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Deuterium/Hydrogen Ratio in DKDP Crystals by Laser Photothermal Radiometry

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Abstract—A nondestructive technique is proposed for determining the fraction of deuterium in DKDP crystals by photothermal radiometry, which involves measurement of the thermal heating induced by IR laser pulses close in frequency to the second harmonic of the fundamental O–H mode. This technique relies on the dependence of the 1.34-μm absorption on deuterium concentration.

INTRODUCTION

Electrooptic and nonlinear optical properties of deuterated potassium dihydrogen phosphate (DKDP) crystals depend in large measure on the deuterium-to-total-hydrogen atomic ratio. Therefore, the ability to measure and control deuterium content of DKDP crystals is crucial to the performance of choppers, deflectors, frequency converters, and other optical devices fabricated from these crystals.

It is well known that deuterium concentration in DKDP single crystals is always lower than that in the growth solution by a value that depends on crystal growth conditions. Therefore, deuterium concentration should be measured in the grown crystals rather in solution; moreover, it is desirable to trace deuterium distribution over a crystal, since it may be nonuniform as a result of changes in growth conditions.

The known procedures for measuring deuterium concentration in DKDP crystals have a number of inherent drawbacks. Gravimetry of the starting material and thermal decomposition products ensures a fairly high measurement accuracy but is not always acceptable because of the material destruction.

Deuterium concentration can also be determined by near-IR spectroscopy using the second harmonic of the fundamental O–H mode. Since the frequency of molecular and lattice vibrations depends on the mass of vibrating atoms, the range of strong absorption in deuterium-rich crystals is shifted to longer wavelengths. The dependence of the 1.5-μm absorption on deuterium concentration can be successfully used to analyze deuterated water [1]. This method is, however, less convenient in studies of crystals, since it requires special specimens with highly parallel, polished faces. Another limitation of this method is the necessity of using long specimens. For example, Bespalov *et al.* [2] measured IR absorption on crystals up to 8 cm long. Deuterium-rich crystals pose particular problems, since, in this case, Fresnel's losses dominate over absorption, reducing measurement accuracy.

To overcome these difficulties, we propose here a nondestructive technique for determining the fraction of deuterium, γ, in DKDP crystals by photothermal radiometry, which involves measurement of the thermal heating induced by IR laser pulses close in frequency to the second harmonic of the fundamental O–H mode. This technique relies on the dependence of the 1.34-μm absorption on deuterium concentration.

EXPERIMENTAL SETUP

The experimental arrangement is shown in Fig. 1. Polarized radiation from a cw Nd-doped yttrium aluminate laser (*1*) operating at $\lambda = 1.34$ μm is electromechanically chopped (*2*) at frequency *f*. Sequential radiation pulses heat the probed area (*3*), inducing a periodic variation in surface temperature. The alternating component of the thermal radiation signal from the crystal surface is recorded with a lithium tantalate IR sensor (*5*). To improve sensitivity, thermal radiation is focused by an objective (*6*) consisting of germanium lenses, which also protect the IR sensor from the scattered 1.34-μm radiation. The modulation frequency $f = 2.3$ Hz was chosen so as to eliminate the effect of surface finish [3]. The lens (*7*) focusing the laser beam to the crystal surface also ensures substantial divergence of the beam in the crystal bulk; as a result, the backside of the crystal, even unfinished, has no effect on the measurement results.

To improve sensitivity, we use synchronous signal detection (*4*). Note that the measurement technique in

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question requires extremely high sensitivity, because, to avoid crystal cracking, the amplitude of variations in surface temperature should be limited (~0.1°C in our experiments).

RESULTS AND DISCUSSION

To best demonstrate the potential of laser photothermal radiometry for determining deuterium concentration in DKDP, we examined more than ten crystals with γ in the range from 75 to 97%. After photothermal measurements, γ values were determined by weighing the original sample and thermal decomposition products to within ≈0.3% accuracy. To study the effect of surface finish, we tested both as-polished surfaces of 80- to 100-Å roughness and surfaces after long-term exposure to humid air with etch pits up to tenths of a micron deep.

The amplitude U of thermal radiation pulses was found to depend linearly on γ in the range from 75 to 97%:

$$U(\theta) = k(\theta)(100 - \gamma), \quad (1)$$

where $k(\theta)$ is a coefficient that depends only on the orientation of the polarization plane of laser radiation with respect to crystallographic axes of the crystal. Figure 2 displays the dependences of U on the angle θ between the polarization plane and the Y axis for two crystals with $\gamma_1 = 80\%$ and $\gamma_2 = 92\%$. The curves *1* and *2* show the signal measured with the laser beam normal to the z-cut of the crystals; curves *3* and *4* show analogous dependences for the x-cut. Within the present experimental accuracy (≈2%), the latter two curves can be represented by

$$U(\theta) = A\cos^2\theta + B\sin^2\theta, \quad (2)$$

where A and B are constants. This type of dependence shows clear evidence that the thermal radiation pulse is due primarily to heating of the material bulk. The angular dependence of U reflects the difference in the ordinary and extraordinary absorption coefficients of the uniaxial crystal DKDP. No influence of surface finish is detected.

