Ultrasonic measurement of the elastic constants of sodium *p*-nitrophenolate dihydrate single crystals

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Sodium *p*-nitrophenolate dihydrate single crystals possess excellent nonlinear optical properties such that they can be used for optical second-harmonic generation. It belongs to the orthorhombic system with the space group $Ima2$. Slow evaporation or slow cooling techniques can be used to grow good optical quality single crystals from supersaturated solution. All the nine elastic constants of this crystal have been measured using an ultrasonic technique. Samples for measurements have been cut along desired crystallographic axes and the pulse echo overlap technique has been used to measure longitudinal and shear ultrasonic wave velocities along appropriate symmetry directions in the crystal. The McSkimin Δt criterion has been applied to determine the round trip travel time accurately, from which the nine elastic constants have been evaluated. Temperature variation of selected elastic constants in a limited range have also been measured and reported.

I. INTRODUCTION

Single crystals belonging to the family of nonlinear optical materials find wide application in the areas of laser technology, optical communication, optical information storage, and computing. Extensive research in this field[1,2] has revealed that semiorganic compounds possess a higher degree of optical nonlinearity than their inorganic counterparts. Inherent high nonlinearity, ease with which method of synthesis can be varied, and scope to alter their properties by functional substitutions make these materials highly attractive from the technological point of view. Metal complexes of highly polarizable organic molecules, usually known as semiorganics or organometallics, possess favorable physical properties such as a high damage resistance, which are combinations of the properties of both inorganic and organic crystal constituents. Good size optical quality single crystals can easily be grown from the supersaturated solution either by slow evaporation or slow cooling techniques. Perhaps the latter one is the most attractive feature of this class of compounds from a commercial point of view.

The second-harmonic generation efficiency of sodium *p*-nitrophenolate dihydrate (NPNa) single crystal is nearly 1.2 times that of potassium titanyl phosphate (KTP). The powder efficiency for second harmonic generation for NPNa is reported to be 1 m-NA with meta-Nitro Aniline (m-NA) used as the reference sample.[3] Minemoto and co-workers have reported the linear optical properties, the powder efficiency for second-harmonic generation (SHG), and crystallographic characterization of its molecule.[4,5] Intracavity frequency doubling of a diode laser pumped Nd:YVO_4 laser has been demonstrated employing this material and reported in literature.[6]

NPNa, a metal complex of donor-acceptor substituted aromatic compound, belongs to the orthorhombic system with space group representation $Ima2$. The unit cell parameters are reported to be $a=6.892$ Å, $b=19.692$ Å, and $c=6.439$ Å and has four molecules per unit cell.[8] The molecular formula of NPNa is $Na(C_6H_4NO_3)\cdot 2H_2O$. NPNa molecules are arranged as layers perpendicular to the crystallographic *a* direction and this layered packing of molecules is highly favorable for exhibiting an electro-optic effect.[7] A three-dimensional network of bonding is established by the presence of extensive intermolecular and intramolecular hydrogen bonds in almost two perpendicular directions. Large size optical quality single crystals grown are of reasonably high mechanical hardness and do not exhibit any cleavage. A detailed account of the results of various experiments such as crystal growth, morphology, defect characterization by chemical etching, synchrotron topography, optical transmission, and mechanical hardness have been reported by Brahadeeswaran *et al.*[8] It is found that crystals grown from methanol solution exhibit well-developed faces parallel to (010), (011), and (110) planes.

In this paper, we report the values of all the nine second-order elastic constants of NPNa determined from ultrasonic wave velocities of longitudinal and shear modes propagating along different symmetry directions, measured, using the pulse echo overlap technique. Variation of some of the elastic constants with temperature in a limited range are also reported. Experimental details, results obtained, and a brief discussion of the results, are outlined in the following sections.

II. EXPERIMENTAL METHOD

NPNa material is synthesized by dissolving *p*-nitrophenol in water containing one equivalent of sodium hydroxide. The yellow precipitate so obtained is washed and purified by several recrystallizations from water. Water or methanol can be used as the solvent, but it is found that the crystals grown from methanol solution by slow evaporation technique are found to be of good optical quality compared to that grown from an aqueous solution, which loses transparency within

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TABLE I. The nine elastic constants of NPNa at room temperature (300 K).

