TITLE: Investigation of Thermal Annealing by Gamma Irradiation at Room Temperature in LiNbO3 Crystals

Investigation of thermal annealing by gamma irradiation at room temperature in $LiNbO_3$ crystals

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ABSTRACT

An interesting phenomenon of thermal annealing in gamma irradiated undoped, and photorefractive Cu- and Fe-doped, Z-oriented $LiNbO_3$ crystals has been observed. Prior and after each gamma irradiation the crystals were thermally annealed in the air at 800°C for a couple of hours. Optical homogeneity was investigated on the entire areas of $LiNbO_3$ wafers by measuring distributions of birefringence, the principal azimuth, transmission, and parameters associated with birefringence dispersion, and also by measurements of additional absorption in a few wafers' points. It has been rather unexpectedly observed that the classical thermal annealing can lead to a decrease in optical homogeneity in the majority of cases. It is attributed to generation of an internal electric field by the pyroelectric effect, and to the electrooptic effect involved thereafter. On the other hand, the secondary electrons generated by gamma irradiation are believed to increase the optical homogeneity by increasing the crystal's conductivity and dissipating this field. A uniform temperature heating across the wafer generated by this irradiation is also a helpful factor in this gamma-annealing. It has been found that this effect at room temperature is small for gamma irradiation of 10^5 Gy, while increasing the doses to 10^6 Gy and 10^7 Gy can profit in a considerable reduction of the optical inhomogeneity. A certain influence of Cu-doping on this effect has also been observed.

Keywords: thermal annealing, gamma irradiation, doping, electrooptic phenomenon, **B**irefringence **D**ispersion **C**oefficient (BDC).

1. INTRODUCTION

Lithium niobate ($LiNbO_3$) is a promising photorefractive material and is also used e.g. for manufacturing polarizers, electrooptic modulators or acoustooptic devices. Its optical homogeneity is then of primary importance in many practical applications. In this work we investigate the influence of gamma irradiation (1.2 MeV, ^{60}Co source, source yield 1.5 Gy/s) on undoped, and photorefractive Cu- and Fe-doped crystals grown by the Czochralski method from the congruent melt. The influence of gamma irradiation on the optical properties of crystals or devices can be expected in several specific cases including nuclear power stations and laboratories or extraterrestial environment. One might then have expected rather parasitic effects associated with this radiation. However, it was rather unexpectedly observed that thermal annealing applied after each gamma irradiation resulted in a certain increase in the optical inhomogeneity, whereas the gamma irradiation was found to be a fruitful factor in cancelling this effect. One may then suspect that a certain temperature gradients in the samples during the annealing and cooling processes can result in an internal electric field due to the pyroelectric effect, and, therefore, to some parasitic birefringence caused by this field through the electrooptic phenomenon. When such samples are next homogeneously irradiated by gamma rays the secondary electrons generated by this radiation are helpful for relaxation of this electric field. Since samples are also uniformly heated by this radiation it should also imply a positive effect on canceling this parasitic birefringence.

2. EXPERIMENT

The investigated samples (Cu-doped at. 0.05, 0.06, and 0.07 at.%, respectively; and undoped) were cut perpendicularly to the Z-growth direction, being also the direction of their optical axis. They were next mechanically both-sides polished to the thicknesses of 2.1 mm. Also three Fe-doped samples (0.1 at. %, 3.1 mm thick) were cut parallely to the Y-growth

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direction, and perpendicularly to Z. The samples after checking their optical homogeneity were thermally annealed, next they were gamma irradiated at 10^5 Gy, again thermally annealed, again gamma irradiated at 1.065×10^6 Gy, and after the consecutive thermal annealing they were finally gamma irradiated at 10^7 Gy. Prior and after each such operation the samples were checked for their optical homogeneity. The three optical methods have been used : an automated polarimeter (refs. [1,2]) having the capacity of measuring the three maps on the entire sample area (birefringence, the principal azimuth (one of the principal residual stresses in the case of birefringence induced by residual stresses), and transmission), an automated spectropolarimeter (refs. [3-5]) utilizing a novel technique of mapping of parameters associated with the birefringence optical dispersion, and optical spectroscopic measurements of the so-called additional absorption. In the latter case the additional absorption was measured in a few (usually five) sample points, and an average or the most typical result has been taken into consideration. UV-VIS Lambda 900 and Fourier transform IR 1705 Perkin Elmer spectrophotometers have been used in these measurement, as described e.g. in ref. [6]. The values of additional absorption ΔK were calculated according to formula

$$\Delta K(\lambda) = \frac{1}{d} \ln \frac{T_1}{T_2} \quad (1)$$

where λ is wavelength, d is sample thickness, and T_1 and T_2 are the transmissions of the sample measured before and after gamma irradiation, respectively.

