

# A PULSE ECHO DETERMINATION OF THE ELASTIC CONSTANTS OF SODIUM BROMATE

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## ABSTRACT

The elastic constants of sodium bromate ( $\text{NaBrO}_3$ ) single crystals have been determined by the ultrasonic pulse echo method from velocity measurements along [100] and [111] directions. The results [ $c_{11}=5.648$ ,  $c_{12}=2.038$  and  $c_{44}=1.54$ ; in units of  $10^{10}$   $\text{N/m}^2$  at  $25^\circ\text{C}$ ] are compared with other available data. The elastic constants of sodium bromate are discussed in relation to those of sodium chlorate.

## 1. INTRODUCTION

Sodium bromate  $\text{NaBrO}_3$  crystallises in the cubic tetrahedral group. A study of the elastic wave velocities in  $\text{NaBrO}_3$  and in the isomorphous  $\text{NaClO}_3$  was originally suggested<sup>1</sup> in order to detect possible deviations from the classical elastic behaviour, but a precision pulse echo study<sup>2</sup> of  $\text{NaClO}_3$  showed no departures greater than 0.1% from classical theory. The present study of  $\text{NaBrO}_3$  was part of the programme. Even though the substance has been investigated earlier<sup>3-5</sup>, no accurate pulse echo determination of  $c_{ij}$  has been carried out so far and further, these earlier determinations show rather large variations among themselves. Hence an investigation of the elastic constants by the precision ultrasonic pulse echo technique was considered worthwhile and, in view of the discordance among the earlier values mentioned above, the new results are briefly reported here.

## 2. MEASUREMENTS AND RESULTS

A cubic crystal has three independent elastic constants  $c_{11}$ ,  $c_{12}$  and  $c_{44}$ . Incidentally, the present study showed that in  $\text{NaBrO}_3$ , as in  $\text{NaClO}_3$ , no observable deviations occur from the classical infinitesimal theory of elasticity. A similar situation of agreement with classical theory to within 0.1% has been observed in a few other cases where careful and specific studies were made<sup>6-8</sup>. It must therefore be concluded that at present the classical theory is perfectly adequate.

Single crystals of sodium bromate, approximately  $15 \times 15 \times 8 \text{ mm}^3$  in size, were grown by slow evaporation of the aqueous solution. Velocities of

longitudinal and transverse acoustic waves along the  $[100]$  and  $[111]$  directions were measured by a pulse echo technique using unrectified pulses at 10 MHz. The details of the set up are found elsewhere<sup>9</sup>. The longitudinal and shear wave velocities along the  $[100]$  direction readily yield  $c_{11}$  and  $c_{44}$  respectively, while  $c_{12}$  emerges out from velocity measurements in the  $[111]$  direction. The present value of  $c_{12}$  is the average of those obtained from longitudinal and shear wave velocities along the  $[111]$  direction, the values between themselves agreeing to within 0.04%. The absolute accuracy of the present arrangement is  $\pm 0.1\%$  in  $c_{11}$  and  $c_{44}$  and  $\pm 0.2\%$  in  $c_{12}$ .

TABLE I  
Elastic Constants of  $\text{NaBrO}_3$

Author	Method	$c_{11}$	$c_{12}$	$c_{44}$	$k$
Mason	Resonance	6.16	2.36	1.54	27.6
Sundara Rao	Wedge	5.45	1.91	1.50	32.4
Bechmann	Resonance	5.73	1.76	1.52	32.4
Bridgman	Static compression	—	—	—	44.1
Present values	Pulse echo	5.64 <sub>g</sub>	2.03 <sub>g</sub>	1.54 <sub>7</sub>	30.8 <sub>5</sub>

Table I furnishes the present values of the elastic constants  $c_{ij}$  and the cubic compressibility  $k$  of sodium bromate, together with the results of the earlier workers. The  $c_{ij}$  values are expressed in  $10^{10} \text{ N/m}^2$ , while the compressibility is in units of  $10^{-14} \text{ m}^2/\text{N}$ . Mason's and Bechmann's compliance values were matrix-inverted to obtain the stiffness coefficients.

A comparison of the present values with those of others clearly shows a good agreement in the case of  $c_{44}$ .  $c_{11}$  lies mid-way between the values of Sundara Rao and Bechmann, while Mason's value is too large by about 10%. The present value of  $c_{12}$  is virtually the mean of the three earlier values as is also the case with the cubic compressibility  $k$ . Bridgman's measurement of the compressibility at high pressure gives a rather high  $k$ . Bridgman's value is the isothermal compressibility, while the others are adiabatic values. But  $k$  (isothermal) is larger than  $k$  (adiabatic) by only a few per cent. It is commonly found in a number of other cases that static measurements give a rather large value of  $k$ , probably because of appreciable plastic deformation in the measurement of (linear) compressibility at high pressures. However, it has not been possible to explain the discrepancies among the earlier measurements of elastic constants. The wedge method is admittedly susceptible to large errors of the order of 5–10% in  $c_{11}$  and  $c_{44}$ , but the resonance methods used by Mason and by Bechmann are generally regarded as correct to within about 1%.

The effect of piezo electricity on elastic constants, as with  $\text{NaClO}_3^2$  and other non-ferroelectric crystals<sup>11</sup>, is too small to be detected experimentally in the present case.