At the same time, one should keep in mind that the surface layer of crystals consists of deformed material containing microcracks, dislocation networks, and elastically strained regions, which extend deeper into the bulk than the cracking layer. It is reasonable to expect that diffusive exchange in the near-surface region proceeds at an increased rate, thus reducing deuterium concentration upon a long-term exposure to ordinary water vapor. Assuming that, as a result of ion exchange, the entire surface layer consists of undeuterated KDP with an ordinary absorption coefficient $\alpha^{o}_{\gamma=0} = 0.35$ cm^{-1} at $\lambda = 1340$ nm, the limiting surface absorption coefficient can be found as

$$\beta = \alpha^{o}_{\gamma=0} d, \quad (3)$$

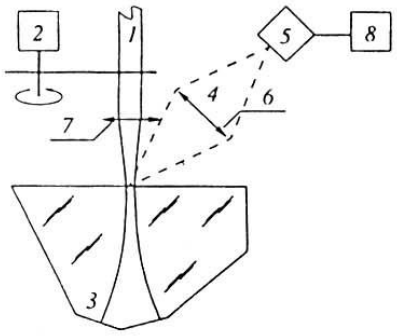

Fig. 1. Experimental arrangement: (*1*) laser radiation, (*2*) chopper, (*3*) crystal, (*4*) thermal radiation, (*5*) pyroelectric detector, (*6*) IR objective, (*7*) lens, (*8*) selective nanovoltmeter.

where d is thickness of the surface damage layer.

Surface absorption has no effect on photothermal radiometry results [3] if

$$\beta \ll \frac{\pi}{2}\sqrt{a\tau}\alpha, \quad (4)$$

where $a \approx 0.0062$ cm^2/s is the thermal diffusivity of the material calculated from the data given in [4, 5], $\tau = 0.2$ s is the laser pulse duration, and α is the volume absorption coefficient.

Therefore, the contribution of the surface damage layer is insignificant if

$$d \ll \frac{\pi}{2}\sqrt{a\tau}\frac{\alpha}{\alpha^{o}_{\gamma=0}}. \quad (5)$$

Obviously, d should be smaller in measurements on heavily deuterated crystals ($\gamma \approx 95\%$), since they have a smaller ordinary absorption coefficient: $\alpha \approx 0.02$ cm^{-1}. Therefore, in determining deuterium concentration in DKDP crystals by laser photothermal radiometry, the uncertainty due to the surface damage layer can be neglected if d is less than 30 μm. (Note for comparison that, in crystals finished by a conventional procedure to 100-Å roughness, the surface damage layer is ~3 μm thick.) In measurements on samples with lower deuterium concentrations, thicker deformed layers are permissible. In any case, the preparation of the sample surface for determining deuterium concentration in DKDP by photothermal radiometry can be confined to rough polishing.

Thus, laser photothermal radiometry provides a means for determining the fraction of deuterium in DKDP crystals in the range 75–97% with an accuracy of 2% by using the calibration dependence (1) rewritten in the form

$$\gamma = 100 - k'(\theta)U(\theta), \quad (6)$$

where $k'(\theta) = \dfrac{1}{k(\theta)}$.

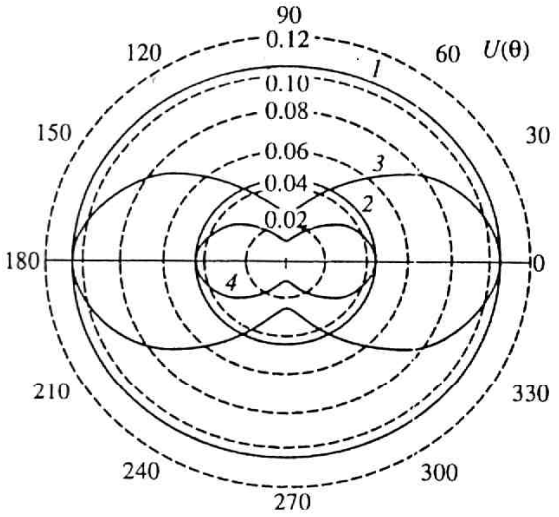

Fig. 2. Amplitude of the thermal radiation signal, U, from two DKDP crystals heated with linearly polarized 1.34-μm laser radiation (θ is the angle between the polarization plane and the y axis of the crystal): (*1*, *2*) incident laser beam normal to the z-cut, $\gamma_1 = 80\%$, $\gamma_2 = 92\%$; (*3*, *4*) incident laser beam normal to the x-cut of the same crystals.

Obviously, the use of $U(\theta)$ values calibrated in arbitrary units provides correct results when measurements are carried out under fixed conditions. At the same time, since the amplitude of the alternating component of the thermal radiation signal is proportional to the volume absorption coefficient α, expression (6) can be transformed to a more general form using the $U(\alpha)$ dependence found in additional experiments [3]:

$$\gamma = 100 - k''(\theta)\alpha(\theta), \qquad (7)$$

with an angle-dependent coefficient $k''(\theta)$. For extraordinarily polarized laser radiation incident at $\theta = 90°$, we obtain

$$\gamma = 100(1 - 8.0\alpha^e), \qquad (8)$$

where α^e (cm^{-1}) is the absorption coefficient for an extraordinary wave. In practice, however, direct use of relation (6) is preferred, since it allows one to eliminate the error introduced by the measured $U(\alpha)$ dependence.

CONCLUSION

Our results demonstrate the potential of laser photothermal radiometry for nondestructive determination of deuterium concentration in DKDP crystals. This technique allows measurements to be performed on roughly polished crystals, without stringent requirements to the flatness of the probed area.

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