Popovkin, V.I. Belousov, and A.V. Novoselova, *Russian Journal of Inorganic Chemistry* 20 (6) 825 (1975).

[8] D. Cubicciotti and F.J. Keneshea, Jr., *J. Phys. Chem.* 63, 295 (1959).

[9] B.J. Curtis and H.R. Brunner, *Mat. Res. Bull.*, Vol. 9, 715-720 (1974).

[10] T. Komatsu and Y. Kaifu, *Journal of the Physical Society of Japan,* Vol. 40 No. 4, 1062 (1976).

[11] S. Takeyama, K. Watanabe, and T. Komatsu, *Japanese Journal of Applied Physics,* Vol. 29, No. 4, 710 (1990).

[12] M. Schieber, T.J. Davies, W.F. Schnepple, P.T. Randke, and R.C. Carlston, *Journal of Applied Physics,* Vol. 45, No. 12, 5371 (1974).

[13] A. Burger, D. Nason, L. van den Berg, and M. Schieber, "Growth of Mercuric Iodide," Chapter Four in "Semiconductors for Room Temperature Nuclear Detector Applications" in Semiconductor and Semimetals, Academic Press, 1995, Ed. T.E. Schlessinger and R.B. James.

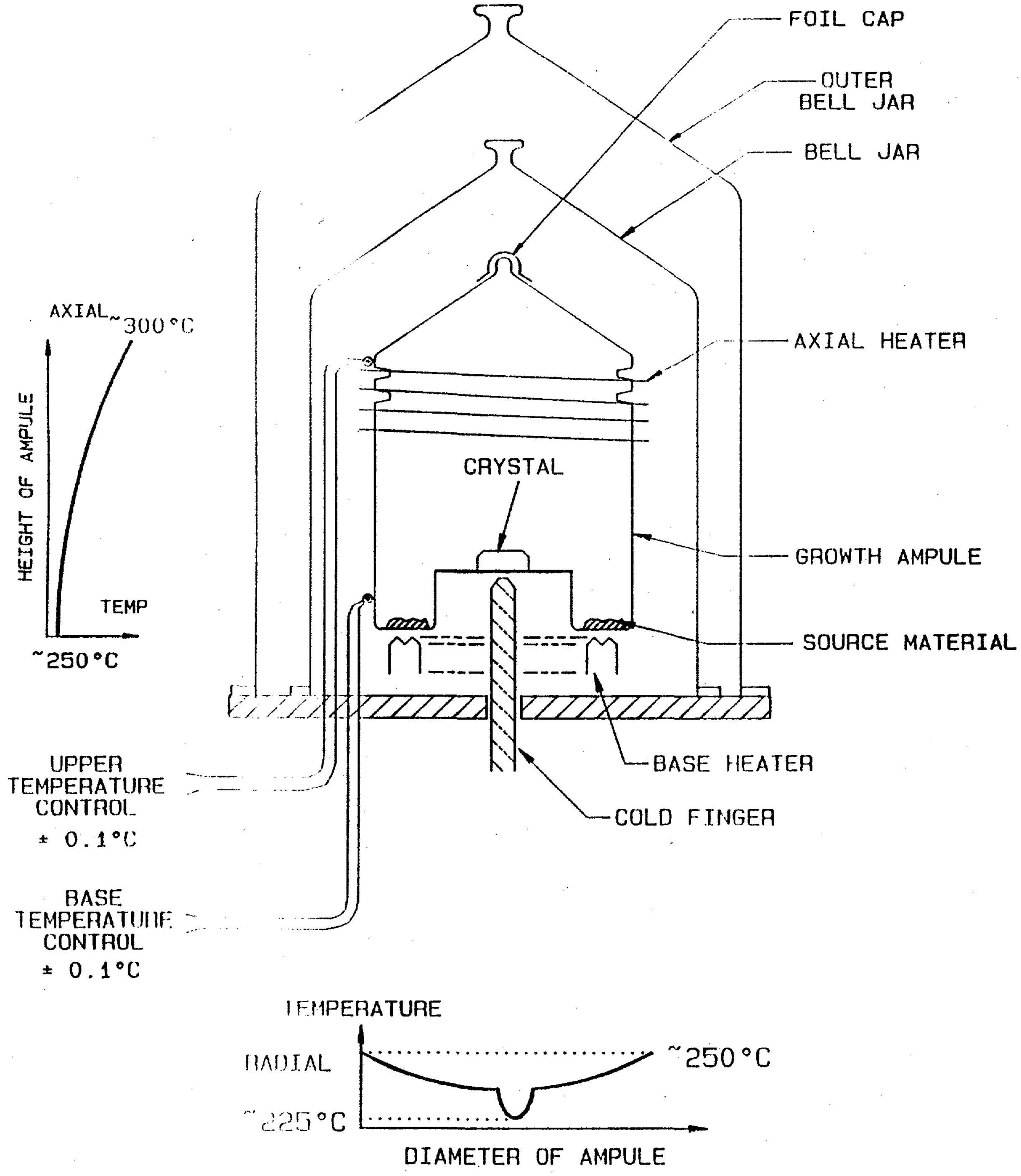
[14] D. Nason, Y. Biao, and A. Burger, accepted for publication in *Journal of Crystal Growth.*

