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ON THE NATURE OF STRIAE IN STRONTIUM BARIUM NIOBATE

R.R. MONCHAMP, G.B. MIHALIK AND L.A. FRANKS

Material Sciences Department, EG&G/Energy Measurements, Inc.

Goleta, California, 93117

ABSTRACT

Strontium barium niobate crystals were grown by the Czochralski technique. These crystals were 15-20 mm in diameter and 25 to 75 mm long. Two types striae, designated as coarse an fine, were characterized. The coarse striae are optically dense and are spaced by 100 to 500 μm apart; the fine striae are optically less dense and spaced 5-50 μm apart. The origins of the striae are attributed to thermal fluctuations in the melt related to the control system and to rotation of the growing crystal in non-isothermal radial gradients. Analysis of the crystals would indicated that the coarse striae may contain increased concentrations of sodium.

INTRODUCTION

Several investigators [1-4] have reported on the formation of striae in Czochralski grown strontium barium niobate (SBN) crystals. Our research, like most of the published work has been performed on SBN crystals of the 61% strontium composition. As with other crystalline materials, the SBN striae are most likely due to impurities and induced by thermal instabilities in the melt. We too have observed striations in SBN and herein attempt to quantify and correlate the observations of striae to crystal growth parameters.

We have noted two types of striae in SBN. The first type are widely spaced, 100 to 500 μm apart. These striae are due to temperature fluctuations in the melt and are related to the temperature control process. These coarse striae generally appeared to be broader and of greater optical density than the finer striae. Often, the coarse striae appeared to be irregularly spaced making quantification difficult. This irregularity results from the interaction of the automatic diameter control with the temperature control system.

The second type of striae are much finer, 5 to 50 μm apart. These are due to the rotation of the crystal in the radial gradient in the melt and have been described by many authors.

This type of striae does appear to be more regularly spaced. They also appeared to be fainter or less optically dense.

EXPERIMENTAL

A Crystar Inc. pulling apparatus was used for the crystal and withdrawal mechanism. In all of the experiments, 50 mm diameter by 50 mm tall platinum crucibles were recessed into the cavity of zirconia insulated growth station (Figure 1). The growing crystal mass was sensed with a Hottinger Baldwin Messtechnik mass measurement system and the signal was used as feedback to control the diameter automatically. A thirty kilowatt r-f generator was the power supply. An Accufiber Inc. thermal sensor was used to measure the temperature for the control loop. Initially, the sensor was placed in contact with the bottom of the crucible and the Accufiber Inc. control system was employed for temperature regulation. In later experiments, the temperature of the surface of the melt was measured and controlled with an adaptive temperature control program written at EG&G/EM-LVO [5].

The starting materials were Johnson Matthey, Inc., 99.997% $BaCO_3$, 99.995% $SrCO_3$ and Hermann C. Starck, Gmbh., 99.997% Nb_2O_5. Crystal were pulled at rates varying from 1 to 20 mm/hr and rotation rates were varied from 5 to 60 rpm. As with other Czochralski growers of SBN our crystals were grown in the <001> direction. The grown crystals were 15-20 mm in diameter and 25 to 75 mm long. The interface as normally planar. Only at rotation

