

Piezoelectric Properties of Potassium Niobate Single Crystals with Various Domain Configurations

Satoshi Wada, Kazuma Muraoka, Hirofumi Kakemoto, Takaaki Tsurumi
and Hirohiko Kumagai*

Department of Metallurgy and Ceramics Science, Graduate School of Science and Engineering,
Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, JAPAN.

Fax: +81-3-5734-2514, e-mail: swada@ceram.titech.ac.jp

*Asahi Techno Glass Co., 50-1 Gyouda, Funabashi, Chiba 273-0044, JAPAN.

Fax: +81-47-421-2058, e-mail: hirohiko_kumagai@atgc.co.jp

Domain configurations of potassium niobate (KNbO_3) single crystals were investigated as a function of temperature, crystallographic direction and electric field. When temperature was increased from -100°C to 500°C , its domain configuration was changed at the following three phase transitions, *i.e.*, (1) -19°C assigned to phase transition from $3m$ to $mm2$, (2) 230°C assigned to phase transition from $mm2$ to $4mm$, and (3) 450°C assigned to phase transition from $4mm$ to $m3m$. Piezoelectric properties of KNbO_3 single crystals were investigated as a function of crystallographic orientations, *i.e.*, $[110]_c$ of polar direction and $[001]_c$ of nonpolar direction. Prior to piezoelectric measurement, KNbO_3 crystals were poled using the 2-step poling method, and then two kinds of domain configurations were induced. KNbO_3 crystals poled along $[110]_c$ showed almost single-domain state apparently while the $[001]_c$ poled KNbO_3 crystals exhibited the complicated domain configuration, which cannot be assigned crystallography. The $[110]_c$ poled KNbO_3 crystals exhibited electromechanical coupling factor k_{31} of 28.9% and piezoelectric constant d_{31} of 18.4 pC/N while the $[001]_c$ poled KNbO_3 crystals exhibited k_{31} of 31.2% and d_{31} of 51.7 pC/N. The piezoelectric constant d_{31} along nonpolar $[001]_c$ direction was 2.8 times higher than that along polar $[110]_c$ direction.

Key words: potassium niobate, single crystal, domain configuration, piezoelectric property

1. INTRODUCTION

Domain configuration is one of the most important factors to determine ferroelectric related properties, especially piezoelectric property. Recently, domain engineering using ferroelectric single crystals is developing rapidly. Engineered domain configuration is one of the domain engineering, and its application to ferroelectric single crystals can make the piezoelectric property much larger¹⁻⁵⁾. However, the domain configuration is strongly dependent of the crystal structures of ferroelectric single crystals, *i.e.*, there were different engineered domain configurations. In this study, KNbO_3 single crystal was chosen as a ferroelectric single crystal. This is because KNbO_3 single crystals are orthorhombic $Amm2$, and possess 4 kinds of domain structures, *i.e.*, 60° , 90° , 120° and 180° domains. Therefore, KNbO_3 single crystal has very complex domain structures.

Ferroelectricity of KNbO_3 was first observed by Matthias⁶⁾, and up to date, a lot of studies on KNbO_3 have been reported. However, there have been just a few reports about piezoelectricity of KNbO_3 single crystals⁷⁻⁹⁾. There are two reasons why the reports on the piezoelectricity of KNbO_3 crystals were so limited. One is the difficulty in the crystal growth of KNbO_3 single crystals with sufficient electrical resistance to measure piezoelectric property due to the high volatility of potassium during the growth process. The other is the difficulty in the poling treatment, *i.e.*, reconstruction of domain configuration. Because of these two reasons, not all piezoelectric properties of KNbO_3 single crystals have been determined even at present. However, recently,

KNbO_3 single crystals with a low dielectric loss below a few % were grown, and to make a single-domain state of KNbO_3 single crystal, a new 2-step poling method was proposed¹⁰⁾. Therefore, using these KNbO_3 single crystals, it is very important that a relationship between domain configurations and piezoelectric properties of KNbO_3 single crystals is investigated.

In this study, piezoelectric properties of KNbO_3 single crystals are investigated as a function of crystallographic orientations, such as $[110]_c$ of polar direction and $[001]_c$ directions. The $[001]_c$ direction was chosen to induce the engineered domain configuration, and subscript *c* means a cubic notation system. Moreover, the domain configurations are observed as a function of temperature, crystallographic orientation and electric field.

