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16. Abstract (Limit: 200 words)

During the period July 15 through August 14, 1991, excimer laser ablation of a high purity, hexagonal boron nitride (HBN) target was continued to synthesize CBN thin films on silicon substrate; the films were characterized with SEM, Raman spectroscopy, x-ray diffraction and IR spectroscopy. Today our results indicate that the laser grown films were predominantly amorphous boron nitride rather than CBN. We had a discussion with Dr. Gary Doll and his research group (they are actively involved in growing CBN films using laser ablation) at General Motors Research Laboratory to identify the issues involved in growing CBN films. A summary of discussion and the work to be done in the next month are presented.

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Report Documentation Page

SBIR Phase I Research Progress Report # 2

Summary of Work Performed

In the previous report (June 15 - July 14, 1991), we have demonstrated the growth of boron nitride films on Si <100> and Si <111> substrates using excimer laser ablation methodology. The films contained particulates and peeled off at the center of deposited zone. Although film thickness was not measured, it appeared to be in the microns range.

Excimer laser ablation experiments were continued to produce particle-free, strongly adherent CBN films. Table 1 lists the experimental conditions that we have employed. Visual and SEM examination of the samples show the following parametric effects:

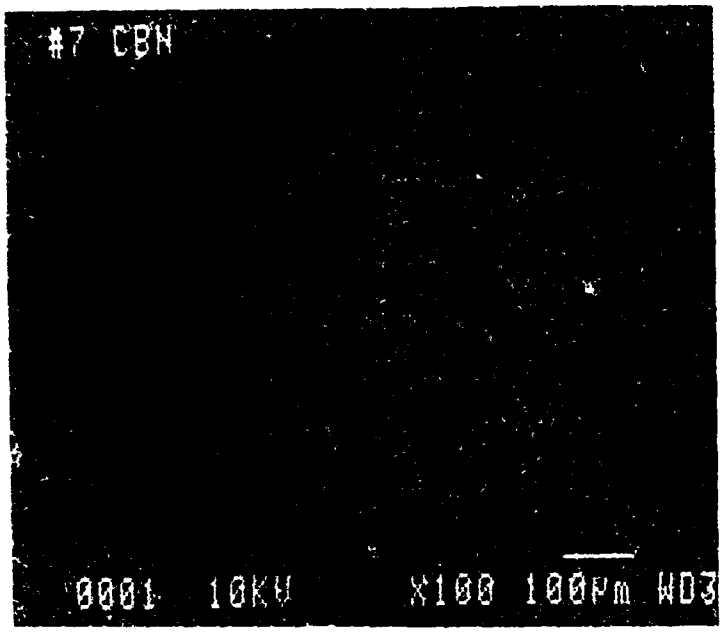
1. An increase in laser energy density resulted in thicker films and large number of particulates. In addition, film cracking and fracture were observed.
2. When the distance between the target and the substrate decreases, thicker and loosely attached films with large number of particulates were obtained.
3. Substrate temperature did not affect the film properties including the adherence
4. In all the experiments, the film exhibited fringes of multiple colors

Wavelength dispersive X-ray analysis (attached with SEM) of the laser grown films indicated the presence of boron and nitrogen, and the absence of oxygen. Figure 1 presents the SEM micrographs of two samples, # 7 and # 10, at low magnification. Sample # 10 shows particle-free, smooth surface in contrast to sample # 7 essentially due to the effect of low energy density. At higher magnifications (see Figure 2), localized microcracking and microstripping of the film are observed in sample # 7 in contrast to sample # 10 suggesting that lower energy density is preferred.

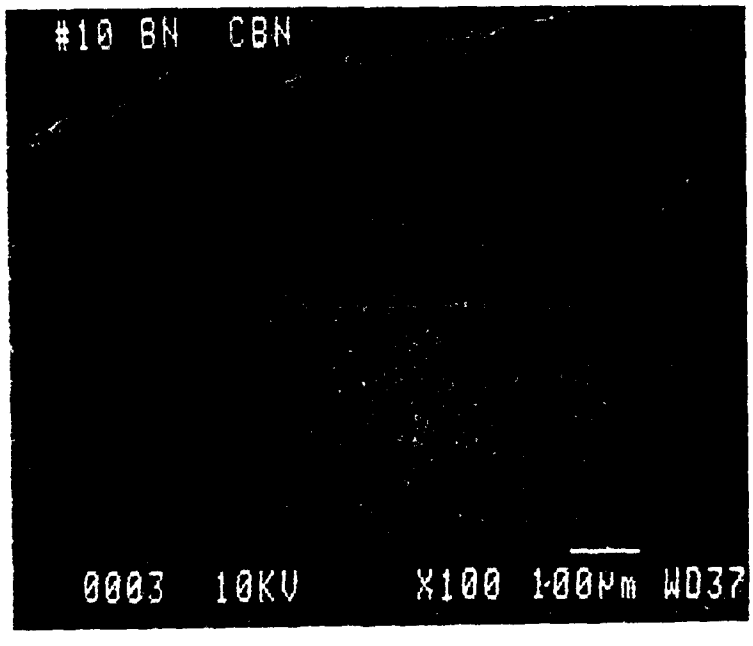
Table 1. Experimental conditions and observations

Laser: 248-nm KrF Excimer Lens: 100 mm Focal length lens
Spot size: 4.5 mm x 1.5 mm Target: Hexagonal BN rod rotated at 50 rpm
Pulse length: 23 nsec Pulse rate: 5 pulses per sec
Degree of vacuum: 10^{-7} torr
Sample: Silicon, polished and etched in HF acid for 30 secs