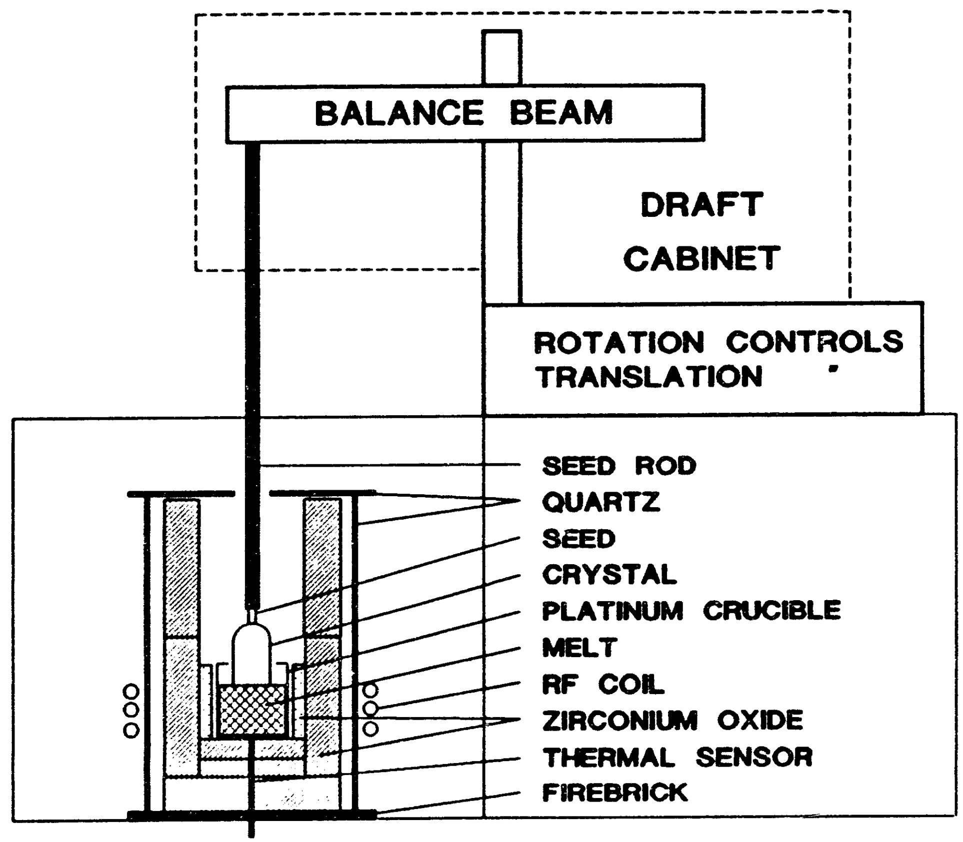

Figure 1. Sketch of Czochralski crystal growth apparatus.

rates of 50-60 rpm did the interface become concave in the center of the crystal; the peripheral interface surfaces remained flat. The striae were perpendicular to the growth axis and clearly demarcated the growth interface.

After growth two opposing sides of the crystal were lapped and polished to produce inspection flats. The crystals were examined with an optical microscope and the striae photographed and counted.

RESULTS AND DISCUSSION

From the striae spacings on the photographs and the rotation rates and pull rates used to grow the crystals, the rates of formation of striae were calculated. In the case of the coarse striae in many crystals, the striae were not always evenly spaced either in localized sections or throughout the length of the crystals. Also the number of coarse striae per photograph were many fewer than those for fine striae leading to poorer statistics in the coarse striae calculations. Furthermore, because of subtle variances in the nature of Czochralski experiments, e.g. station set-ups, melt heights, the striae spacings were found to vary considerably from run to run even though the growth parameters were ostensibly the same. This was found to be especially true for the coarse striae which will be shown were dependent on the temperature control. The fine striae spacings, dependent on pull and rotation rates also varied from run to run but less so than the coarse striae. In this case it appeared that station set-up, influencing the radial thermal gradients of the melt may have been influential in the variation for the spacings for the same growth parameters but for different experiments.

Coarse Striae - As indicated above, the variation in striae spacing varied significantly from run to run. However, in some experiments the pull rate was varied during the same growth experiment and the striae data were more consistent. Figure 2 show two sets of data. The data designated as 60 rpm were derived from three different experiments. The data for the 20 mm/hr data were all taken from the same experiment during the same day. The initial pull rate was 10mm/hr and was subsequently slowed to 6 and then 3 mm/hr. Figure 3 a,b,c are the photomicrographs of the striae from this experiment. It is clear from these photographs that as the pull rate decreased the striae spacing decreased - 489, 333, 159 μm, respectively. From the spacing data and the pull rates, the rates of striae formation were calculated for which 0.341, 0.300 and 0.315 stria/min, respectively, were obtained. Similar temperature traces with frequencies of 0.3 Hz/min were obtained for 10 and 6 mm/hr pull rates. In cases where the striae spacing was found to be to irregular to characterize, the corresponding temperature and power traces where also found to be irrgeular.

