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**GROWTH OF KNbO₃ THIN FILMS ON MgO
BY PULSED LASER DEPOSITION**

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Abstract

Crystalline and stoichiometric KNbO₃ thin films have been grown on (100) oriented MgO substrates by pulsed laser deposition technique. Electron microprobe analysis and Rutherford backscattering spectroscopy of the films show a progressive loss of K with increasing substrate-target distance. To compensate for this K loss the ceramic KNbO₃ targets were enriched with K₂CO₃ powder, pressed at room temperature and sintered at 650° C. For a substrate-target distance of 6 cm, targets with [K]/[Nb] molar ratio = 2.85 yield stoichiometric KNbO₃ films. A partial oxygen pressure of 2 x 10⁻² mbar was optimum for growing transparent films. Films grown between 650 and 700° C show the KNbO₃ crystalline phase with its (110) axis preferentially oriented perpendicular to the surface of the substrate. At these temperatures KNbO₃ diffusion into the MgO substrate is observed. Films grown from KNbO₃ single crystal targets only contain a Mg₄Nb₂O₉ crystalline layer.

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Although both the electro-optical and nonlinear optical properties of bulk KNbO_3 single crystals compare rather favourably with other optoelectronic materials, the widespread application of KNbO_3 crystals for optical devices is limited because of the difficulty, and cost, of growing large single crystals. Moreover, KNbO_3 undergoes structural and ferroelectric phase transitions at 225°C . During cooling through this temperature, the nucleation of several types of domains may introduce cracking in the sample thereby increasing loss via light scattering, and this therefore severely limits the practical production of waveguides by diffusion of metals, and ion exchange techniques. So far, optical waveguides in bulk KNbO_3 crystals have been reported only by low temperature techniques, i.e. electro-optic light confinement ¹ and He^+ ² or proton ³ implantation.

Different methods have been used to produce epitaxial KNbO_3 films on substrates suitable for waveguiding applications. Thick films have been grown by liquid phase epitaxy (LPE) ⁴, producing waveguides which were multimode, due to the relatively large thickness of the films (some few microns). In order to produce monomode waveguides, thinner films have been produced by ion beam sputtering ⁵ and by rf-diode sputtering ⁶.

Moreover, the epitaxial growth of ferroelectric layers on semiconductor substrates allows other applications such as ferroelectric permanent memories, piezoelectric sensors or the integration of nonlinear optical media with semiconductor light sources. This integration has been realized using pulsed laser deposition (PLD) to grow BaTiO_3 ⁷ and LiNbO_3 ⁸ onto buffer layers of MgO on (001) and (111) oriented GaAs wafers respectively.

PLD has been also successfully used to grow a variety of dielectric and

ferroelectric oxides directly on insulating substrates for optoelectronic applications: LiNbO_3 ⁹ and LiTaO_3 ¹⁰ on sapphire; BaTiO_3 on (100) MgO , (110) SrTiO_3 and (100) LiF ¹¹; $\text{Bi}_{12}\text{GeO}_{20}$ on (100) ZrO_2 ¹² or $\text{KTa}_{0.67}\text{Nb}_{0.33}\text{O}_3$ on (110) SrTiO_3 ¹³. The latter material is cubic at room temperature ($\text{Pm}\bar{3}\text{m}$ space group) and hence does not exhibit any linear electro-optic effect¹¹. To our knowledge, the successful growth of KNbO_3 by PLD has not been reported.

In this letter we report on the PLD growth of epitaxially oriented KNbO_3 thin films on MgO single crystals substrates. The choice of MgO as a substrate fulfils the refractive index requirement for waveguide application, since its refractive index, $n_{\text{MgO}} = 1.735$ (at 633 nm) is smaller than any of the three values of refractive index of KNbO_3 (ranging from 2.169 to 2.331 at 633 nm). Moreover, MgO is cubic with a room temperature lattice parameter $a = 4.213 \text{ \AA}$. For the deposition temperatures used in this work, $T \approx 650^\circ \text{C}$, KNbO_3 is also cubic crystal with $a \approx 4.03 \text{ \AA}$ which is only about 5% smaller than the MgO lattice at this temperature, $a \approx 4.24 \text{ \AA}$, allowing a reasonable lattice match between the substrate and film. Films from 100 to 1000 nm thickness have been prepared at an average deposition rate of 18 nm/min (0.15 \AA /pulse). This deposition rate is 60 times faster than that obtained by rf sputtering⁶ and should scale readily with higher laser repetition rates.