Sample Number	Substrate Temp. ^{o}C	Beam-target Distance, mm	Energy Density, J/cm^2	No. of Pulses	Observations and comments
1	400	6	5.5	18,000	Improper target rotation, thick film, film fracture at the center
2	100	6	5.5	18,000	Improper target rotation, thick film
4	200	6	5.5	18,000	Thick film, film breakage at the center
5	100	18	4.4	9,000	Smooth uniform film
6	400	18	4.4	9,000	Smooth uniform film
7	250	18	4.4	9,000	Smooth uniform film
8	Repeat sample # 7				Same as # 7
9	250	18	2.9	9,000	Extremely thin film
10	250	18	3.7	9,000	Smooth thin film



(a)



(b)

Figure 1. SEM micrographs of samples (a) # 7 and (b) # 10
Magnification: 100 X

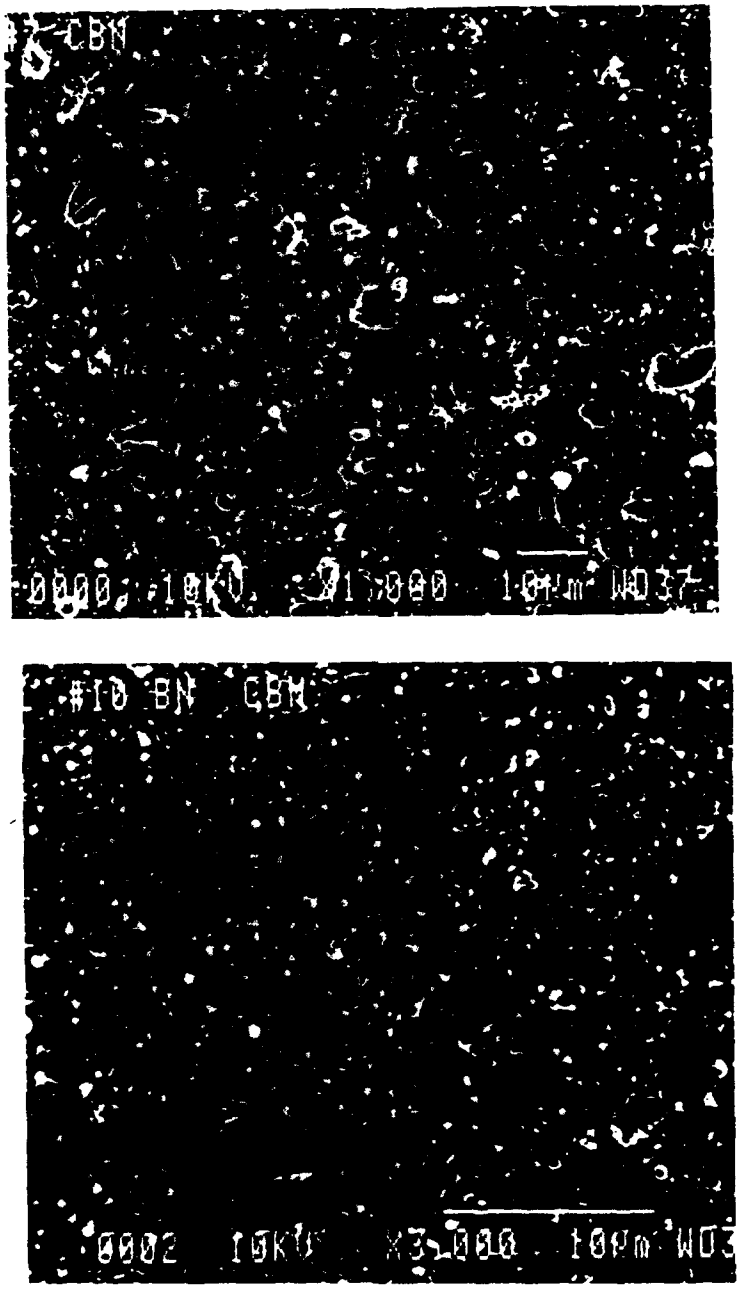


Figure 2. SEM micrographs of samples (a) # 7 and (b) #10
Magnification: 1,000 X

X-ray diffraction using copper K alpha radiation (wavelength = 1.5418 angstroms), Raman spectroscopy and IR spectroscopy analysis were performed on samples # 4, 6, 7, 9 and 10. X-ray diffraction patterns of samples # 4, 6 and 9 were similar and exhibited no peaks in the diffraction patterns (see Figure 3). Samples # 7 and 10 also did not exhibit peaks corresponding hexagonal, wurtzite or cubic structure of BN (see Figures 4 and 5). It is clear that the films grown via laser processing were amorphous rather than crystalline.

Raman spectroscopy analysis of the films (shown in Figures 6 through 8) do not indicate any evidence of cubic or hexagonal BN. IR spectrums were obtained for the target and samples # 4, 7, 10 and are given in Figures 9 through 11. IR spectroscopy is sensitive to the determination of chemical bonding rather than crystal structure. As seen in Figure 9, sp^2 bonding, characteristic of HBN target, has peaks at 1370 and 770 cm^{-1} (sp^3 bonding is characteristic of CBN and has a peak near 1100 cm^{-1}). IR spectrums of sample # 7 superimposed on the target, and samples # 4 and 10 do not indicate the presence of sp^3 bonding (see Figures 10 and 11). Although IR spectrums show some evidence of sp^2 bonding, the stoichiometry should be considered in order to derive the structural aspect.

In summary, the films grown by excimer laser ablation of a high purity hexagonl boron nitride were amorphous in nature and no cubic or hexagonal form was detected.

Discussion With Dr. Doll

Dr. Gary Doll and his research group are actively involved in synthesis of CBN films using excimer laser ablation; in fact, they claim that they are the first to synthesize epitaxial CBN thin films. We had a long discussion with him about his work and also went through the papers published by him in this area.

