Acta Cryst. (1977). A33, 261–264

Solution Growth and Some Physical Properties of a New Lithium Iodate–Iodic Acid Solid Solution

BY S. A. HAMID, G. KUNZE AND G. REUTER

Kristallographische Abteilung am Mineralogischen Institut der Technischen Universität, 3 Hannover, Welfengarten 1, Germany (BRD)

(*Received* 2 *August* 1976; *accepted* 23 *September* 1976)

A method is described for the growth from aqueous solution of $Li_{1-x}H_xIO_3$ single crystals. Unit-cell parameter, low-frequency resistivity and the temperature dependence of the $\alpha-\beta$ transition for several x values were determined. With an increase in x there is an increase in a_0 and a decrease in c_0 compared with the lattice constants of $LiIO_3$. The maximum increase in a_0 is 0·082 Å and the maximum decrease of c_0 is 0·219 Å.

Introduction

Crystals of α-$LiIO_3$ with the space group $P6_3$ (Rosenzweig & Morosin, 1966) have important electro-optical properties (Nath & Haussühl, 1969; Nash, Bergman, Boyd & Turner, 1969). Crystal-growth experiments have been made by Haussühl (1968). Unlike potassium iodate, $LiIO_3$ does not combine with iodic acid to form hydrogen compounds of the type $K_mH_n(IO_3)_{m+n}$ where $n=1,2,3$ and $m=1$ (Hamid & Kunze, 1976). The low-frequency dielectric behaviour, piezoelectric constant (g_{33}), IR and Raman spectra of the solid solution have been studied by Hamid & Kunze (1977). The newly formed crystals show anomalous dielectric behaviour for $x \leq 0{\cdot}2$ and a strong piezoelectric effect. A correlation between the dielectric properties and the atomic arrangement has been shown by the same authors. During the present study crystal-growth conditions, X-ray diffraction, low-frequency resistivity and the $\alpha-\beta$ phase transition are investigated.

Experimental

The material used in all experiments was obtained from the manufacturers (Merck) in small-crystal form and was prepared by neutralization of iodic acid solution with lithium hydroxide. To several 0·1 l aliquots of supersaturated solution of $LiIO_3$ different quantities of iodic acid were added (0·025, 0·050, 0·100, 0·125 kg). These solutions were heated to 40 °C and then cooled to 30 °C. The solutions were decanted and seeded with small crystals of $Li_{1-x}H_xIO_3$ obtained from a fast evaporation of the same solution. The solution was isothermally evaporated at 30 °C. The lithium content was determined by atomic absorption spectrometry and the iodine content by titration with sodium thiosulphate. Thermogravimetric investigations showed that the crystals do not contain H_2O. The variation of the lattice constants with the value of x in the formula $Li_{1-x}H_xIO_3$ was studied with a focusing Guinier-type camera. Single crystals were studied with a Buerger precession camera. The low-frequency resistivity was measured in the range 5–500 kHz. The temperature dependence of the $\alpha-\beta$ transition was determined by measuring the relative dielectric constant at 10 kHz. Silver paste was used to make electrical contact with the samples.

Results and discussion

Lithium iodate and iodic acid are very soluble in water, *i.e.* about 0·084 kg of $LiIO_3$ and 0·285 kg HIO_3 in 0·1 kg H_2O at room temperature and their solubility curves have a negative thermal coefficient. Therefore, isothermal evaporation is the most desirable among

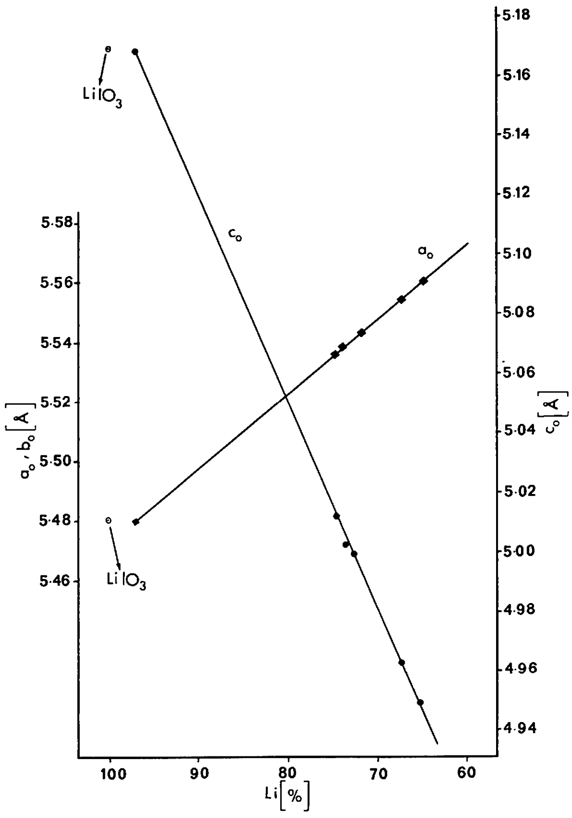

Fig. 2. Lattice parameters *versus* Li content.

