

CONF-980731--

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JUN 12 1998

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Submitted to

Optical Diagnostic Methods for Inorganic Transmissive Materials, ed. by R. U. Datla and L. M. Hanssen, International Symposium on Optical Science, Engineering, and Instrumentation, SPIE, 43rd Annual Meeting
 July 19-24, 1998
 San Diego, CA

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June 1998

Prepared by
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 managed by
 LOCKHEED MARTIN ENERGY RESEARCH CORP.
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 U.S. DEPARTMENT OF ENERGY
 under contract DE-AC05-96OR22464

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Transient grating in a KNbO₃/KTaO₃ superlattice

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ABSTRACT

Time-resolved degenerate-four-wave-mixing (DFWM) techniques have been used to characterize the nonlinear optical response of a KNbO₃/KTaO₃ superlattice grown by pulsed laser deposition on a 1 mm thick, (001)-oriented KTaO₃ substrate. With a 30 psec pulsed laser, the difference in the nonlinear optical response between bulk KTaO₃ and the superlattice was measured. Results indicate that a significant contribution to the response signal is due to the KNbO₃ superlattice. The $\chi^{(3)}$ value was estimated to have increased by 2 orders of magnitude compared to the bulk crystal.

Key words: superlattice, KNbO₃/KTaO₃, thin film, grating, wave mixing, PLD

1. INTRODUCTION

Potassium tantalate and potassium niobate are of particular interest among perovskite-structure ABO₃ materials because their para- or ferroelectric properties can be drastically altered by small changes in structure - introduced either mechanically, by stress¹, or chemically, by introducing other ions. Pure KTaO₃ is a cubic-symmetry crystal with a mean B-O distance of $a = 1.99 \text{ \AA}$, and is always in the paraelectric phase. By contrast, pure KNbO₃ changes its phase from cubic (O_h , $Pm3m$) into tetragonal (C_{4v} , $P4mm$) at 704 K, and into orthorhombic (C_{2v} , $Amm2$) at 498 K, and finally becomes rhombohedral (C_{3v} , $R3m$) with a mean B-O distance of 2.85 \AA at 265 K in a ferroelectric phase. The development of pulsed laser deposition (PLD) in the last decade has permitted the successful preparation of niobate and tantalate thin films deposited onto a variety of substrates. This offers new opportunities to study the variation of optical properties with structural changes. PLD-grown KTN (KTa_{1-x}Nb_xO₃) thin films have shown changes in the second-order electro-optical coefficients² from bulk crystal values. Other thin films and superlattices, such as SBN³, SBT⁴, BTO/STO⁵ prepared by PLD also show dramatic changes in their properties. We have systematically studied the nonlinear optical (NLO) properties of pure KTaO₃ and KNbO₃, as well as mixed crystal KTN⁶, among which KNbO₃ exhibited a particular sensitivity of NLO response with respect to its optical orientation.⁷

In this work, a superlattice with excellent crystalline quality and consisting of alternating layers of paraelectric KTaO₃ and ferroelectric KNbO₃ (KNO/KTO superlattice) was grown on a KTaO₃ (001) substrate by PLD. The lattice mismatch is less than 0.5%. The alternating KNbO₃ and KTaO₃ films were grown using a KrF excimer ($\lambda = 248\text{nm}$) laser as a light source. The superlattice consists of a total of 8 layers with thicknesses of 40 nm (KTaO₃) and 30 nm (KNbO₃). The fabrication details have been given elsewhere¹.

2. EXPERIMENTAL

The NLO response of the superlattice was characterized using a degenerate-four-wave-mixing (DFWM) technique. A frequency-trippled Y₃Al₅O₁₂:Nd laser operated at 355 nm with pulse width of 30 ps was used for optical parametric generation. The output wavelength can be continuously tuned from 400 to 700 nm. In order to determine which wavelength can be best used for characterization, the two-photon absorption (TPA) effect was tested. With the laser tuned at 450 - 525 nm, significant TPA would cause a change in spectral width of the DFWM signal, as observed in a pure KNbO₃ crystal.⁶ On the other hand, tuning the wavelength beyond 560 nm caused the DFWM signal to become too weak in the transverse geometry. Therefore the final measurement was conducted at 532 nm. Fig. 1 shows the experimental setup for characterization of the