Dr. Doll has grown BN films on silicon using excimer laser ablation of pyrolytic BN to a thickness of about 1200 angstroms which he has claimed as epitaxial CBN film on Si <100> based on X-ray diffraction data. TEM and IR spectroscopy confirmed the presence of CBN in his samples. However, he said to us that his recent analysis with synchotron radiation of such films revealed that most of the film (about 1100 A) contained amorphous structure rather than crystalline. He also observed that the films were not stoichiometric ($BN_{0.75}$) inspite of the presence of nitrogen during the experiment.

Dr. Doll has recommended us to use pyrolytic BN target instead of high purity hexagonal BN target (HBC grade from Union Carbide which we are using in our experiments) because HBC grade tends to flake off easily and produce more particulates in the film. In addition, films produced using pyrolytic BN have low oxygen content, structurally superior than other targets, and optically smooth. He also suggested the following:

1. Initial surface condition of silicon is critical and should be free from oxygen; an etching time of 10 minutes in HF solution is recommended.
2. Flow of nitrogen at 10 sccm for a pressure of 30 mtorr will aid in reducing the particulate formation
3. Si <100> is preferable to Si <111> as a substrate
4. High substrate temperatures (600^{o}C or more) should reduce the degradation of the film by moisture

Work to be done for the next month

We have considered Dr. Doll's suggestions and ordered pyrolytic BN target from Union Carbide. We are expected to receive it in three weeks. We have examined carefully our results and Dr. Doll's work. We have also reviewed the work by Mineta et al [1] who used a continuous wave CO_2 laser to evaporate HBN targets in conjunction with an ion source (to produce ionized species of nitrogen) for deposition of CBN on silicon. Essentially the CO_2 laser was used as an evaporation source while the nitrogen ions were used to impart energy to the film so that cubic structure of BN can be obtained.

It appears from our work and Dr. Doll's work that excimer laser ablated species do not have sufficient energy to convert the amorphous to cubic form. The kinetic energy of laser-generated species increases as photon energy increases. The possibility of employing a 193-nm excimer should be considered or superimposing two laser beams may be considered.

The objective is to enhance the mobility and energy of laser-induced species from the target. We intend to use a dual beam approach involving a Nd:YAG beam (3 J at 1 pps) and the 248-nm excimer beam to irradiate the target. The Nd:YAG beam by virtue of its high energy density can produce a high density of ionized, excited state, atomic and high kinetic energy species. Nd:YAG evaporated species can be easily dissociated by KrF-excimer beam to produce high energy species. The plasma formation may cause these species to assume a large velocity similar to the effects observed in ion-beam deposition namely enhanced adatom mobility, breaking of weak bonds etc. Results of such experiments will be presented in the next report.

[1] S. Mineta, M. Kohata, N. Yasunaga, and Y. Kikuta., Thin Solid Films, Vol 189, 125 (1990).

