

**Growth of Er:LiNbO<sub>3</sub> single crystal thin film with high crystal quality  
by LPE method**

Tong-Ik Shin<sup>a</sup>, Hyun Lee<sup>a</sup>, Joong-Won Shur<sup>a</sup>, Byungyou Hong<sup>b</sup> and Dae-Ho Yoon<sup>a</sup>

<sup>a</sup>School of Metallurgical and Materials Engineering, Sungkyunkwan University,

Suwon 440-746, Korea

<sup>b</sup>School of Electrical and Computer Engineering, Sungkyunkwan University,

Suwon 440-746, Korea

**Abstract**

It was grown Er<sub>2</sub>O<sub>3</sub> doped LiNbO<sub>3</sub> single crystal thin films with high crystal quality by liquid phase epitaxial(LPE) method. Er<sub>2</sub>O<sub>3</sub> was doped with a concentration of 1, 3, and 5 mol% respectively. After the growth of single crystal thin film, we examined the crystallinity and the lattice mismatch along the c-axis between the film and the substrate with the variation of Er<sub>2</sub>O<sub>3</sub> dopant using X-ray double crystal technique. There were no lattice mismatches along the c-axis for the undoped and the films doped with 1 and 3mol% of Er<sub>2</sub>O<sub>3</sub>. For 5mol% of Er<sub>2</sub>O<sub>3</sub> doped film, there was a lattice mismatch of  $7.86 \times 10^{-4}$ nm along the c-axis.

## LPE 법에 의한 고품질 Er:LiNbO<sub>3</sub> 단결정 박막의 성장

신동익<sup>a</sup>, 이 현<sup>a</sup>, 서중원<sup>a</sup>, 홍병유<sup>b</sup>, 윤대호<sup>a</sup>

<sup>a</sup> 성균관대학교 금속·재료공학부, 수원 440-746, 한국.

<sup>b</sup> 성균관대학교 전기전자 및 컴퓨터공학부, 수원 440-746, 한국.

### 요 약

Liquid phase epitaxial (LPE)법으로 고품질을 갖는 Er<sub>2</sub>O<sub>3</sub>가 첨가된 LiNbO<sub>3</sub> 단결정 박막을 성장시켰다. Er<sub>2</sub>O<sub>3</sub>는 1, 3, 5mol%으로 변화를 주어 첨가 시켰다. 단결정 박막을 성장시킨 후 X-ray double crystal technique 으로 첨가물의 증가에 따른 박막의 결정성 및 substrate와 박막 간의 lattice mismatch에 대해 고찰하였다. Undoped 박막과 Er<sub>2</sub>O<sub>3</sub>이 1, 3mol% 첨가된 박막은 c-축을 따라 lattice mismatch가 발생하지 않았다. 그러나 Er<sub>2</sub>O<sub>3</sub>를 5mol% 첨가 시킨 박막은 substrate와 박막 사이에 lattice mismatch가  $7.86 \times 10^{-4}$  nm 만큼 발생하였다.

## 1. Introduction.

Recently, LiNbO<sub>3</sub> crystal has been widely studied for applications in optical device due to its excellent electro-optical, acousto-optical and nonlinear-optical properties[1]. Rare-earth ion doped LiNbO<sub>3</sub> could be used for integrated optical amplifiers and laser materials. In particular, the recent advances in the LiNbO<sub>3</sub> waveguide fabrication and the improvement in the doping technique with Er ions had made it possible to obtain the new integrated device based on optical pumped Er doped LiNbO<sub>3</sub> lasers such as acousto-optically tunable lasers[2], DBR lasers[3] and mode locked lasers[4] exploiting the excellent electro-optic and acousto-optic properties of LiNbO<sub>3</sub> crystal[5]. Indeed the first mode-locked waveguide laser and amplifiers based on Er doped LiNbO<sub>3</sub> have already been fabricated[6].

Although, several doping(Er) techniques have been studied for a few years, we still have lots of problem solved such as device fabrication processes, increase of cost and so on. Er doped LiNbO<sub>3</sub> thin film was grown for the usage of fabrication of optical waveguide by vertical Liquid Phase Epitaxial (LPE) method. LiNbO<sub>3</sub> of congruent composition grown by Czochralski(CZ) method has been the most popular material for optical use and many attempts have been made to improve the quality of these bulk crystal[7-9]. Achieving improved crystal perfection and optical quality (such as resistance to optical damage[10]) has become more important with the successful development of device fabrication processes. LPE

techniques are the most promising for improving the quality of grown crystal, because film growth can be achieved at much lower temperature (~950 °C) than that (~1253 °C) of the CZ method. In the lower temperature, the number of defects that are developed in the crystal is less because films of incongruent (approximately stoichiometric) composition can be grown. Especially LPE method has no difficulty in adding dopant[11-14].