No.	Direction of wave propagation	Direction of polarization	Measured ultrasonic velocity ($m\,s^{-1}$)	Mode velocity-elastic constant relation	Elastic constant (GPa)
1	[100]	[100]	$V_1=4402\pm4$	$C_{11}=\rho v_1^2$	$C_{11}=26.38\pm0.05$
2	[010]	[010]	$V_2=4032\pm4$	$C_{22}=\rho v_2^2$	$C_{22}=22.11\pm0.04$
3	[001]	[001]	$V_3=5937\pm6$	$C_{33}=\rho v_3^2$	$C_{33}=47.95\pm0.10$
4	[001]/[010]	[010]/[001]	$V_4=2259\pm2$	$C_{44}=\rho v_4^2$	$C_{44}=6.94\pm0.01$
5	[100]/[001]	[001]/[100]	$V_5=1518\pm2$	$C_{55}=\rho v_5^2$	$C_{55}=3.14\pm0.01$
6	[010]/[100]	[100]/[010]	$V_6=1470\pm2$	$C_{66}=\rho v_6^2$	$C_{66}=2.94\pm0.01$
7	[110]	QL	$V_7=5945\pm6$	$C_{12}=f_{ab}$[a]	$C_{12}=107.7\pm1.08$
8	[011]	QL	$V_8=5518\pm6$	$C_{23}=f_{bc}$[a]	$C_{23}=78.35\pm0.78$
9	[101]	QL	$V_9=3381\pm3$	$C_{13}=f_{ac}$	$C_{13}=-2.53\pm0.03$

[a] $f_{ab}=\{[c^2C_{11}+s^2C_{66}-\rho v_7^2][c^2C_{66}+s^2C_{22}-\rho v_7^2]/c^2s^2\}^{1/2}-C_{66}$;
$f_{bc}=\{[c^2C_{22}+s^2C_{44}-\rho v_8^2][c^2C_{44}+s^2C_{33}-\rho v_8^2]/c^2s^2\}^{1/2}-C_{44}$;
$f_{ac}=\{[s^2C_{11}+c^2C_{55}-\rho v_9^2][s^2C_{55}+c^2C_{33}-\rho v_9^2]/c^2s^2\}^{1/2}-C_{55}$.
s and c are the sine and cosine of the angle of rotation with the respective axes. The angles of rotation are indicated in Fig. 1.

30 min after removal from the mother solution. The supersaturated solution prepared in jacketed vessels is kept in a bath maintained at a constant temperature of 45 °C with a controlling accuracy of ±0.01 °C. For fair mixing of the supersaturated solution and to ensure uniform growth, the suspended seed crystal has been rotated with definite periodic reversals with definite stop periods between two successive reversals. In order to reduce nonuniformity of supersaturation at different areas of the growing faces of the sample, and for faster mass transport for increased growth rate, the motion of the crystal relative to the solution must be ensured without causing turbulence. For this, the seed holder is rotated and the rotations are reversed periodically. Keeping the seed holder stationary for 2 sec between successive rotation reversals eliminates the possibility of occurrence of turbulence. Single crystals of size $22\times17\times16\,mm^3$ have been grown over a period of 2 weeks, with well-developed (010), (110), and (011) faces.

Determination of the nine elastic constants of a crystal belonging to the orthorhombic system requires at least 12 sound velocity measurements for their evaluation, which permit cross-checking of some of the values. All the nine elastic constants of NPNa, viz, C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{23}, and C_{13} have been determined by measuring ultrasonic wave velocities along required propagation directions. Samples with dimensions in the range 0.5–0.9 cm have been cut using a slow speed diamond wheel saw. These samples with parallel faces perpendicular to the [100], [010], [001], [110], [101], and [011] directions have been lightly polished preserving the parallelism between the opposite faces. Density of the crystal has been measured to be 1.36 $g\,cm^{-3}$.

X- and *Y*-cut quartz transducers of resonant frequency 10 MHz have been used to generate ultrasonic waves of longitudinal and transverse polarizations. Silicone grease is found to be a suitable bonding medium to transmit ultrasonic wave pulses into the sample. Ultrasonic pulse echo overlap (PEO) technique[9] is employed to measure the round trip travel time accurately, which is used to evaluate the mode velocity. Standard expressions available in literature[10] are used to evaluate the elastic constants from velocity data. The technical details of the PEO technique are discussed at length in literature.[11] A MATEC model 7700 pulse modulator and receiver system with its associated subunits have been used to carry out these measurements. The McSkimin Δt criterion[12,13] has been applied to identify the correct overlap of the echoes and to correct for the phase change introduced by the bonding medium on the ultrasonic pulses. The accuracy in these measurements is better than 0.2% in the values of diagonal elastic constants and better than 1% for off-diagonal constants, considering all sources of errors in the measurements.

The temperature dependence of selected elastic constants of NPNa crystals have been measured by keeping the crystal transducer assembly in a temperature-controlled oven. Variations in the round trip travel time are recorded for both lon-

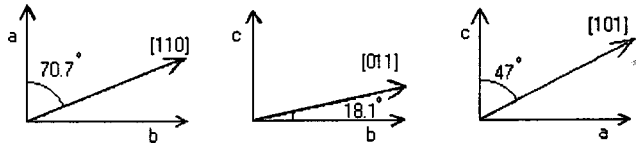

FIG. 1. The angles of rotation chosen from the respective axis.

