J. Fiz. UTM. Vol. 3. (2008) 90-94

INVESTIGATION ON THE GROWTH AND LUMINESCENCE SPECTRA OF CONGRUENT $LiNbO_3$ CRYSTAL OBTAINED IN AIR ATMOSPHERE BY CZOCHRALSKI METHOD

Hamdan H.K[1,2], Ngurah Made D.P[3], M. Radzi Sudin[1], Mohamad Khairi Saidin[1] and Md Supar Rohani[1]

[1]Physics Department, Faculty of Science
University Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia
[2]Physics Education Department, Faculty of Science and Mathematics Education
IKIP PGRI Semarang, Indonesia
[3]Physics Department, Faculty of Science and Mathematics
UNNES Semarang, Indonesia
Email coesma@yahoo.com

ABSTRACT

Single crystal of Congruent $LiNbO_3$ (CLN) was grown by the Czochralski method in an air atmosphere with ADC (Automatic Diameter Control) r.f. heating. In this study, the optimum conditions required to grow high quality CLN single crystal are described. The high quality CLN single crystal with growth direction of $\langle 001 \rangle$ was produced by effective control of growth conditions. The luminescence spectra from $LiNbO_3$ is due to change–transfer in the niobate octahedron, and is strongly affected by the concentration of Li vacancies. For CLN single crystal at room temperature under 300nm wavelength excitation, the emission maximum is 760 nm. There are significant differences between the intensity of component emission band in the X, Y and Z cut crystals. Luminescence decay times and intensity variations gives a qualitative measure of both purity and crystal quality.

***Keywords*: Congruent $LiNbO_3$, Crystal growth, Czochralski method, Luminescence spectra.

INTRODUCTION

The Czochralski technique is widely known for growing single crystals from the melt. There are about 70% of the crystals are used in practical devices, therefore, this can be the main reason for using this technique as it can grow a huge amounts of material [1]. $LiNbO_3$ has been selected by researchers due to its technological applications [2].

Lithium niobate (labeled as $LiNbO_3$, LN) single crystal exhibits excellent electro-optics, ferroelectric, piezoelectric, acoustic and nonlinear properties [3]. Nominally pure congruent $LiNbO_3$ crystals (labeled as CLN) generally have good quality and compositional uniformity, exhibit a high concentration of intrinsic defects, namely Nb occupied Li site (Nb_{Li}) and Li vacancy (V_{Li}) according to Li-site vacancy model [4], are always present in the crystals. In this paper, we describe the growth of CLN single crystal by the Czochralski method in an air atmosphere with ADC (Automatic Diameter Control) r.f. heating. The luminescence of CLN were measured and discussed.

EXPERIMENT PROCEDURE

Crystal growth and sample preparation

Crystals of CLN were grown using the radio frequency (r.f) heated Czochralski crystal puller. The system is computer controlled involving weighing the crucible and the melt to generate identical conditions and sizes. Computer controlled growth conditions are tabulated in Table 1. The melts were prepared in air from polycrystalline CLN powder with nominal composition 48.6mol% Li_2O and 51.4mol% Nb_2O_5 [5] and contained in platinum crucible. The platinum crucible was placed at the center of work coil and surrounded with ZrO_2 grains. Then, the crucible was heated to the requited computer by the adjusting the r.f. generator output. The temperature of the wall crucible was monitored by a B- typed thermocouple. To reduce the radial temperature gradient above the melt surface, the ZrO_2 tube insulator is used to surround the heating zone and improve the thermal insulations. Once the melts reach the melting point (about 1250 °C for LN [6]) the seed <001> orientation, is lowered and rotates at 15 rpm until the tip touched the melt. The seed then slowly pulled up at about 2 mmh^{-1} whilst remains rotated at 15 rpm. The pulling speed will define the crystal shape and diameter which normally has been preset in the growth parameter. After completion of the growth run, the crystal was cooled at a rate of about 50°C/h down to room temperature and rotated at about 15 rpm.

Table 1. The growing conditions of CLN crystal

Growth temperature	Growth rate	Crystal rotating rate	Crystal pulling rate
1250°C	0.1 mmh^{-1}	15 rpm	2-8 mmh^{-1}

Sample measurements

The as-grown crystal was cut into about 10 mm plates along X-axis, Y-axis, Z-axis and polished to optical grade. Optical properties luminescence spectra will be measured by using Perkin Elmer LS 55 Luminescence Spectrometer in the range from 200-900nm.

