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GROWTH OF $KNbO_3$ THIN FILMS ON MgO BY PULSED LASER DEPOSITION

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Abstract

Crystalline and stoichiometric $KNbO_3$ 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 $KNbO_3$ targets were enriched with K_2CO_3 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 $KNbO_3$ films. A partial oxygen pressure of 2×10^{-2} mbar was optimum for growing transparent films. Films grown between 650 and 700° C show the $KNbO_3$ crystalline phase with its (110) axis preferentially oriented perpendicular to the surface of the substrate. At these temperatures $KNbO_3$ diffusion into the MgO substrate is observed. Films grown from KNbO3 single crystal targets only contain a $Mg_4Nb_2O_9$ 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]; $Bi_{12}GeO_{20}$ on (100) ZrO_2 [12] or $KTa_{0.67}Nb_{0.33}O_3$ on (110) $SrTiO_3$ [13]. The latter material is cubic at room temperature ($Pm\bar{3}m$ space group) and hence does not exhibit any linear electro-optic effect [11]. 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, $n_{MgO} = 1.735$ (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 Å. For the deposition temperatures used in this work, T ≈ 650° C, $KNbO_3$ is also cubic crystal with a ≈ 4.03 Å which is only about 5% smaller than the MgO lattice at this temperature, a ≈ 4.24 Å, 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 Å/pulse). This deposition rate is 60 times faster than that obtained by rf sputtering [6] and should scale readily with higher laser repetition rates.

The films have been deposited using the arrangement in figure 1. $KNbO_3/K_2CO_3$ ceramic and $KNbO_3$ single crystal targets were ablated by focusing the light from a pulsed KrF excimer laser (Lambda Physik, model LPX, λ = 248 nm). The laser provided pulses of 20 ns width and ≃ 200 mJ of energy per pulse. The ablation threshold of $KNbO_3$ single crystal targets was found to be 200

mJ/cm^2 but to achieve the deposition rate above, a flux of 5 J/cm^2 was used to ablate single crystals and 2.5 J/cm^2 for the ablation of ceramic targets. Typically, the chamber was initially evacuated to 1×10^{-4} mbar with a turbo molecular pump and later back-filled with oxygen to the required pressure, 2×10^{-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 CO_2 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., $LiNbO_3$ [7] and $KTa_{0.7}Nb_{0.3}O_3$ [10], have indicated the loss of light elements (Li and K) during deposition. To compensate for this, a segmented $50\%KNO_3/50\%KTa_{0.7}Nb_{0.3}O_3$ target was used to achieve stoichiometric $KTa_{0.67}Nb_{0.33}O_3$ film growth [10]. For target-substrate distances of 60 mm we found a similar problem when $KNbO_3$ 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 $KNbO_3$ 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 $KNbO_3$ 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 $KNbO_3$ and K_2CO_3 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 KO_2 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 $KNbO_3$ 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 $KNbO_3$ 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 $KNbO_3$. Most of the peaks observed fit well with those expected from

crystals of the $Mg_4Nb_2O_9$ strucutre [15]. The only exception is the peak at $2\Theta = 47^o$, 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], $Mg_5Nb_4O_{15}$ [17] or $(MgNb)_{12}O_{29}$ [18].

Figure 3(b) shows a x-ray diffraction spectrum of a film grown from a ceramic target ([K]/[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 RUMP [19] analysis software. The experimental data of figure 4(b) are well modelled by assuming a 240 nm thick layer of $KNb_{0.99}O_3$ 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 $KNbO_3$ + 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

$KNbO_3$ single crystal target (figure 4(a)) shows that the film is composed of a single layer of $Mg_4Nb_2O_9$, 310 nm thick, in addition to a region of 380 nm where a linear diffusion of $Mg_4Nb_2O_9$ and MgO has been assumed.

In summary, we have reported the growth of stoichiometric and preferentially oriented crystalline $KNbO_3$ 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° C. These films are potentially suitable for optoelectronic applications. The interdiffusion of $KNbO_3$ and MgO must be taken into account in future work in relation with the substrate-film boundary and the refractive index profile.