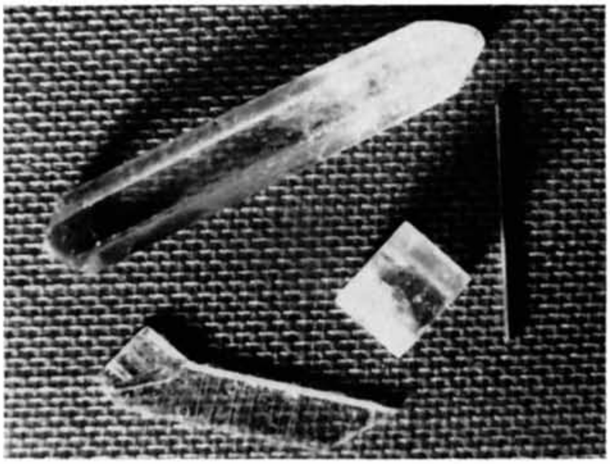

Fig. 1. $Li_{1-x}H_xIO_3$ single crystals (scale 3:1).

several solution growth methods. $Li_{1-x}H_xIO_3$ single crystals of several sizes and high optical quality have been grown from aqueous solutions (Fig. 1). Table 1 gives information about crystal growing conditions, formula, unit-cell parameter and point group. The cell parameters have been refined by a least-squares method. The crystals grow as hexagonal prisms of different sizes. The evaporation rate was varied according to the HIO_3 content in the solution.

The newly formed crystals were chemically analysed (Li, I) and then X-rayed. The cell dimensions of $Li_{1-x}H_xIO_3$ were determined for several x values (Table 1). It was found that there is a linear relation between the cell parameter (a_0, c_0) and the Li content (Fig. 2). Further, it was observed that with increasing values of x in $Li_{1-x}H_xIO_3$, a decrease of 0·219 Å in c_0 was accompanied by an increase of 0·082 Å in a_0. The intensities of the powder and single-crystal patterns were found to be different from those of $LiIO_3$. This difference is clearly demonstrated in the relations I_{300}/I_{103} and I_{112}/I_{201} which have for $LiIO_3$ the values 0·47 and 1·68 respectively. The observed and calculated lattice spacing d_o and d_c and the relative intensities I/I_0 are given in Table 2. Precession photographs for $x=0{\cdot}33$ of the $0kl$ layer showed after 90 h weak spots at $00l$ for $l=2n+1$. This indicates the disappearance of the symmetry element 6_3. Another explanation for the halving of the reciprocal lattice c^* would be an ordered distribution of Li^+ and H^+ along the **z** direction which, however, cannot be distinguished by X-rays from a statistical distribution of these atoms along this lattice direction because of the weak atomic scattering amplitudes. In particular, for the statistical occupation of the Li^+/H^+ sites the mean atomic scattering amplitudes of a compound $Li_{1-x}H_xIO_3$ can be written in the form

$$\bar{f}_{Li,H}=(1-x)f_{Li^+}+xf_{H^+}; \qquad (1)$$

the atomic scattering amplitudes of I and O are the same as in the ordered structure. Applying this equation for the compounds $Li_{0{\cdot}67}H_{0{\cdot}33}IO_3$ and $LiIO_3$ gives $F_{002}=72$ and $F_{002}=72{\cdot}4$ for the disordered and ordered structures respectively. The difference between the two values is negligible in such a manner that it cannot be correlated with that of the observed intensity. Therefore the above mentioned weak reflexions can only be produced by a change in the atomic arrangement of the IO_3 pyramid. This idea may be supported by considering the IR and Raman spectra. In both cases new modes were observed which may be due

Table 1. *Crystal growing condition, chemical formula, lattice parameters and point group of some* $Li_{1-x}H_xIO_3$ *compounds*