Figure 3. X-ray Pattern of Sample #4

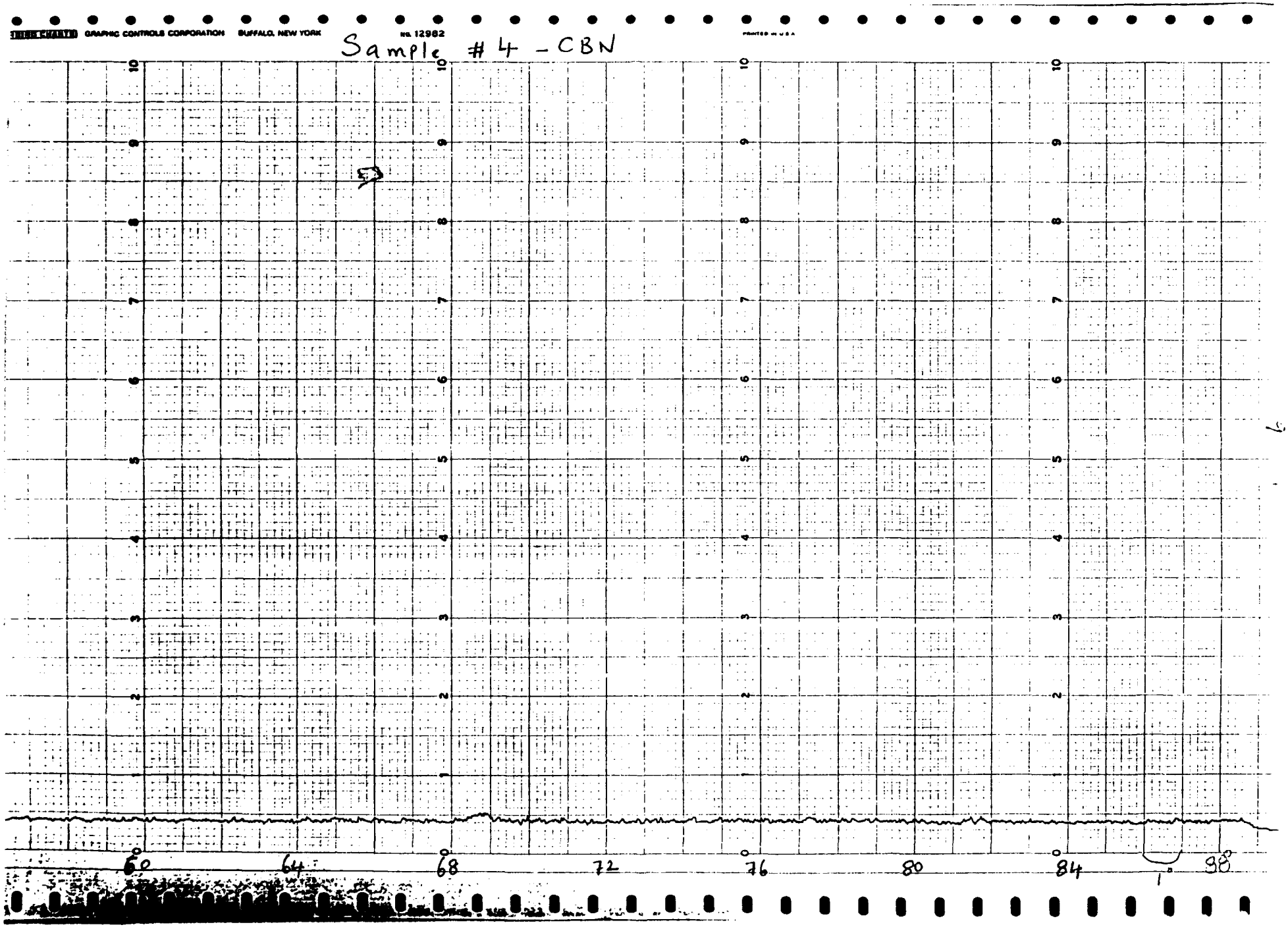
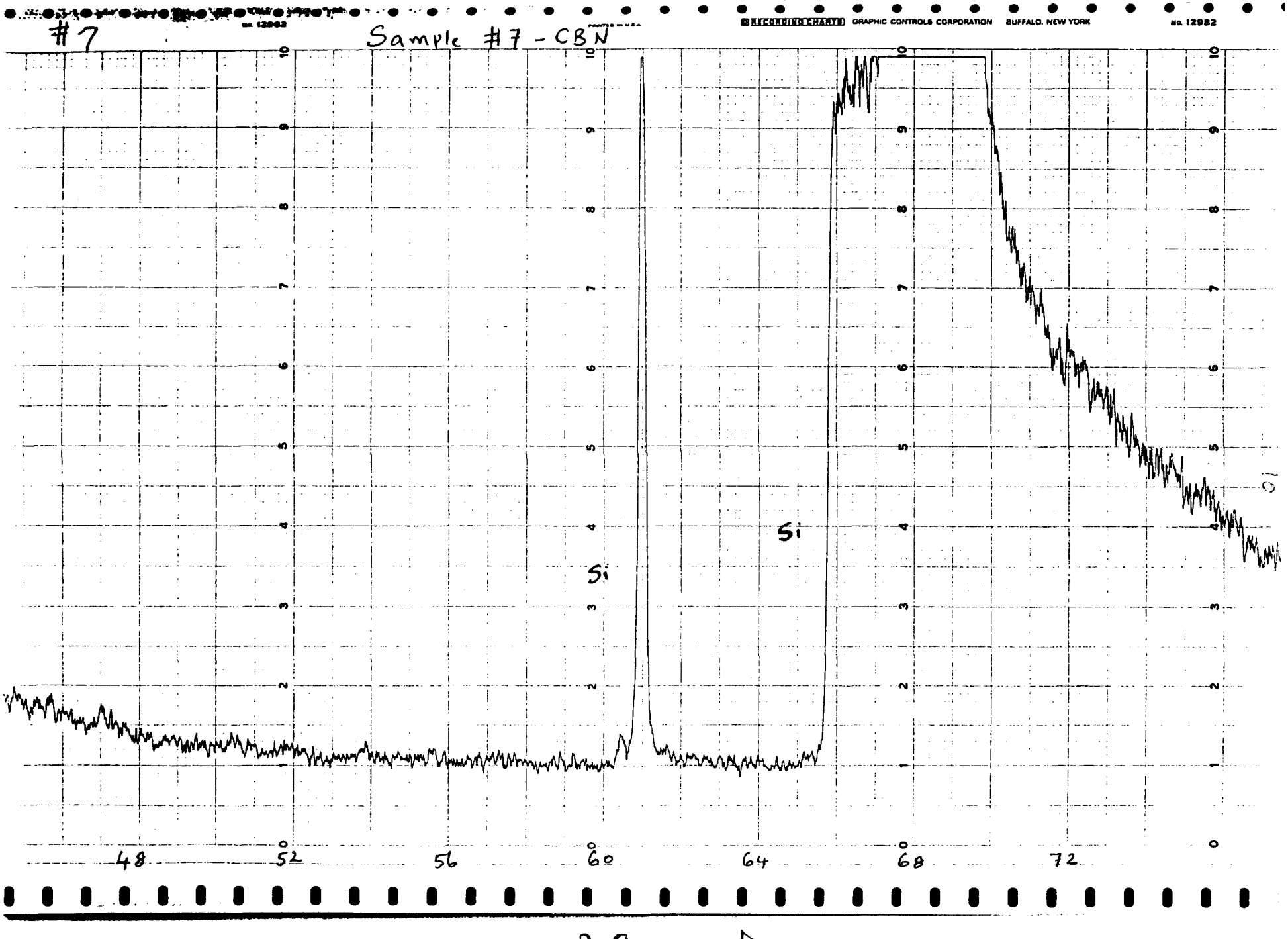


