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A TECHNIQUE TO OPTICALLY DETERMINE THE STOICHIOMETRY OF C_Z GROWN LITHIUM NIOBATE CRYSTALS

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Czochralski법으로 성장시킨 $LiNbO_3$단결정의 화학양론 (Stoichiometry)을 결정하기 위한 광학적 방법

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ABSTRACT

In growing single crystals, which exhibit incongruent melting behavor, it is extremely difficult to maintain the stoichiometry of its chemical compositions for given crystals. For instance, $LiNbO_3$ is a typical one which exhibits such incongruent melt, especially with a large solid solution region that makes it difficult to maintain the chemical compositions. Such a variation can then cause a serious problem for the practical applications in designing a precision electro/optic device.

Of the known methods of determining its composition and quality, an optical technique of measuring refractive index of the crystals has been implemented. This technique is also capable of determining optical uniformity of the grown crystals and the chemical compositions. The technique used for such characterizations is herein described and some of the results are discussed.

요　　약

비균질 용융을(incongruent melting behavior)보이는 단결정제조에 있어 화학성분을 일정성분비로 유지하는 것은 매우 어렵다. $LiNbO_3$는 이러한 성질을 보이는 대표적인 예인데 넓은 고용(固溶)영역에서 일정성분비를 유지하기 힘들다. 정밀전기/광학장치에 있어 이런 변수는 치명적이라 할 수 있다. 결정의 조성과 질을 결정하는 방법으로 굴절율(n)을 측정하는 광학적 방법이 수행되어 왔다. 이

방법으로 성장결정의 광학적 균질성과 화학조성을 알아낼 수 있다. 여기서는 그런 특성분석에 사용되는 기술을 설명하고 그 결과들을 제시해 보았다.

1. INTRODUCTION

Synthetically grown crystals are no longer only academically interested, but rather practical interests have been strongly focused throughout world, ever since the capability of growing silicon single crystals has been commercially demonstrated. Recently, other categories of single crystals (oxide compounds) have become attractive for industrial applications, and the crystal growing activity has been intensified. For example a new group of superconductor single crystals, La/NdSrCu oxides [1] have been recently grown by TSFZ(Traveling Solvent Floating Zone) technique in Professor Kojima Lab., Yamanashi University.

It was first such a large bulk crystal grown by the TSFZ technique, and an accurate measurement of its basic as well as functional properties was possible.

In growing high temperature melting oxide crystals, it is important to understand its thermodynamic behavior, expecially with high vapor pressure chemical compounds. Much effort has been made in growing such crystals in optical quality [2].

It is known that chemical, mechanical or thermal treatment may cause an alteration of refractive index near the surface of the substrates which may be used in making electro-optice devices. For example, surface Li out diffused during heat treating causes its chemical composition change, and hence it produces inoperable devices by deterioration of optical performance.

Electro-optic devices have been successfully fabricated by implementing a technique analogous to the silicon wafer processing ; silicon substrate processing. Li_2O single crystals as big as 75mm diameter with 125mm long boules are commercially available for making electro-optic devices. A typical substrate is about 1mm thick 75mm in diameter. The refractive index (N) measuring procedure should be able to handle such a geometry and nondestructive as well. A prism technique, in which eight couples into the sample [3], the light reflected from the interface between the prism and substrate is monitored (Fig. 1) and the angle at which the total internal reflection shows a sharp break is determined. From this angle the refractive index can be obtained. This technique offers two modes of operation : high accuracy in the measurements and reference obtainable. A special technique (prism coulping) to monitor optical quality and indirectly check its stoichiometry of electro-optical quality crystals is here described and results are discussed.

2. DESCRIPTION OF THE METHOD

A. An arrangement of the substrate sample with a rutile (TiO_2) prism is shown in Fig. 1. The prims is coupled to a well polished niobate substrate with a spacing of a fraction of wavelength. The laser light reflected from the prism-substrate interface is monitored by a large area detector. A typical example of intensity of light, which is reflected from the prism substrate interface as a function of the angle is presented in Fig. 2. This method can also be extended to a boule of single crystals to monitor optical uniformity.

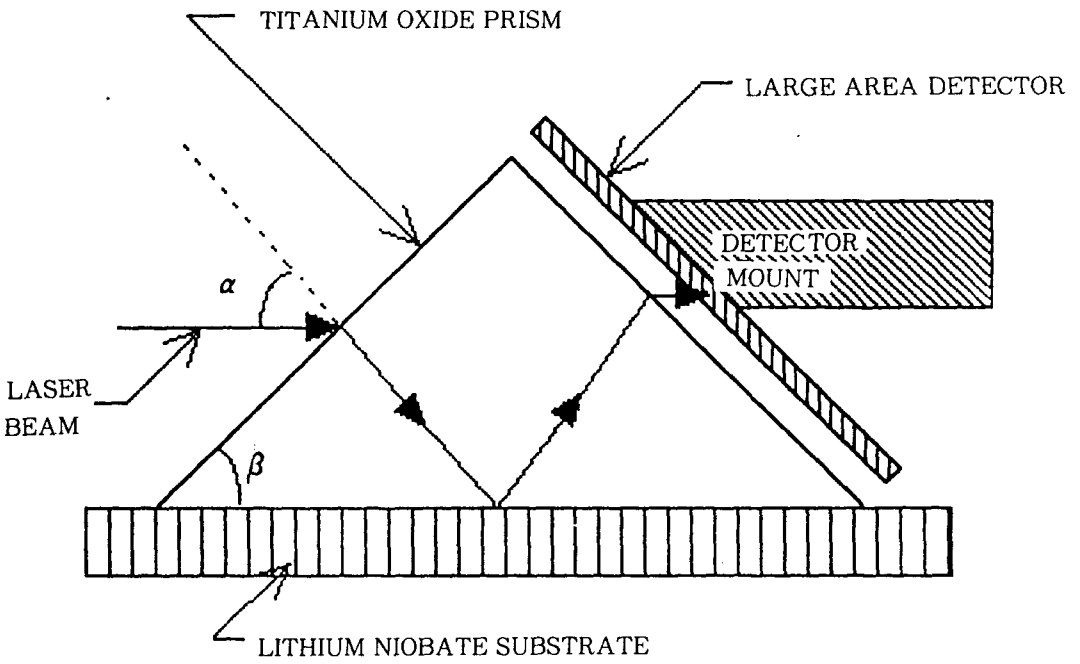


Fig. 1. A TiO_2 Prism Coupler for Meauring Reflectivity for Substrate.