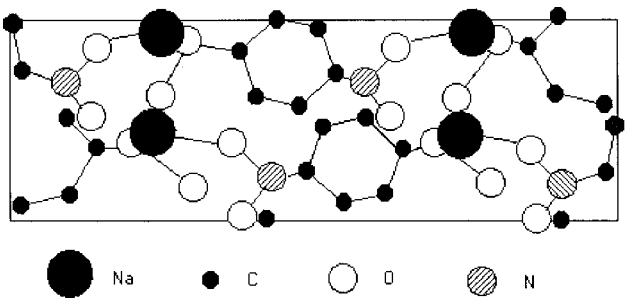

FIG. 2. Packing diagram of NPNa molecules in the *b*-*c* plane.

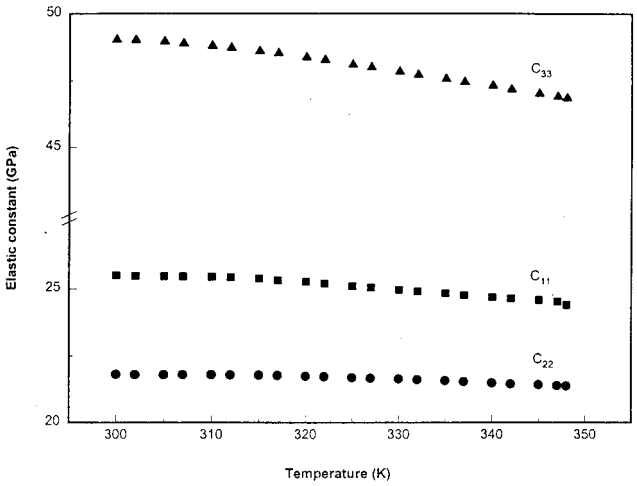

FIG. 3. Variation of elastic constants C_{11}, C_{22}, and C_{33} with temperature.

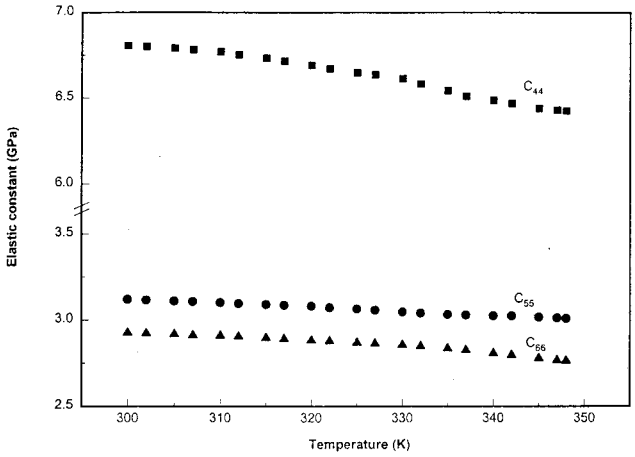

FIG. 4. Variation of elastic constants C_{44}, C_{55}, and C_{66} with temperature.

gitudinal and transverse waves in the temperature range 300–348 K. Thermal expansion of the crystal is neglected in these measurements. Measurements have been limited to 348 K, since at still higher temperatures, the crystal turns red upon dehydration.

III. RESULTS AND DISCUSSION

The complete set of elastic constants of NPNa, determined from ultrasonic wave velocity measurements, are tabulated in Table I along with the velocities of various modes involved. Figure 1 defines the angles of rotation from the respective axes. Calculated values of C_{12} and C_{23} are very large compared to the values of other constants. The off-diagonal constant C_{13} is found to take negative value. The fact that NPNa has a layer structure perpendicular to the crystallographic *a* axis explains these numbers. The crystal structure of NPNa indicates that the oxygen of the water of crystallization is hydrogen bonded to the phenolate oxygen and the infinitely extending hydrogen bond chains form a network in the *b*-*c* plane. The packing diagram of NPNa molecules as viewed perpendicular to the (100) plane is shown in Fig. 2. This can be the reason for high values for C_{12} and C_{23}. Such layered structures with a three-dimensional network of bonding predicts reasonably high mechanical strength along the layers.

The temperature dependence of six of the elastic constants measured by the pulse comparison method is shown in Figs. 3 and 4. All these elastic constants slowly decrease with increase of temperature, which is the general behavior exhibited by most solids. This crystal does not exhibit any elastic anomaly in the 300–348 K temperature range over which the elastic constants have been measured.

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