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Piezoelectric, Electro-optic, Dielectric, Elastic and Thermoelastic Properties of Hexagonal $Cs_2S_2O_6$, $LiClO_4.3H_2O$, $LiClO_4.3D_2O$, and $Ba(NO_2)_2.H_2O$

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Complete tensor sets of piezoelectric, electro-optic, dielectric, elastic and thermoelastic properties were measured on hexagonal $Cs_2S_2O_6$, $LiClO_4.3H_2O$, $LiClO_4.3D_2O$, and $Ba(NO_2)_2.H_2O$. The space-group symmetry of $Cs_2S_2O_6$ and $Ba(NO_2)_2.H_2O$ has been definitely established, by X-ray work in combination with the measurement of polar properties, to be $P6_3mc$ and $P6_1$ ($P6_5$), respectively, contrary to earlier X-ray determinations. $LiClO_4.3H_2O$ and $LiClO_4.3D_2O$ possess almost identical physical properties, with the exception of density and density-dependent properties. The very small differences correspond to those observed in other hydrates and deuterates. Most components of the piezoelectric and electro-optic tensors do not exceed the effective values of other crystals already in technical use. However, an exceptionally strong longitudinal piezoelectric effect is observed in $Cs_2S_2O_6$ ($d_{333} = -41$ e.s.u. dyn^{-1}, electromechanical coupling coefficient k_t $-$ 0·25), which together with other favourable acoustic and optical properties supports the application of this new material for acousto-optical devices in the high-frequency range.

Hitherto only a few polar crystals with hexagonal symmetry have been investigated with respect to their macroscopic properties. In this paper complete tensor sets of electrical and mechanical properties of four polar hexagonal crystals are reported. They all are easily obtained from aqueous solutions as large single crystals of high optical quality, and therefore deserve further consideration for applications in technical devices. Preliminary piezoelectric tests had revealed that the point symmetry for $Cs_2S_2O_6$ given in the literature as 62 (Hägg, 1932) is incorrect. Therefore, the symmetry properties of all four species had to be checked by X-ray diffraction and macroscopic properties. Some properties of $Ba(NO_2)_2.H_2O$ have already been reported by Gladkii & Zheludev (1967), but not all in complete tensor sets.

Crystal growth and measurements

Single crystals with diameters up to several cm have been grown from aqueous solutions by the usual evaporation technique at constant temperature. The growth experiments were carried out between 30 and 40 °C with resulting growth rates of *ca* 0·3 mm d^{-1}. The starting materials were produced by standard chemical processes: $Cs_2S_2O_6$ by reaction of Cs_2SO_4 with an aqueous solution of $BaS_2O_6.2H_2O$; $LiClO_4.3D_2O$ by dissolution of dehydrated $LiClO_4$ in D_2O; $Ba(NO_2)_2.H_2O$ by crystallization from an aqueous solution of $NaNO_2$ and $BaCl_2$ at *ca* 5 °C and manual selection of the yellowish crystals. The observed forms, ordered by their morphological rank, are listed in Table 1.

Table 1. *Observed forms as grown from pure aqueous solutions, ordered by morphological rank, lattice constants a_1 and a_3 (20 °C), space-group symmetry and measured density ρ (20 °C)*

	$Cs_2S_2O_6$	$LiClO_4.3H_2O$	$LiClO_4.3D_2O$	$Ba(NO_2)_2.H_2O$
Forms as grown	$(001), (00\bar{1})$ $\{100\}, \{101\}$ $\{10\bar{2}\}, \{10\bar{3}\}$	$\{100\}, \{101\}$ $\{10\bar{1}\}$	$\{100\}, \{101\}$ $\{10\bar{1}\}$	$\{100\}, \{101\}, \{10\bar{1}\}$ $(001), \{102\}$
Space group (point group)	$P6_3mc$ ($6m$)	$P6_3mc$ ($6m$)	$P6_3mc$ ($6m$)	$P6_1$ (6)
a_1 (Å)	6·357	7·716	7·717	7·076
a_3 (Å)	11·539	5·450	5·451	17·898
ρ(g cm^{-3})	3·503	1·898	1·967	3·179