In this case the prism is coupled the boule through a small window polished (Z) along its length as shown in Fig. 3. The method is nondestructive and accurate way of analyzing boules and determining its usability. A selected $LiNbO_3$ crystal boule, which has melt composition ; 48.00mol Li_2O & 52.00mol Nb_2O_5 was measured for the reflectivity in the same manner for the substrate as a function of the angle. To compare its uniformity on two spots ; seed and tail were checked for four different crystal boules.

B. Fig. 4 shows a schematic representation of refractive index measuring system and in Fig. 5 a schematic representation of the electronic system for the measurement. The equation relating the refractive index of the substrate to the critical angle (the break of the reflected intensity) is expressed below :

$$N = \sin\alpha \cos\beta + (N^2p - \sin^2\alpha)^{1/2} \sin\beta.$$

Where N is the refractive index for polarization of the laser used. TiO_2 prism has its faces parallel to the optic axis of the materials. A TE polarized wave senses a prism the range of index of 2.865, while a TM polarized wave senses a prism index of 12.583. For a TiO_2 prism the range of refractive indices that can be measured depends upon which polarization is employed.

3. RESULTS AND DISCUSSION

A. From the coupler the intensity of reflected

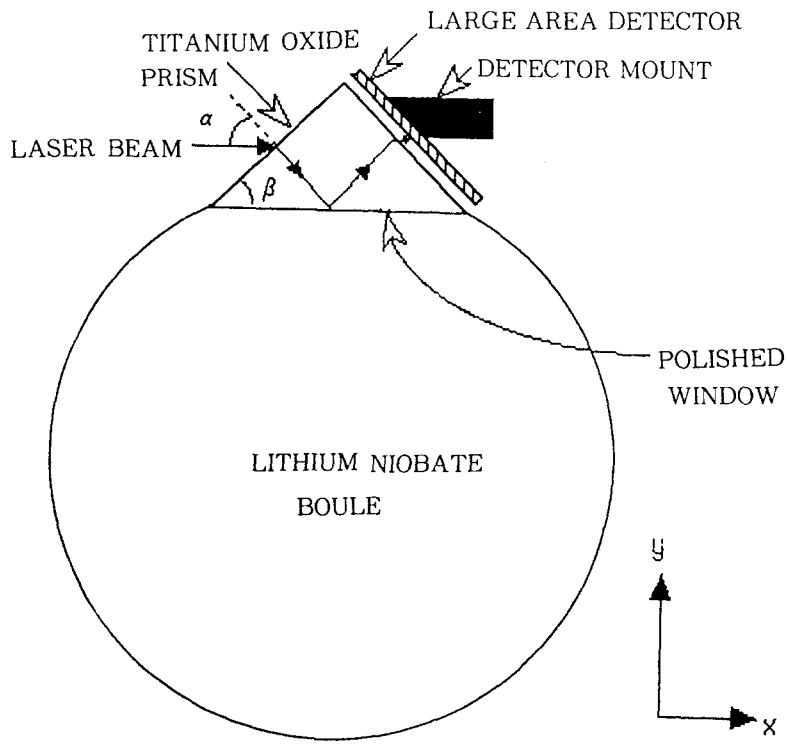
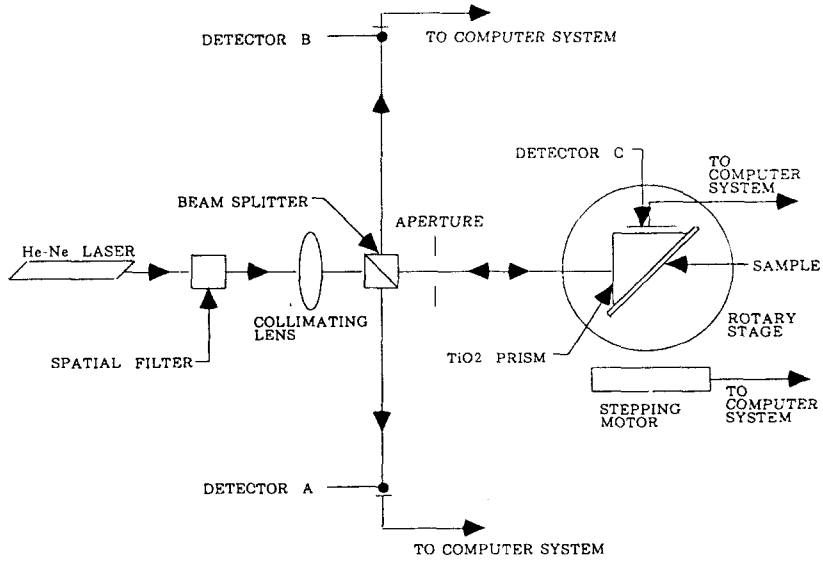


Fig. 2. An Arrangement of the Prism Coupler for $LiNbO_3$ Boules.



Schematic representation of refractive index measuring system.