In this work, LiNbO<sub>3</sub> thin films were grown by changing the amount of Er<sub>2</sub>O<sub>3</sub> as much as 1, 3, and 5 mol% and it was observed how the crystallinity, which has an effect on optical properties, was varied an aspect according to the amount of dopant.

## 2. Experimental procedure

LiNbO<sub>3</sub> epitaxial films were grown on z-cut LiNbO<sub>3</sub> substrate using LPE method. The substrate size was 20mm×5mm×0.5mm. For liquid phase epitaxy, the choice of a suitable flux is very importance. Baudrant et al.'s solvent study[13, 15] has shown that a Li<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> mixture was the most convenient flux for LiNbO<sub>3</sub> compared to other solvents such as LiBO<sub>2</sub>, KBO<sub>2</sub>, LiMoO<sub>4</sub> and K<sub>2</sub>WO<sub>4</sub> because LiVO<sub>3</sub> is deliquescent and is easily washed away from the as grown specimen with water. The composition of fluxed melts was 20mol% LiNbO<sub>3</sub>-80mol% LiVO<sub>3</sub>. Er<sub>2</sub>O<sub>3</sub> was doped with a concentration of 1, 3, and 5 mol% respectively. The

exact temperature control is important too. Therefore, we made LPE furnace designed specially. A schematic diagram of LPE furnace apparatus was shown in Fig 1. In the furnace, the noted points indicate the location of thermocouple. The temperature of the melt was controlled by thermocouple attached just above the melt vertically. LPE furnace was vertical type which has 3 zone heater to minimize the temperature gradient.

The film growth was performed by a conventional method[1]. Fig. 2 shows a growth condition. The melt was held at about 1160 °C for 5 hours. During this time, it was stirred for 3 hours to make homogeneous state, and then cooled down to about 870 °C at a rate of 60 °C/h, and then held for over 3 hours. In this state, spontaneous nucleation did not occur in the melt : that is, the melt was in a homogeneous supercooled state. And next, the melt was cooled down to the growth temperature (860 °C) at a rate of 200 °C/h and held for 20min and substrate was dipped into the melt for the film growth. In this situation, nucleation occurred in the melts and on the crucible wall, and the uniform supercooled state was broken.

Lattice constant was evaluated using X-ray diffraction method. Also, we examined the crystallinity and the lattice mismatch along the c-axis between the film and the substrate with the variation of Er<sub>2</sub>O<sub>3</sub> dopant using X-ray double crystal technique. The c-axis was determined by a (00 $\bar{1}$ 2) diffraction spot. The incident CuK <sub>$\alpha$ 1</sub> X-ray was reflected from a GaAs single crystal oriented to (004) which plays a role of monochrometer. Crystallinity of the film was evaluated based on the full width at half maximum(FWHM) of the peak. The

lattice mismatch along the c-axis was evaluated from the difference between the substrate and the film diffraction angle:

$$\Delta a_c/a_c = -\Delta \theta / \tan \theta_B \quad (1)$$

where  $\Delta a_c$  is the lattice mismatch between the film and the substrate.  $a_c$  is the lattice constant of substrate.  $\theta_B$  is the Bragg angle for the (0012) reflection and  $\Delta \theta$  is the separation between the diffraction peaks.

### 3. Results and discussion

#### 3.1. Crystallinity of Er : LiNbO<sub>3</sub> thin film

It is well known that crystallinity of thin film depends on film thickness. Kawaguchi et al.[1] reported that when the thickness of thin film was about 20 ~ 30  $\mu\text{m}$ , the crystallinity and surface morphology was excellent. So, the thickness of thin film grown was kept at about 20 ~ 25  $\mu\text{m}$  and the growth rate was about 1 ~ 1.2  $\mu\text{m}/\text{min}$  for this work.