RESULT AND DISCUSSION

Contrary to the results given by Garrett *et al*, [7,8] no difficulties were experienced using platinum crucibles to contain the melt. The pure melts are completely transparent. The quality of crystals grown by the Czochralski technique is related to the shape of the liquid–solid interface during the growth process [9]. Fig.1 present is CLN crystal which has been grown with a power control during growth process. In the same figures are shown the pulling rate has been changed during the growth process from 2 to 8 mmh^{-1}.

In this crystal there are three parameters which could affect the domain structure, (1) the temperature variation, (2) the off-centered crystal geometry and (3) the variation of the rotation rate [10,11]. As can be observed in Fig.1, the temperature fluctuations create a periodical variation in the growth rate and thus a periodical change in the crystal diameter. As the growth progress, the diameter of the growing crystal is controlled by adjusting the crucible temperature. Lowering the heating power will accelerate the crystallization and lead to a diameter increase, while increasing the power will act to decrease the crystal diameter [6].

The crystals formed are transparent, clear, bubble-free, twin-free, and crack-free. In order to improve the quality of the CLN structure, a regular temperature variation of about 5°C at the solid-liquid interface during the growth process was imposed. After the required crystal length has been achieved, the crystal is separated from the melt by accelerated pulling, tapering the crystal bottom to avoid heat shock is typically into not necessary. After completion of the growing crystal, the crystal is slowly cooled to room temperature and rotated at rate 15 rpm in order to avoid thermally induced cracking.

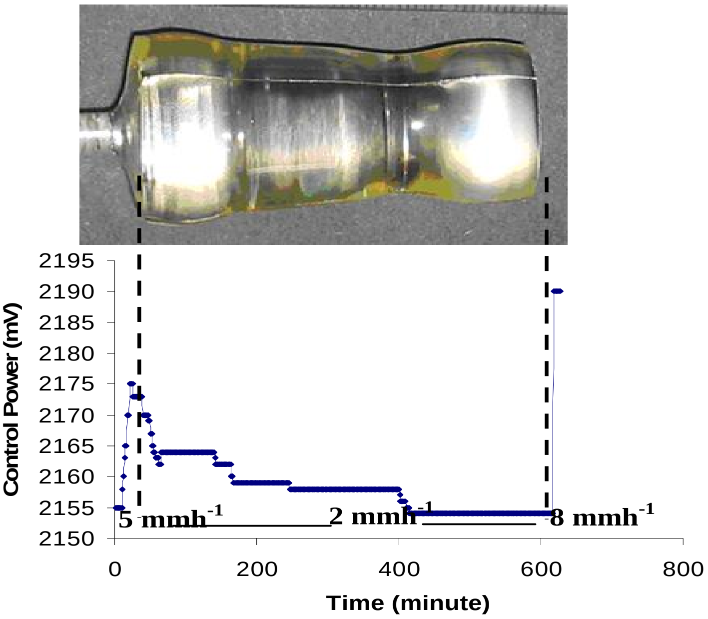

Figure 1: Photograph of CLN crystal, with the control power and pulling rate (mm/h) during the growth process.

For a crystalline material such as LN it is informative to view luminescence emission spectra of CLN crystal from different crystal faces at room temperature. The major orientations of X-, Y-, and Z- cut CLN were excited and each produced significantly different spectra. Fig. 2 shows the initial signals obtained at room temperature from three orientations of the CLN crystal technologies samples. The relative intensities of the component features are noticeably different and at room temperature proton excitation does not significantly modify this picture.

Luminescence spectra at room temperature under 300nm wavelength excitation in CLN show a strong emission near 760 nm. This appears to be due to Nb_{Li}^{4+} sites, such a proposition is supported by the appearance of the signal in reduced crystals and in those that have lost lithium by heat treatment or changes in the Li:Nb stoichiometry [12]. One might expect that in a anisotropic crystal structure such as LN, the luminescence would be polarized. Hence, one might offer more specific defect models. Few studies of this anisotropy have been made but the ion beam work shows clear evidence for polarized emission. Indeed there are significant differences between the intensity of component emission band in the X (or a-axis), Y(or b-axis) and Z (or c-axis) cut crystals.