HIO_3*	Rate of evaporation (mm d^{-1})	L [mm]	F [mm^2]	Formula	a_0 (Å)	c_0 (Å)	Point group
0·025	0·3	20	8	$Li_{0{\cdot}985}H_{0{\cdot}015}IO_3$	5·4803 (6)	5·1689 (9)	6
0·050	0·2	15	10	$Li_{0{\cdot}96}H_{0{\cdot}04}IO_3$	5·4822 (2)	5·186 (1)	6
0·080	0·15	15	6	$Li_{0{\cdot}74}H_{0{\cdot}26}IO_3$	5·5491 (3)	5·0115 (5)	6
0·100	0·1	10	8	$Li_{0{\cdot}7}H_{0{\cdot}3}IO_3$	5·494 (6)	4·9817 (9)	6
0·125	0·08	9	4	$Li_{0{\cdot}67}H_{0{\cdot}33}IO_3$	5·5544 (4)	4·9626 (8)	6
>0·125	—	6	1	$Li_{0{\cdot}65}H_{0{\cdot}35}IO_3$	5·5605 (4)	4·9489 (6)	6

* In kg per 0·1 l supersaturated solution of $LiIO_3$.

Table 2. *Observed and calculated lattice spacing* d_o *and* d_c *(in* 10^{-3} *Å) and relative intensities* I/I_0

	$Li_{0{\cdot}97}H_{0{\cdot}03}IO_3$				$Li_{0{\cdot}74}H_{0{\cdot}26}IO_3$				$Li_{0{\cdot}67}H_{0{\cdot}33}IO_3$		
hkl	d_o	d_c	I/I_0	*hkl*	d_o	d_c	I/I_0	*hkl*	d_o	d_c	I/I_0
100	4756	4745	14	100	4799	4796	14	100	4825	4810	28
101	3499	3495	100	101	3466	3462	100	101	3455	3454	100
110	2741	2739	20	110	2769	2769	29	110	2777	2777	26
002	2584	2584	67	002	2501	2501	10	002	2481	2481	9
111	2421	2420	2	111	2422	2422	5	111	2423	2424	2
200	2374	2373	7	200	2398	2398	12	200	2404	2405	9
102	2269	2269	11	102	2218	2217	12	102	2204	2205	10
201	2157	2156	18	201	2162	2162	25	201	2163	2164	24
112	1880	1879	25	112	1856	1855	32	112	1851	1850	22
210	1794	1794	2	210	1814	1813	7	210	1818	1818	4
202	1746	1747	5	202	1731	1731	5	202	1727	1727	3
211	1695	1695	22	211	1705	1704	27	211	1707	1707	21
103	1619	1619	9	300	1599	1599	10	300	1603	1603	6
300	1582	1582	7	103	1575	1575	8	103	1564	1564	6
212	1473	1473	5	212	1468	1468	7	212	1466	1467	5
203	1394	1394	8	220	1385	1385	5	220	1389	1389	4
220	1369	1369	4	203	1369	1368	9	203	1363	1363	5
302	1349	1349	7	302	1347	1347	6	302	1347	1347	4
310	1316	1316	1	310	1331	1330	2	310	1334	1334	2
311	1275	1275	9	311	1285	1286	11	311	1288	1288	9

either to removing the degeneracy of the IO_3 internal modes or to inserting protons in the $LiIO_3$ structure (Hamid & Kunze, 1977).

Low-frequency resistivity (ϱ_{33},ϱ_{11}) of single crystals parallel to [100] and [001] has been measured in the range 50–500 kHz. Figs. 3 and 4 show curves of ϱ_{33} and ϱ_{11} for several x. With increasing x in the formula ($Li_{1-x}H_xIO_3$) there is an increase in ϱ_{33} and a decrease in ϱ_{11}. Moreover space-charge effects in static fields have been observed. They lead to considerable charge displacements in the crystal and to a time dependence of the current. The increase of ϱ_{33} with increasing x can be explained as a recombination of the current carriers. This phenomenon has been discussed by Hamid & Kunze (1977) on the model representation of the dielectric behaviour of $Li_{1-x}H_xIO_3$. The frequency dependence of ϱ_{33} can be simulated by an RC circuit (Fig. 5). Volger (1960) derived the following equation for a two-layer dielectric:

$$\varrho'(\omega)=\frac{\varrho_s+\varrho_\infty\tau_p^2\omega^2}{1+\tau_p^2\omega^2}, \qquad (2)$$

where ϱ_s = static resistivity, ϱ_∞ = high-frequency resistivity, τ_p = relaxation time, ω = angular frequency.