Fig. 3 shows lattice mismatch between the substrate and the thin film by X-ray rocking curves(XRC). From this Figure, it was observed in undoped, 1 and 3mol% Er<sub>2</sub>O<sub>3</sub> doped LiNbO<sub>3</sub> thin film that there were no difference in the Bragg angle(lattice mismatch) between

the substrate and the thin film ( $\Delta \theta_B$ ). But 5mol% Er<sub>2</sub>O<sub>3</sub> doped LiNbO<sub>3</sub> thin film had lattice mismatch between the substrate and the thin film. When  $\Delta \theta_B$  was a 101.25 arcsec by Eq. (1), the lattice mismatch was  $7.86 \times 10^{-4}$  nm. From this result, if Er<sub>2</sub>O<sub>3</sub> is doped over the 5mol%, it is expected that the crystallinity is worse and lattice mismatch is increased.

Fig. 4 shows the dependence of FWHM on the amount of Er<sub>2</sub>O<sub>3</sub> dopant by XRC. It indicates crystal quality of LiNbO<sub>3</sub> single crystal thin film dependent on the amount of Er<sub>2</sub>O<sub>3</sub> dopant. When the epitaxial thin film was undoped, and doped with 1 and 3mol% Er<sub>2</sub>O<sub>3</sub>, the crystallinity was better than the substrate. (For example, the FWHM of the undoped, 1, and 3mol% Er<sub>2</sub>O<sub>3</sub>-doped film was 27.3, 29.2, and 30.2 arcsec respectively. And the FWHM of substrate was 31.2 arcsec.) However, crystallinity of 5mol% Er<sub>2</sub>O<sub>3</sub> doped LiNbO<sub>3</sub> thin film was worse than substrate.

### 3.2. Lattice constant of Er : LiNbO<sub>3</sub> thin film

Fig. 5 shows the change of lattice constant of the c-axis with amount of Er<sub>2</sub>O<sub>3</sub> dopant. From this result, it is shown that the lattice constant of c-axis decreases with increased amount of Er<sub>2</sub>O<sub>3</sub> dopant. The lattice constant of undoped, 1, and 3mol% Er<sub>2</sub>O<sub>3</sub> doped LiNbO<sub>3</sub> thin films was little bit smaller than substrate. But, in the case of 5mol% Er<sub>2</sub>O<sub>3</sub> doped LiNbO<sub>3</sub> thin film,

lattice constant was much smaller than substrate. Most impurities lie at the Li octahedron along the c-axis[16-19]. The transition metals substitute for Li at the regular position very approximately, whereas Er ions shift their position by a few Å toward the nearest oxygen plane[17-19]. Therefore, as amount of Er<sub>2</sub>O<sub>3</sub> dopant was increased, the lattice constant of c-axis was decreased. This result is in good agreement with those from XRC analysis, and indicates that the observed changes in separation of diffraction peak between the substrate and the grown film are caused due to changes of the lattice constant of the thin film.

#### 4. Summary

Er<sub>2</sub>O<sub>3</sub> doped LiNbO<sub>3</sub> single crystal thin films with high crystallinity were grown by LPE method. For the undoped, 1, and 3mol% of Er<sub>2</sub>O<sub>3</sub> doped films, the crystalline quality of grown films was better than that of LiNbO<sub>3</sub> substrate. However, for 5mol% of Er<sub>2</sub>O<sub>3</sub> doped film, crystalline quality was decreased. There were no lattice mismatches along the c-axis for the undoped and films doped with 1, and 3mol% of Er<sub>2</sub>O<sub>3</sub>. For 5mol% of Er<sub>2</sub>O<sub>3</sub> doped film, there was a lattice mismatch of  $7.86 \times 10^{-4}$ nm along the c-axis. Further, lattice constant of the c-axis with amount of Er<sub>2</sub>O<sub>3</sub> dopant was decreased.



