SECOND HARMONIC GENERATION IN SQUARIC ACID

K. BETZLER

and

D. BÄUERLE
Angewandte Physik, Johannes Kepler Universität, 4045 Linz, Austria

Received 6 December 1978

From the temperature-dependent optical second harmonic generation in squaric acid we conclude that no local symmetry breaking occurs in the high temperature phase of this material.

In the last years squaric acid, H$_2$SQ, (3, 4-dihydroxy-3-cyclobutene-1, 2-dione) has found increasing interest, because, as is generally assumed, it shows quasi two-dimensional behaviour near a second order antiferrodistortive phase transition at about $T_{c,H} \approx 370$ K. The crystal is built of layers wherein C$_4$O$_4$ molecules are linked by hydrogen bonds to 4 neighbouring C$_4$O$_4$ groups. In the high temperature phase the crystal structure is body centered tetragonal with I4/m (C$_{4h}$) symmetry [2,3]. The hydrogen atoms are supposed to be at the center of the O—H—O bonds on the average. In the low temperature phase, which has monoclinic structure with P2$_1$/m (C$_{2h}$) symmetry, the hydrogen atoms are displaced from the center on the average, thereby producing a polarization proportional to the displacement. The planar ferroelectric layers are antiferroelectrically stacked. In deuterated crystals, D$_2$SQ, the transition temperature shifts to $T_{c,D} = 516$ K. This large shift in transition temperature indicates that an ordering process of the protons of the O—H—O bonds drives the phase transition, and that, possibly, the tunneling of the protons is important.

Recently, Nakashima and Balkanski [3] investigated the temperature dependence of Raman active modes. The increase in the band width of the external modes with temperature below $T_c$ was explained by disordering of hydrogen atoms. On the other hand Thackeray et al. [4] suggest that the results of the X-ray and the Raman scattering experiments obtained in the high temperature phase can be explained by orientational disorder, whereby the molecules, i.e. the direction of the C=C bonds, continuously change orientation.

In this note we report on temperature-dependent optical second harmonic generation (SHG) in H$_2$SQ. The experimental setup was described elsewhere [5]. The crystals used in the experiments were transparent and colorless platelets of about 5 X 5 X 1 (b-direction) mm$^3$. The samples were prepared by cleaving crystals which were grown from aqueous solution by the usual method described in ref. [6].

Fig. 1 shows the intensity of the SHG as function of temperature. The propagation of light was parallel to the crystal b-direction. No phase matching was achieved. Below the phase transition the intensity of the SHG increases approximately linearly with increasing temperature. Near $T_{c,H}$ there is a sharp drop in intensity with an inflection point at about 370 K. At higher temperatures the SHG signal vanishes within the accuracy of the measurements. As expected for a second order phase transition, no hysteresis was observed in the curvature for rising and falling temperatures.

Since the structure of H$_2$SQ has inversion symmetry both in the high temperature and the low temperature phase, no SHG in lowest order is expected in
Because the observed SHG intensity is "relatively strong" and seems to increase linearly with temperature below about 340 K, the second mechanism discussed seems to be dominating. From the absence of SHG intensity above the phase transition, we conclude that no symmetry breaking as discussed by Thackeray et al. [4] takes place. We therefore believe that the 245 cm$^{-1}$ Raman line should indeed be assigned to a $A_g$ bulk mode of the crystal, as suggested by Nakashima and Balkanski [3].

We are grateful to Professor J. Petersson and Dipl. Phys. H.D. Maier for valuable discussions, and for supplying the crystals used in the experiments. For one of us (D.B.) it is a pleasure to thank the Linzer Hochschulfonds for financial support.

References

[1] For a review see e.g. J. Feder, Ferroelectrics 12 (1976) 71.