The films have been deposited using the arrangement in figure 1. $\text{KNbO}_3/\text{K}_2\text{CO}_3$ ceramic and KNbO_3 single crystal targets were ablated by focusing the light from a pulsed KrF excimer laser (Lambda Physik, model LPX, $\lambda = 248 \text{ nm}$). The laser provided pulses of 20 ns width and $\approx 200 \text{ mJ}$ of energy per pulse. The ablation threshold of KNbO_3 single crystal targets was found to be 200

mJ/cm² but to achieve the deposition rate above, a flux of 5 J/cm² was used to ablate single crystals and 2.5 J/cm² for the ablation of ceramic targets. Typically, the chamber was initially evacuated to 1 x 10⁻⁴ mbar with a turbo molecular pump and later back-filled with oxygen to the required pressure, 2 x 10⁻² mbar. At this pressure, transparent films were produced with an optical absorption edge at 300 nm. Films prepared at lower oxygen pressures appeared dark, and exhibited broad optical absorption features in the visible spectral region.

In order to obtain homogeneous films as required for waveguide applications the substrate was held 60 mm away from the target. Films deposited to room temperature were amorphous. Crystalline films were prepared by heating the substrate with a 10 W CO₂ laser as shown in figure 1, so that the film is directly heated and also simultaneously annealed during deposition. The temperature of the substrate was monitored with a chromel-alumel (K-type) thermocouple glued to the reverse side of the substrate with silver paint.

Previous reports on the growth of niobium oxides, i.e., LiNbO₃⁷ and KTa_{0.7}Nb_{0.3}O₃¹⁰, have indicated the loss of light elements (Li and K) during deposition. To compensate for this, a segmented 50%KNO₃/50%KTa_{0.7}Nb_{0.3}O₃ target was used to achieve stoichiometric KTa_{0.67}Nb_{0.33}O₃ film growth¹⁰. For target-substrate distances of 60 mm we found a similar problem when KNbO₃ single crystals targets were used. The K deficiency of the films is a function of the substrate-target distance, due very likely to the complicated plume dynamics. Figure 2 shows the [K]/[Nb] molar ratio calculated by scanning electron microprobe analysis for films deposited on glass substrates, as a function of the substrate-target distance. From figure 2, it is seen that films grown from KNbO₃ single

crystal targets may have [K]/[Nb] ratios close to 1 only when the substrates are placed close to the target. However, because of the small angular spread of the plume, the uniformity of these films will be poor. Homogeneous films can be prepared by increasing the substrate-target distance, but the films prepared are K-deficient (figure 2). Moreover, films produced on hot (765° C) MgO using KNbO₃ single crystal targets do not contain any potassium, and only a Nb-rich layer is produced at the substrate surface.

To maintain the correct [K]/[Nb] ratio in the deposited film, K-rich ceramics were prepared by mixing KNbO₃ and K₂CO₃ powders in various ratios. The mixture was pressed at room temperature and later heated at 650° C to remove the carbon. During this process, some KO₂ loss is also expected, so the [K]/[Nb] composition of the targets was subsequently analyzed by electron microprobe. This analysis showed that the carbon concentration of the target used was below the detection limit of the microprobe analysis. It was determined empirically, that ceramics with a composition of [K]/[Nb] = 2.85 lead to correct stoichiometric film growth.

Figure 3 shows a comparison of the x-ray diffraction spectra observed for films grown from KNbO₃ single crystal and K-rich ceramic targets on hot MgO single crystal substrates. Grazing incidence x-ray scattering spectra were taken with a D-500 Siemens diffractometer, using the K_α emission from a Cu anode.