Fig. 3. Schematic Arrangement of Refrative Index Measuring System

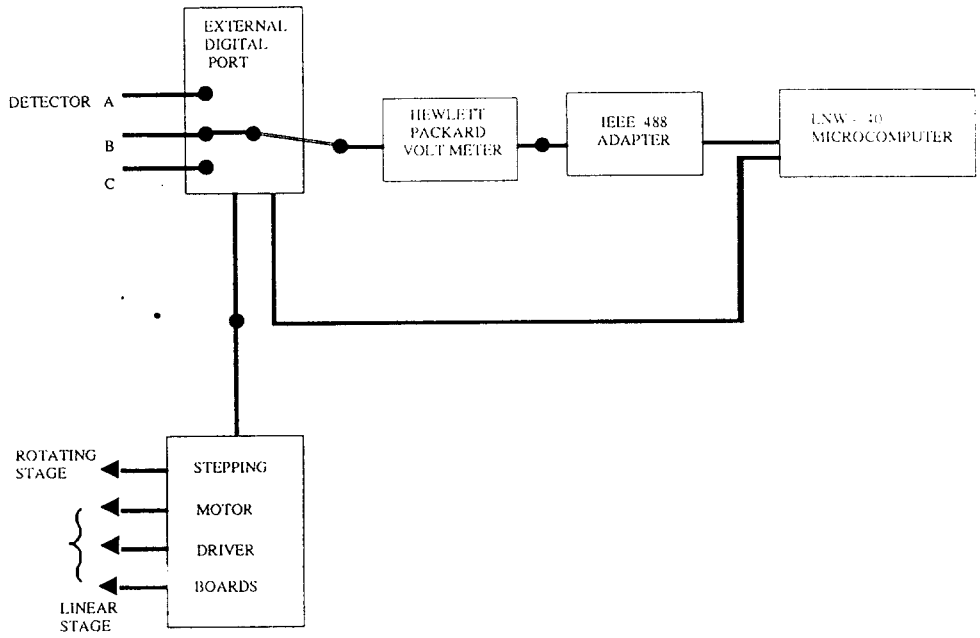


Fig. 4. Schematic Arrangement of the Electronic System.

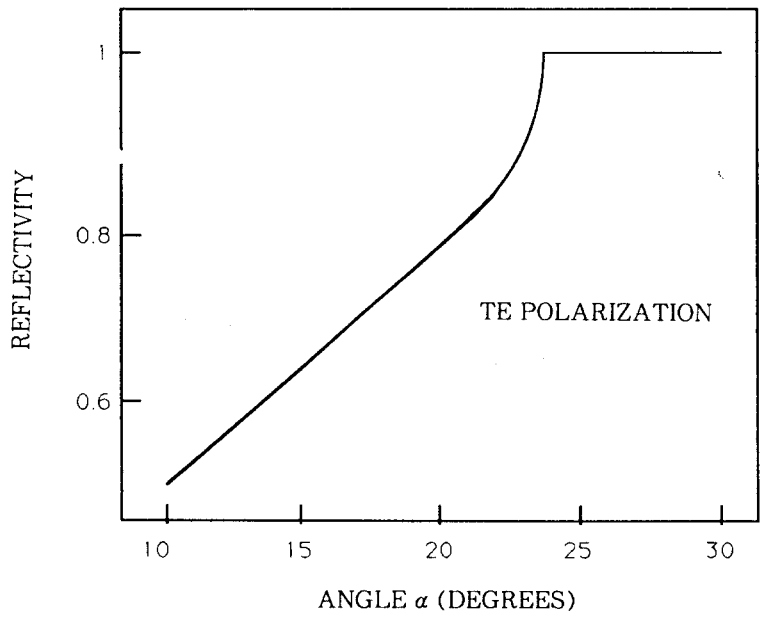


Fig. 5. Reflectivity from the Prism-Substrate Interface vs Angle for TE.

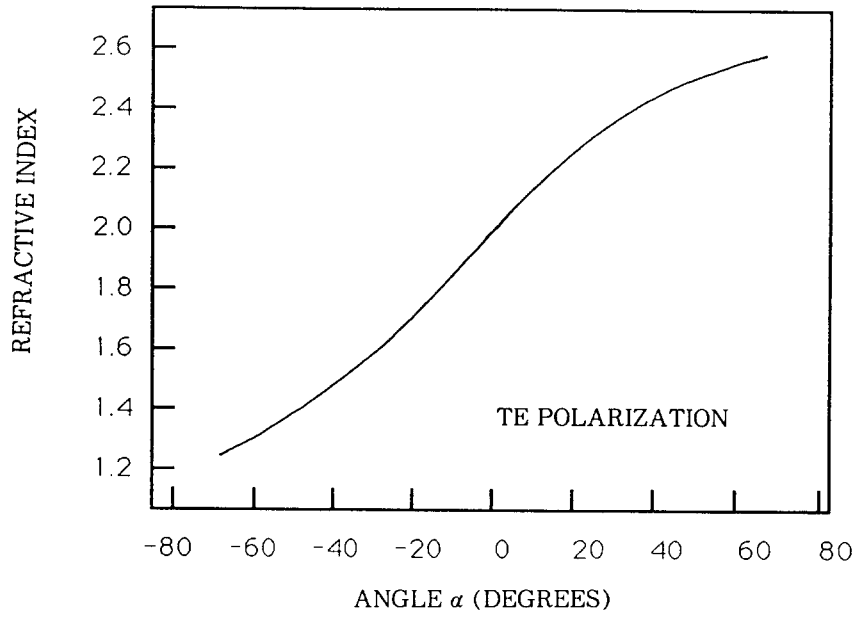


Fig. 6. Refractive Index vs Angle for TE.