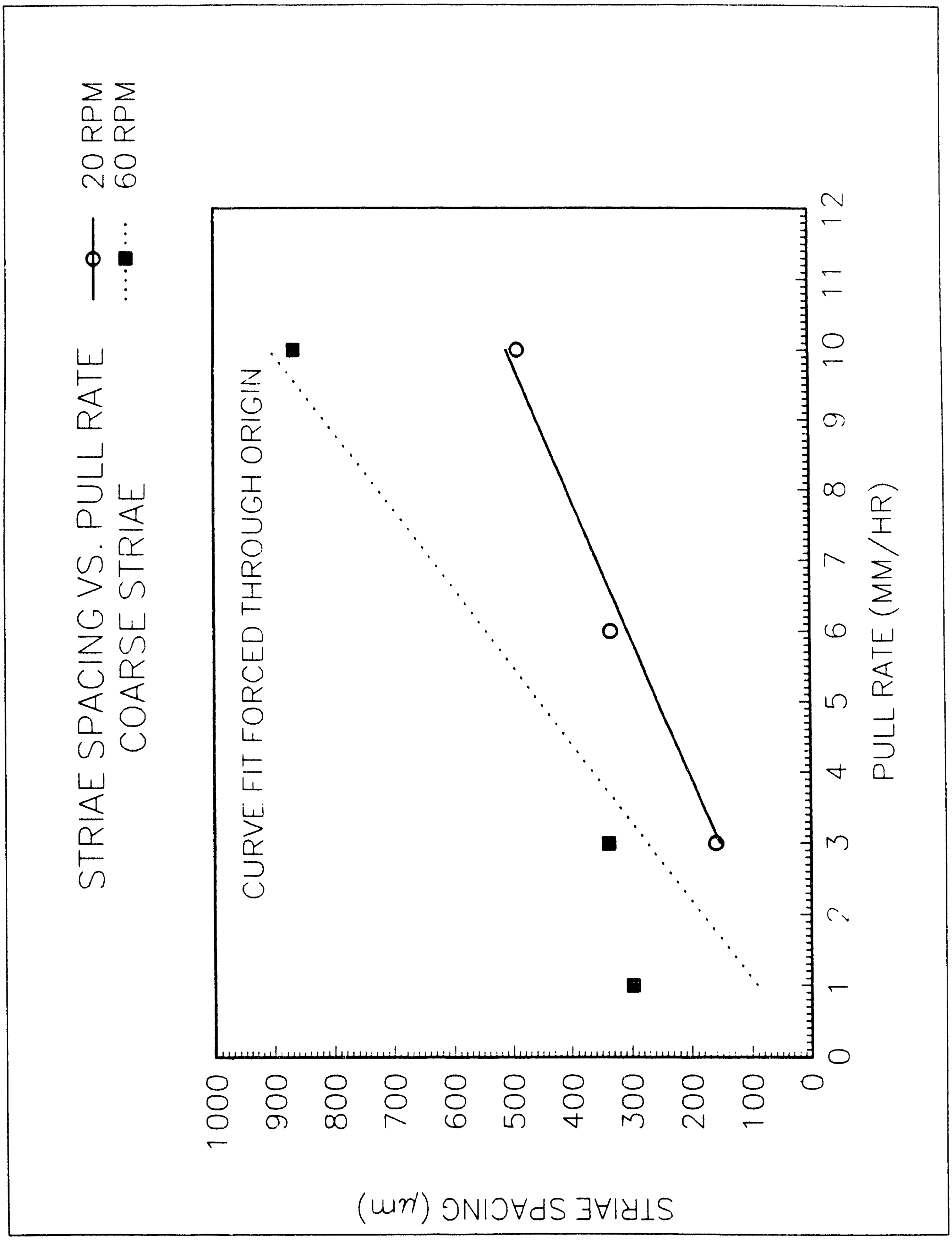

Figure 2. Striae spacing data at various pull rates at 20 and 60 rpm.

(a)

(b)

(c)

Figure 3. Photomicrographs of a crystal showing striae from three sections grown at (a) 10 mm/hr, (b) 6 mm/hr and (c) 3 mm/hr.