## References

- [1] T. Kawaguchi, D.H. Yoon, M. Minakata, Y. Okada, M. Imaeda and T. Fukuda, *J. Crystal Growth* 87 (1995) 152.
- [2] H. Suche, *Proc. ECIO 95* (1995) 565.
- [3] R. Groβ et al., *Proc. ECIO 95* (1995) 571.
- [4] S. Bosso et al., *Proc. ECIO 94* (1994) 353.
- [5] I. Baumann et al., *Appl. Phys. A64* (1997) 33.
- [6] H. Suche, I. Baumann, D. Hiller, and W. Sohler, *Election. Letter* 29 (1993) 1111.
- [7] B.C. Grabmaier and F. Otto, *J. Crystal Growth* 79 (1988) 682.
- [8] K. Kitamura, J.K. Yamamoto, N. Lyi and S. Kimura, *J. Crystal Growth* 116 (1992) 327.
- [9] S. Kan, M. Sakamoto, Y. Okano, K. Hoshikawa and T. Fukuda. *J. Crystal Growth* 119 (1992) 215.
- [10] A. Askin, G.D. Boyd, J.M. Dziedzic, R.G. Smith, A.A. Ballman, J.J. Levinstein and K. Nassau, *Appl. Phys. Letter* 9 (1966) 72.
- [11] A.A. Ballman, H. Broun, P.K. Tien and S. Riva – Sanseverino, *J. Crystal Growth* 29 (1975) 289.
- [12] S. Kondo, S. Miyazawa, S. Fushimi and K. Sugill, *Appl. Phys. Letters* 26 (1975) 489.
- [13] A. Baudrant, H. Vail and J. Daral, *Mater. Res.* 10 (1975) 1373.

- [14] A. Yamada, H. Tamada and M. Daitoh, *J. Crystal Growth* 48 (1993) 132.
- [15] A. Baudrant, H. Vaid and J. Daval, *J. Crystal Growth* 43 (1978) 197.
- [16] L. Rebouta, J. C. Soares, M. F. da Silva, J. A. Sanz-Garcia, E. Diéguez, and F. Agulló-López, *J. Mater. Res.* 7 (1992) 130.
- [17] L. Rebouta, P. J. M. Smulder, D. O. Boerma, F. Agulló-López, M. F. da Silva, and J. C. Soares, *Phys. Rev.* 48 (1993) 3600.
- [18] A. Loenzo, H. Jaffrezic, B. Roux, G. Boulon, and J. Garcia-Solé, *Appl. Phys. Lett.* 67 (1995) 3735.
- [19] L. Rebouta, M. F. da Silva, J. C. Soares, D. Serrano, E. Diéguez, F. Agulló-López, and J. Torenero, *Appl. Phys. Lett.* 70 (1997) 1070.

## List of Figures.

Fig. 1 A schematic diagram of LPE furnace.

Fig. 2 A growth condition for Er : LiNbO<sub>3</sub> thin film by LPE method.

Fig. 3 X-ray rocking curves of film with amount of Er<sub>2</sub>O<sub>3</sub> dopant ; (a) Substrate, (b)  
Undoped, (c) 3mol% Er<sub>2</sub>O<sub>3</sub>, (d) 5mol% Er<sub>2</sub>O<sub>3</sub>.

Fig. 4 Crystallinity of LiNbO<sub>3</sub> single crystal thin film with amount of Er<sub>2</sub>O<sub>3</sub> dopant by X-ray  
double crystal method.

Fig. 5 Lattice constant of the c-axis with amount of Er<sub>2</sub>O<sub>3</sub> dopant.