The electron microprobe analysis of films grown from KNbO₃ single crystal targets shows that the K concentration in the film is negligible, and the x-ray diffraction peaks observed in figure 3(a) do not correspond to those expected from the desired KNbO₃. Most of the peaks observed fit well with those expected from

crystals of the $\text{Mg}_4\text{Nb}_2\text{O}_9$ structure¹⁵. The only exception is the peak at $2\theta = 47^\circ$, corresponding to an interplanar distance of 1.93 Å. The origin of this peak remains uncertain, but it is likely it may be related to other Mg/Nb oxides; such as MgNb_2O_6 ¹⁶, $\text{Mg}_5\text{Nb}_4\text{O}_{15}$ ¹⁷ or $(\text{MgNb})_{12}\text{O}_{29}$ ¹⁸.

Figure 3(b) shows a x-ray diffraction spectrum of a film grown from a ceramic target ($[\text{K}]/[\text{Nb}] = 2.85$) at 650°C . This spectrum shows a dominant peak corresponding to the (110) interplanar distance of KNbO_3 and its harmonic (220); a peak corresponding to an interplanar distance of 1.94 Å is also present as in figure 3(a), suggesting that some Nb diffusion into the MgO substrate has taken place.

Those two films were further analyzed using Rutherford Backscattering Spectroscopy (RBS). Figure 4 shows the RBS spectra of the films grown from single crystals (figure 4(a)) and ceramic (figure 4(b)) targets. Comparison of both spectra shows that the peak associated with the presence of K in the film grown from the ceramic target is not present in the film grown from the KNbO_3 single crystal target. This result, as expected, agrees with the electron microprobe analysis and with the x-ray diffraction spectra shown in figure 3.

The RBS spectra of figure 4 have been simulated using the RUMP¹⁹ analysis software. The experimental data of figure 4(b) are well modelled by assuming a 240 nm thick layer of $\text{KNb}_{0.99}\text{O}_3$ on top of a 170 nm thick layer where a linear interdiffusion between KNbO_3 and MgO has occurred. The thin layer (40 nm thick) of $\text{KNbO}_3 + \text{C}$ (in the ratio 1:10), on top of the layers above was included because of the carbon coating of the sample for the previous electron microprobe analysis. The fit obtained for the RBS spectrum corresponding to the film grown from a

KNbO₃ single crystal target (figure 4(a)) shows that the film is composed of a single layer of Mg₄Nb₂O₉, 310 nm thick, in addition to a region of 380 nm where a linear diffusion of Mg₄Nb₂O₉ and MgO has been assumed.

In summary, we have reported the growth of stoichiometric and preferentially oriented crystalline KNbO₃ films on (100) MgO substrates by pulsed laser deposition technique. This has been achieved using K-rich ceramic targets ([K]/[Nb] = 2.85), an oxygen pressure of 2×10^{-2} mbar and heating the substrates to 650-700^o C. These films are potentially suitable for optoelectronic applications. The interdiffusion of KNbO₃ and MgO must be taken into account in future work in relation with the substrate-film boundary and the refractive index profile.