In conjunction with this data we also examined the temperature fluctuations during growth. A typical example of the data obtained is shown in Figure 4. These data were taken while the crystal was being pulled at 3 mm/hr. The temperature cycle frequency is 0.3 Hz/min. The thermal perturbations of the melt result from either noise in the r-f generator output and/or to changes in temperature set-point dictated by the temperature control algorithm and by the automatic diameter control program. Similar data were obtained with the same the frequency of temperature cycling at the other pull rates (10 and 6 mm/hr). In all cases the rate of striae formation agreed with the rate of temperature fluctuation; thus we conclude that the coarse striae formation are induced by the cycling of the temperature control.

The data for 60 rpm (Figure 2) were taken from three separate experiments where various pull rates were employed. In this case the spread of the data is greater than in the case of the 20 rpm data. This spread is due to the slight variations of the three experimental set-ups. The difference in slopes of the two curves is merely indicative of the difference in temperature cycle periods resulting from the interaction of the different stirring rates with the convective currents.

Fine Striae - Examples of fine striae can be seen in between the coarse striae in Figure 3. Since more striae appear in the photographed image and the fine striae are more regular spaced, the striae space data are statistically somewhat better.

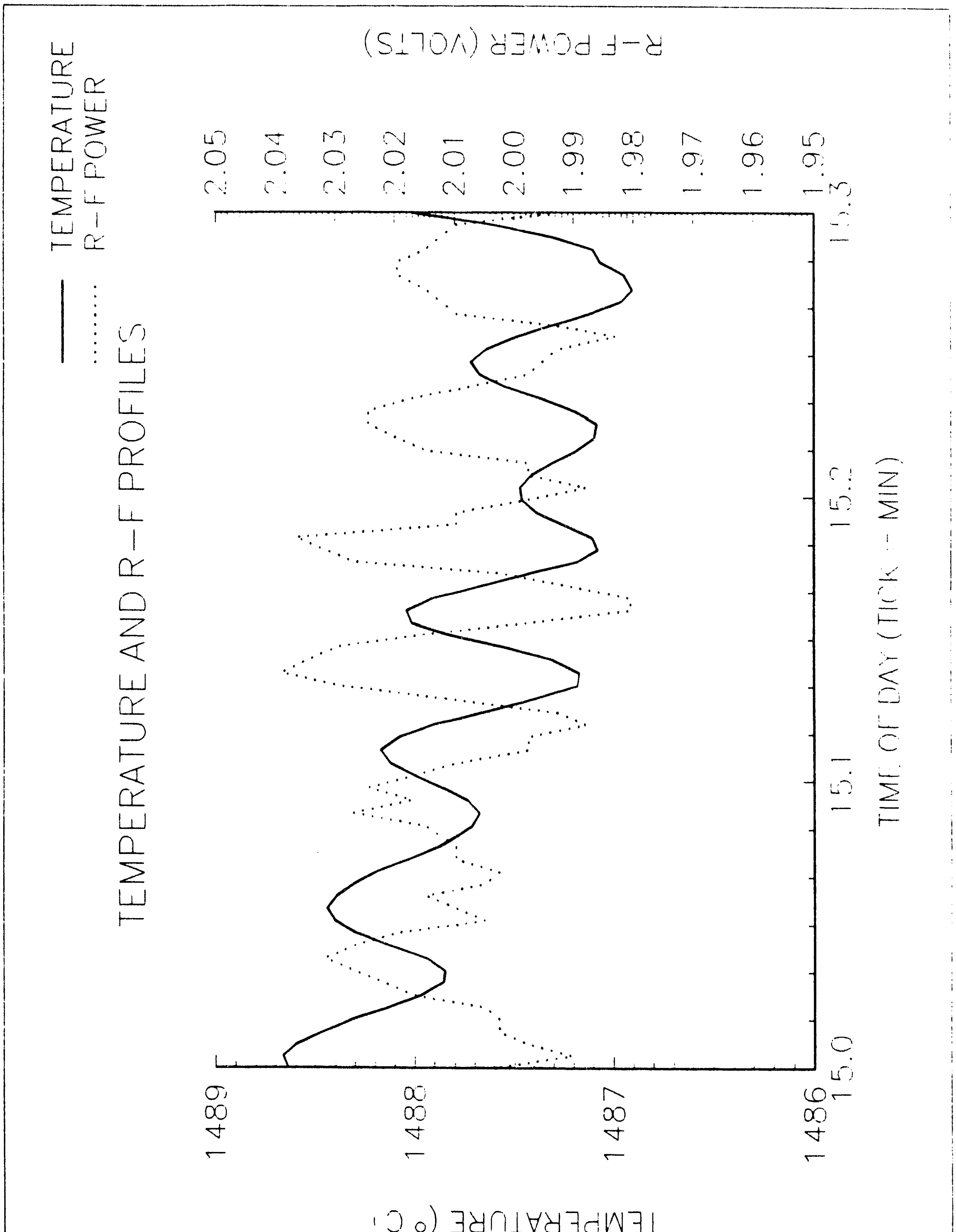