2. EXPERIMENTAL

KNbO_3 single crystals were prepared by a top-seeded solution growth (TSSG) method at Asahi Techno Glass, Ltd. The TSSG-grown KNbO_3 crystals were perfectly transparent and colorless. The details of the preparation of KNbO_3 single crystals and their characterization have been described elsewhere¹¹⁾. These crystals were oriented along $[110]_c$ and $[001]_c$ directions.

Domain configurations of KNbO_3 single crystals were observed under crossed nicols using a polarizing microscope (Nikon LABOPHOT2-POL) with a cryostat. For the domain observation, temperature was changed from -190°C to 600°C , and electric field was also changed from 0 to 2kV/mm.

Prior to piezoelectric measurements, KNbO_3 single

crystals was poled using the 2-step poling method¹⁰. KNbO₃ single crystals were shaped as rectangular bars of size 4.0x1.2x0.4 mm³. After poling treatment, these domain configurations were observed using a polarizing microscope. Piezoelectric properties of the poled KNbO₃ single crystals were measured by a conventional resonance method¹². The length extensional mode, k_{31} mode, was chosen as the piezoelectric property. Impedance ($|Z|$) and phase (θ) were measured as a function of frequency to determine the resonance frequency (f_s) and the antiresonance frequency (f_p). These values were substituted in an exact formula solution listed in EMAS-610021), and finally, d_{31} , k_{31} , elastic compliance coefficient s_{11}^E and mechanical quality factor Q_m were calculated.

3. RESULT AND DISCUSSION

3.1 Domain configuration of KNbO₃ single crystals

Figure 1 shows the domain structures expected in the monoclinic KNbO₃ single crystal. There are four kinds of domain structures, i.e., (1) 180° domain structure with W_w walls, (2) 90° domain structure with W_f walls of $\{100\}_c$, (3) 60° domain structure with W_f walls of $\{110\}_c$ and (4) 120° domain structure with W_f walls of $\{110\}_c$.¹³ These four domains are randomly distributed in the crystal. It is known that there is S-type wall in monoclinic KNbO₃ crystal, but we do not focus S-type wall in this study.

To confirm the above expected domain configurations, the domain structure of KNbO₃ crystal was observed at 25°C using the KNbO₃ crystal with 50 μm -thickness.

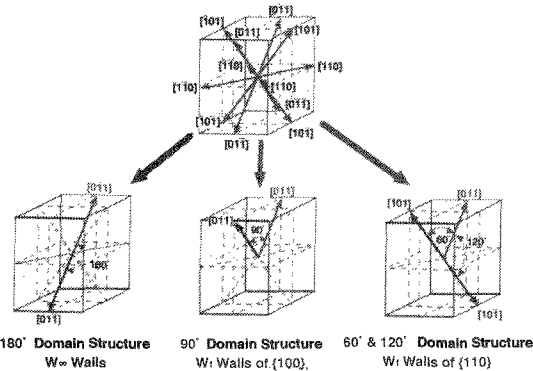


Fig. 1 Schematic domain structure expected for monoclinic KNbO₃ single crystal; (a)-180° domain structure with W_w walls, (b) 90° domain structure with W_f walls of $\{100\}_c$ and (c) 60° and 120° domain structures with W_f walls of $\{110\}_c$.

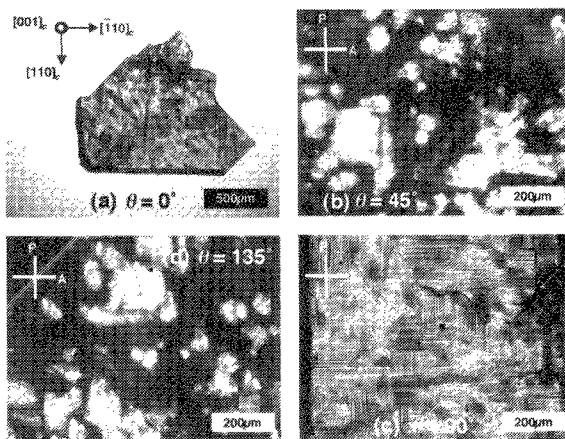


Fig. 2 Domain configuration of $[001]_c$ oriented KNbO₃ single crystal at 25°C.