NLO response of the superlattice sample. The laser beam is split into two pump beams and a probe beam, the latter carrying 10% of the total laser power. The probe goes through an optical delay line and is then incident on the sample from the substrate side. The two pump beams are crossed on the film at an angle, interfering to form a transient grating in the film. The delay line in one of the pump beam paths is used to ensure simultaneity of the pulses at the sample. The beam size of the probe is about 50% that of the pump. Thus, the probe can uniformly sense the susceptibility within the interference region of the two pump pulses. DFWM methods for thin films have been amply discussed in the literature.^{8,9} All the beams in our experiment were in backward phase conjugation configuration, which can allow higher signal-to-noise ratio. The difference in index of refraction between substrate and film, or between two different layers, is expected to be very small in our case, so that any influence due to this source would be negligible. Further, beam-crossing was carefully adjusted. The two beams were separated on the film surface while measuring the substrate signal, whereas they were crossed in the thin film layers while measuring the film response. Therefore, the influence due to the substrate on the thin film could be reduced.

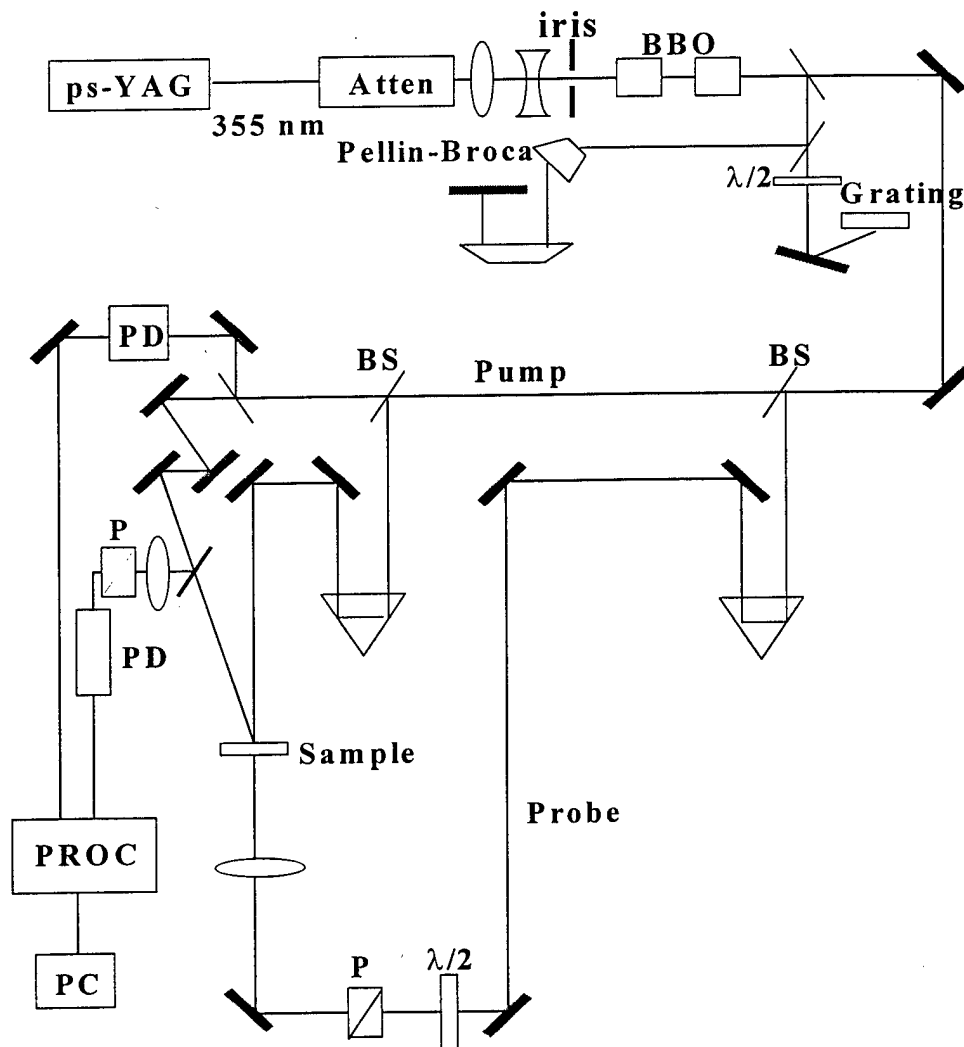


Figure 1. Experimental setup for picosecond pulsed-laser DFWM.