FIGURE 4 X-ray pattern of Sample #7



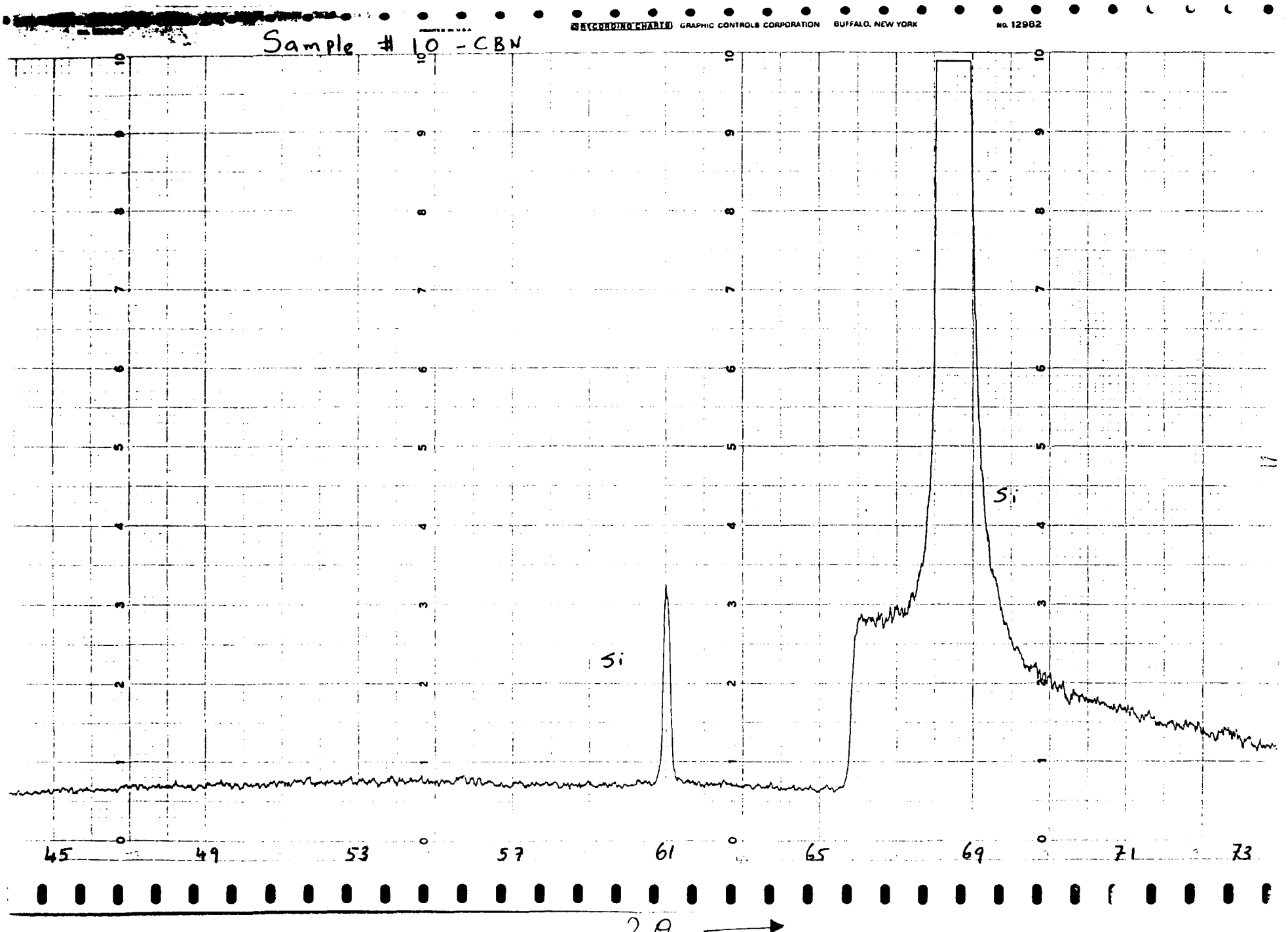
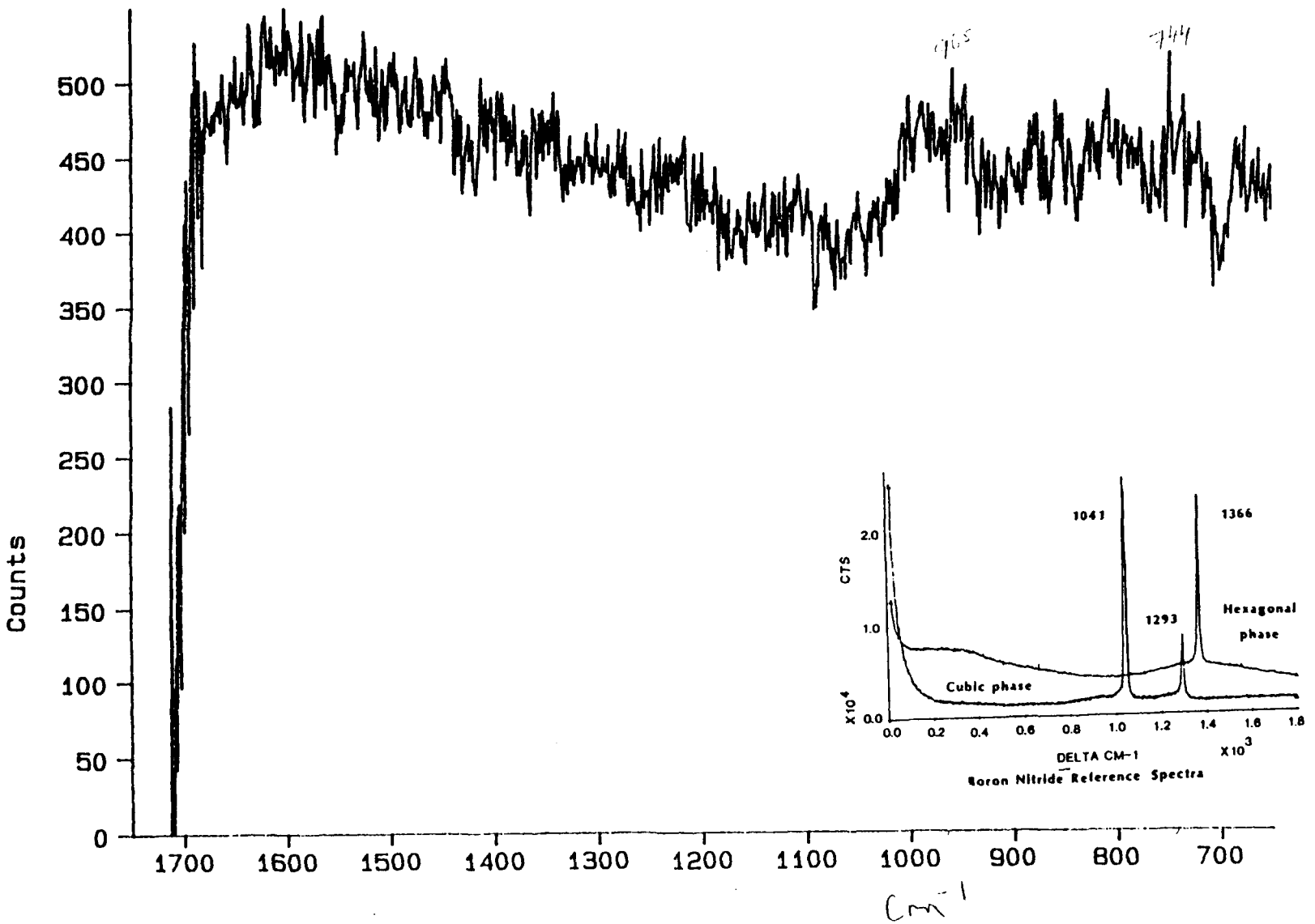

