Acta Cryst. (1977). A**33**, 320–322

Elastic, Thermoelastic, and Dynamic Piezoelectric Properties of Trigonal Potassium Bromate

By S. Haussühl

Institut für Kristallographie der Universität zu Köln, 5 Köln 1, Germany (BRD)

(*Received* 25 *June* 1976; *accepted* 24 *October* 1976)

The elastic moduli, their temperature derivatives, and the dynamic piezoelectric constants of trigonal potassium bromate, point group 3*m*, were measured by ultrasonic methods. The coupling coefficient k_t for longitudinal waves which propagate parallel to the threefold axes is 0·58. As the damping coefficient for these waves is extremely small, even at high frequencies up to 100 MHz, trigonal potassium bromate is preferentially suitable for highly efficient generators and sensors of ultrasonic waves. The dielectric constants are relatively small and no disturbing electric conductivity occurs as, for example, in lithium iodate. Therefore this material is superior to most other crystals in its use for such devices. All thermoelastic constants are negative, and it is not possible to cut a crystal with temperature-independent properties.

Growth properties, static piezoelectric constants and non-linear optical properties of $KBrO_3$ single crystals, point symmetry group 3*m*, were reported in an earlier paper (Haussühl, 1971). In the meanwhile still larger and better crystals of optical quality with dimensions up to several cm could be grown from aqueous solutions, working with the method of controlled temperature lowering between *ca* 40 and 30°C with growth velocities of *ca* 0·1 mm d^{-1}. With additives of *ca* 3 g HNO_3 and 5 g KBr per litre solution, an essential improvement of the crystal quality could be achieved. The main forms developed are, in trigonal-hexagonal notation: pyramids $\{1\bar{1}1\}$ and $\{\bar{1}1\bar{1}\}$, prism $\{110\}$, pyramids $\{102\}$ and $\{\bar{1}0\bar{2}\}$, pedion (001), ordered by their morphological rank.

The axes $\mathbf{e}_i$ of the Cartesian reference system are connected with the crystallographic axes $\mathbf{a}_i$ according to $\mathbf{e}_1\|\mathbf{a}_1$, $\mathbf{e}_3\|\mathbf{a}_3$, $\mathbf{e}_2=\mathbf{e}_3\times\mathbf{e}_1$. The axis $\mathbf{a}_3$ runs parallel to the threefold axis, the axis $\mathbf{a}_1$ is perpendicular to a mirror plane. The orientation of the specimens was done with the aid of the natural faces and by optical means. The specimens for the elastic measurements had the form of rectangular parallelepipeda with dimensions of *ca* 10 × 10 × 10 mm. For the determination of the dielectric properties and the electromechanical coupling coefficient k_t, thin plates with a thickness between 0·5 and 0·8 mm and diameters between 15 and 20 mm were used.

In piezoelectric crystals there exists a strong coupling between mechanical and electric quantities, expressed by the following relations:

$$\sigma_{ij}=c^E_{ijkl}\varepsilon_{kl}-e_{mij}E_m\,,\qquad D_i=e_{ikl}\varepsilon_{kl}+\epsilon^{\varepsilon}_{im}E_m\,,\quad \operatorname{div}\mathbf{D}=0\,.^*$$

Magnetic interactions are neglected. The elastodynamic equations for the propagation of plane waves are (Kyame, 1949; Meier & Schuster, 1953)

$$\sum_{j,k,l,m,n}^{1,2,3}\left[-\varrho v^2\delta_{ik}+\left(c^E_{ijkl}+\sum_{r,s}^{1,2,3}\frac{1}{\epsilon^{\varepsilon}_{rs}g_rg_s}\,e_{mij}e_{nkl}g_mg_n\right)g_jg_l\right]\xi_k=0$$

with $i=1,2,3$. The above symbols have the following meaning, where the indexed ones are tensor components: σ_{ij} stress tensor, ε_{ij} strain tensor, c^E_{ijkl} elastic tensor at constant electric field, e_{ijk} piezoelectric tensor, E_i electric field, D_i electric displacement, $\epsilon^{\varepsilon}_{ij}$ dielectric permittivity tensor at constant strain, ϱ density, v velocity of a plane elastic wave with propagation vector $\mathbf{k}$, δ_{ij} Kronecker delta, g_i unit vector parallel to wave vector $\mathbf{k}$, ξ_i mechanical displacement vector.