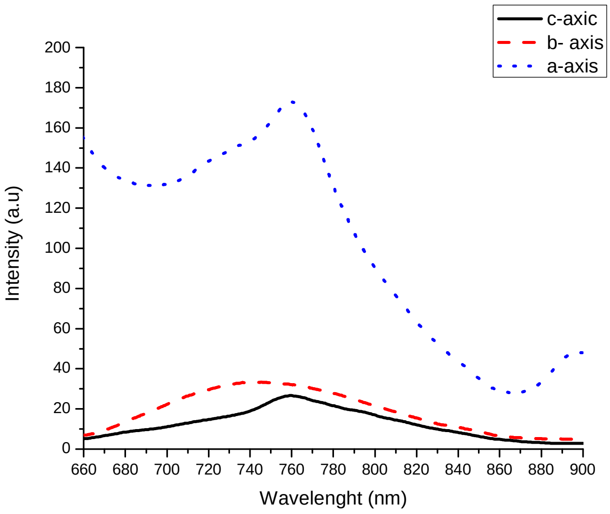

Figure 2: Room temperature luminescence of CLN (c-axis, b-axis and a-axis) with excitation wavelength is 300 nm.

Proton excitation of pure LN did not produce evidence for the free-Li line signals but the lines were immediately apparent in Mg-doped samples [13]. Thus the Mg impurities appear to displace Li from lattice sites and the mobile Li then condenses into metallic precipitates. Furthermore, Mg has an effect on the activation energy of the luminescence efficiency.

CONCLUSION

In conclusions, CLN bulk crystals have been successfully grown with ⟨001⟩ oriented seed from the melt by Czochralski method. The crystals grown was transparent, bubble-free, twin-free, and crack-free under optimum growth parameters. The luminescence emission spectra from LN is due to change–transfer in the niobate octahedron, and is strongly affected by the concentration of Li vacancies. For CLN single crystal at room temperature under 300nm wavelength excitation, the emission maximum is 760 nm. Luminescence decay times and intensity variations gives a qualitative measure of both purity and crystal quality.

ACKNOWLEDGEMENTS

The authors wish to thank the Ministry of Science, Technology and Innovation for their financial support under Vote UTM 74529.

REFERENCES

[1] M. T. Santos, J. C. Rojo, L. Arizmendi, E. Dieguez, *Journal of Crystal Growth*,142 pp.103, 1994.

[2] K. Kawasaki, Y. Okano, S. Kan, M. Sakamoto, K. Hoshikawa, T. Fukuda, *Journal of Crystal Growth*,119, pp. 317, 1992.

[3] T. Zhang, B. Wang, S. Q. Fang, Y. Q. Zhao, F. R. Ling, Y. H. Xu, *Journal of Materials Science*, 39, pp. 5799-5801, 2004.

[4] N. Iyi, K. Kitamura, F . Izumi, J . K. Yamamoto, T. Hayashi, H. Asano, S. Kimura, *Journal Solid State Chem*., 101, pp 340, 1992.

[5] H. Chen, H. Xia, J. Wang, J. Zhang, J. Xu, S. Fan, *Journal of Crystal Growth,* 256, pp. 219-222, 2003.

[6] D.H. Jundt, G.Foulon, *Properties of Lithium Niobate,* Short Run Press Ltd, Exeter, England, 2002.

[7] J.D. Garrett, M. Natarajan-Iyer, J.E. Greedan, *Journal of Crystal Growth,* 41, pp. 225, 1977.

[8] D.S. Robertson, I.M. Young, *Journal of Materials Science*, vol 17, pp 1729-1738, 1982.

[9] A. Golubovic, R. Gajic, I. Hnic, A. Valcic, *Journal Serb. Chem. Soc.* 69 (6), pp 493-502, 2004.

[10] S.H. Lee, Y.J. Kim, S.H. Cho and E.P. Yoon, *Journal of Crystal Growth*, 125, pp 175-180, 1992.

[11] V. BermuH dez, M.D. Serrano, P.S. Dutta, E. DieH guez, *Journal of Crystal Growth*,203, pp. 179-185, 1999.

[12] P.D. Townsend, *Properties of Lithium Niobate,* Short Run Press Ltd, Exeter, England 2002.

[13] P.W. Haycock, P D Townsend, *Journal. Physics C**:** Solid State Physics*, 20**,**319-327, 1987.