RECORDING CHARTS GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK No. 12982
Sample # 10 - CBN
Si
Si
45
49
53
57
61
65
69
71
73
2θ

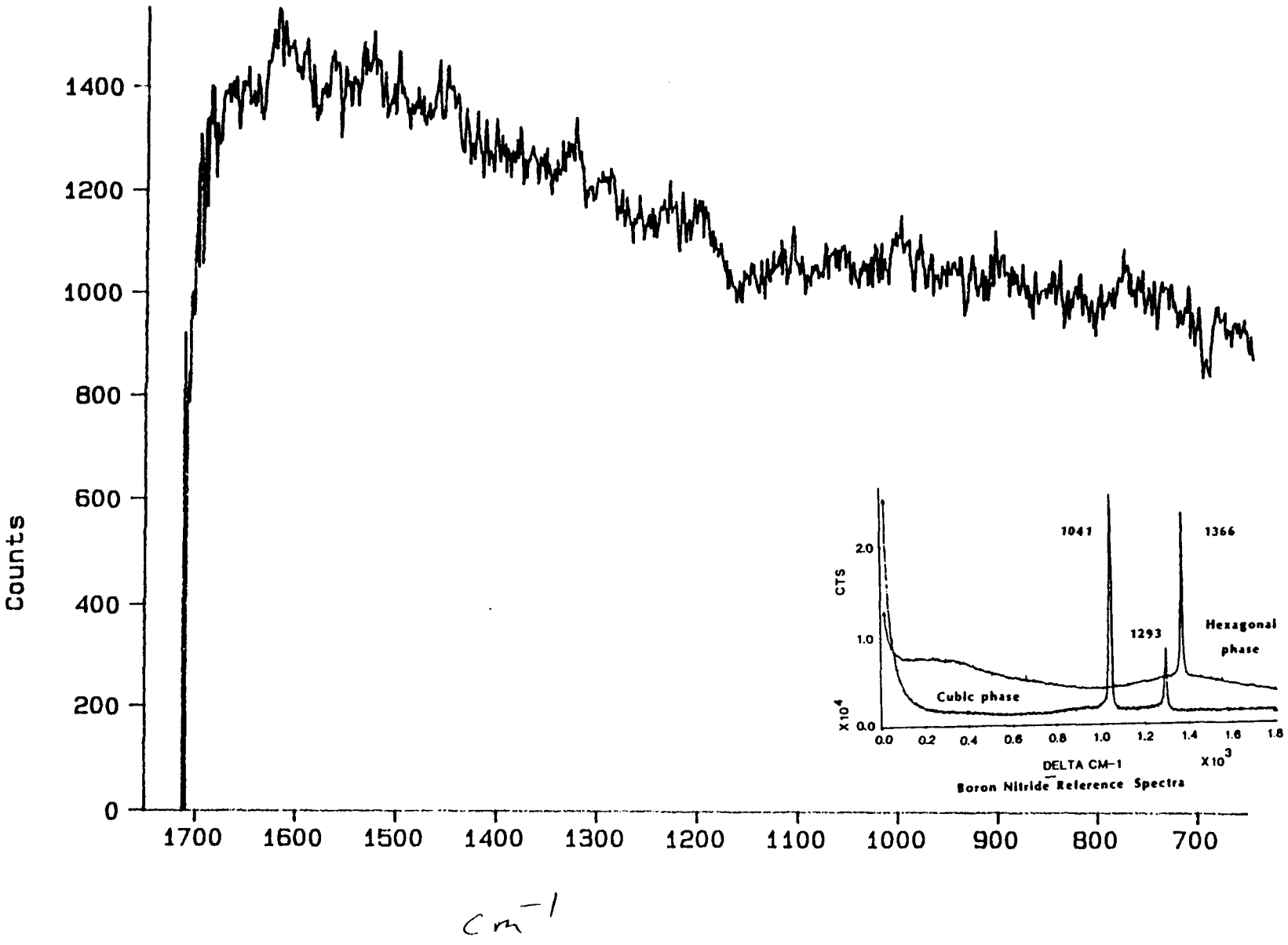