Table 2. *Methods of measurement*

Property	Definition	Method
Piezoelectric constants d_{ijk}	$D_i = d_{ijk}\,\sigma_{jk}$; D_i components of electric displacement vector, σ_{jk} components of mechanical stress tensor	Static longitudinal and transverse piezoelectric effects in [100], [001] and intermediate directions
Linear electro-optic constants r_{ijk}	$\Delta a_{ij} = r_{ijk} E_k$ with $\Delta a_{ij} = a_{ij} - a^0_{ij}$; a_{ij} components of optical polarization tensor; E_k components of electric field vector	Changes of optical path lengths upon application of static electric fields (Bohatý, Haussühl & Nohl, 1974)
Dielectric constants ε^{rel}_{ij}	$D_i = e_{ikl}\,\varepsilon_{kl} + \varepsilon^{\varepsilon}_{im} E_m$; e_{ikl} components of piezoelectric **e** tensor; ε_{kl} components of mechanical strain tensor, $\varepsilon^{\varepsilon}_{im}$ components of dielectric tensor at constant strain	Thin plates of different orientations in a zero-compensation capacitor bridge; diameter–thickness ratio > 10 (Haussühl, 1957)
Elastic constants c^E_{ij} at constant electric field (Voigt notation)	$\sigma_{ij} = c^E_{ijkl}\,\varepsilon_{kl} - e_{mij} E_m$	Diffraction of monochromatic light by ultrasonic waves at frequencies between 5 and 30 MHz (Schaefer–Bergmann method); resonance frequencies of plane-parallel plates (Haussühl, 1956, 1977)
Thermoelastic constants T_{ij}	$T_{ij} = \mathrm{d} \log c_{ij}/\mathrm{d}T$; T = temperature	Change of resonance frequencies of plane-parallel plates upon variation of temperature between −20 and +20 °C (Haussühl, 1959)
Electromechanical coupling coefficient k_t	$k_t^2 = \frac{c^D_{33} - c^E_{33}}{c^D_{33}}$ (for hexagonal crystals); c^D_{33} elastic constant at constant electric displacement	Anharmonicity of resonance frequencies of thin plates (Onoe, Tiersten & Meitzler, 1963)
Coefficients of thermal expansion α_{ij}	$\varepsilon_{ij} = \alpha_{ij}\,\Delta T$	Fizeau interferometer between −20 and +20 °C

The existence of a polar hexagonal axis in $Cs_2S_2O_6$ is recognized by the nonequivalent pyramids $\{101\}$, $\{10\bar{2}\}$ and $\{10\bar{3}\}$. Therefore, the space groups $P6_32$ or $P\bar{6}2c$ proposed by Hägg (1932) are incorrect. On $LiClO_4.3H_2O$ and $LiClO_4.3D_2O$ the morphological polarity is not easily detected because of the occurrence of both pyramids $\{101\}$ and $\{10\bar{1}\}$. $Ba(NO)_2.H_2O$ exhibits its polarity by the pedion (001). The correlate pedion $(00\bar{1})$ was never observed. Often also the pyramid $\{102\}$ is developed. Furthermore, the crystal volume grown on the pyramid $\{101\}$ possesses a much higher quality (no veils and microcracks) than that on the pyramid $\{10\bar{1}\}$. The presence of a strong longitudinal piezoelectric effect in all four crystals confirms the existence of a polar hexagonal axis. Optical activity was found only in $Ba(NO_2)_2.H_2O$ which had been investigated already by Burkov, Kizel', Perekalina, Kozlova & Semin (1973). Therefore point symmetry 6 must be assigned to $Ba(NO_2)_2.H_2O$ in contradiction to point symmetry 62 suggested from X-ray diffraction work by Ferrari & Cavalca (1948). It should be mentioned that the polar properties reported by Gladkii & Zheludev (1967), namely a longitudinal piezoelectric effect and a strong pyroelectric effect along [001], indicated already the polar character of the sixfold axis. The IR studies of Brink & Falk (1971) also had made point symmetry 6 more probable.