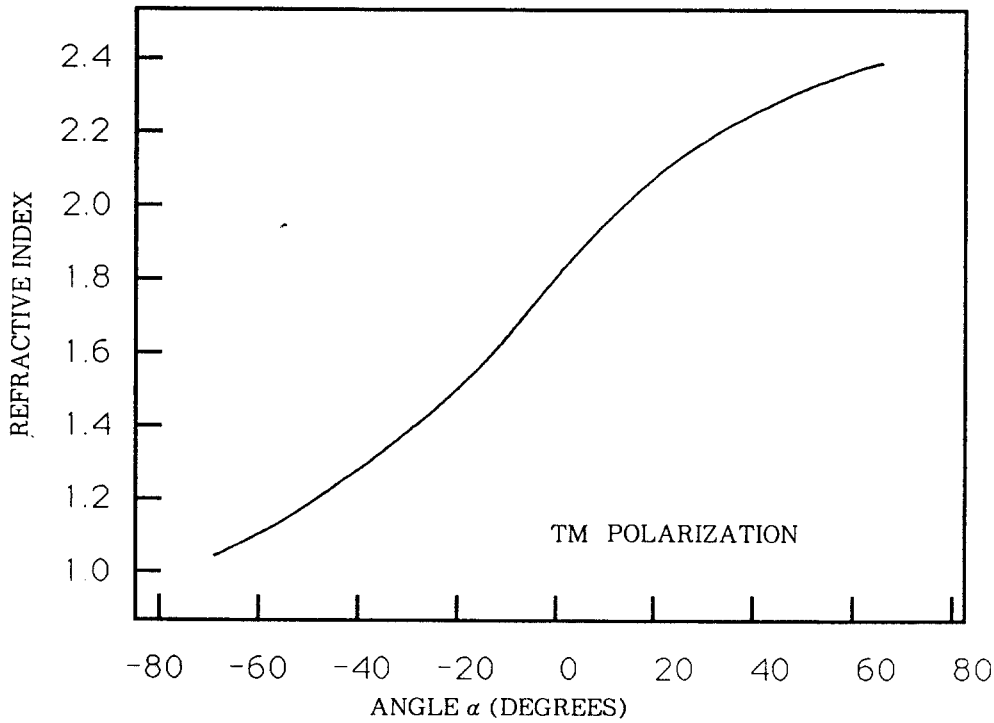


Fig. 7. Refractive Index vs Angle for TM.

light as a function of the angle shows a sharp intensity drop. The sharpness of the edge determines the accuracy by which the critical angle can be measured.

B. The refrative indices for both TE and TM polarizations were measured and plotted as a function of the angle as shown in Fig. 6 and 7. In both cases, β was at 45°. The sensitivity, $\triangle\theta/\triangle N$ is about twice as great for TM as for TE polarization. It is also found that the lower limit in index for the TM polarization is 1.00. For both polarizations (TE, TM), a linear trend in the plots of the refractive index as a function of the angle can be discerned. Information concerning the relationship between melt stoichiometry and refractive index can be obtained from the work of Bergman and coworkers [4]. In Fig. 7 the plot can be seen based upon the wavelength of the measurements of 6328 A. Effect of its stoichiometry (Li/Nb) on No was found to be little, while it showed a linear change in Ne. Despite little change in No, it is still useful for checking spot anomaly.

C. Since a reference curve has been established, the samples, substrates were measured for its reflectivity as the function of angle. A typical measurement on a nominal congruent composition substrate yields followings :

$$Ne = 2.2019 +/- .0003$$
$$No = 2.2963 +/- .0003$$

These values can be compared with that of the previously measured by Nelson and Mikulyak [5]. An accuracy of +/−.0003 is considered to be excellent. Interpolation of their data (Fig. 8) is below:

$$Ne = 2.2030$$
$$No = 2.2869$$

No agrees within error, but Ne is slightly off. This may be due to a difference in stoichiometry. Fig. 9 shows intensity break angles for TM polarization for index range 2.198 and $\beta = 45°$.

D. Actual measurements of $LiNbO_3$ substrates are graphically presented in Fig. 10, and 11. The Z axis of the substrate is parallel to the symmetry axis of the prism and the polarization is TM. Fig. 10a represents reflectivity change as the function of the angle (α) for a typical $LiNbO_3$ substrate. It shows a sharp intensity break, indicating an excellent uniformity. On the other hand, Fig. 10b shows a noticeably different reflectivity pattern from the normal sample, since an acid treated substrate was tested under the same condition as the normal substrate. It is interesting to find a pattern obtained from a substrate which was heat treated for making waveguide devices using $LiNbO_3$ substrates. In the pattern which was based on TE mode, two modes ; A, B, were found with corresponding angles, 15° and 23°. For the first angle, its reflective index corresponds 2.287.

E. The reflectivity measured on a boule crystal as a function of the angle is graphically shown in Fig. 12. It is interesting to note that the substantial difference in the position of the breaks for the seed and tail end of the boule is found in the reflectivity plot. It certainly suggests that optical uniformity is not even from the seed to the tail ends, and such a highly inhomogeneous boule should not be