The spectrum obtained for the substrate was compared to that from bulk KTaO_3 crystal and found to be the same. The pump-pulse intensity was typically 30 - 50 mJ/cm^2 . The polarization for all measurements was perpendicular to the incidence plane for all beams (ssss). In this case, the time-resolved NLO response obtained can adequately measure the film's NLO properties.

3. TRANSIENT GRATING

Fig. 2 shows the DFWM signal of the KTaO_3 substrate, KNO/KTO superlattice, and a CS_2 reference crystal-versus-probe-pulse delay in a ± 250 psec region. The diffraction signal intensity is normalized. For the film sample, the laser intensity was typically 50 mJ/cm^2 while for CS_2 it was 30 mJ/cm^2 . Within the 500ps time scale, for either KNO/KTO or CS_2 one can see an instantaneous nonlinear optical response signal with a half width of about 35 psec located at zero delay of the probe pulse. This coherent signal is associated with the inherent third-order susceptibility $\chi^{(3)}$ of the measured material. The signal width is close to the autocorrelation width of the three pulses. In the superlattice, two more interesting features are observed.

First, a significant enhancement of $\chi^{(3)}$ was found for the superlattice film. The value of $\chi^{(3)}$, which is evaluated by calculating the coherent signal intensity was found to be increased by 2 orders of magnitude in the transverse configuration, compared to the bulk sample. When the two pump pulses are polarized in the same direction, the coherent signal component is directly related to the third-order susceptibility by^{10,11}

$$\eta = \exp(-ad/\cos\theta) \sin^2(d\pi\Delta n/\lambda\cos\theta) , \quad (1)$$

where

$$\Delta n = \frac{12\pi}{n_0 \langle E^2 \rangle} \chi^{(3)} , \quad (2)$$

E is optical electric field, d is the grating thickness, and 2θ is the crossing angle of the two pump pulses. Considering the alternating layers' nature and a total 30 nm thickness of the KNbO_3 crystalline layers in the film, we obtained the following values: for KTaO_3 substrate : $\chi_{1111} = \chi_{2222} = \chi_{3333} = 0.32 \times 10^{-13} \text{ cm}^3 \text{ erg}$; for the KNO/KTO superlattice thin film: $\chi = 0.93 \times 10^{-11} \text{ cm}^3 \text{ erg}$.