In order to establish the correct space groups of all four crystals under investigation, an X-ray determination employing the Bragg method on large single crystals was carried out. The extinction of reflections $(h_1 h_1 h_3)$ with h_3 odd leads unambiguously to space group $P6_3mc$ for $Cs_2S_2O_6$, $LiClO_4.3H_2O$, and $LiClO_4.3D_2O$, which is fully compatible with all physi-

Table 3. *Piezoelectric constants* d_{ijk} (20°C), *linear electro-optic constants* r_{ijk} (20°C), *dielectric constants* $\varepsilon_{ij}^{\text{rel}}$ (20°C), *coefficients of thermal expansion* α_{ij} (0°C), *elastic constants* c_{ij}^{E} (20°C), *thermoelastic constants* $T_{ij} = \text{d} \log c_{ij}/\text{d}T$ (0°C), *and electromechanical coupling coefficient* k_t (20°C)

Units: d_{ijk} in 10^{-8} e.s.u. dyn^{-1}; r_{ijk} in 10^{-10} cm V^{-1}; α_{ij} in 10^{-6} deg^{-1}; c_{ij} in 10^{11} dyn cm^{-2}; T_{ij} in 10^{-3} deg^{-1}. Limits of probable relative error (%) are given in parentheses.

Property	$Cs_2S_2O_6$	$LiClO_4.3H_2O$	$LiClO_4.3D_2O$	$Ba(NO_2)_2.H_2O$
d_{113}	+2·5 (10)	−0·65 (50)	−0·2 (100)	+3·1 (10)
d_{311}	+0·9 (20)	+3·52 (10)	+3·4 (10)	+5·2 (10)
d_{333}	−41 (4)	−16·1 (5)	−17 (5)	−9·8 (5)
d_{123}	0	0	0	−1·4 (20)
r_{113}	−6·17 (3)	4·04 (4)	4·29 (3)	3·47 (3)
r_{311}	−1·3 (10)	0·74 (25)	0·91 (10)	−0·41 (25)
r_{333}	−4·85 (3)	6·61 (4)	6·67 (3)	3·31 (4)
r_{231}	0	0	0	−0·85 (25)
$\varepsilon_{11}^{\text{rel}}$ (10 MHz)	4·89 (1)	5·70 (1)	5·66 (1)	7·56 (1)
$\varepsilon_{33}^{\text{rel}}$ (10 MHz)	6·37 (1)	7·66 (1)	7·70 (1)	6·78 (1)
α_{11}	45·8 (2)	52·6 (2)	54·7 (1)	15·3 (3)
α_{33}	46·6 (2)	81·2 (2)	76·3 (2)	76·0 (2)
c_{11}^{E}	3·040 (0·2)	4·086 (0·2)	4·083 (0·2)	5·422 (0·2)
c_{33}^{E}	1·761 (0·2)	2·589 (0·2)	2·566 (0·2)	2·992 (0·2)
c_{12}^{E}	1·594 (1)	1·768 (1)	1·757 (1)	2·750 (1)
c^{E}	0·826 (1)	0·780 (1)	0·773 (1)	1·775 (1)
c_{44}^{E}	0·816 (0·5)	0·727 (1)	0·730 (1)	1·118 (1)
c_{66}^{E}	0·723 (0·5)	1·159 (0·5)	1·163 (0·5)	1·336 (0·5)
T_{11}	−0·91 (2)	−1·22 (2)	−1·23 (2)	−0·925 (2)
T_{33}	−0·59 (2)	−1·11 (2)	−1·11 (2)	−1·02 (2)
T_{12}	−0·94 (3)	−1·11 (3)	−1·13 (3)	−0·24 (20)
T_{13}	−0·79 (4)	−1·24 (4)	−1·27 (4)	−0·10 (50)
T_{44}	−1·08 (4)	−1·07 (4)	−1·00 (4)	−1·50 (4)
T_{66}	−0·88 (2)	−1·30 (2)	−1·30 (2)	−1·61 (2)
k_t	0·25 (4)	0·083 (5)	0·095 (5)	0·034 (5)

cal properties reported here. The earlier data for $LiClO_4.3H_2O$ of West (1934) and Swanson, Gilfrich, Cook, Stinchfield & Parks (1959) are confirmed. The extinction of reflections ($00h_3$) with $h_3 \neq 6n$ (n integer) together with the observed optical activity, the non-vanishing piezoelectric constant d_{123} and electro-optic constant r_{231} (see Table 3) shows that $Ba(NO_2)_2.H_2O$ belongs to space group $P6_1$ ($P6_5$).