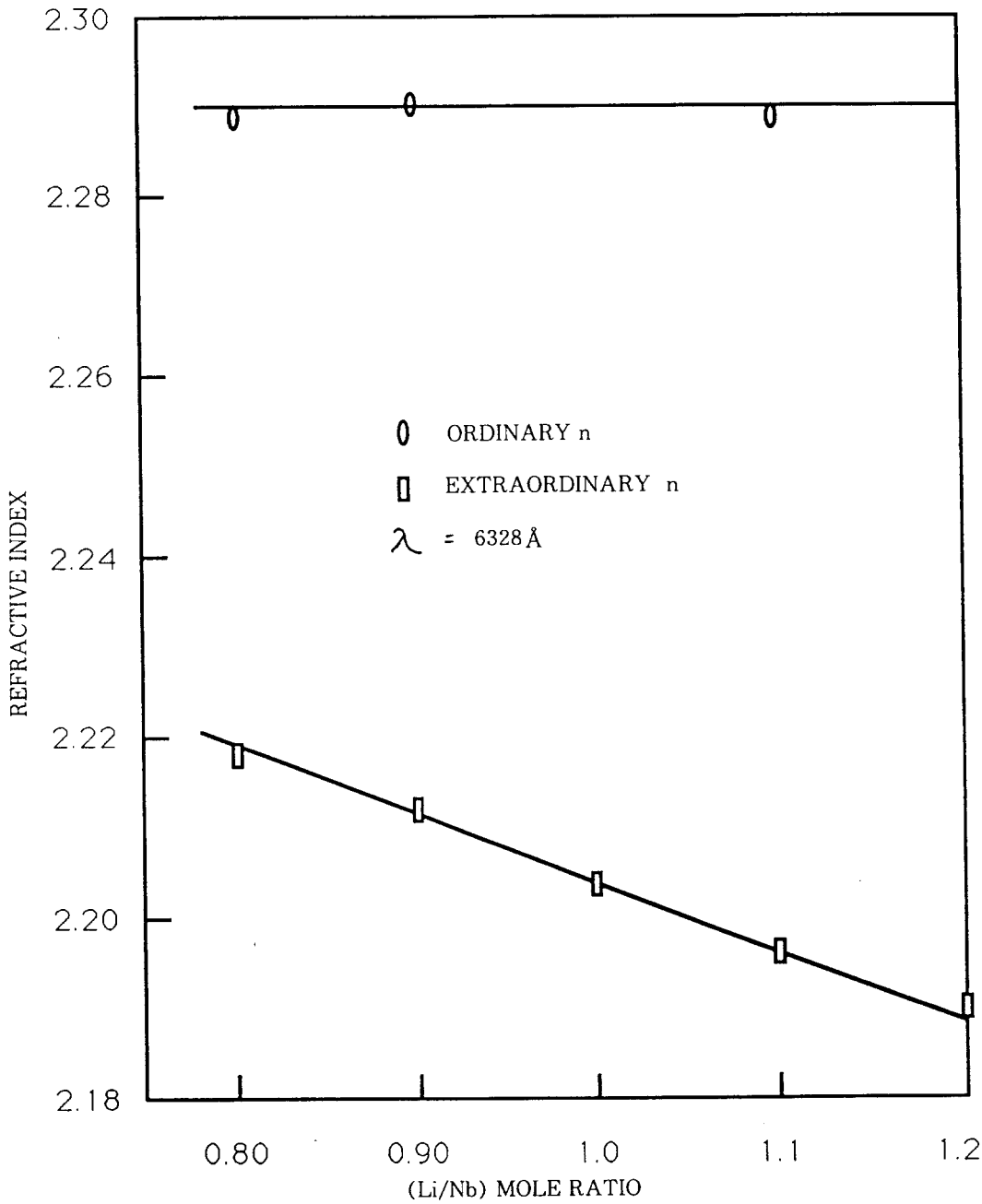


Fig. 8. Refractive Index vs Melt Composition for $LiNbO_3$.

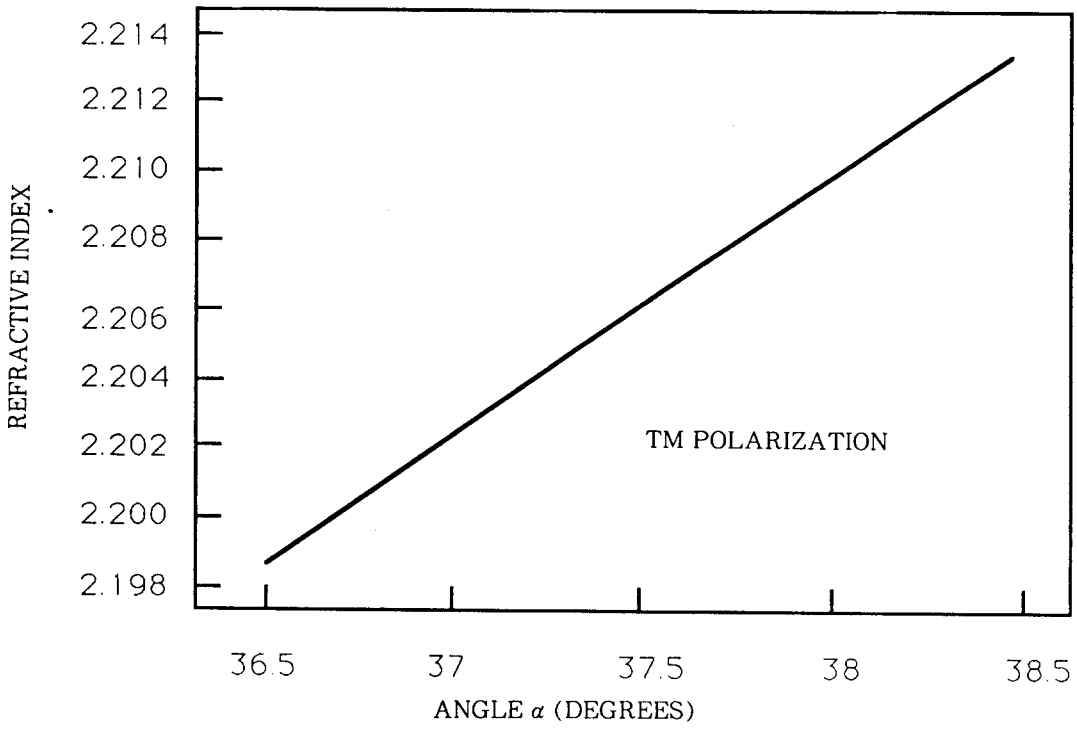


Fig. 9. Intensity Break Angles for TM.