Figure 4. Typical temperature data during which the crystal was being pulled at three mm/hr. Period of data is ~ 0.3 Hz/min. R-f power is also displayed showing the response of the control system.

Typically, the spacing between these fine striae were found to be 5 - 50 μm apart. We, like others, attribute their origin to the crystals rotation in a radial thermal gradient of the melt. In Figure 5 are plotted spacing between striae and the distance the crystal traveled during one revolution. Data were collected from various runs with different pull and rotation parameters. The slope of the line (linear best fit of the data) in Figure 4 is about 0.5. This implies that there were two stria formed in growth per revolution. We measured the radial gradients in our station set-ups and indeed observed two alternating "hot spots" and two "cold spots"; the ΔT's for the spots were 5-8 °C. While we cannot explain this type of non-isothermal radial gradient it does account for the generation of two stria per revolution.

Analytical Results - Among the analysis performed on the crystals the following were the most informative relative to striae. A sample analyzed at Ledoux & Co. using spark source mass spectroscopy (SSMS), revealed several impurities. Among them sodium at 0.5 ppm was most interesting. Also they did not detect iron; their limit was 0.5 ppm.

We submitted crystal samples containing striae to Sandia National Laboratories (Livermore) where they were analyzed by particle induced x-ray emission (PIXE). With 40 μm thick sample, they were able to obtain penetration and determined that iron was the main contaminant at 150 ± 50 ppm. They did not, however, detect any periodicity of the iron. Just barely above there