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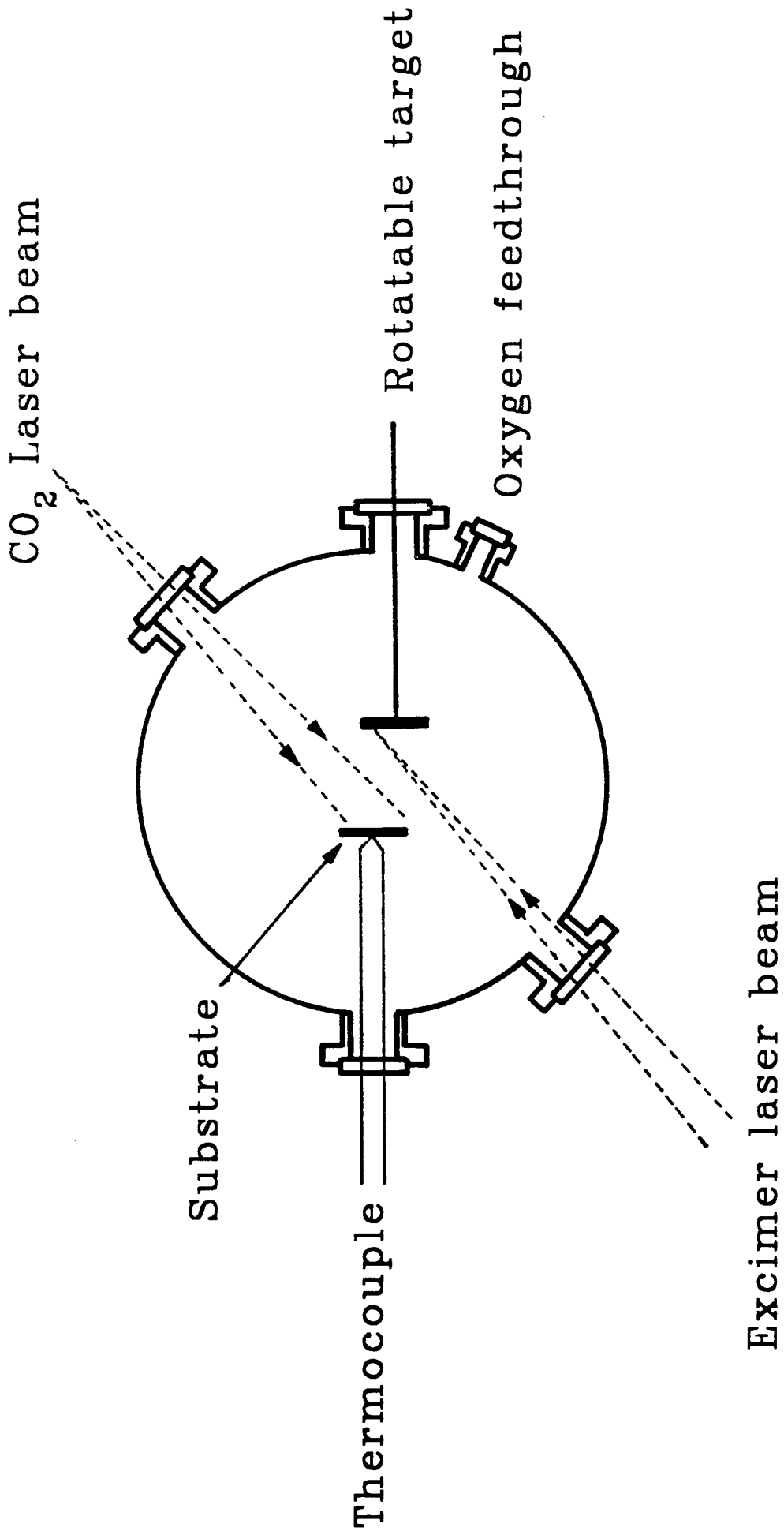
Figure Captions