Simultaneously, better data for the lattice constants were obtained (Table 1). The densities measured on large single crystals with the buoyancy method agree well with these lattice constants within the limits of error of *ca* 0·1%.

The methods of measurement employed in this investigation are listed in Table 2, which also contains references where these methods are described in detail. In all cases the axes $\mathbf{e}_i$ of the Cartesian reference system are chosen to be $\mathbf{e}_1$ parallel to $\mathbf{a}_1$, $\mathbf{e}_3$ parallel to $\mathbf{a}_3$. The dimensions of the specimens ranged between 10 and 15 mm in the case of rectangular parallelepipeda used mainly for piezoelectric, electro-optic and elastic measurements. The plated specimens necessary for measuring dielectric and electromechanical coupling properties had diameters up to 20 mm and thicknesses between 0·8 and 2 mm. The results obtained are given in Table 3 together with the limits of error.

Discussion

As a first result the almost identical behaviour of all macroscopic properties of $LiClO_4.3H_2O$ and $LiClO_4.3D_2O$ should be mentioned. Within the limits of experimental error there are no observed differences, except of course in the densities and related properties, such as sound velocities. The tendency observed in other isotypic hydrate–deuterate pairs, like the alums and Schlippe's salt, seems to exist also here. The deuterate possesses slightly larger lattice constants and smaller elastic longitudinal resistances (c_{11} and c_{33}), but higher elastic shear resistances (c_{44} and c_{66}) (Haussühl, 1970).

At present the interpretation of the polar properties of $Cs_2S_2O_6$ and $Ba(NO_2)_2.H_2O$ on a structural basis must be postponed, since the choice of space-group symmetry in the earlier structure determination was incorrect and a redetermination has not yet been undertaken. Therefore, we must confine the discussion to the macroscopic properties, their anisotropy, and their applicability in technical devices.

A surprisingly strong longitudinal piezoelectric effect, expressed by d_{333}, is observed in $Cs_2S_2O_6$: *ca* six times larger than that of α-quartz or other dithionates, such as those of $K_2S_2O_6$ or $CaS_2O_6.4H_2O$ type, which belong to point symmetry 32.

By virtue of the relatively high electromechanical coupling coefficient $k_t = 0{\cdot}25$ and the low velocity of longitudinal sound waves propagating along the sixfold axis, single crystals of $Cs_2S_2O_6$ might find applications in the construction of self-excited acousto-optic deflectors in the high-frequency range. This is supported by their quasi-isotropic thermal expansion, good cutting and polishing properties, and excellent optical homogeneity. All other piezoelectric effects in $Cs_2S_2O_6$ and the other crystals under investigation are too small to be superior to other crystals in technical applications. The linear electro-optic constants of all four crystals do not even approach one half of the values of KH_2PO_4. They therefore are not of direct technical interest.

A common feature is observed in thermal expansion and longitudinal elastic resistances. The ratios α_{11}/α_{33} and c_{33}/c_{11} are <1. This reflects the validity of Grüneisen's rule in anisotropic media. It should be emphasized that in hexagonal crystals contrary anisotropic effects are extremely rare.

The magnitude of the elastic constants, especially the volume compressibility derived from the elastic constants, is qualitatively explainable by comparison with chemically related compounds like Cs_2SO_4 in the case of $Cs_2S_2O_6$ or $Ba(NO_3)_2$ in the case of $Ba(NO_2)_2.H_2O$. The method to be employed has been outlined earlier (Haussühl, 1965). The thermoelastic behaviour agrees with that of other stable crystals, even in the case of the hydrates with their slightly elevated values.

Finally, concerning the pyroelectric effect, it should be remarked that only $Ba(NO_2)_2.H_2O$ exhibits a strong pyroelectric effect (Gladkii & Zheludev, 1967) which exceeds the pyroelectric effect of the other three crystals by more than two orders of magnitude. In all cases of high pyroelectric effects certain dielectric instabilities are involved, as in triglycine sulphate, $BaMgF_4$ and many other ferroelectric crystals. The unexpected dielectric anisotropy $\epsilon_{11}/\epsilon_{33}$, which does not comply with the elastic anisotropy, and also the extreme ratio α_{11}/α_{33} may be considered as an indication of the existence of such anomalous interactions in $Ba(NO_2)_2 \cdot H_2O$.

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