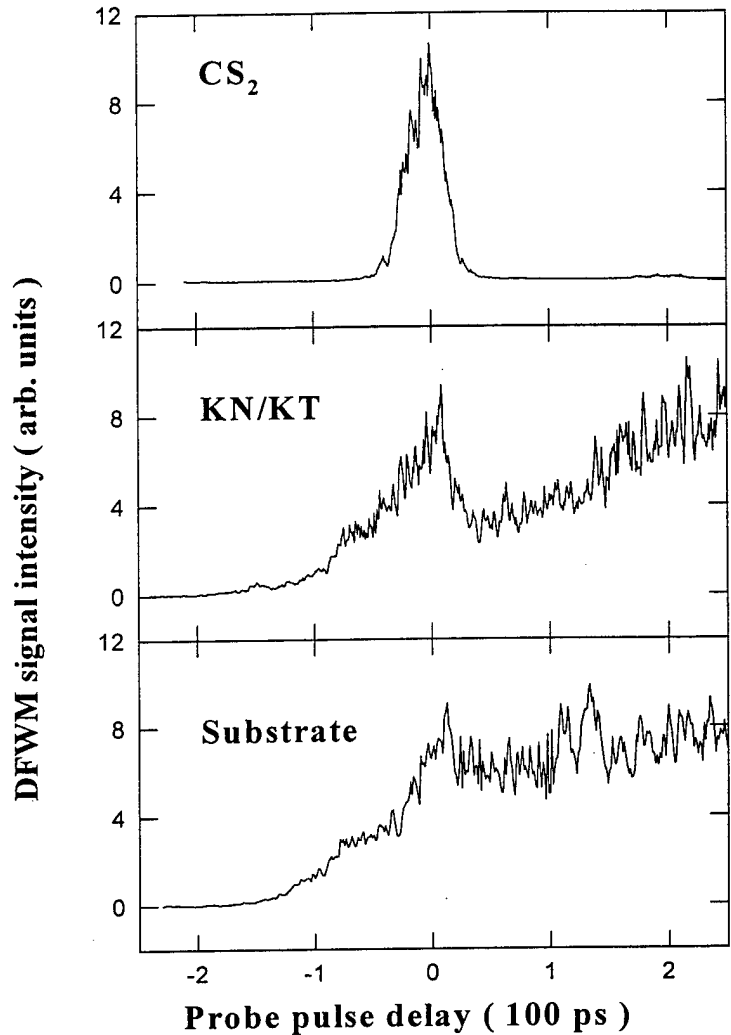


Figure 2. Time-resolved DFWM spectra show the coherent NLO response for the $\text{KNbO}_3/\text{KTaO}_3$ superlattice. The response signal from CS_2 at zero-delay is taken as a reference. In the substrate of pure KTaO_3 crystal the coherent signal is overwhelmed by the long-lived signal component.

Second, the coherent signal for the KNO/KTO superlattice was found to be followed by a buildup of a long-lived, yet distinguishable signal. Further, the buildup feature can be enhanced by exposure to laser pulses for longer time. At the beginning of the experiment, the coherent signal behaved similarly to that of the CS₂ standard sample, showing a symmetric narrow peak overlapped on a shoulder at positive delay. The shoulder gradually rose with time. After a certain dose of laser exposure, the signal intensity of the shoulder could reach a relatively stable maximum value. Each time the sample was repositioned, the buildup of the long-lived signal repeated the same pattern. It is, therefore, understood as a local structure change (not a permanent grating) induced by the two pump pulses.

The intrinsic nonlinear optical response signal generated in this circumstance can be analyzed as the probe beam diffracted by the grating formed by the two pump pulses A and B, which intersect at an angle of 2θ inside the thin film. The grating vector is $q = \pm (k_A - k_B)$, confined in the film along the x direction. The electric field amplitude A is

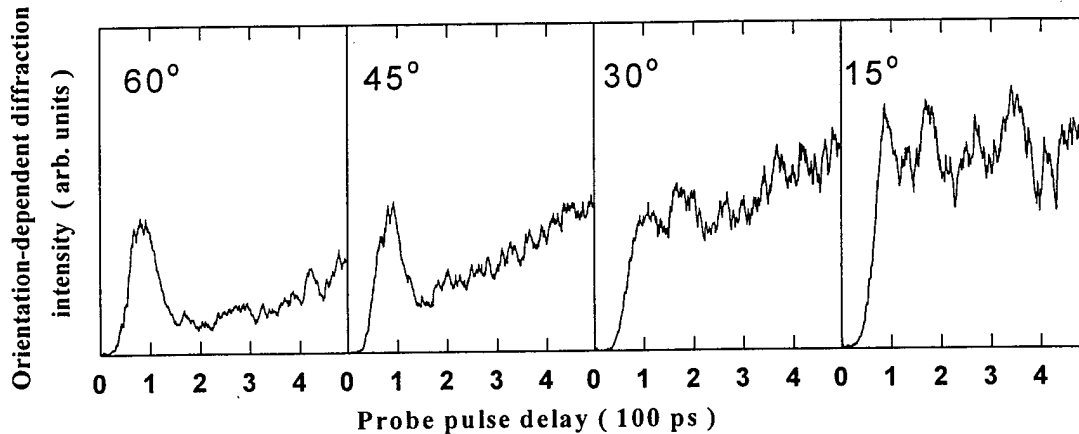
$$A = A_A e^{+ikx} + A_B e^{-ikx} , \quad (3)$$

where k represents the wavevector. The light intensity is then modulated as

$$I = I_A + I_B + 2\Delta I \cos(2kx) , \quad (4)$$

where $\Delta I = 1/2n\epsilon_0 A_A \cdot A_B$. In our experiment, $I_A = I_B$, so $I = 2I_A(1 + \cos(qx))$ for identical polarizations (ss) of A_A and A_B . The diffracted signal intensity is directly related to the third-order susceptibility as expressed by Eq.(1). However, since the ferroelectric crystalline KNbO₃ layers were not poled into a single domain, the intense optical electric field of the laser pulses may induce local polarization transversely. The characteristic orientation dependence for DFWM in KNbO₃ single-domain crystal was reported before.⁷ As shown in Fig. 3, the behavior of the long-lived signal component buildup depends on the orientation of the crystal C-axis with respect to the grating vector. When the angle ϕ (between C-axis and grating vector) equals 90°, only a narrow coherent response signal could be observed. However, when ϕ decreases towards 0°, the buildup rises. The signal intensity of the long-lived component can be simply characterized as varying with $(\cos \phi)$ as characterized