Acknowledgements

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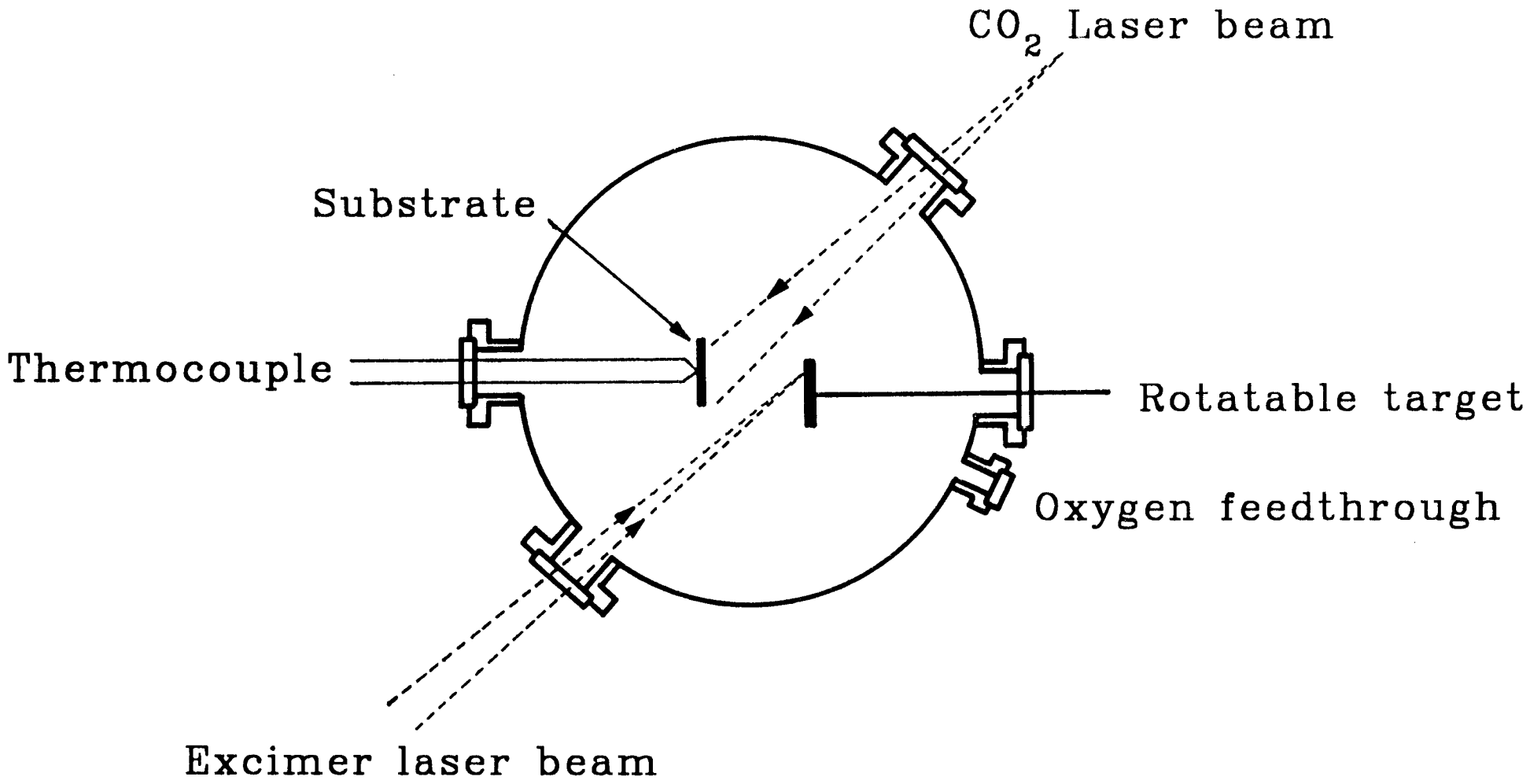
Figure Captions