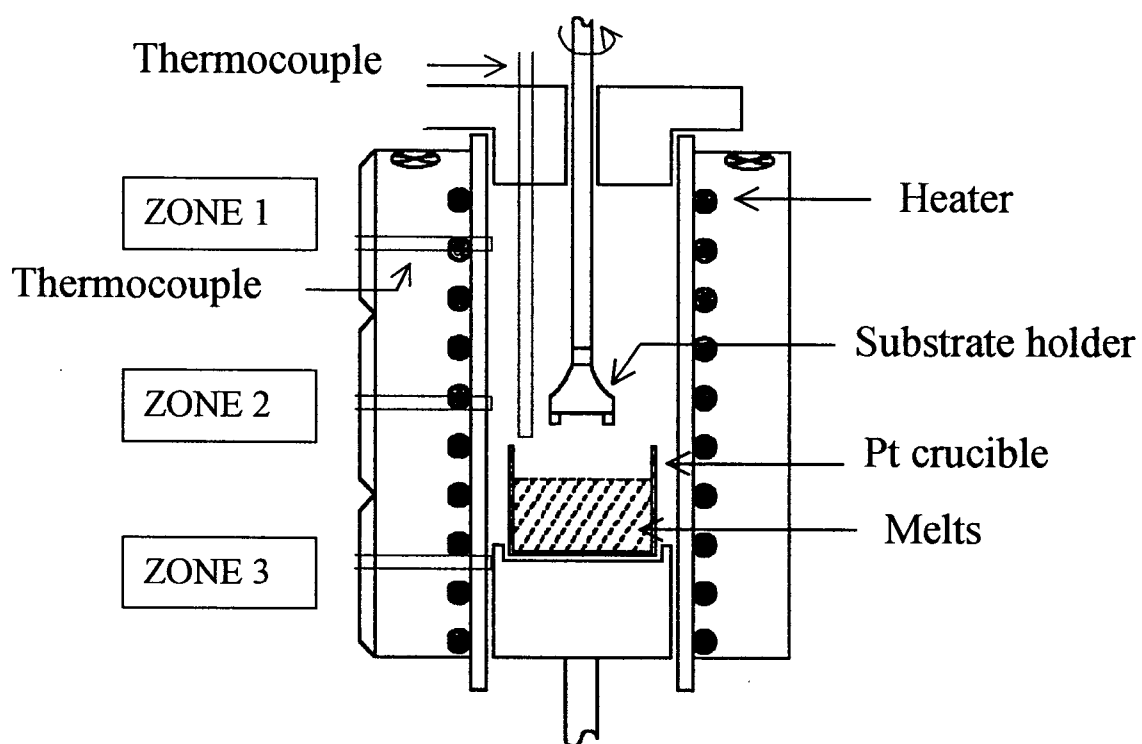


Fig. 1 T. I. Shin.

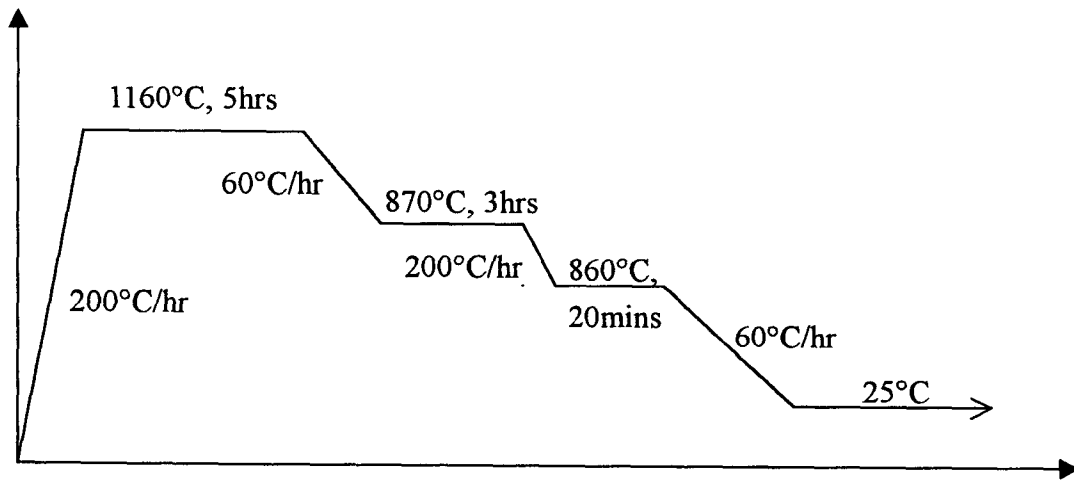


Fig. 2 T. I. Shin.

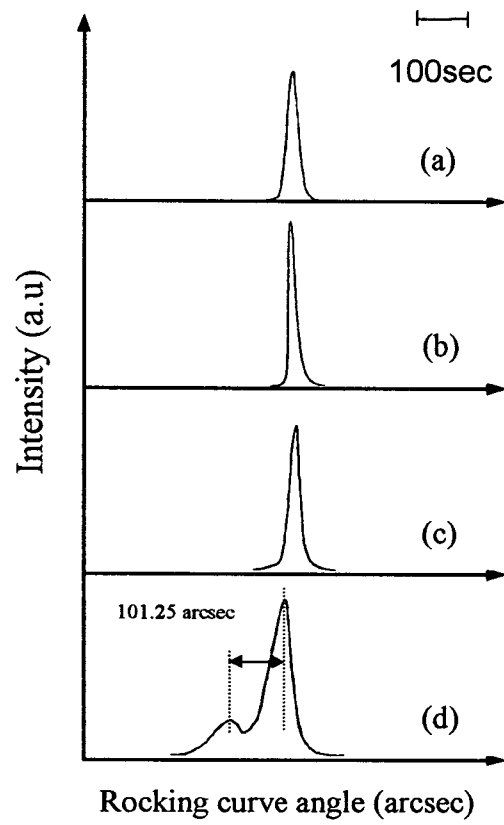


Fig. 3 T. I. Shin.