Due to the shortage of space in this paper on the following maps (figs. 1 to 8) one can note only the results for one sample only (no. 4, Cu-doped at 0.06 at. %) achieved with the use of the automated spectropolarimeter, since it has been found to be the most characteristic for this experiment. The remaining results of the birefringence, principal azimuth, and transmission mapping are supporting those shown on these maps for this sample. However, since the technique of mapping of parameters associated with birefringence dispersion is quite a new one, a few words have to be said on it here.

It can be shown (e.g. in ref. [3]) that the so-called **B**irefringence **D**ispersion **C**oefficient (BDC) in sample cut out from an isotropic crystal, or, alternatively, cut perpendicularly to the Z-optical axis in an anisotropic crystal, is a function of the stress-optic coefficients C_i, i.e.

$$BDC(\lambda_i) = \frac{\Delta n(\lambda_i)}{\Delta n(\lambda_{i+1})} = \frac{C_i}{C_{i+1}} \quad (2)$$

where Δn is birefringence, and the wavelength increment λ_{i+1}-λ_i was adjusted to 10 nm in this experiment. The stress-optic coefficients of the crystal are defined by the direct relation of birefringence to (residual) stresses σ

$$\Delta n_i = C_{ij} \sigma_j \quad (3)$$

where the matrix notation like that used e.g. in ref. [7] has been applied. In contrary to such parameters like the piezooptic(al) π_{ij}, or elastooptic(al) p_{ij} coefficients, which have been usually measured by many investigators for describing the elastooptic properties of crystals, the piezooptic coefficients C_{ij}, closely related to π_{ij}, and being a good alternative for them (using C_{ij} one does not need to know or measure the refractive index of the ordinary ray) have been, however, mentioned only in a few papers on optics (e.g. refs. [8,9]). It can be also shown (ref. [5]) that the so-called **R**elative **D**ifferential **B**irefringence **D**ispersion (RDBD) (unshown in this work, since its maps and their cross-sections are close in shape to the BDC's ones) is another important function (relative dispersion) of the stress-optic coefficient :

$$RDBD(\lambda_i) = \frac{\Delta n(\lambda_i) - \Delta n(\lambda_{i+1})}{\Delta n(\lambda_i)(\lambda_{i+1} - \lambda_i)} = \frac{1 - \frac{1}{BDC(\lambda_i)}}{\lambda_{i+1} - \lambda_i} = \frac{1}{C_i} \frac{dC}{d\lambda}\Big|_{\lambda_i} \quad (4)$$

In fig. 1 one can see the BDC map for the investigated sample after it had been gamma irradiated at 1×10^5 Gy. The map has been calculated for λ_i=760 nm using eq. (2), and so has been the following maps and cross-sections shown in this work. The BDC horizontal cross-section of the map in fig. 1 is shown in fig. 2. All the horizontal and also vertical cross-

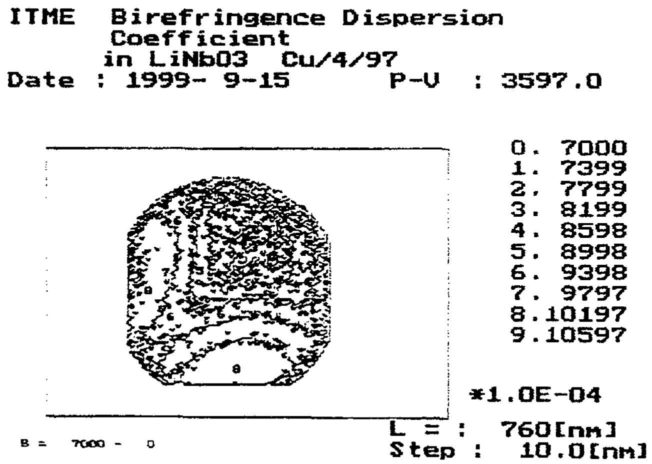

Fig. 1. BDC distribution in Cu (0.06 at. %) doped, Z-cut $LiNbO_3$ after gamma irradiation at $1x10^5$ Gy.