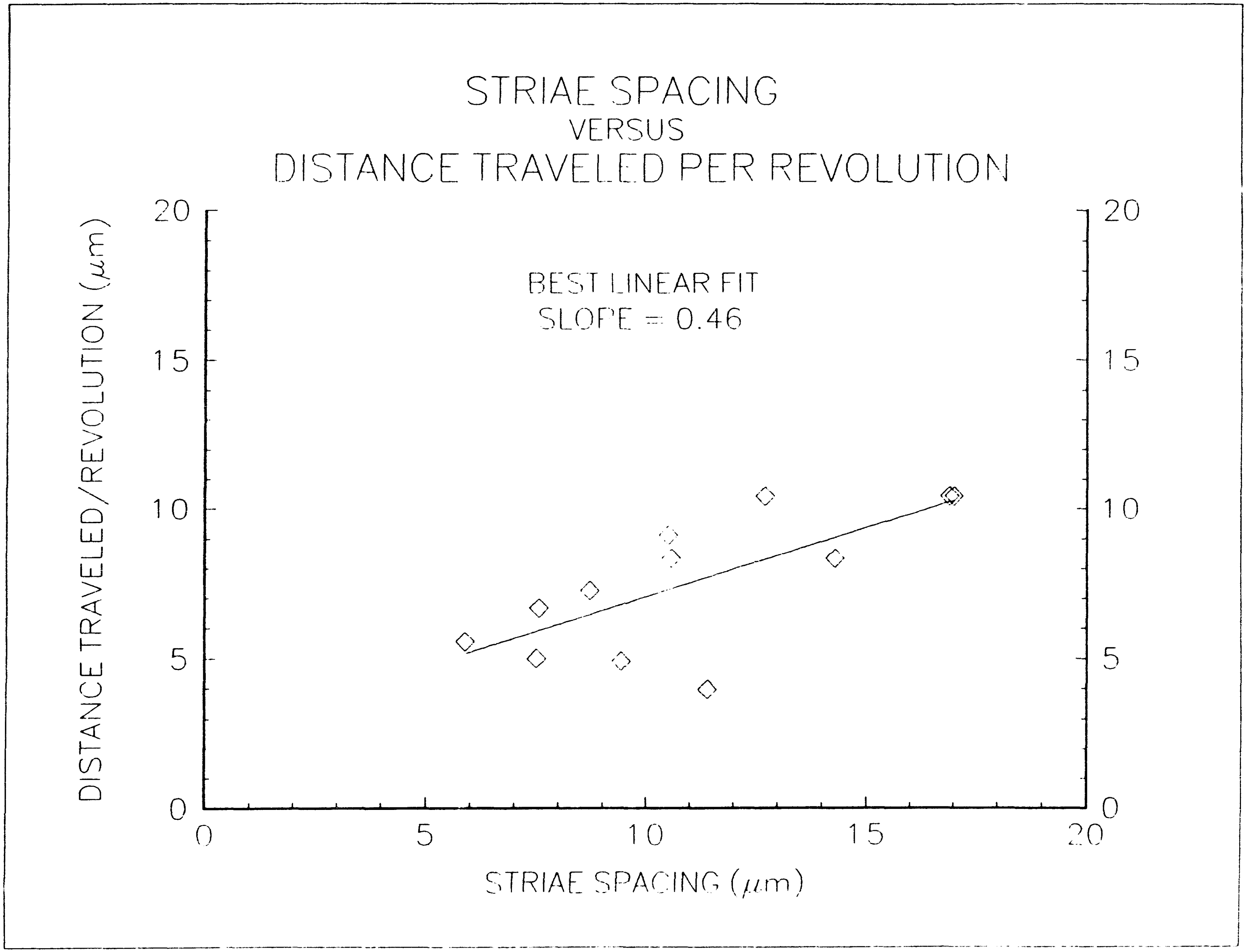

Figure 5. Plot of striae spacing and distance traveled per rotation. Slope of ~ 0.5 accounts for the formation of two striae per rotation.

detection limits, they did detect sodium which may have been periodic, but the signals were too weak to conclude this with certainty.

We also submitted a striae containing sample to EG&G - Mound National Laboratory for x-ray photoelectron spectroscopy (XPS). Figure 6 is a montage of the sodium peak of the spectrum they obtained on the sample. It appears that there is some periodicity. The data would suggest a spacing of about 0.5 mm which places it at the upper level spacing of the coarse striae we observe with optical microscopy.

Other researchers [3], using a secondary ion microscope analyzer "Cameca SMI 300", have reported K and Ca to be the impurities in their crystals associated with striae with spaces of 25 μm corresponding to fine rotational striae. They report their sample's K and Ca levels were 600 and 60 ppm, respectively, by SSMS. Our SSMS results gave K and Ca levels of 0.2 and <1 ppm, respectively.

Clearly, more in depth and careful analytical work is necessary to delineate the various impurities which are responsible for both the coarse and fine striae associated with striae.