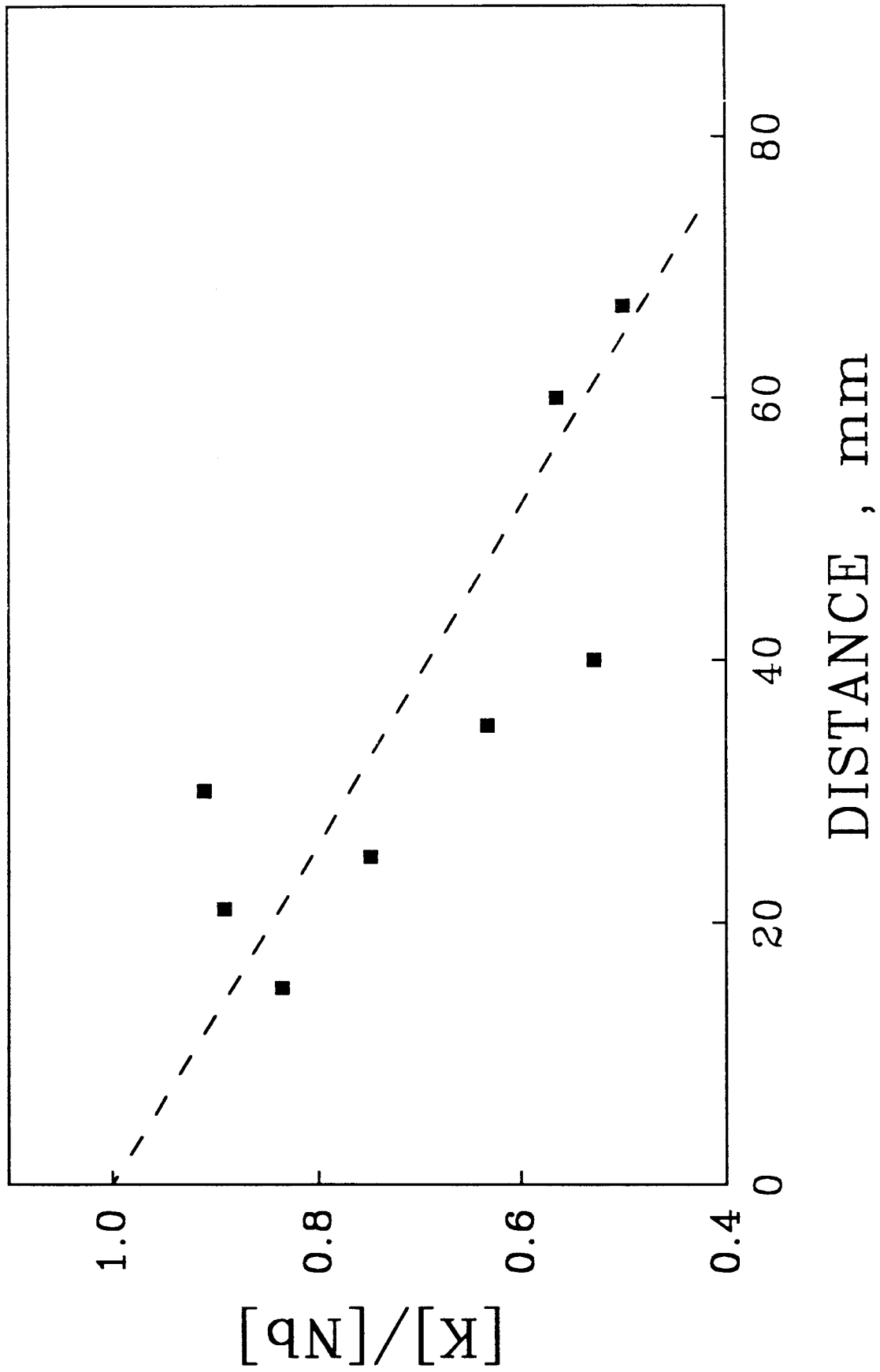
Figure 1. Experimental arrangement used for pulsed laser deposition and heating the MgO substrate with a CO₂ laser.

Figure 2. Ratio of potassium, [K], and niobium, [Nb], concentration of the films as a function of the substrate-target distance used for deposition. The [K]/[Nb] ratio has been calculated by electron microprobe analysis. The line is not a best fit, but an aid for the eye.