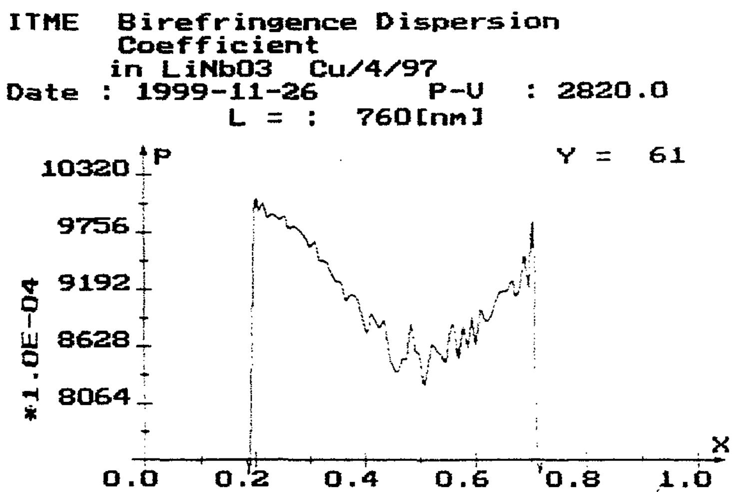

Fig.2. Horizontal cross-section of the map shown in fig. 1.

sections are plotted along the diameter of the quasicircular sample. In figs. 3 and 4 one can see for comparison the horizontal and vertical cross-sections, respectively, of the BDC map (unshown here) after the sample had been thermally annealed at 800°C for 4 hours. Such BDC horizontal and vertical cross-sections for the sample gamma irradiated at $1.065x10^6$ Gy are shown in figs. 5 and 6, whereas only the BDC horizontal cross-sections of this sample again thermally annealed, and next gamma irradiated at $1x10^7$ Gy are shown in figs. 7 and 8, respectively.

As it clearly comes out from fig. 3 the thermal annealing of this sample after gamma irradiation at $1x10^5$ Gy had only a minor influence on optical homogeneity of this sample. The reason is an insignificant influence of this dose on the optical homogeneity of the sample that prior to this irradiation had been also thermally annealed. However, the dramatic and positive changes in the BDC distribution can be seen after the sample had been next gamma irradiated at $1.065x10^6$ Gy (figs. 5 and 6 compared to figs. 3 and 4, respectively). The horizontal BDC cross-section shown in fig. 5 is almost flat, and so is also approximately flat the respective vertical cross-section (fig. 6). The rocking curves that can be seen in the vertical cross-sections come solely from the background, not from the sample. Also the rocking curves seen on the left, and on the right hand side, respectively, in the horizontal cross-sections come out from some reflections at the border of the sample and its holder.

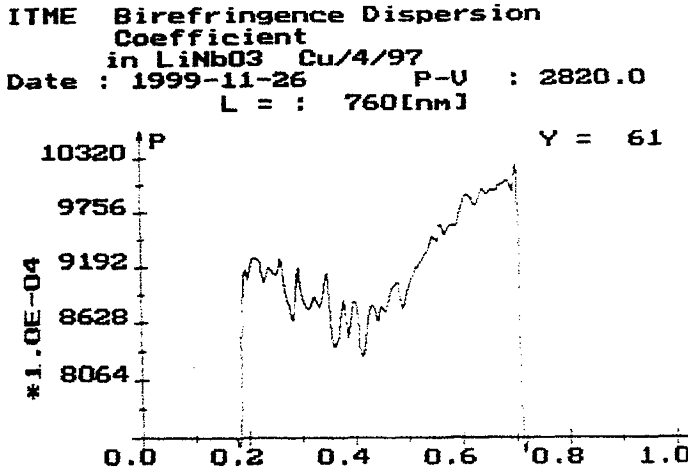

Fig. 3. Horizontal cross-section of the BDC map (unshown in this work) for the sample thermally annealed after gamma irradiation at 10^5 Gy.