Figures 2 (a)-(d) show the domain structures of this crystal observed under crossed nicols. When the rotation angle θ was 0°, all of the crystal became bright. This means that this position was a diagonal position. On the other hand, when the crystal was rotated by θ of 45°, most of the crystal became dark. This means that this position was an extinction position. Some parts of the crystal were always bright despite of crystal rotation. This suggests that along a thickness direction, there were some laminated domain structures. Moreover, crystallography, these domain walls assigned to $\{100\}_c$ and $\{110\}_c$. Thus, the domain configurations of KNbO₃ crystal observed at 25°C satisfied the crystallographic domain structure expected for monoclinic ferroelectrics.

3.2 Temperature dependence of domain configuration

Temperature dependence of dielectric permittivity of KNbO₃ crystals measured at 100 kHz in the cooling process was reported¹⁰. In this report, three dielectric peaks were clearly observed, and each peak was assigned to a phase transition behavior, i.e., (1) 436°C assigned to phase transition from $m3m$ to $4mm$, (2) 208°C assigned to phase transition from $4mm$ to $mm2$, and (3) -60°C assigned to phase transition from $mm2$ to $3m$. On the other hand, in the heating process, three dielectric peaks were also observed, but these peaks shifted to higher temperatures, i.e., (1) -19°C assigned to phase transition from $3m$ to $mm2$, (2) 230°C assigned to phase transition from $mm2$ to $4mm$, and (3) 450°C assigned to phase transition from $4mm$ to $m3m$. Therefore, it is expected that the domain configurations of KNbO₃ crystals strongly depend on temperature. Thus, temperature dependence of domain configuration was investigated in the heating process.

Figures 3 (a)-(d) show temperature dependence of the domain configuration observed under crossed nicols. The domain structure observed below -19°C was assigned to rhombohedral $3m$ domain configuration with (1) 71° domain structure with W_f walls of $\{110\}_c$ and (2) 109° domain structure with W_f walls of $\{100\}_c$ as shown in Fig. 3 (a). The domain structure observed from -19°C to 230°C was assigned to monoclinic m domain configuration as the above-mentioned as shown in Fig. 3 (b). Moreover, the domain structure observed from 230°C to 450°C was assigned to tetragonal $4mm$ domain configuration with (1) 90° domain structure with W_f walls of $\{110\}_c$ as shown in Fig. 3 (c). Finally, no domain structure observed above

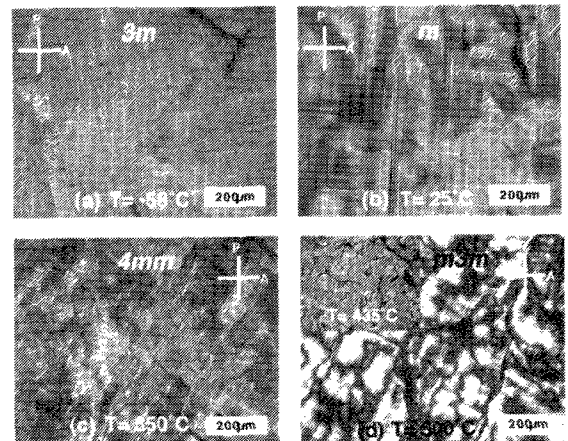


Fig. 3 Temperature dependence of domain configuration for $[001]_c$ oriented KNbO₃ single crystal in the heating process.

450°C was assigned to cubic $m\bar{3}m$ structure. Therefore, the temperature dependence of the domain configuration completely agreed with the temperature dependence of dielectric permittivity.

3.3 Poling of KNbO_3 single crystals using the 2-step poling method and their domain configurations

The KNbO_3 crystals were poled along $[110]_c$ and $[001]_c$ directions using the 2-step poling method. At first, changes of domain configuration before and after poling along $[110]_c$ direction were investigated using the polarizing microscope. Figures 4 (a)-(d) show the domain structure of $[110]_c$ oriented KNbO_3 crystals before poling. In Fig. 4 (a), many fine domains and many surface scratches were clearly observed. When the $[110]_c$ direction of the crystal was adjusted to the analyzer direction (the angle between analyzer and $[110]_c$ direction, ϕ , of 0°), some parts of the crystal became to dark partially. This means that at ϕ of 0° , the some parts of the crystal was in an extinction position.¹⁴⁾ Successively, when the crystal was rotated by 45° (ϕ of 45°), most of the crystal was in a diagonal position,¹⁴⁾ and then, at ϕ of 90° , the crystal partially moved to the extinction position, again. The domain observation revealed that this KNbO_3 crystal before poling was multi-domain state.