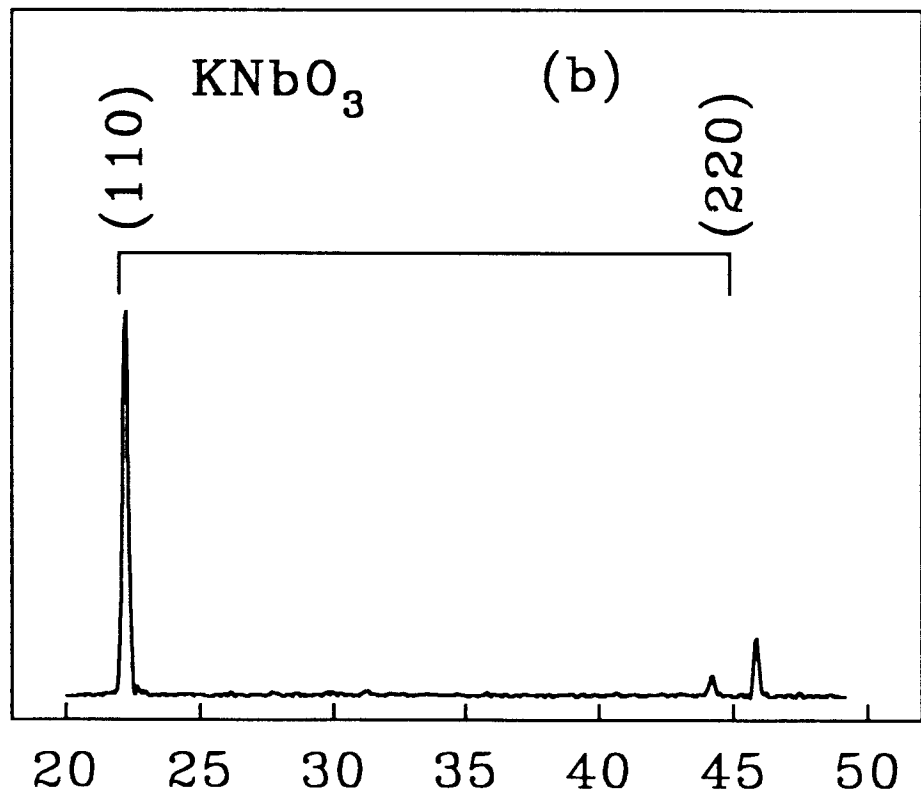
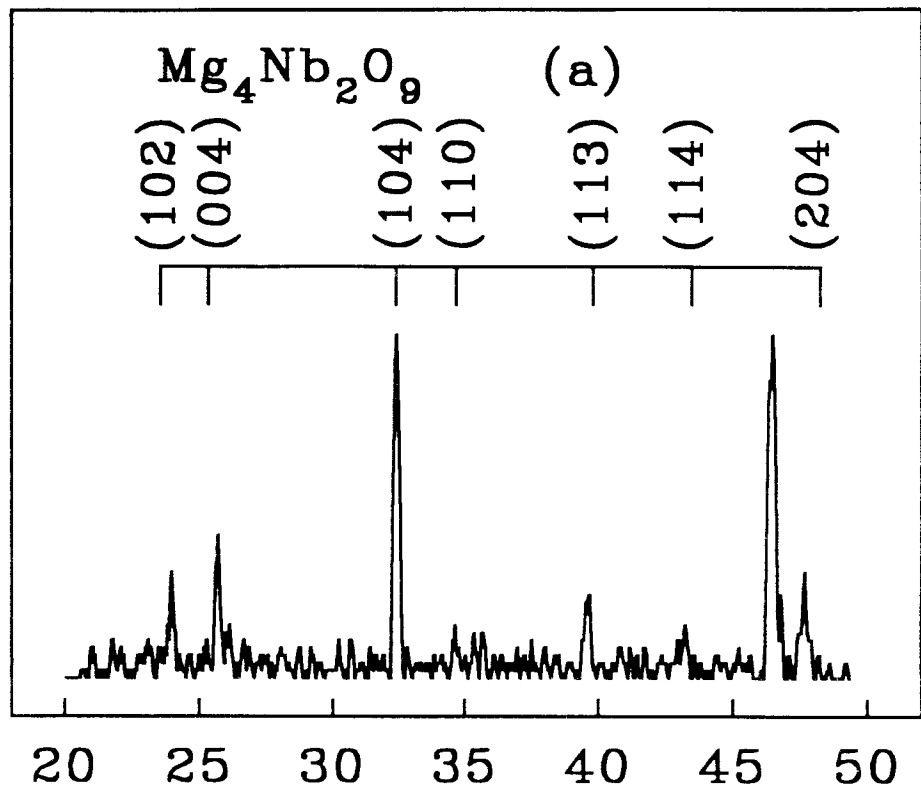
Figure 3. X-ray diffraction patterns of the films formed on (100) MgO single crystal substrates. (a) Film deposited at 765° C from a KNbO₃ single crystal target. (b) Film deposited at 650° C from a ceramic target with [K]/[Nb] = 2.85. The diffraction peaks identified have been marked.