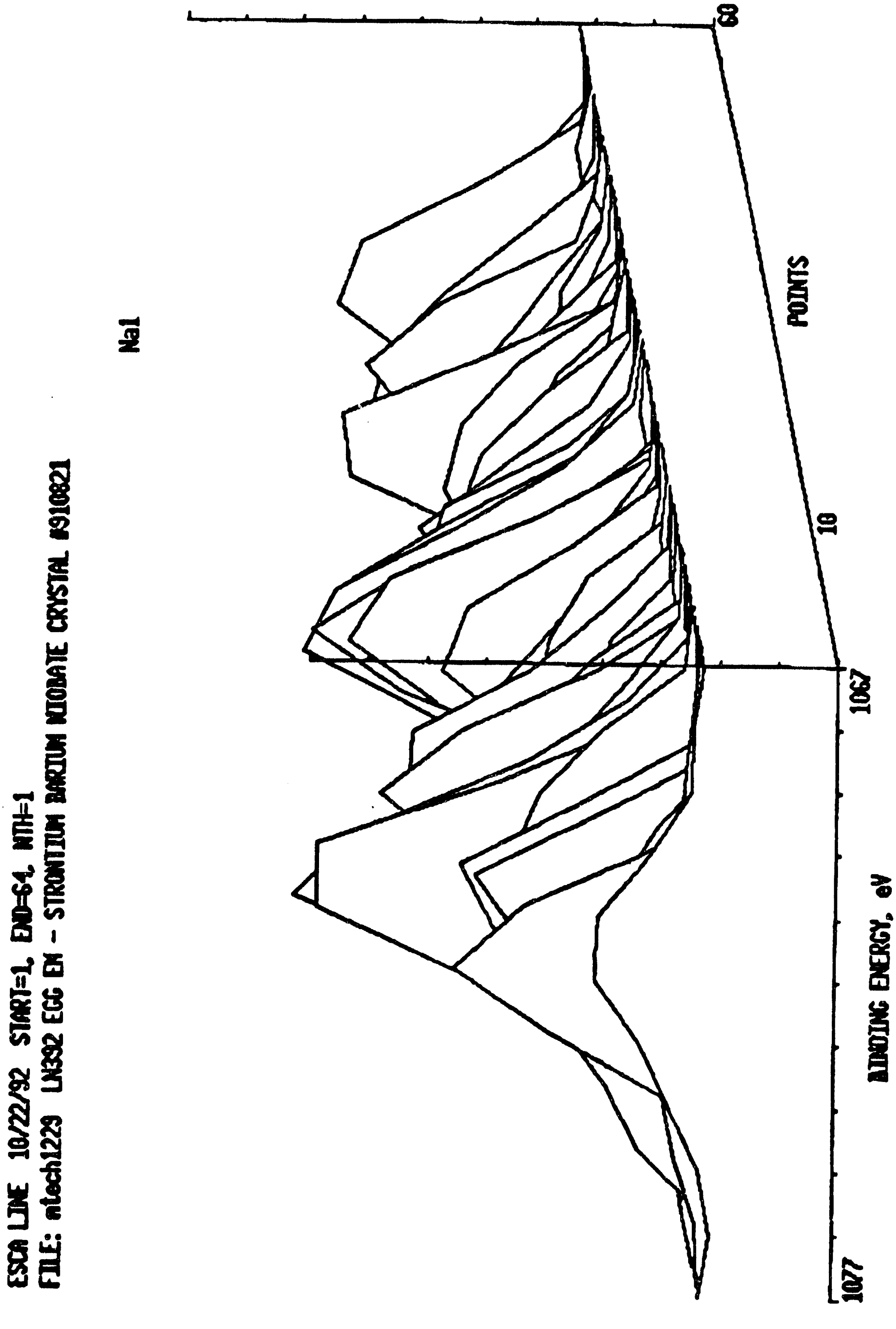

Figure 6. Montage of sodium spectrum from x-ray photoelectron spectroscopy data.

CONCLUSIONS

Two types of striae have been observed in SBN crystals. The coarse ones are optically dense, spaced 100 to 500 μm apart and are induced by temperature fluctuations of the melt resulting from temperature and diameter control functions. The fine striae, 5-50 μm apart, are attributed to rotation of the growing crystal in a temperature field in which has two highs and two lows with ΔT's of 5-8 °C. Of the impurities detected in the crystal, sodium is the one most likely to be associated with the coarse striae in our crystals.

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REFERENCES

[1] Ratnakar R. Neurgaonkar and Warren K. Cory, J. Opt. Soc. Am., **B 3**, (1986) 274.

[2] J.C. Brice, O.F. Hill, P.A.C. Whiffin and J.A. Wilkinson, J. Crystal Growth **10** (1971) 133.

[3] Claude Brehm, Jean-Yves Boniort and Pierre Margotin, J. Crystal Growth **18** (1973) 191.

[4] Jeffrey P. Wilde, Lambertus Hesselink and Robert S. Feigelson, J. Crystal Growth **113** (1991) 337.

[5] To be published.

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