On the other hand, Figs. 5 (a)-(d) show the domain structure of $[110]_c$ oriented KNbO_3 crystals after poling, under crossed nicols. Numerous scratches were observed near the surface of the crystal, but there was no domain wall over the crystal. The electric field was applied along the $[110]_c$ direction. When the $[110]_c$ direction of the

crystal was adjusted to the analyzer direction (the angle between analyzer and $[110]_c$ direction, ϕ , of 0°), the entire crystal became to dark at the same time. This means that at ϕ of 0° , the entire crystal was in an extinction position.¹⁴⁾ Successively, when the crystal was rotated by 45° (ϕ of 45°), the entire crystal was in a diagonal position,¹⁴⁾ and then, at ϕ of 90° , the entire crystal moved to the extinction position, again. Under crossed nicols, the observation of no domain wall indicates that there was no domain assigned to non- 180° domains. Moreover, the simultaneous extinction of the entire crystal suggested that the crystal resembled a single domain state apparently.

Similar changes of domain configuration before and after poling along $[001]_c$ direction was observed. Figures 6 (a)-(d) show the domain structure of $[001]_c$ oriented KNbO_3 crystals before poling. In Fig. 6 (a), many domain structures and some surface scratch were clearly observed. When the $[110]_c$ direction of the crystal was adjusted to the analyzer direction (the angle between analyzer and $[001]_c$ direction, ϕ , of 0°), some parts of crystal became to dark partially. This means that at ϕ of 0° , the some parts of the crystal was in an extinction position.¹⁴⁾ Successively, when the crystal was rotated by 45° (ϕ of 45°), most of the crystal was in a diagonal position,¹⁴⁾ and then, at ϕ of 90° , the crystal partially moved to the extinction position, again. The domain observation revealed that this KNbO_3 crystal before poling was multi-domain state.

On the other hand, Figs. 7 (a)-(d) shows the domain state after poling along $[001]_c$ direction under crossed nicols. In addition to numerous scratches near the surface, a very fine domain configuration was observed over the crystal.

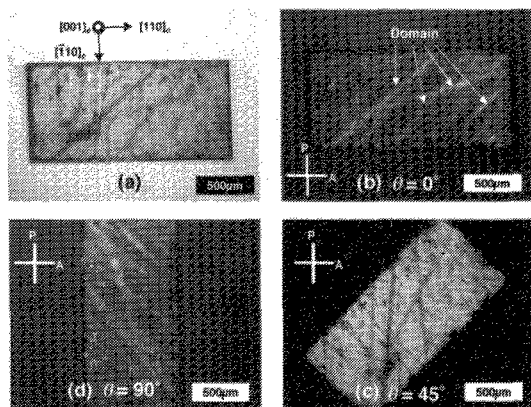


Fig. 4 Domain observation of the $[110]_c$ nonpoled KNbO_3 crystal at various rotation angles (ϕ).

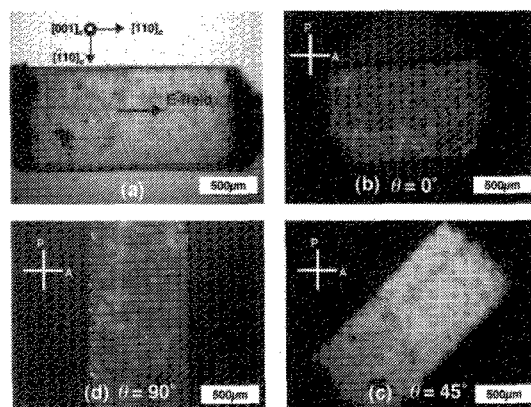


Fig. 5 Domain observation of the $[110]_c$ poled KNbO_3 crystal at various rotation angles (ϕ).