For the complete evaluation of all elastic and piezoelectric coefficients the following strategy, which has been proved earlier on other strongly piezoelectric crystals like $K_3Cu(CN)_4$, $LiIO_3$, and $Al(IO_3)_3.2HIO_3.6H_2O$ (Haussühl, 1967, 1970, 1972), is employed. In the first step, the complete set of dielectric coefficients $\epsilon^{\varepsilon}_{ij}$ is determined under 'clamped' conditions for the frequency range considered. In the 20 MHz range, in which the present investigation was carried out, the 'clamped' coefficients are approximately equal to the free coefficients. In the second step, static piezoelectric coefficients, defined by $\Delta D_i=d_{ijk}\Delta\sigma_{jk}$ for constant electric field, are measured. The third step covers the measurement of propagation velocities of ultrasonic waves in certain directions. These directions should be almost uniformly distributed in space. The number of different directions depends on the point symmetry of the crystal under investigation. For non-piezoelectric triclinic crystals, examples for this procedure were given earlier (Haussühl & Siegert, 1969; Küppers & Siegert, 1970). In the case of piezoelectric crystals, the number of different directions must be enlarged appreciably and also the accuracy must be higher if all elastic and piezoelectric

---

* Summation according Einstein convention.

coefficients are to be determined. In the present case the measurements were carried out with three methods: (*a*) diffraction of light by standing ultrasonic waves at frequencies between 15 and 28 MHz (Schaefer–Bergmann method), (*b*) observation of resonance frequencies of thick plates, (*c*) observation of resonance frequencies of thin plates with a thickness:diameter ratio of less than 0·1. For (*b*) the Schaefer–Bergmann equipment may be used; also in the case of piezooptically non-active waves as described earlier (Haussühl, 1975). The resonance frequencies under (*c*) are detected from the frequency dependence of the electrical impedance of the metallized plates. The temperature derivatives of the velocities are obtained from the temperature variation of the resonance frequencies with methods (*b*) and (*c*). In Table 1 the observed values of ϱv^2 at 20 and -20 °C are listed for different directions with the appropriate displacement vectors.

In crystals of point symmetry $3m$ the complete evaluation of elastic and piezoelectric coefficients can easily be solved without computer aid. In our case the procedure is as follows. The elastic constants c^E_{11}, $c^E_{66}=(c^E_{11}-c^E_{12})/2, c^D_{33}, c^E_{44}$ and c^E_{14} are directly obtained from measurements No. 1, 6, 7, 8, 14, 17 (Table 1). The constants c^E_{33} and e^2_{333} are derived by the relations

$$c^E_{33}=c^D_{33}-e^2_{333}/\epsilon^{\varepsilon}_{33}=c^D_{33}(1-k_t^2)\,,$$

inserting the measured values for the coupling coefficient $k_t=0{\cdot}58$ and the dielectric constant $\epsilon^{\varepsilon}_{33}=6{\cdot}09\epsilon^0$, ϵ^0 being the vacuum dielectric constant. k_t was determined by the method of Onoe, Tiersten & Meizler (1963) which is based on the anharmonicity of resonance frequencies of thin plates. Then the only unknown elastic constant left is c^E_{13}. An approximate value for c^E_{13} is c^E_{44} according to the Cauchy relation. With this set of elastic constants and the already known static piezoelectric constants d_{imn} (Haussühl, 1971), approximate values for the coefficients e_{ijk} are derived from the relation

$$e_{ijk}=\sum_{m,n}^{1,2,3} d_{imn}c^E_{mnjk}\,.$$

Inserting now these coefficients and the dielectric constants $\epsilon^{\varepsilon}_{11}=6{\cdot}59\epsilon^0$ and $\epsilon^{\varepsilon}_{33}$ as given above in the basic equations for measurements No. 9, 10, 11, 12, 13, 15, 16, 18, 19 one obtains a mean value $c^E_{13}\simeq 1{\cdot}50$. With this value and with the condition that the different measurements should yield the same c^E_{13}, an improved set of e_{ijk} and a better c^E_{13} is obtained. After two runs of this type the following results for 20 °C were compatible with the limits of experimental errors: $c^E_{11}=4{\cdot}313, c^E_{12}=1{\cdot}438; c^E_{13}=1{\cdot}515; c^E_{14}=-0{\cdot}035, c^E_{33}=2{\cdot}40$; $c^E_{44}=1{\cdot}655$ (10^{11} dyn cm^{-2}), and $e_{113}=1{\cdot}02$; $e_{112}=-0{\cdot}20$; $e_{311}=0{\cdot}62$; $e_{333}=2{\cdot}40$ (10^5 e.s.u. cm^{-2}).