[15] To be submitted to *Powder Diffraction.*

[16] J. Trotter and T. Zobel, *Zeitschrift für Kristallographie,* Bd. 123, S. 67 (1966).

[17] M. Schieber, C. Ortale, L. van den Berg, W. Schnepple, L. Keller, C.N.J. Wagner, W. Yelon, F. Ross, G. Georgeson and F. Milstein *Nuclear Instruments and Methods in Physics Research*, A283, 172 (1989).

[18] K. James, private communication.



BiI_3 CRYSTAL VAPOR GROWTH FURNACE

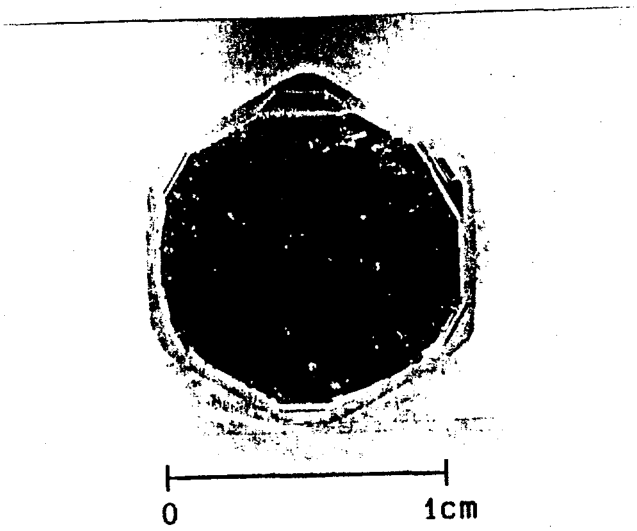
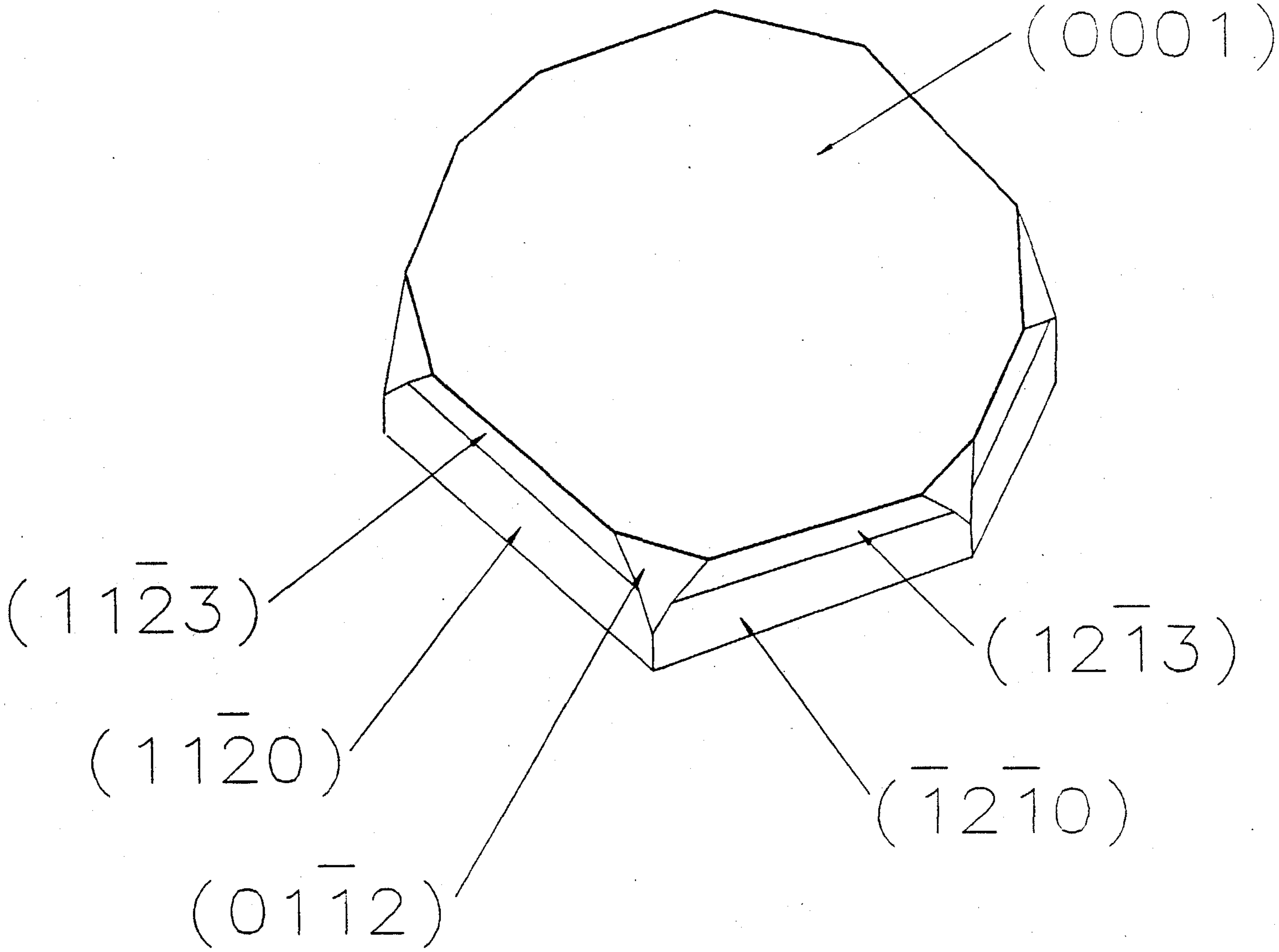
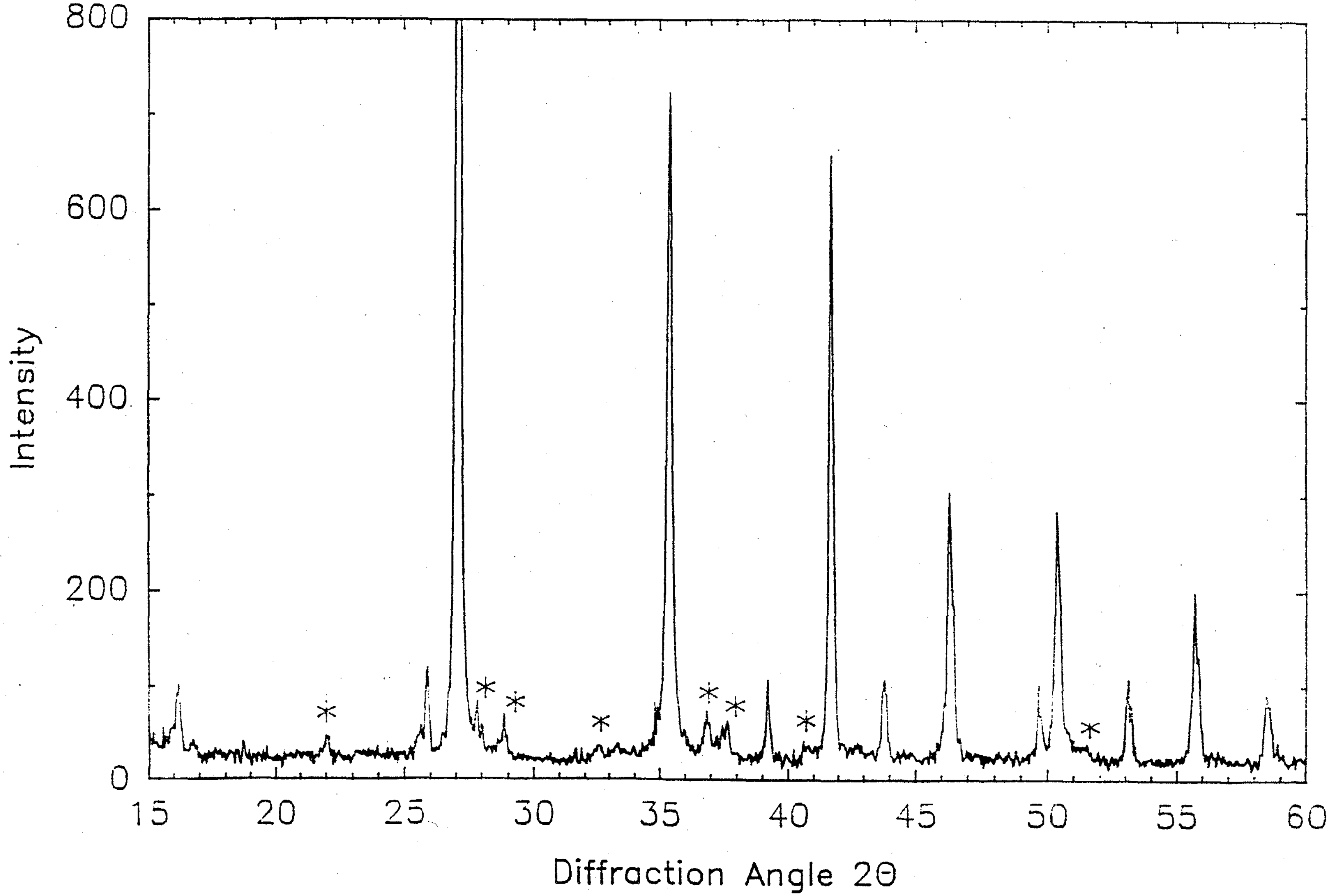