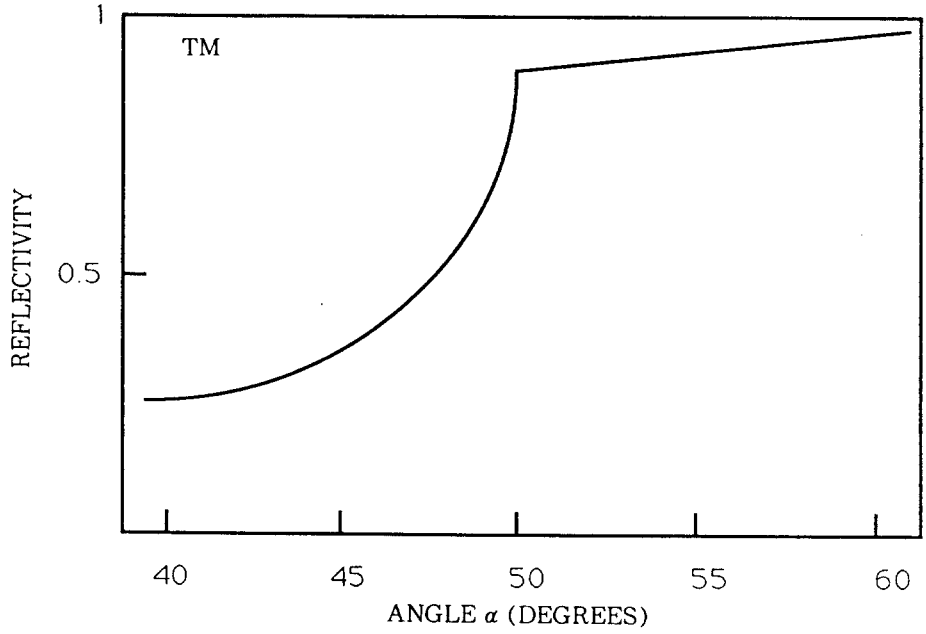


Fig. 10a. Intensity Break vs Angle for $LiNbO_3$ Substrate.

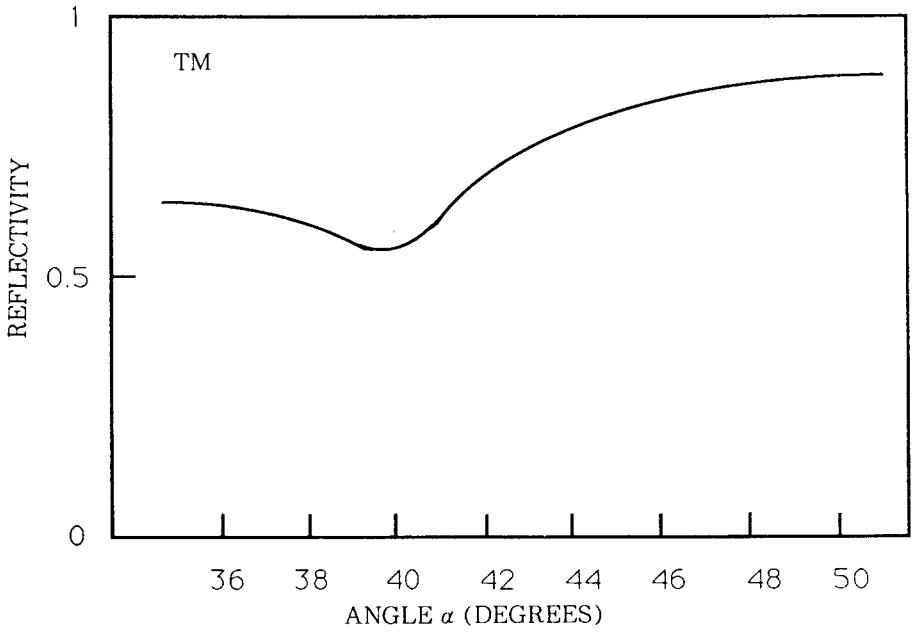


Fig. 10b. Intensity Break vs Angle for the Acid Treated Substrate.

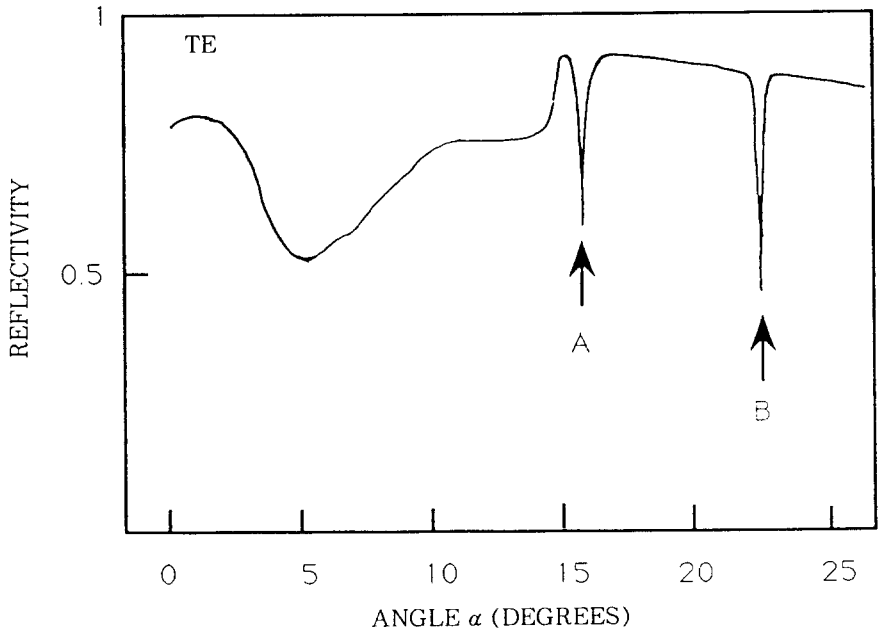


Fig. 11. Intensity Break vs Angle for A $LiNbO_3$ Substrate with TM.