In order to achieve a refinement from the whole overdetermined system of measurements (Table 1) a computer program for least-squares estimation of nonlinear parameters, which we had successfully applied for the evaluation of elastic constants in non-piezoelectric triclinic crystals (Haussühl & Siegert, 1969), was extended to piezoelectric crystals introducing the full piezoelectric interaction as noted in the basic equations. The first runs with arbitrary initial values yielded only unsatisfactory results because the φ^2 value (sum of squares of residuals) remained too high. We found that the parameter output depended strongly on the initial guess values, if all parameters were allowed to

Table 1. *Measured values of* ϱv^2 *in* $KBrO_3$ *at* 20 *and* -20 °C

$\mathbf{g}=[g_1, g_2, g_3]$ unit propagation vector, $\boldsymbol{\xi}=[\xi_1, \xi_2, \xi_3]$ unit vector of mechanical displacement. g and $\boldsymbol{\xi}$ are noted in the Cartesian reference system; v in 10^5 cm s^{-1}; c_{ij} in Voigt notation.

No.	$[g_1,g_2,g_3]$	$[\xi_1, \xi_2, \xi_3]$	Type of wave	ϱv^2 (20 °C)*	ϱv^2 (-20 °C)†	Relation between v and elastic constants
1	[1, 0, 0]	[1, 0, 0]	longitudinal	4·314	4·464	$\varrho v^2=c^E_{11}$
2	[1, 0, 0]	$[0, a, b]$	transverse	1·432	1·492	see basic equations
3	[1, 0, 0]	$[0, \bar{b}, a]$	transverse	1·849	1·923	see basic equations
4	[0, 1, 0]	$[0, c, d]$	quasi-longitudinal	4·318	4·480	see basic equations
5	[0, 1, 0]	$[0, \bar{d}, c]$	quasi-transverse	1·438	1·497	see basic equations
6	[0, 1, 0]	[1, 0, 0]	transverse	1·853	1·929	$\varrho v^2=c^E_{66}$
7	[0, 0, 1]	[0, 0, 1]	longitudinal	3·602	3·730	$\varrho v^2=c^D_{33}$
8	[0, 0, 1]	[1, 0, 0]	transverse	1·655	1·715	$\varrho v^2=c^E_{44}$
9	[0, −0·6157, 0·788]	$[0, e, f]$	quasi-longitudinal	4·565	4·741	see basic equations
10	[0, −0·6157, 0·788]	$[0, \bar{f}, e]$	quasi-transverse	0·968	—	see basic equations
11	[0, 0·788, 0·6157]	$[0, g, h]$	quasi-longitudinal	4·857	5·031	see basic equations
12	[0, −0·5225, 0·8526]	$[0, i, j]$	quasi-longitudinal	4·399	4·574	see basic equations
13	[0, −0·5225, 0·8526]	$[0, \bar{j}, i]$	quasi-transverse	1·035	1·061	see basic equations
14	[0, −0·5225, 0·8526]	[1, 0, 0]	transverse	1·638	1·694	$v^2=g_2^2c^E_{66}+g_3^2c^E_{44}+2g_3g_3c^E_{14}$
15	[0, 0·8434, 0·5373]	$[0, k, l]$	quasi-longitudinal	4·829	5·016	see basic equations
16	[0, 0·8434, 0·5373]	$[0, \bar{k}, l]$	quasi-transverse	1·111	—	see basic equations
17	[0, 0·8434, 0·5373]	[1, 0, 0]	transverse	1·474	1·526	$v^2=g_2^2c^E_{66}+g_3^2c^E_{44}+2g_2g_3c^E_{14}$
18	[0, 0·7071, 0·7071]	$[0, m, n]$	quasi-longitudinal	4·813	4·990	see basic equations
19	[0, −0·7071, 0·7071]	$[0, p, q]$	quasi-longitudinal	4·658	4·841	see basic equations

* With $\varrho(20\,°\mathrm{C})=3{\cdot}255$ g cm^{-3}.

† For density and thickness corrections the values of thermal expansion $\alpha_{11}=52$ and $\alpha_{33}=21\times10^{-6}$ deg^{-1}, as obtained with a Fizeau interferometer, were used.