Figure 1. Experimental arrangement used for pulsed laser deposition and heating the MgO substrate with a CO_2 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 $KNbO_3$ 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 $KNbO_3$ single crystal target. (b) Film deposited at 650° C from a ceramic target with [K]/[Nb] = 2.85.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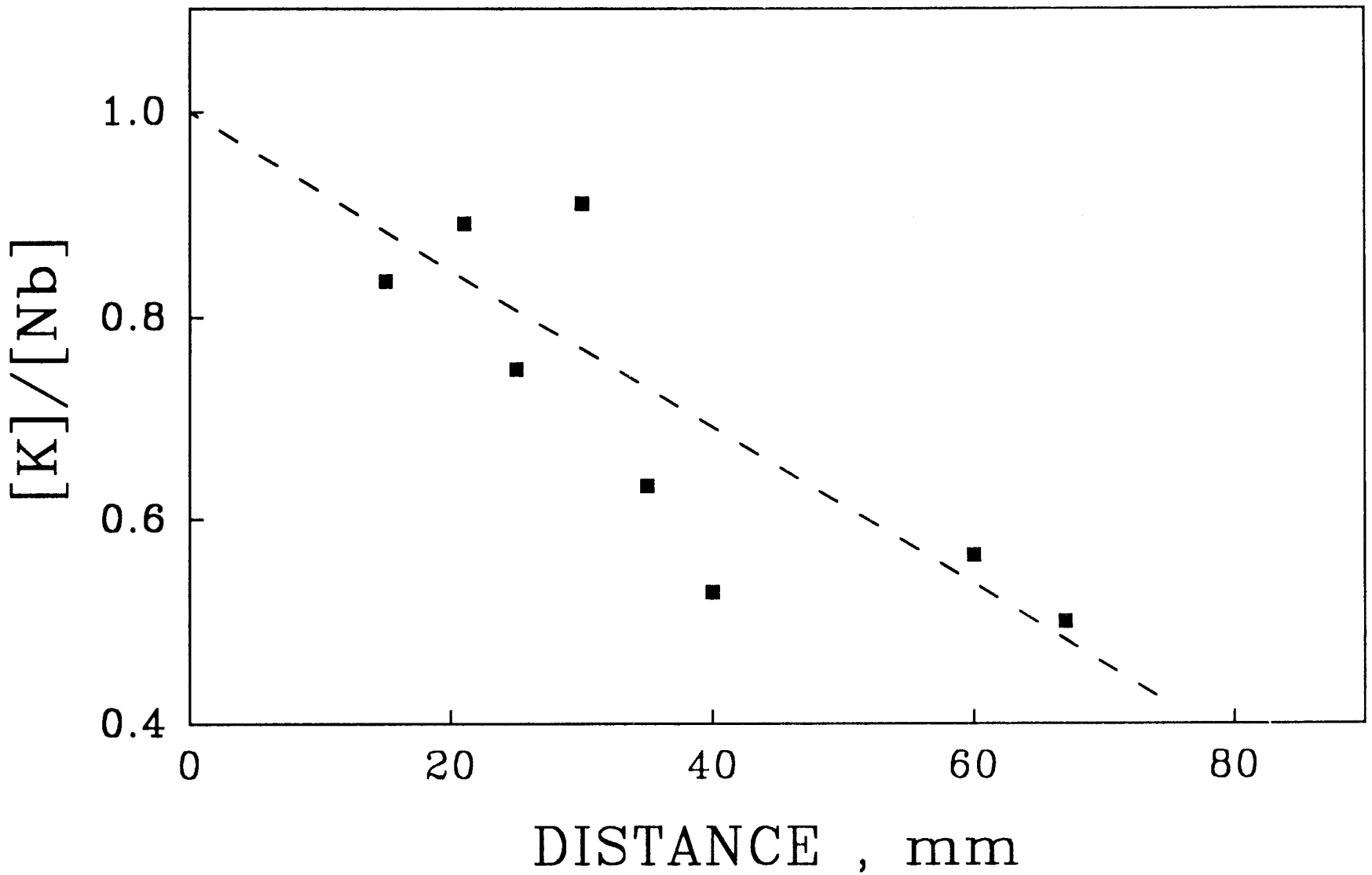
Substrate
Thermocouple
Rotatable target
Oxygen feedthrough
Excimer laser beam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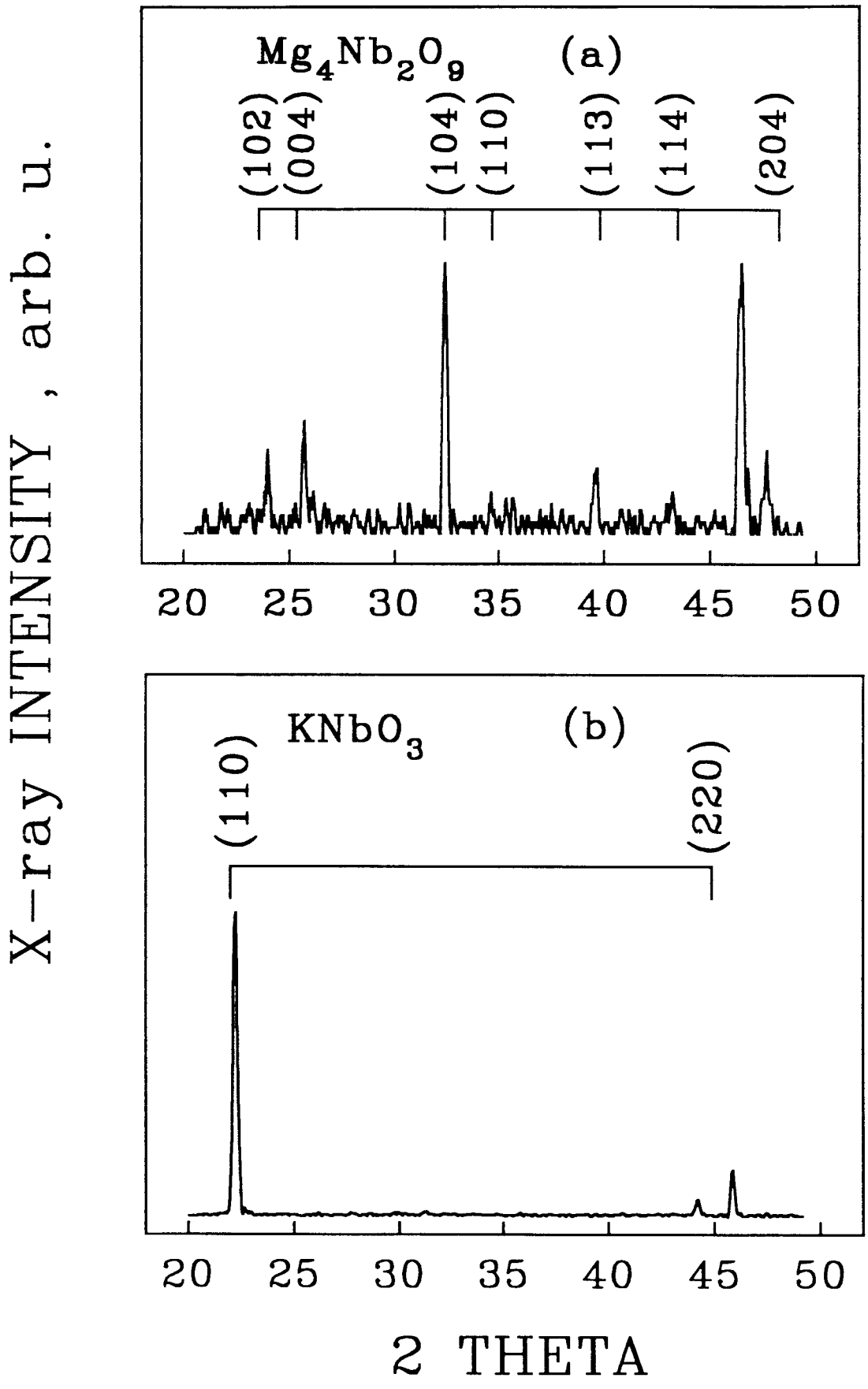
0.6
0.4
[K]/[Nb]
0
20
40
60
80
DISTANCE , mm