Figure 3. DFWM signal intensity of a KNbO₃ single domain crystal versus probe pulse delay at the angle ϕ varying from 60° to 15°.



in the literature⁷.

Compared to the orientation dependence of NLO response for the ferroelectric KNbO₃ crystal, the buildup behavior

observed in the KN/KT superlattice is, therefore, believed to originate from the laser-induced local structure change.

4. TRANSIENT GRATING DECAY

The long-lived response signal as shown in Fig.4 is actually not associated with the inherent third-order susceptibility of the material. It does relate to the change in polarizability of material in the excited state, due to laser excitation, versus the ground state. As discussed in [6], this signal component is attributed to the population grating produced by the interference of the two crossed laser pulses. In the bright region of the grating, the intrinsic interband transition occurs between the valence band, which consists of $p\pi$ orbitals of the oxygen electrons, and the conduction band, which consists of $d\zeta$ orbitals of Nb electrons. The free carriers created in the conduction band become trapped at Nb^{5+} centers to form a charge transferred vibronic exciton (CTVE)¹². The contrast of the grating is provided by the difference in ligand positions around excited Nb^{4+} ions in the bright regions and unexcited Nb^{5+} ions in the dark regions. This signal component has a risetime of several tens of picoseconds which corresponds to the free carrier lifetime in the $KNbO_3$ crystal. The $Nb^{4+}-O^-$ exciton decays with a typical time scale of tens of nanoseconds either by fluorescence or trapping at defect sites. On the other hand, however, experiment has shown that the decay rate of CTVE in $KTaO_3$ is 1.6×10^8 /s, lower than its counterpart of 4.3×10^8 /s in $KNbO_3$.⁷ In the KN/KT superlattice, the measured rate is 1.9×10^8 /s, i.e. less than the value for the bulk sample.

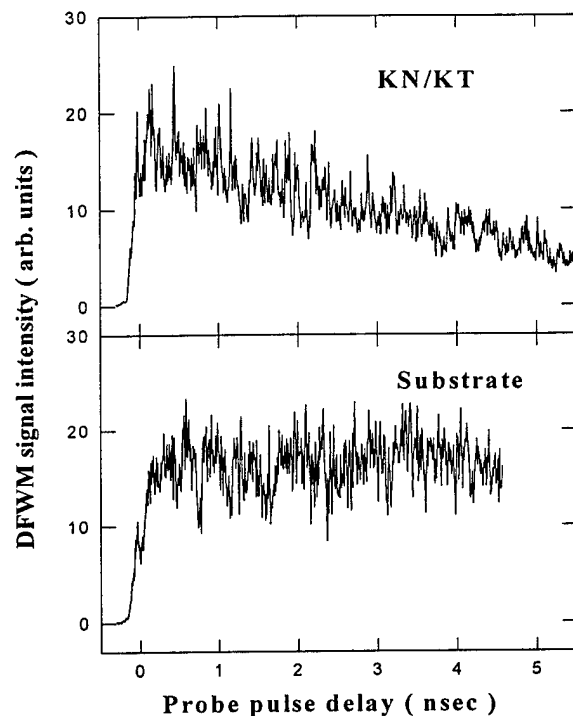


Figure 4. Time-resolved DFWM spectra of KN/KT superlattice and $KTaO_3$ substrate in 6 nanoseconds.

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4. ACKNOWLEDGMENTS

This work was supported by US DoE (Grant DE-FRO2-94ER757640), US ARO (Grant DAAH04-96-10416), NASA-URC (Grant NCCW-0088) and NSF (Grant EHR-9108775)

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M98005662



Report Number (14) ORNL/CP--98.324
CONF-980731

Publ. Date (11) 199806
Sponsor Code (18) DOE/ER, XF
UC Category (19) UC-400, DOE/ER

19980707 017

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