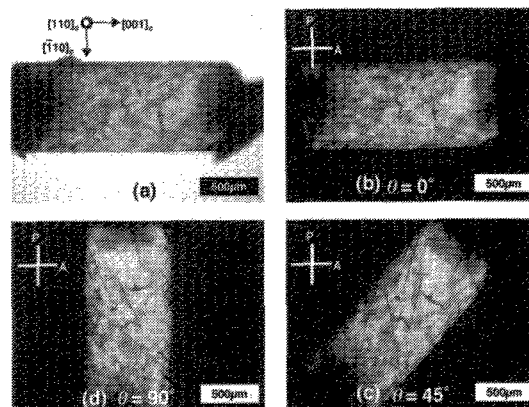


Fig. 6 Domain observation of the $[001]_c$ nonpoled KNbO_3 crystal at various rotation angles (ϕ).

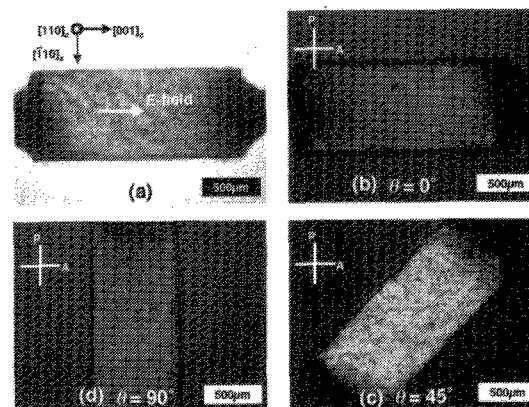


Fig. 7 Domain observation of the $[001]_c$ poled KNbO_3 crystal at various rotation angles (ϕ).

The electric field was applied along the $[001]_c$ direction. Crystallographically, these domain walls were assigned to non- 180° domain walls such as 60° , 90° and 120° walls. In Fig. 7, at ϕ of 0° , the entire crystal was in the diagonal position while at ϕ of 45° , the crystal moved to the extinction position.¹⁴⁾ Moreover, by 90° , the same phenomena was repeated. It should be noted that though the crystal was composed of a lot of fine domains, the entire crystal was oriented in the extinction and diagonal position simultaneously. This phenomenon was explained by a simple model. Before poling, the monoclinic crystal had 12 polar vectors with an equivalent magnitude and different directions. However, $[001]_c$ poled KNbO_3 crystal was composed of just eight polar vectors, except for four polar vectors with four directions of $[110]_c$, $[1-10]_c$, $[-110]_c$ and $[-1-10]_c$. Considering this model, the result of the domain observation in Fig. 7 is completely explained. However, the domain structure in Fig. 7 cannot be assigned crystallographically.

3.4 Piezoelectric properties of KNbO_3 single crystals

Figure 8 shows frequency dependence of $|Z|$ and θ for the $[110]_c$ poled KNbO_3 crystal. In Fig. 8, the phase angle θ approached around 88° . The resonance frequency f_s and the antiresonance frequency f_p estimated from Fig. 8 were 785.5 Hz and 813.5 Hz, respectively. Similar investigation was performed for the $[001]_c$ oriented KNbO_3 crystals. Figure 9 shows frequency dependence of $|Z|$ and θ for $[001]_c$ poled KNbO_3 crystal. In Fig. 9, θ reversed from -90° to around 86° . The resonance frequency f_s and the antiresonance frequency f_p estimated from Fig. 9 were 688.8 Hz and 717.7 Hz, respectively.

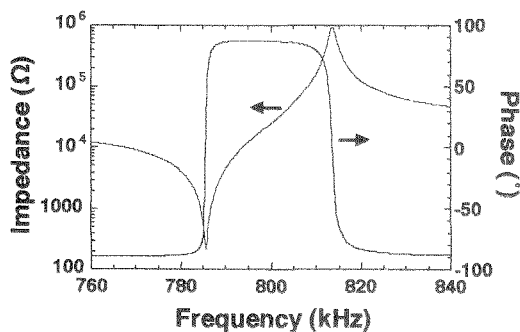


Fig. 8 Frequency dependence of $|Z|$ and θ measured at 25°C for $[110]_c$ oriented KNbO_3 crystals poled using 2-step poling method.