Table 2. *Elastic constants* c_{ij}^E *at* 20 *and* −20 °C, *thermoelastic constants* $T_{ij} = \mathrm{d}\log c_{ij}^E/\mathrm{d}T$ *at* 0 °C, *and piezoelectric constants* e_{ijk} *of* $KBrO_3$

Units: c_{ij} in 10^{11} dyn cm^{-2}; T_{ij} in 10^{-3} deg^{-1}; e_{ijk} in 10^5 e.s.u. cm^{-2}. Limits of probable relative error are given in parentheses.

ij	c_{ij}^E (20 °C)	c_{ij}^E (−20 °C)	T_{ij} (0 °C)
11	4·312 (0·3 %)	4·468 (0·3 %)	−0·89 (5 %)
12	1·439 (0·5 %)	1·480 (0·5 %)	−0·70 (8 %)
13	1·547 (1 %)	1·562 (1 %)	−0·24 (20 %)
14	−0·034 (10 %)	−0·026 (10 %)	−6·67 (—)
33	2·360 (0·5 %)	2·435 (0·5 %)	−0·78 (6 %)
44	1·655 (0·5 %)	1·719 (0·5 %)	−0·95 (6 %)
66	1·437 (0·5 %)	1·494 (0·5 %)	−0·97 (6 %)

ijk	e_{ijk} (20 °C)	e_{ijk} (−20 °C)
112	−0·205 (10%)	−0·21 (20 %)
113	1·00 (5 %)	1·04 (5 %)
311	0·51 (10 %)	0·61 (10 %)
333	2·43 (3 %)	2·48 (3 %)

vary. With the above-listed 'hand-calculated' initial values an acceptable φ^2 of $0{\cdot}002 \times 10^{22}$ dyn^{22} cm^{-4} could be obtained for the 20 and −20 °C sets of measurements. These parameters are listed in Table 2 together with their temperature derivatives and the limits of probable relative error.

Elastic and thermoelastic constants of $KBrO_3$ possess the same order of magnitude as chemically and structurally related compounds like $NaBrO_3$ (Haussühl, 1964). The elastic anisotropy, characterized by the ratio c_{33}^E/c_{11}^E, indicates a minimum in the mean chemical bond strength parallel to the threefold axis. According to the Grüneisen relation one would expect that the thermal expansion would exhibit its maximum value in the direction of the threefold axis, but the opposite is observed. A difference occurs also in the deviations from the Cauchy relation $(c_{12}^E - c_{66}^E)$ and $(c_{13}^E - c_{44}^E)$, both of which are slightly negative, contrary to comparable compounds. The temperature derivatives for all elastic wave velocities are negative, therefore no temperature-independent crystal cuts for the generation of sound waves are possible.

Concerning the applicability for technical devices, the piezoelectric properties deserve great interest. First of all, the electromechanical coupling coefficient for longitudinal ultrasonic waves which propagate parallel to the threefold axis, $k_t = 0{\cdot}58$, is one of the highest values known in non-ferroelectric materials. The temperature derivative $\mathrm{d}\log k_t/\mathrm{d}T$ was determined to be $-0{\cdot}57 \times 10^{-3}$ deg^{-1} in the range between −50 and 90 °C, where no anomalous behaviour of k_t could be detected. Therefore, the existence of a phase transition in that temperature region is rather improbable. Measurements of overtone resonances in thin plates up to 100 MHz revealed that ultrasonic waves are only very weakly attenuated even at such high frequencies. There exists no disturbing electrical conductivity, as in the case of $LiIO_3$, and the dielectric constants are rather small. Grinding and polishing properties are excellent. Because of the low water solubility of $KBrO_3$ at room temperature, the polished surfaces remain stable in dry air without taking any further precaution.

All the above-mentioned properties show $KBrO_3$ to be a most suitable material for the fabrication of ultrasonic wave generators and sensors, much superior to most of the other materials in use today.

The author is highly indebted to H. Siegert for developing the computer program.

References

Haussühl, S. (1964). *Phys. kondens. Mater.* **3**, 139–145.

Haussühl, S. (1967). *Z. Kristallogr.* **125**, 184–187.

Haussühl, S. (1970). *Acoustica*, **23**, 165–169.

Haussühl, S. (1971). *Phys. stat. sol. (a)*, **6**, K23–K24.

Haussühl, S. (1972). *Z. Kristallogr.* **135**, 287–293.

Haussühl, S. (1975). *Krist. Tech.* **10**, 1175–1179.

Haussühl, S. & Siegert, H. (1969). *Z. Kristallogr.* **129**, 142–146.

Küppers, H. & Siegert, H. (1970). *Acta Cryst.* A**26**, 401–405.

Kyame, J. J. (1949). *J. Acoust. Soc. Amer.* **21**, 159–167.

Meier, R. & Schuster, K. (1953). *Ann. Phys.* **11**, 397–406.

Onoe, M., Tiersten, H. F. & Meitzler, A. H. (1963). *J. Acoust. Soc. Amer.* **35**, 36–42.