X-ray INTENSITY , arb. u.
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(a)
(102)
(004)
(104)
(110)
(113)
(114)
(204)
20
25
30
35
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45
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$KNbO_3$
(b)
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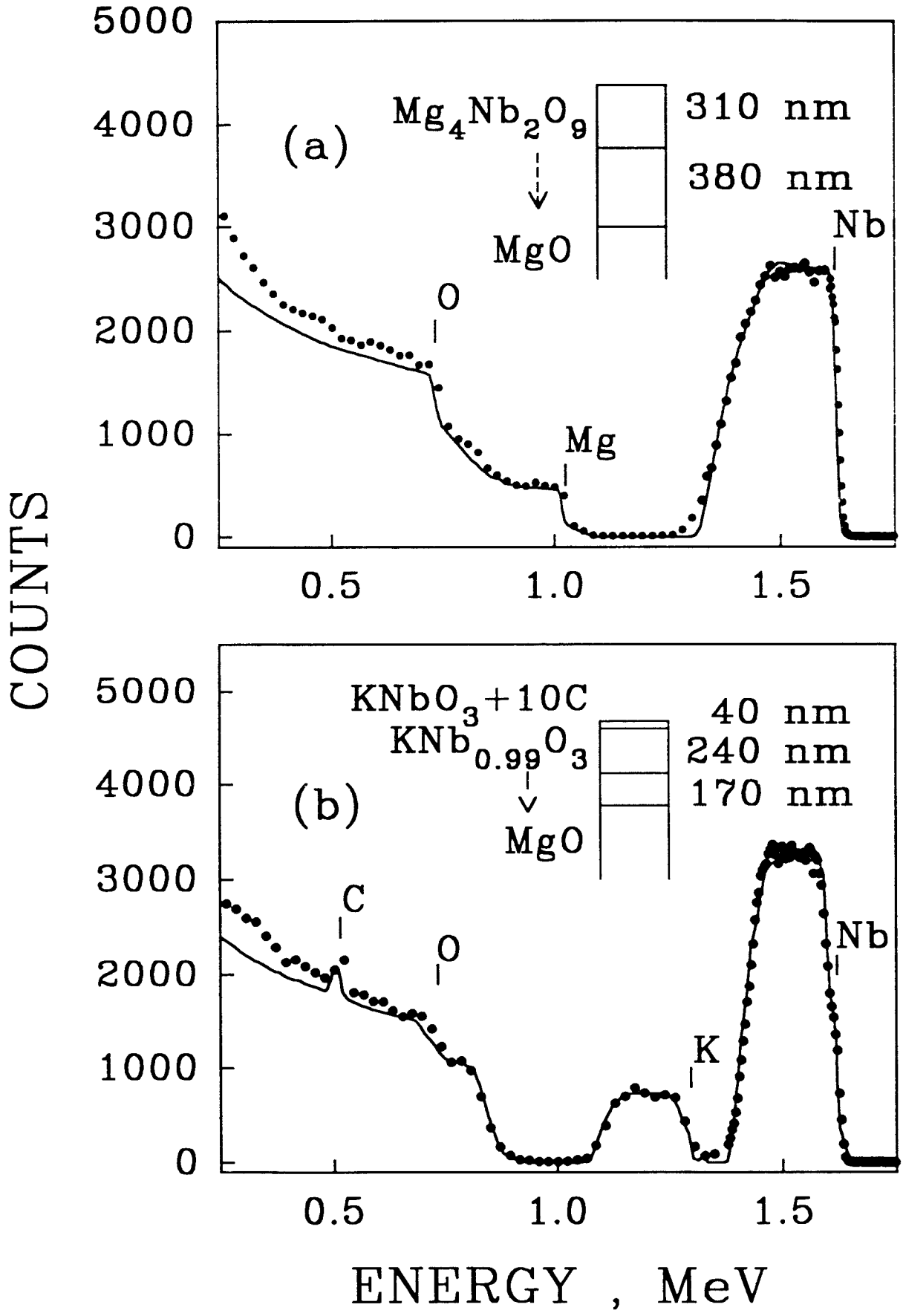
2 THETA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(a)
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380 nm
O
Mg
Nb
0.5
1.0
1.5
5000
4000
3000
2000
1000
0
(b)
$KNbO_3$+10C
$KNb_{0.99}O_3$
MgO
40 nm
240 nm
170 nm
C
O
K
Nb
0.5
1.0
1.5
COUNTS
ENERGY , MeV

Fig 4