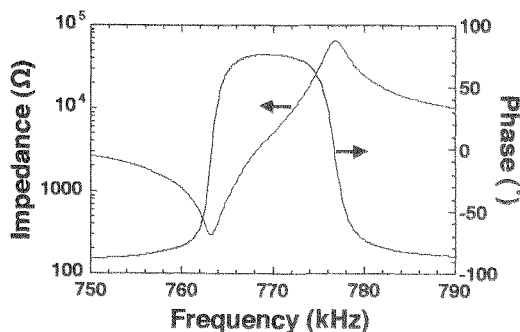


Fig. 9 Frequency dependence of $|Z|$ and θ measured at 25°C for $[001]_c$ oriented KNbO_3 crystals poled using 2-step poling method.

The $[110]_c$ poled KNbO_3 crystals with apparent single-domain state exhibited k_{31} of 28.9% and d_{31} of 18.4 pC/N while the $[001]_c$ poled KNbO_3 crystals with strange domain configuration exhibited k_{31} of 31.2% and d_{31} of 51.7 pC/N. The piezoelectric constant d_{31} along nonpolar $[001]_c$ direction was 2.8 times higher than that along polar $[110]_c$ direction. At present, it is difficult to explain an origin of this difference, *i.e.*, orientation dependence on the basis of a crystallographic engineering or contribution of domain walls. For this purpose, much harder study will be required.

4. CONCLUSION

Domain configurations of KNbO_3 crystals were investigated as a function of temperature, crystallographic direction and electric field. When temperatures were changed from -100°C to 500°C , the domain configuration of KNbO_3 single crystals was also changed at the following phase transitions. Using the 2-step poling method, KNbO_3 crystals were poled, and then their piezoelectric properties of k_{31} modes were measured using a resonance method. KNbO_3 crystals poled along $[110]_c$ showed almost single-domain state apparently while the $[001]_c$ poled KNbO_3 crystals exhibited the complicated strange domain configuration, which cannot be assigned crystallography. The $[110]_c$ poled KNbO_3 crystals exhibited k_{31} of 28.9% and d_{31} of 18.4 pC/N while the $[001]_c$ poled KNbO_3 crystals exhibited k_{31} of 31.2% and d_{31} of 51.7 pC/N. The d_{31} along nonpolar $[001]_c$ direction was 2.8 times higher than that along polar $[110]_c$ direction. On the basis of the above results, we confirm that KNbO_3 crystal is a promising material for piezoelectric application.

5. ACKNOWLEDGMENT

This study was partially supported by (1) a Grant-in-Aid for Scientific Research (11555164) from the Ministry of Education, Sports, Science, Culture and Technology, Japan and (2) TEPCO Research Foundation.

7. REFERENCES

- 1) S.-E. Park and T. R. Shrout: J. Appl. Phys. 82 (1997) 1804.
- 2) S.-E. Park, S. Wada, L.E. Cross and T.R. Shrout: J. Appl. Phys. 86 (1999) 2746.
- 3) S. Wada, S.-E. Park, L. E. Cross and T. R. Shrout: J. Korean Phys. Soc. 32 (1998) S1290.
- 4) S. Wada, S.-E. Park, L. E. Cross and T. R. Shrout: Ferroelectrics 221 (1999) 147.
- 5) S. Wada, S. Suzuki, T. Suzuki, T. Noma, S.-E. Park, L.E. Cross and T.R. Shrout: Jpn. J. Appl. Phys. 38 (1999) 5505.
- 6) B. T. Matthias: Phys. Rev. 75 (1949) 1771.
- 7) E. Wiesendanger: Ferroelectrics 6 (1974) 263.
- 8) P. Gunter: Jpn. J. Appl. Phys. 16 (1977) 1727.
- 9) M. Zgonik, R. Schlessler, I. Biaggio, E. Voit, J. Tscherry and P. Gunter: J. Appl. Phys. 74 (1993) 1287.
- 10) S. Wada, A. Seike and T. Tsurumi: Jpn. J. Appl. Phys. 40 (2001) 5690.
- 11) H. Kumagai, K. Murata, Y. Tanabe and T. Fukuda: Denshidenkitsuushinngakkai, QQE88-43 (1988) 43. [in Japanese]
- 12) EMAS-6100: Standard of Electronic Materials Manufacturers Association of Japan (1993).
- 13) J. Fousek: Czech. J. Phys. B21 (1971) 955.
- 14) E. E. Wahlstrom: Optical Crystallography (John Wiley and Sons, New York, 1979) 5th ed., Chap. 10.

(Received December 21, 2002; Accepted January 31, 2003)