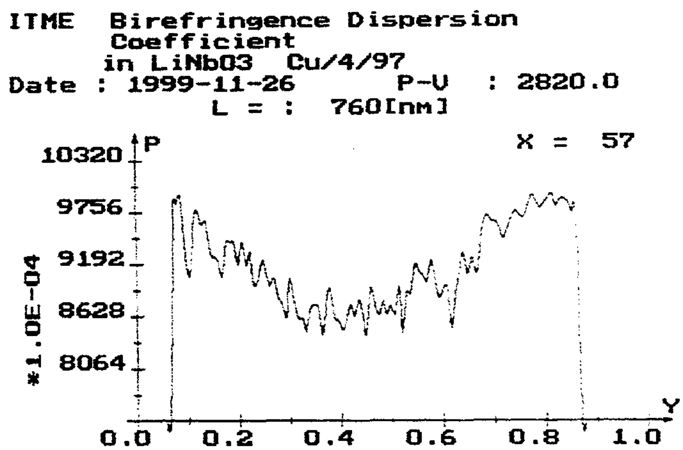

Fig. 4. Vertical cross-section of the BDC map (unshown in this work) for the sample thermally annealed after gamma irradiation at 10^5 Gy.

By comparing fig. 7 and fig. 5 one can observe a considerable decrease in the optical homogeneity when the sample had been thermally annealed after gamma irradiation at 1.06×10^6 Gy. A certain, but small, increase in this homogeneity has been observed (fig. 8) when this sample was again gamma irradiated for a long time at 1×10^7 Gy.

From these results it is evident that thermal annealing leads to degradation of the optical homogeneity in $LiNbO_3$ crystals, what, at first sight, seems to be something unusual in materials engineering. On the other hand, however, gamma irradiation of the thermally annealed samples has been found to be a positive factor in cancelling parasitic birefringence induced by this thermal treatment. Similar results have been observed for another $LiNbO_3$ samples. These results are also in good agreement with measurements carried out in the automated polarimeter (unshown here), and with measurements of the additional absorption (fig. 9). Changes in absorption of the sample shown in this figure are considerable in the visible part of the spectrum (up to about 600 nm). The largest changes are associated with the thermal annealing after gamma irradiation at 10^6 Gy (curve no. 5), and at 10^7 Gy (curve no. 6). This thermal annealing has only a minor influence on the additional absorption after the sample had been gamma irradiated at 10^5 Gy (curve no. 4). A clear positive influence on the additional

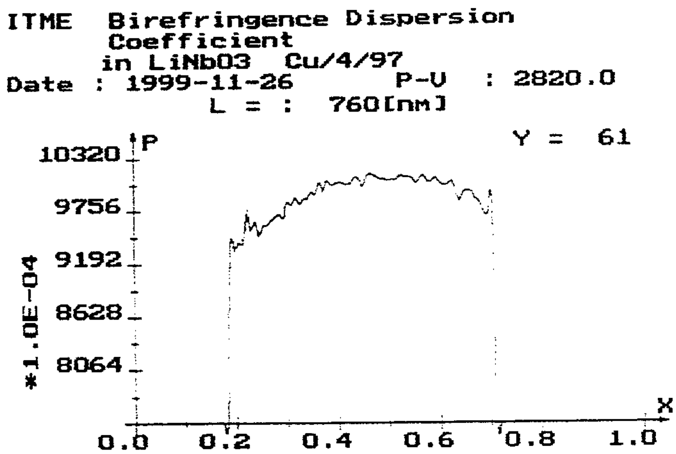

Fig. 5. Horizontal cross-section of the BDC map (unshown in this work) for the sample gamma irradiated at $1.065x10^6$ Gy.