Fig 2a


(0001)
$(11\bar{2}3)$
$(11\bar{2}0)$
$(0\bar{1}\bar{1}2)$
$(12\bar{1}3)$
$(\bar{1}2\bar{1}0)$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600
400
200
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Intensity
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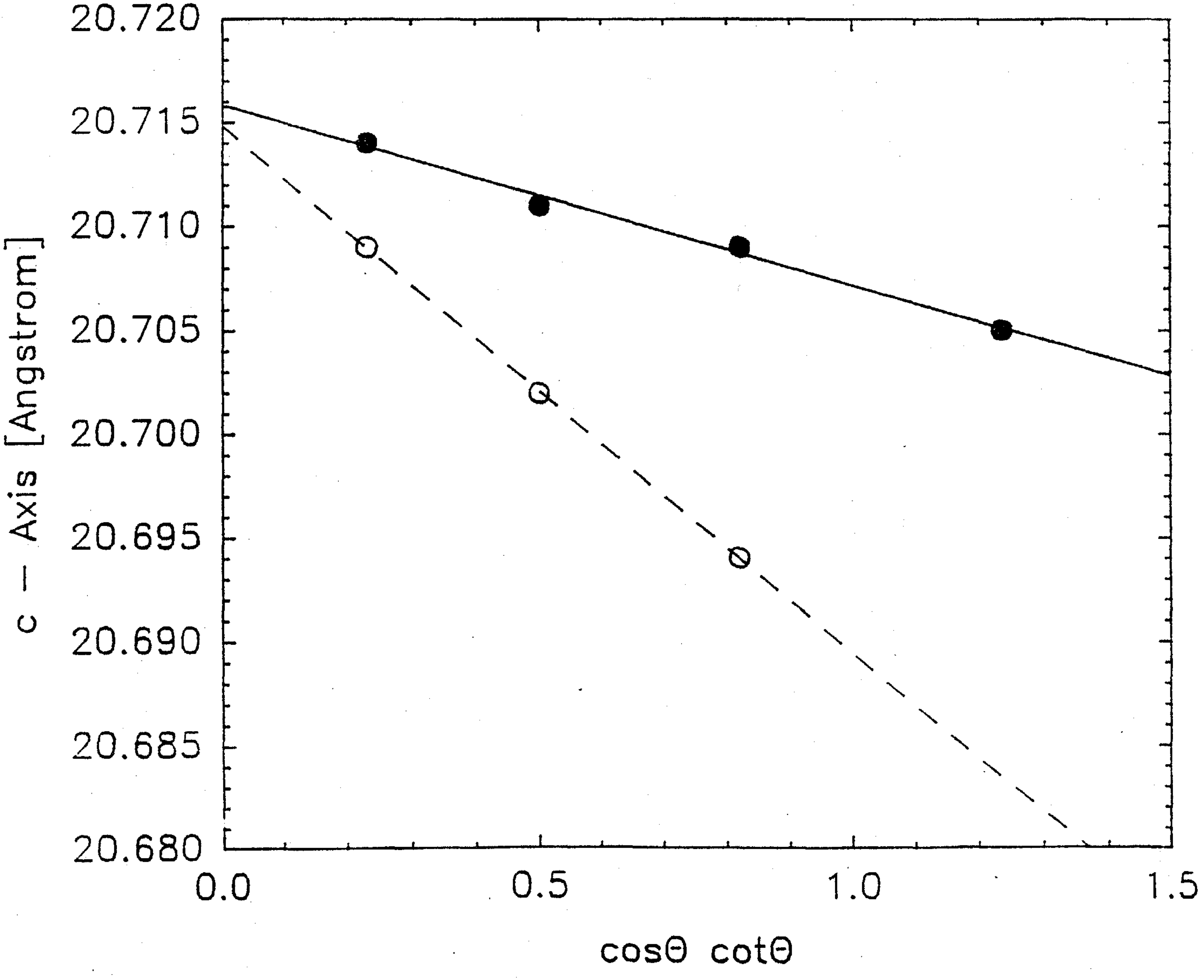
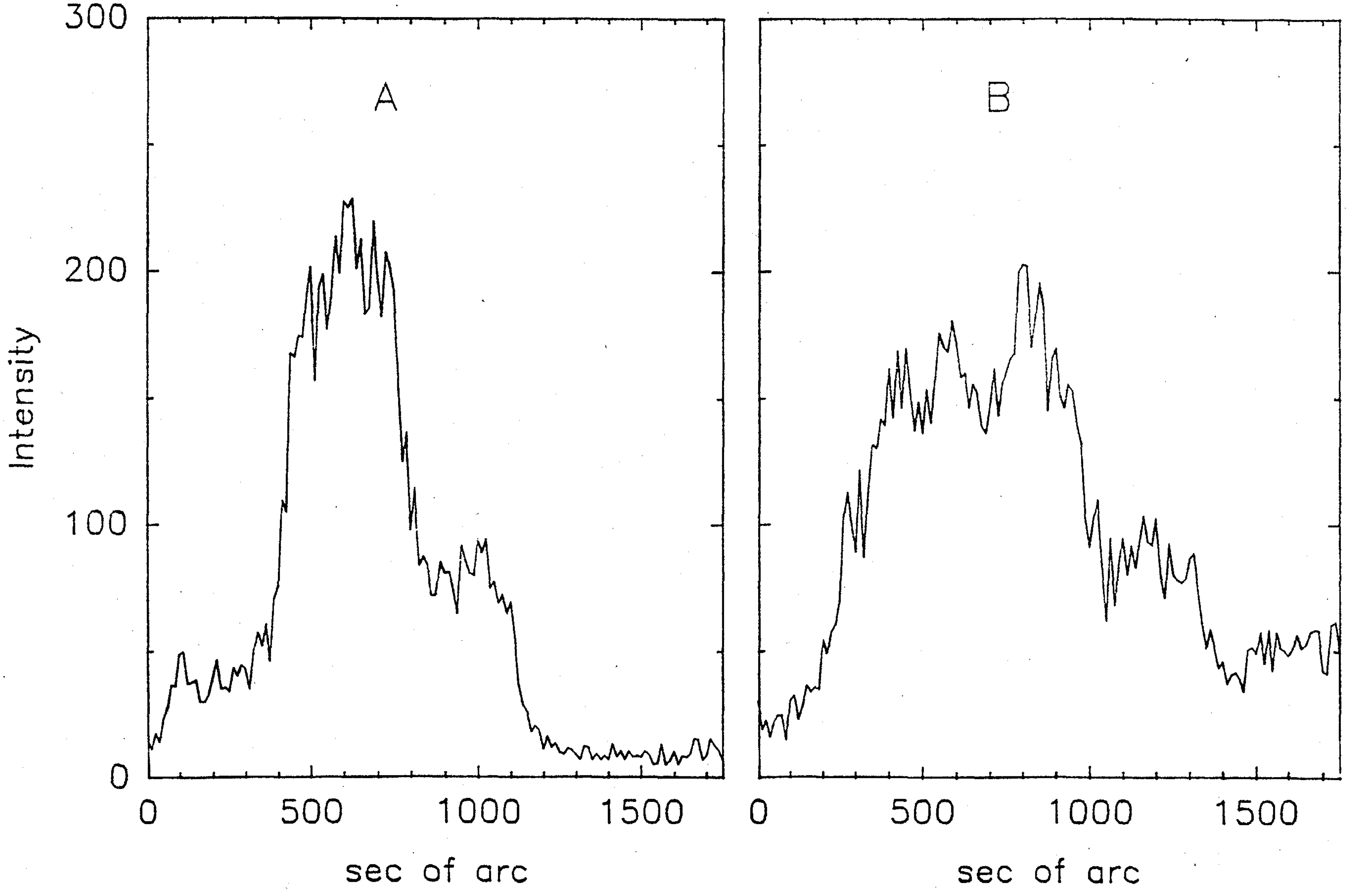
20
25
30
35
40
45
50
55
60
Diffraction Angle 2Θ
*


20.720
20.715
20.710
20.705
20.700
20.695
20.690
20.685
20.680
c — Axis [Angstrom]
0.0
0.5
1.0
1.5
cosΘ cotΘ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200
100
0
Intensity
A
B
0
500
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sec of arc
0
500
1000
1500
sec of arc