### 3. COMPARISON OF THE $c_{ij}$ OF $\text{NaBrO}_3$ WITH $\text{NaClO}_3$

The present experimental investigation definitely establishes the higher elastic constants of the bromate over the chlorate of sodium ( $c_{11} = 4.92$ ,  $c_{12} = 1.42$  and  $c_{44} = 1.15$  in units of  $10^{10} \text{ N/m}^2$  for  $\text{NaClO}_3$  as compared with the corresponding values of 5.65, 2.04 and 1.55 for  $\text{NaBrO}_3$ ). Both sodium chlorate and sodium bromate belong to the cubic tetrahedral (space group  $P 2_1 3$ ) Class; X-ray studies show that the unit cell contains four molecules and has the edges  $a_0 = 6.570 \text{ \AA}$  for  $\text{NaClO}_3^{12}$  and  $a_0 = 5.489 \text{ \AA}$  for  $\text{NaBrO}_3^{13}$ . The densities are  $2485 \text{ kg/m}^3$  for  $\text{NaClO}_3$  and  $3335$  for  $\text{NaBrO}_3$ . The  $\text{ClO}_3^-$  and  $\text{BrO}_3^-$  groups are pyramidal; the oxygen atoms are arranged at the corners of an equilateral triangle, but the cation is displaced from the plane of the triangle, the displacement of the central cation from the basal plane being greater for Br than for Cl. Therefore, the Na-Br distance ( $3.72 \text{ \AA}$ ) is appreciably shorter than the Na-Cl distance ( $4.02 \text{ \AA}$ ).

It should first be noted that, according to the contact law for ionic distances suggested by Bragg<sup>14</sup>, one should expect the elastic constants of the bromate should be smaller because the bromate ion is larger in size. The experimental situation is completely to the contrary. There is evidence from other properties as well that sodium bromate has stronger inter-atomic forces. The melting point of  $\text{NaBrO}_3$  ( $381^\circ \text{C}$ ) is higher than that of  $\text{NaClO}_3$  ( $255^\circ \text{C}$ ). Thermal expansion studies<sup>15, 16</sup> show that the coefficient of thermal expansion as well as its temperature variation is much smaller for the bromate than for the chlorate. The Raman spectra and the low frequency lattice lines ( $< 150 \text{ cm}^{-1}$ )<sup>17</sup> show that the bromate frequencies are only slightly less than chlorate frequencies. If the substantially heavier mass of the bromate ion is taken into account, this would also suggest stronger inter-atomic forces in the bromate. This is probably connected up with the shorter Na-Br bond distance which is only  $3.72 \text{ \AA}$  as compared with the Na-Cl distance of  $4.02 \text{ \AA}$  in the chlorate.

This qualitative relationship between the bond distance and the elastic constant (irrespective of the size of the unit cell) is indirectly supported by the case of sodium chloride and sodium bromide. The inter atomic distances are, for NaCl  $2.81 \text{ \AA}$  ( $a_0 = 5.63 \text{ \AA}$ ) and for NaBr  $2.98 \text{ \AA}$  ( $a_0 = 5.96 \text{ \AA}$ ). The elastic constants  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  are for NaCl respectively 4.93, 1.31 and 1.28 and for NaBr respectively 4.02, 1.15 and 0.99. The melting points are  $801^\circ \text{C}$  for NaCl and  $755^\circ \text{C}$  for NaBr. Thus in this set the larger ion size and the larger inter-atomic distances result in NaBr having weaker bonding and consequently lower elastic constants and lower melting point.

In the case of  $\text{NaClO}_3$ ,  $\text{NaBrO}_3$  set it must therefore be concluded that the shorter Na - Br distance is responsible for the larger elastic constants of  $\text{NaBrO}_3$ , even though its unit cell size and the Br ion size are larger. A full discussion can obviously be made only if the complete lattice dynamics is worked out for this structure. But this is a formidable problem and has not been done so far.

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## NOTE ADDED IN PROOF

Haussühl (Phys. kondens. Materie. 1964, 3, 139) has determined the elastic constants of silver chlorate, sodium chlorate and sodium bromate by the Schaefer-Bergmann method and the results have become available to us very recently. On comparing his values of  $c_{ij}$  of  $\text{NaBrO}_3$  ( $c_{11} = 5.47_8$ ,  $c_{12} = 1.67_8$  and  $c_{44} = 1.50_5 \times 10^{10} \text{ N/m}^2$ ) with the present values,  $c_{11}$  and  $c_{44}$  are slightly less ( $\sim 2 - 3\%$ ) than the new values while  $c_{12}$  is considerably low (by  $\sim 20\%$ ). It is worth noting that Haussühl's values of  $\text{NaClO}_3$  also differ from the pulse-echo and resonance results. For instance, his values of  $\text{NaClO}_3$  ( $c_{11} = 5.00_1$ ,  $c_{12} = 1.54_3$  and  $c_{44} = 1.15_6 \times 10^{10} \text{ N/m}^2$ ) agree somewhat well ( $\sim 1 - 2\%$ ), as far as  $c_{11}$  and  $c_{44}$  are concerned, with the pulse echo values<sup>2</sup> ( $c_{11} = 4.92$ ,  $c_{12} = 1.42$  and  $c_{44} = 1.16 \times 10^{10} \text{ N/m}^2$ ) and those obtained from the resonance method due to Mason<sup>3</sup> ( $c_{11} = 4.89$ ,  $c_{12} = 1.38$  and  $c_{44} = 1.17 \times 10^{10} \text{ N/m}^2$ ) and due to Bechmann<sup>5</sup> ( $c_{11} = 4.99$ ,  $c_{12} = 1.42$  and  $c_{44} = 1.16 \times 10^{10} \text{ N/m}^2$ ). But again in the case of  $c_{12}$  the differences are considerable ( $\sim 10\%$ ). The origin of this discrepancy is not quite known.