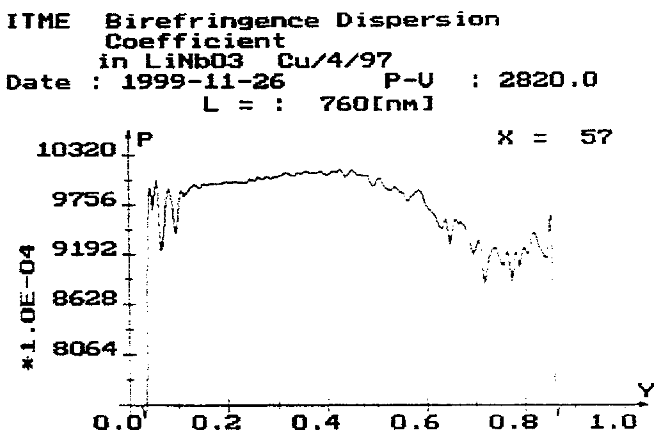

Fig. 6. Vertical cross-section of the BDC map (unshown in this work) for the sample gamma irradiated at $1.065x10^6$ Gy.

absorption from gamma irradiation is also evident in this figure when the sample had been gamma irradiated at 10^6 Gy (curve no. 2), and later irradiated at 10^7 Gy (curve no. 3). The results of these spectroscopic measurements are at least in good qualitative agreement with that achieved by using the (spectro)polarimeters. It is worth noting that the results of the polarimetric measurements in the wavelength region above 600 nm are corresponding with those obtained for shorter wavelengths by the spectroscopic investigations. It means that these measurements are complementary to each other.

It has been also found that the sample doped with 0.07 at. % of Cu seems to be more influenced by gamma irradiation than that doped with smaller amounts of copper. Also a larger influence of gamma irradiation on Cu-doped, than on Fe-doped or undoped samples can be deduced from the results of these investigations. However, this last conclusion needs a further and stronger evidence.

3. SUMMARY AND CONCLUSION

In this work we have shown that the classical thermal annealing, i.e. the annealing of the wafers in a furnace at high temperature, can lead to a certain decrease in the optical homogeneity, while gamma irradiation is a helpful factor in restoring this homogeneity. Thus we can talk about the "thermal annealing by gamma irradiation" because this irradiation also involves a certain temperature increase above the room temperature in the irradiated wafers.

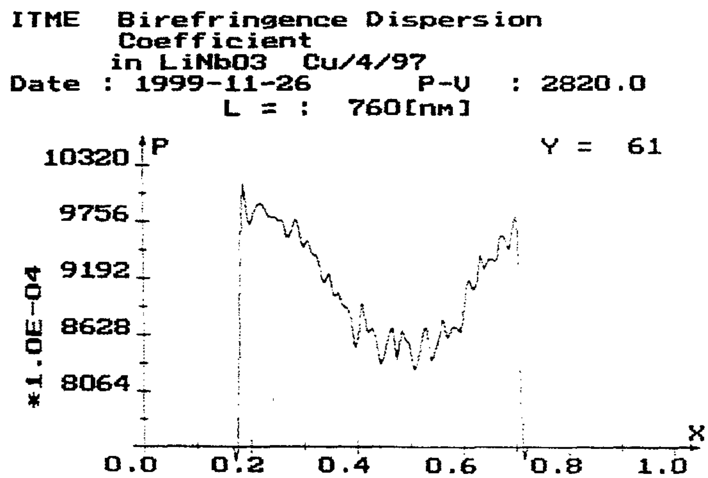

Fig. 7. Horizontal cross-section of the BDC map (unshown in this work) for the sample thermally annealed after gamma irradiation at 1.065×10^6 Gy.