Figure 6 Raman Spectrum of Sample #4

File 12 CBN4 Sample #4



File 9 CBN 7

Figure 7 Raman Specrum
Sample # 7



File 13

Figure 8 Raman Spectrum
Sample #10

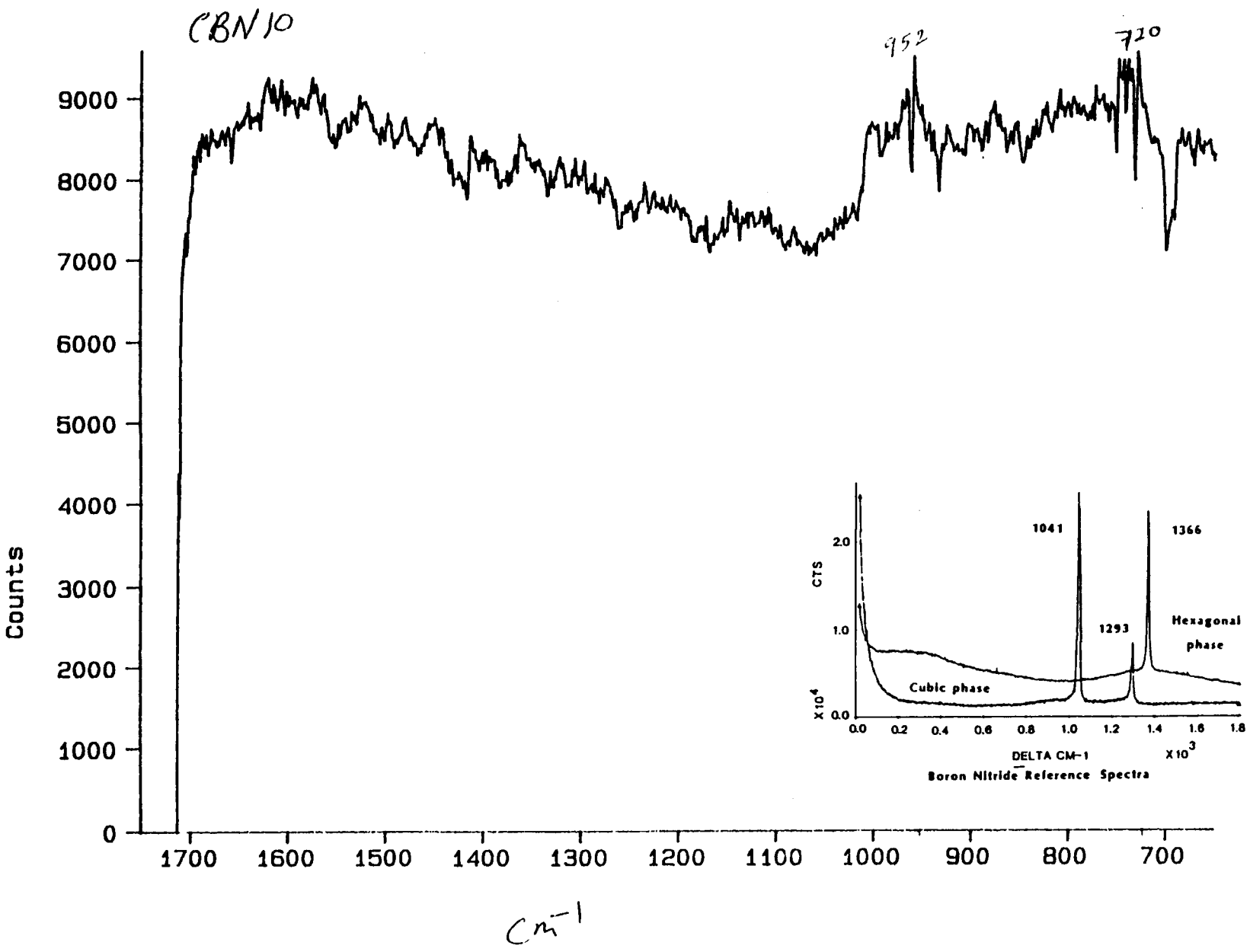