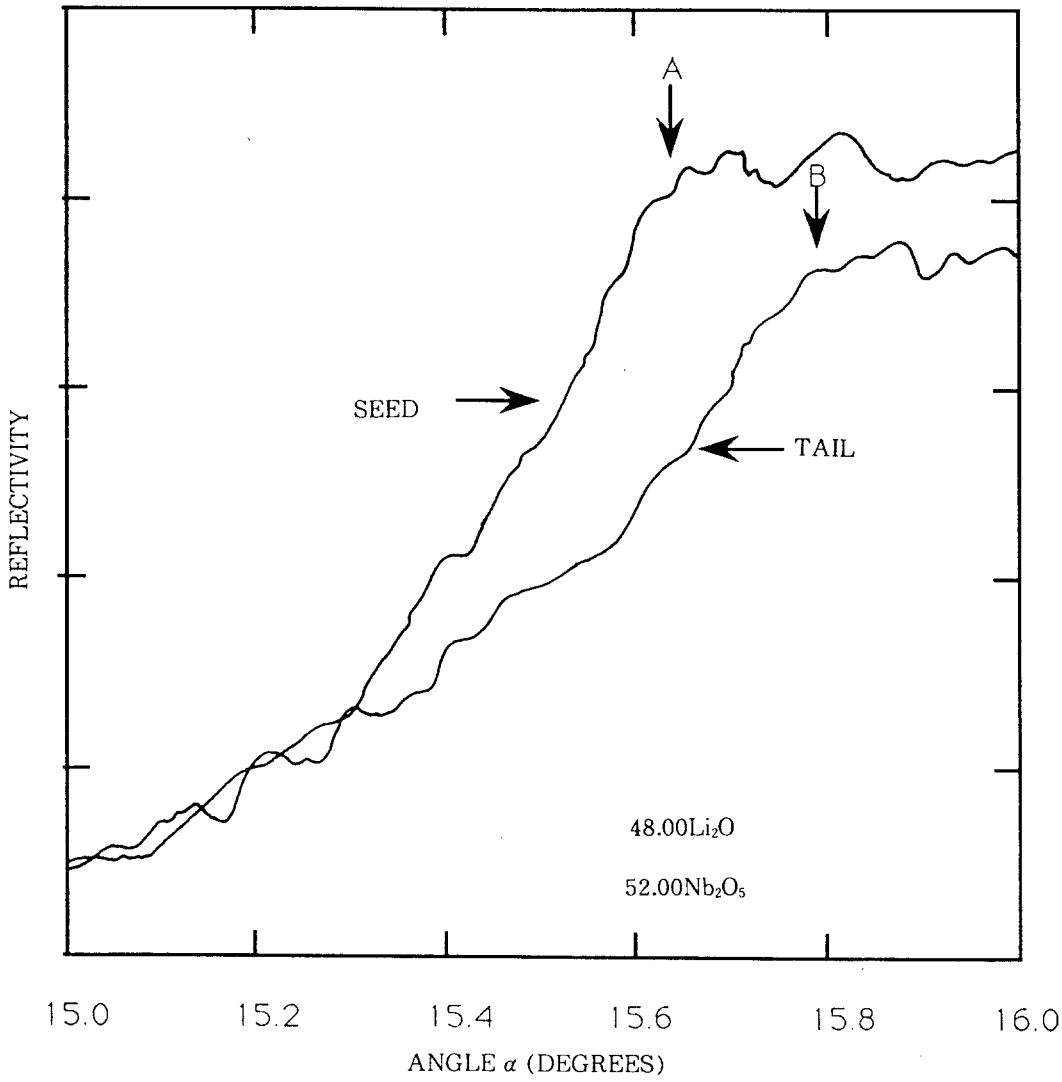


Fig. 12. Intensity vs Angle for A $LiNbO_3$ Boule.

used for device applications.

Fig. 13 shows the refractive index data taken near the seed and near tail ends of four boules. For both ends a drop off in refrative index (Ne) with melt composition is found, and the drop off is more rapid for the tail than seed which is exactly what one would expect from a crystal grown with an incongruent melt composition [6].

F. In fig. 14 the refractive index gradient as a function of the melt composition is shown, which demonstrate its capability of accurately measuring the index gradient. The index gradient extends to negative values of the index, and it suggests that such a boule is suitable for device applications.

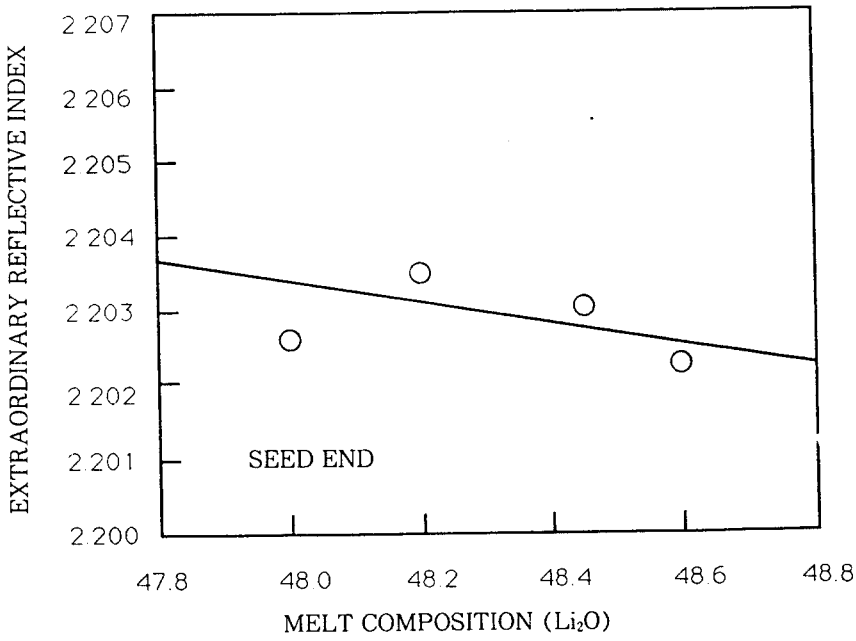


Fig. 13a. Refractive Index, Ne vs Melt Composition for Seed.