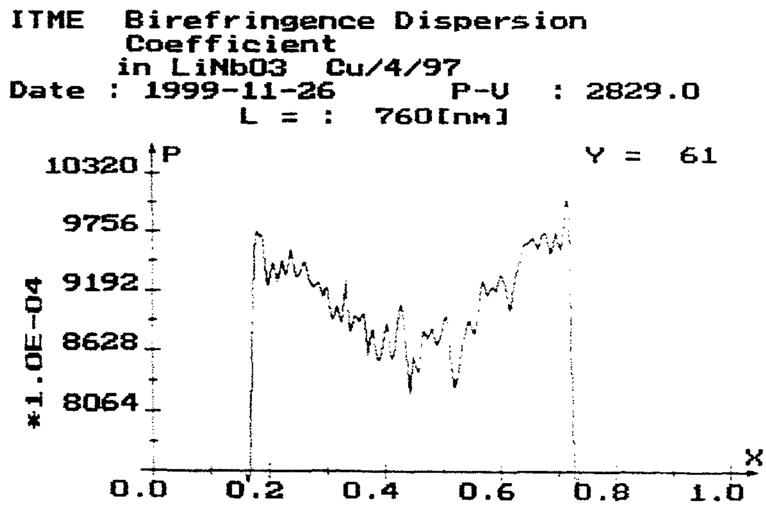

Fig. 8. Horizontal cross-section of the BDC map (unshown in this work) for the sample gamma irradiated at 1×10^7 Gy.

The mechanism of this phenomenon seems to be the electric fields induced in the wafers by the pyroelectric effect, and the electrooptic effect involved thereafter. However, in general case this mechanism is very complicated, and only a simplified qualitative, and to some extent - also a quantitative interpretation is given here.

When the Z-cut $LiNbO_3$ wafer, like in this work, is thermally annealed in the furnace, the critical steps of this operation seem to be the proper annealing itself, and next cooling of the wafer down to the room temperature. The electric field duly involved in these operations should be parallel to the Z-axis, and since the light beam is also parallel to this Z (optical) axis in this experiment, it ideally should then have no influence on the birefringence data at all. However, one can easily imagine that firstly, there is always a certain temperature distribution (a few °C) on the wafer area during the annealing itself, and, secondly, that a certain, but very small, spread distribution of the cooling rate on this area may be also expected in the cooling process. These two effects may result in a certain inhomogeneous distribution of the electric charges on both sides of the wafer, thus generating also some electric field in the X and Y directions. The relaxation of this field while cooling is small. For example, the time constant of this relaxation at 80°C is approx. equal to two hours (ref. [10]), and is of course rapidly increasing with decrease of temperature. It means that in the cooling process (about 24 hours) only a fraction of this electric field can be dissipated. When cooled down to the room temperature, the process of charge relaxation goes on, but extremely slow.

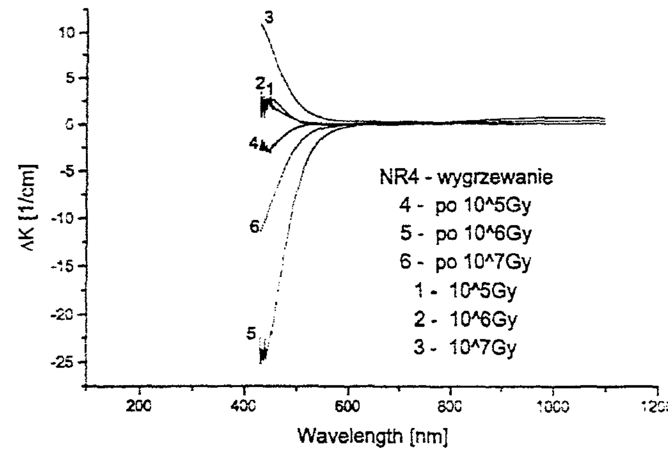

Fig. 9. Additional absorption in Cu (0.06 at. %) doped, Z-cut $LiNbO_3$ wafer prior and after the thermal annealing or gamma irradiations.