Figure 9. IR Spectrum of Sample #7 and HBN Target

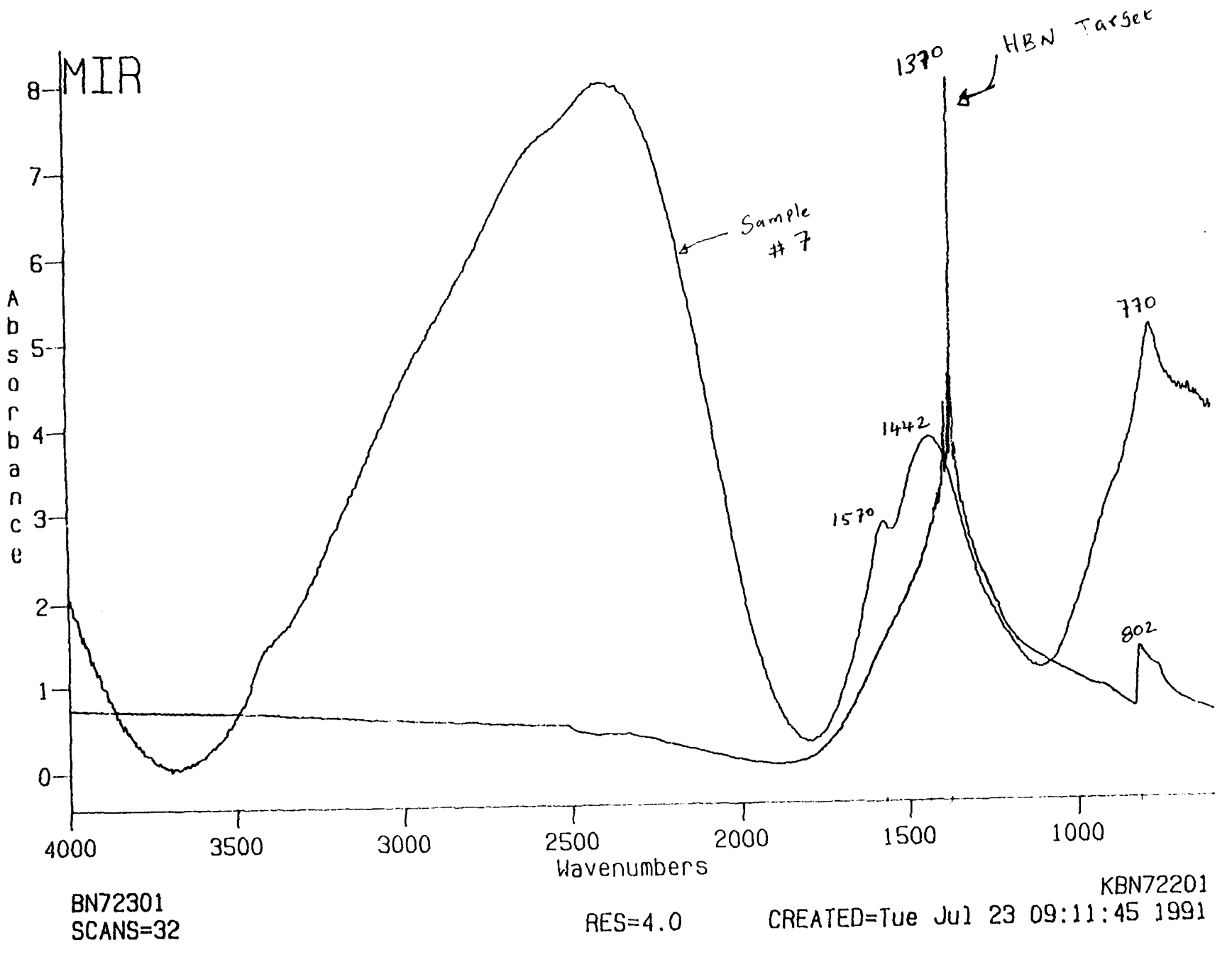


Fig. 10 IR Spectrum of Sample #4

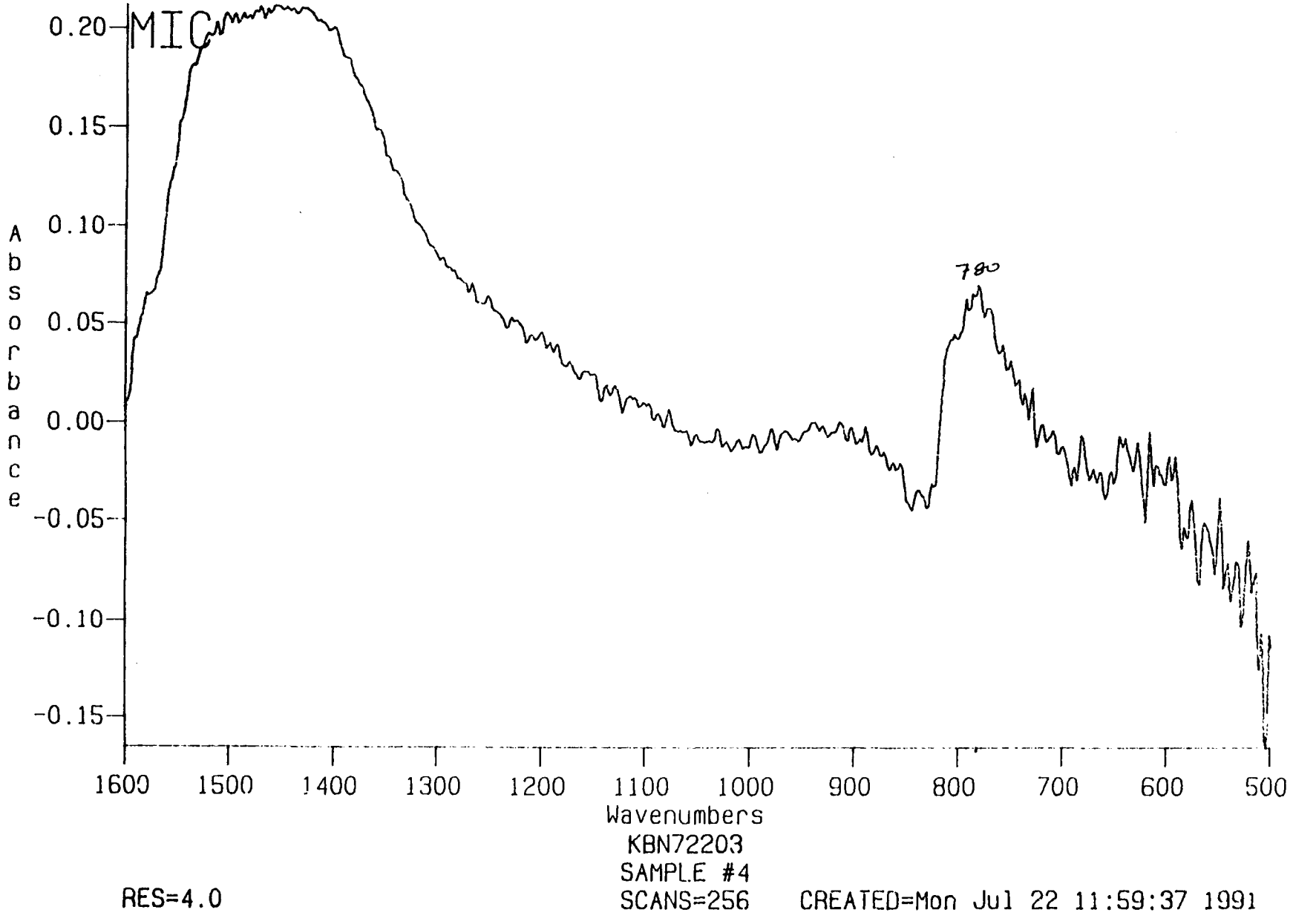


Fig. 11. IR Spectrum of Sample # 10