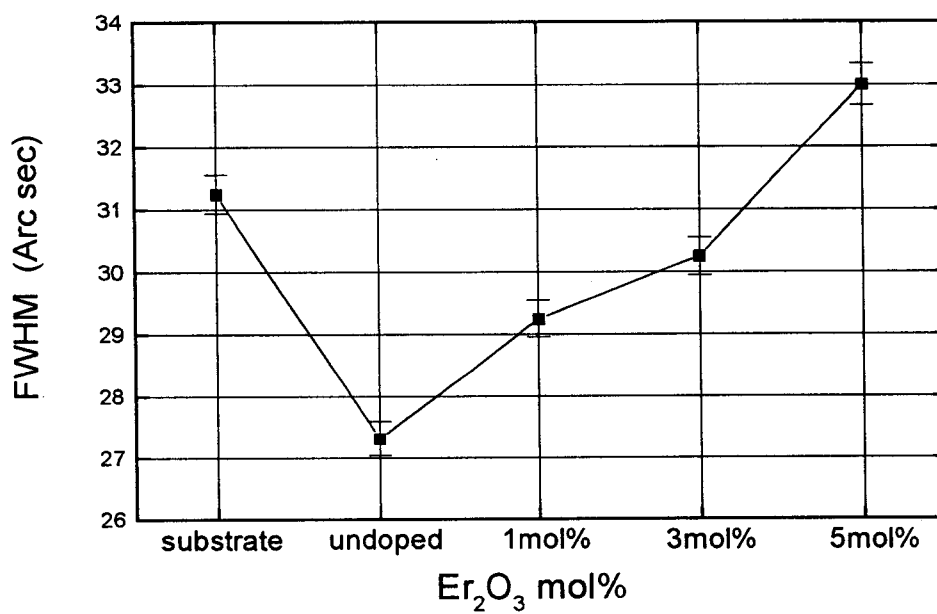


Fig. 4 T. I. Shin.

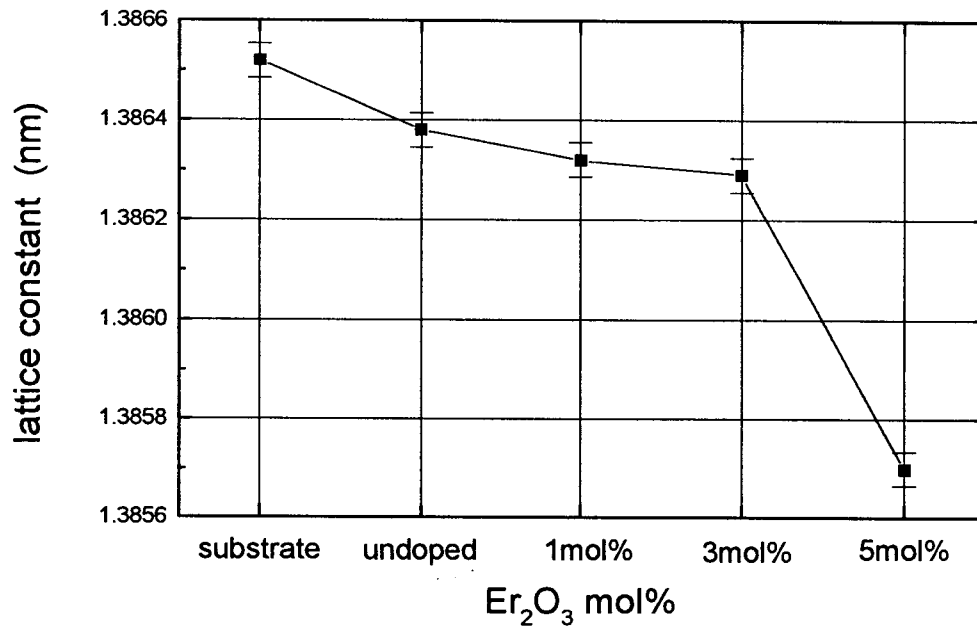


Fig. 5 T. I. Shin.