The magnitude of the electrooptic effect can be estimated from a simple formula $\Delta n = n_o^3 r_{22} E$, where n_o is refractive index of the ordinary ray, r_{22} is electrooptic coefficient in this configuration (Z-cut wafer, light beam parallel to Z, the electric field E perpendicular to Z). Providing a static electric field, like in this example, and 760 nm wavelength from the following data : n_o=2.26 (ref. [11]), and $r_{22}=6.8\times10^{-10}$ cm/V (ref. [12]), one can calculate the constant $n_o^3 r_{22}$ to be 7.85×10^{-9} cm/V. It means then that even such a week electric field, like e.g. 10^4 V/cm acting in the wafer plane, can result in a parasitic birefringence of 7.85×10^{-5}, i.e. the birefringence comparable to that induced by the residual stresses. Usually, the electric fields generated by the pyroelectric effect in $LiNbO_3$ are estimated to be within the range of 10^5-10^8 V/cm. Since in the crossed polarizers configuration of the used polarimeter one could always observe the so-called isoclinic cross associated with principal directions of the residual stresses, it might have been concluded that the additional birefringence due to the pyroelectric and electrooptic effects was weaker than that originally induced by these stresses. Most probably the electric fields generated in our samples at room temperature were then in the vicinity of 10^3-10^4 V/cm.
The effect of cancelling of the electric field by gamma irradiation is primarily associated with a rapid increase in conductivity of the wafers due to the secondary electrons generated by this radiation. Also increase of the wafer's temperature, being the secondary effect of gamma irradiation, and uniformity of this temperature distribution on wafer area, is another helpful factor for migration of the charges and for dissipation of the electric field components parallel to the wafer area.

It was observed that these effect have been significantly large for gamma irradiation at the level of 1.065×10^6 Gy. This figure, or maybe a little smaller one, might then have seem to be something like a threshold in this effect, since the positive influence of gamma irradiation at the level of 1×10^7 Gy has not been so pronounced as that achieved at 1.065×10^6 Gy. The exact magnitude of this threshold is, however, rather difficult to be precisely estimated in these long lasting irradiation experiments.

REFERENCES

1. A.L. Bajor, "Automated polarimeter-macroscope for optical mapping of birefringence, azimuths, and transmission in large area wafers. Part I. Theory of the measurement", *Rev. Sci. Instrum.* **66**, pp. 2977-2990, 1995.
2. A.L. Bajor, M.J. Kukla, T. Pi_tkowski, L. Sałbut, A. Spik, and A. Szwedowski, "ibid. Part II. Measurement setup and results", *Rev. Sci. Instrum.* **66**, pp. 2991-2995, 1995.
3. A.L. Bajor, "Birefringence dispersion inhomogeneity testing in optical materials by imaging polarimetry", in *Optics and Optoelectronics. Theory, Devices and Applications,* edited by O.P. Nijhawan, A.K. Gupta, A.K. Musla, and K. Singh, **Vol. 2**, pp. 1312-1316, Narosa Publ. House, New Delhi, Madras, Bombay, Calcutta, London, 1998.
4. A.L. Bajor, "Testing of optical materials by birefringence dispersion mapping", in press SPIE, 2000.
5. A.L. Bajor, "Birefringence dispersion mapping - a new technique for testing of optical inhomogeneity in crystalline materials", in press SPIE, 2000.
6. I. Pracka, A.L. Bajor, S.M. Kaczmarek, M. Świrkowicz, B. Kaczmarek, J. Kisielewski, and T. Łukasiewicz, "Growth and characterization of $LiNbO_3$ single crystals doped with Cu and Fe ions", *Cryst. Res. Technol.* **34**, pp. 627- 634, 1999.
7. J.F. Nye, *Physical properties of crystals. Their representation by tensors and matrices,* Clarendon Press, Oxford, 1957.
8. P.K. Ajmera, B. Huner, A.K. Dutta, and C.S. Hartley, "Simulation and observation of infrared piezobirefringent images in diametrically compressed semiconductor discs", *Appl. Opt.* **27**, pp. 752-757, 1988.
9. A.K. Dutta, P.K. Ajmera, and B. Huner, "Piezobirefringence effects in GaAs discs subjected to diametrical compression", *J. Appl. Phys.* **65**, pp. 5230-5232, 1989.
10. A.A. Blistanov, E.V. Makarevska, V.V. Geraskin, O. Kamalov, and M.M. Koblova, "The influence of doping on optical quality and on electric conductivity of $LiNbO_3$", *Sol. State Phys. (Sov.),* **20**, pp. 9-12, 1978.
11. D.F. Nelson, and R.M. Mikulyak, "Refractive indices of congruently melting $LiNbO_3$", *J. Appl. Phys.* **45**, pp. 3688-3689, 1974.
12. A. Yariv, and P. Yeh, *Optical Wawes in Crystals,* Wiley-Interscience, New York, 1984.