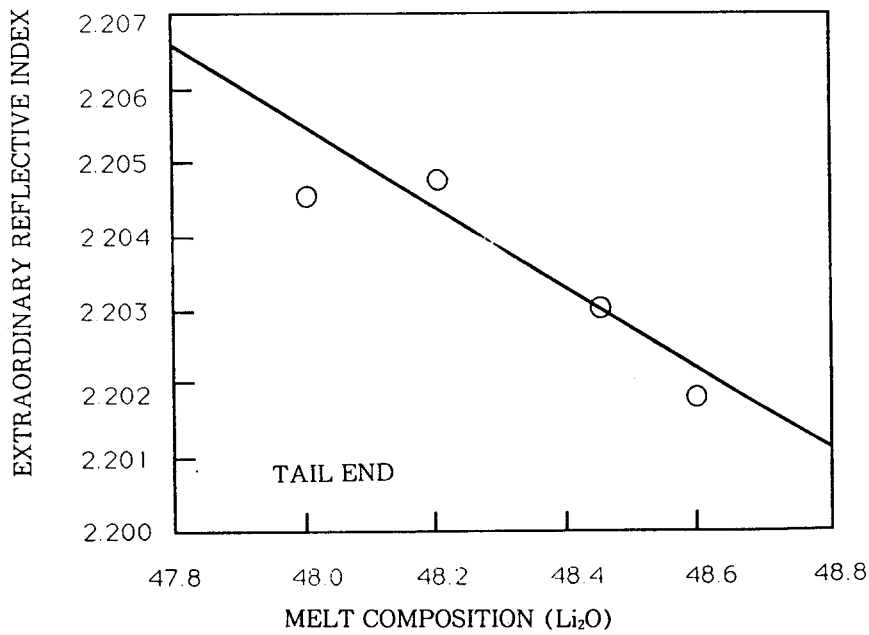


Fig. 13b. Refractive Index, Ne vs Melt Composition for Tail.

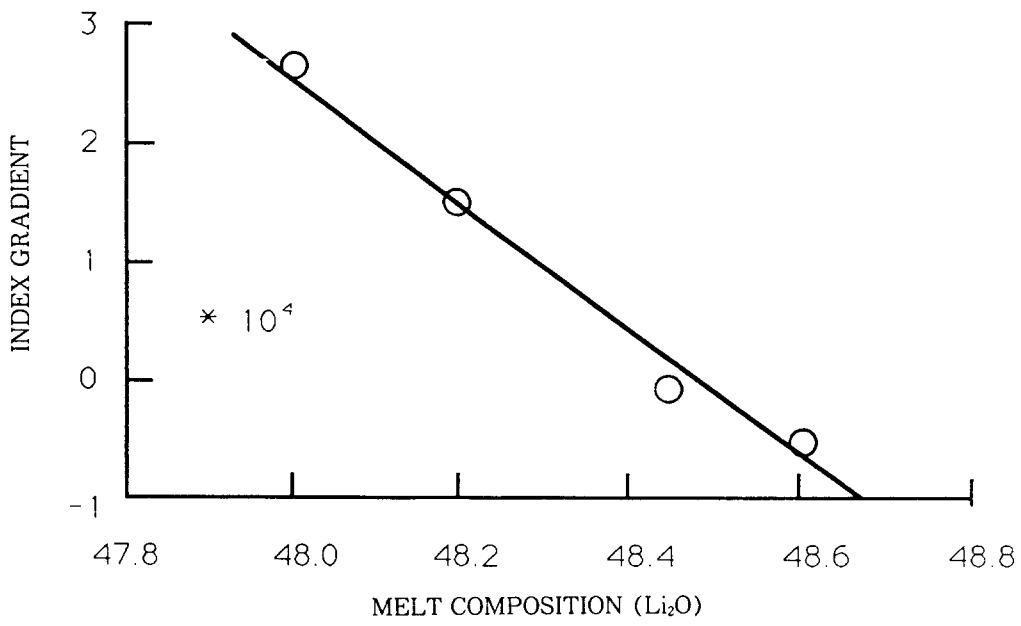


Fig. 14. Refractive Index vs Melt Composition.

A study of Ti diffusion into $LiNbO_3$ as a function of stoichiometry[7] and an interpretation of these data in terms of the defect chemistry of the material [8] demonstrate the importance of compositional uniformity. This refers to uniformity within a substrate as well as from crystal to crystal. The changes as small as 0.1 mol in Li_2O content can affect the resultant waveguide (WG), N and the optical mode size of channel WG by several percent [9].

4. CONCLUSIONS

1. An accurate method of determining the refractive index of thin (1.0mm) substrates of $LiNbO_3$ or other materials of interest to +/− 0.000X was developed.
2. The method can rapidly determine the composition of as received substrates based upon fact that Ne is strongly related to composition.
3. The method lends itself to mapping of the refractive index of the substrates as well as the boules along Z direction.
4. This method is recommended for both academic interests and the practical applications in monitoring optical quality of thin and boule samples for device fabrications.

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