Figure 4. Rutherford Backscattering spectra of the films grown on (100) oriented MgO single crystal substrates. The points are the experimental results and the lines represent the fit obtained assuming the compositions sketched in the figure. (a) Film deposited at 765° C from a KNbO₃ single crystal target. (b) Film deposited at 650° C from a ceramic target with [K]/[Nb] = 2.85.

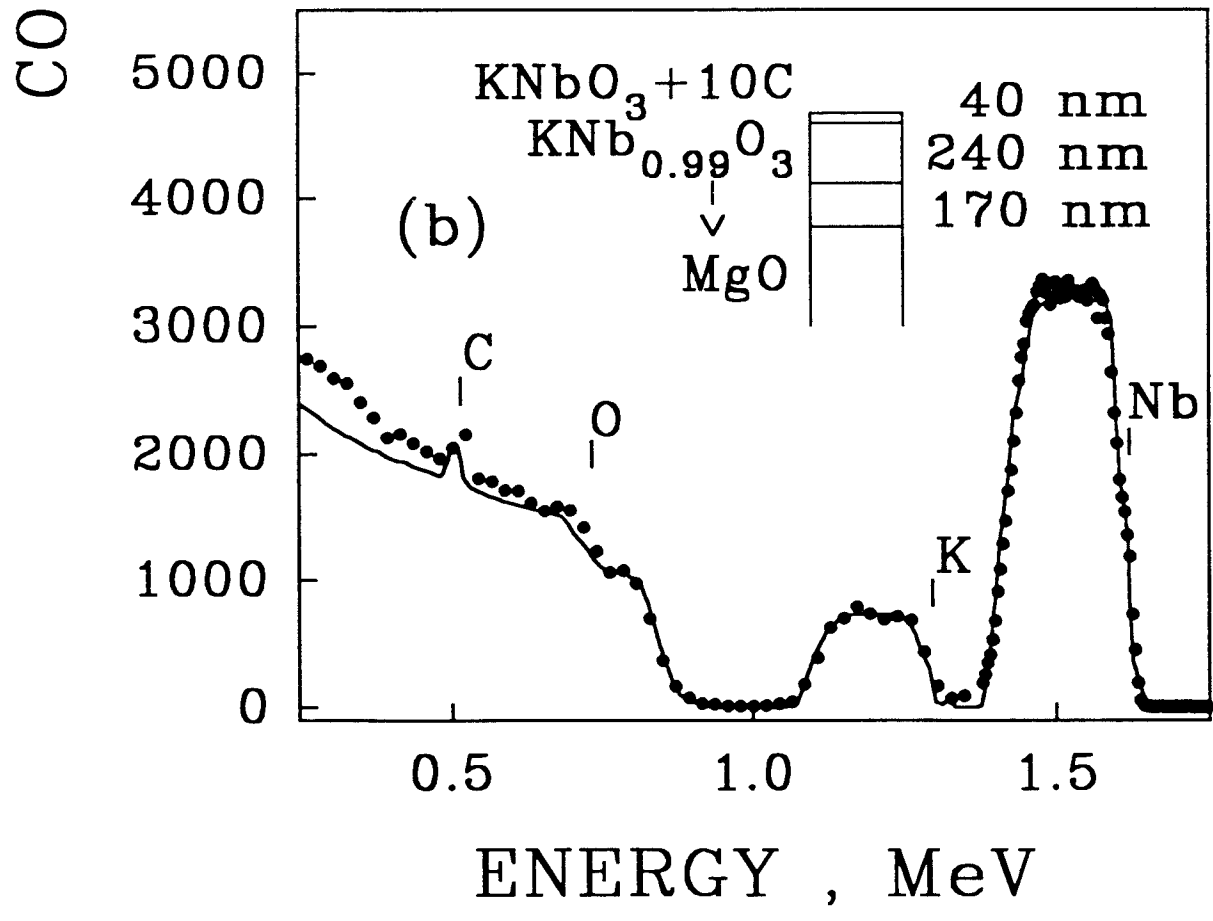
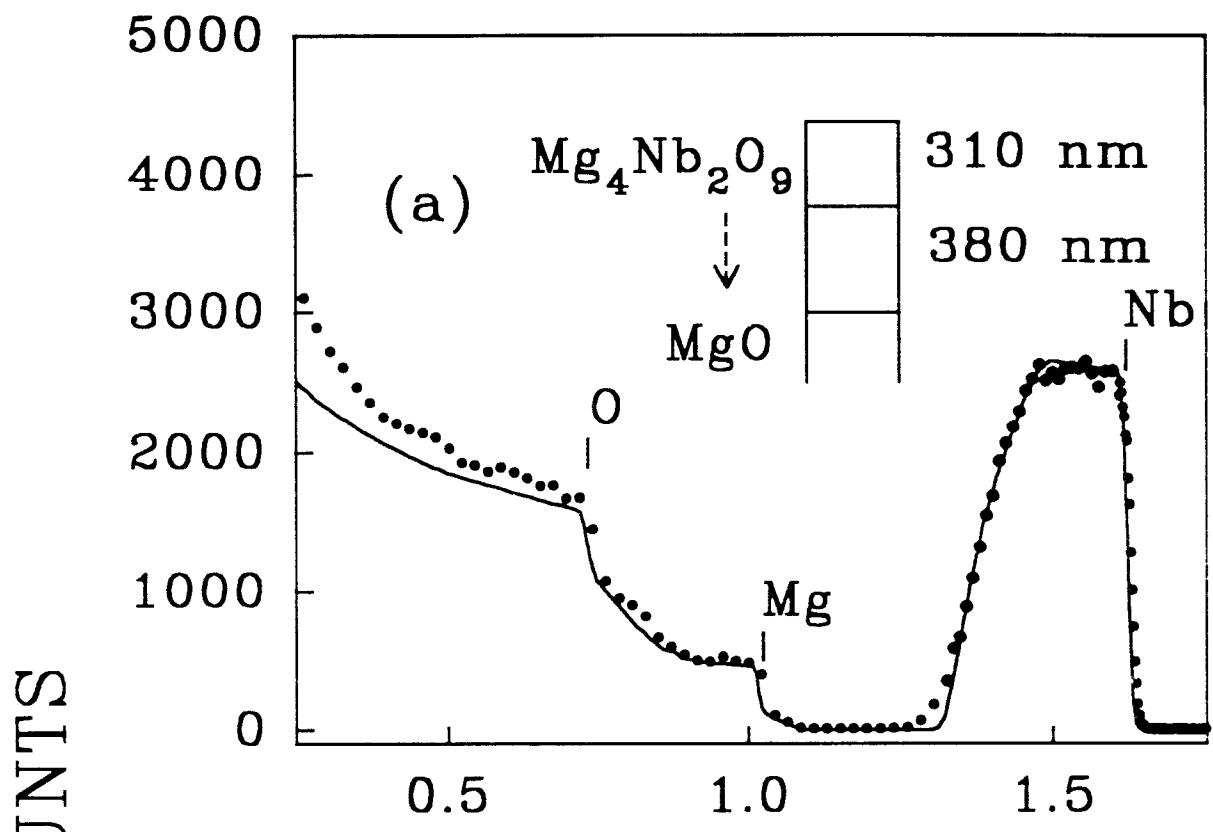




X-ray INTENSITY , arb. u.



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