The $\varrho'(\omega)$ curves of $Li_{1-x}H_xIO_3$ in the range $\varrho_s \le \varrho' \le \varrho_\infty$ are comparable with the $\varrho'(\omega)$ curves, calculated by Volger (1960) on the basis of equation (2). The occurrence of the space-charge polarization focuses interest on the electrical conductivity and the nature of the charge carriers in $Li_{1-x}H_xIO_3$ and $LiIO_3$.

Matsumura (1971) has shown that under normal pressure the hexagonal α-$LiIO_3$ undergoes two phase transitions $\alpha \rightleftharpoons \gamma \rightarrow \beta$. The reversibility of the $\alpha \rightleftharpoons \gamma$ phase transition occurs at about 247 °C followed by an irreversible transformation to the tetragonal β-phase at 285 °C. For $Li_{1-x}H_xIO_3$ the temperature dependence of the relative dielectric constant ε_{rel} has been measured for several x (Fig. 6). First we observed increasing values of C_T/C_{Tr}. After reaching a maximum at a distinct temperature the curves decrease to small values. The maxima of these (C_T/C_{Tr}) curves (Fig. 6) correspond to the $\alpha \rightarrow \beta$ transition point. Increasing the x value shifts the maxima to lower temperatures. The transition point was found to vary to the extent of 15 °C for compounds having the same x values. Broader maxima are noticed when $x \ge 0{\cdot}26$. The crystals were X-rayed after cooling them from 260 °C to room temperature. It was found that all samples had changed to the tetragonal β-phase. Weak reflexions probably corresponding to HIO_3 were noticed. From X-ray studies it was found that the $\alpha \rightleftharpoons \gamma$ transition is absent and the maxima in Fig. 6 are interpreted as the β-phase transition. The early $\alpha \rightarrow \beta$ phase transition is accompanied by lowering of the melting point of $Li_{1-x}H_xIO_3$. This lowering of the melting point is also found to increase with increasing x. It is recorded by Arend, Remoissenet & Staehlin (1972) that the reversible $\alpha \rightleftharpoons \gamma$ transition could not be observed when

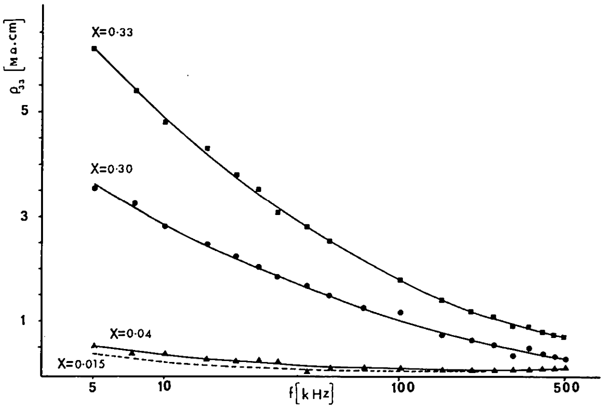

Fig. 3. Low-frequency resistivity (ϱ_{33}) *versus* log frequency.

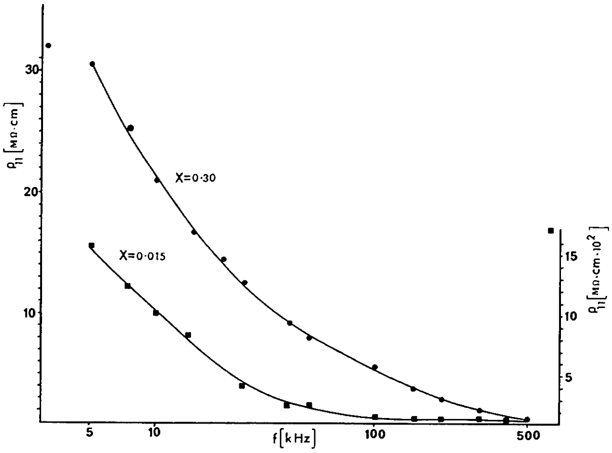

Fig. 4. Low-frequency resistivity (ϱ_{11}) *versus* log frequency.

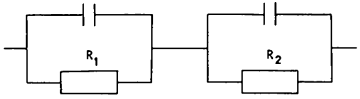

Fig. 5. Equivalent circuits of two-layer dielectric.

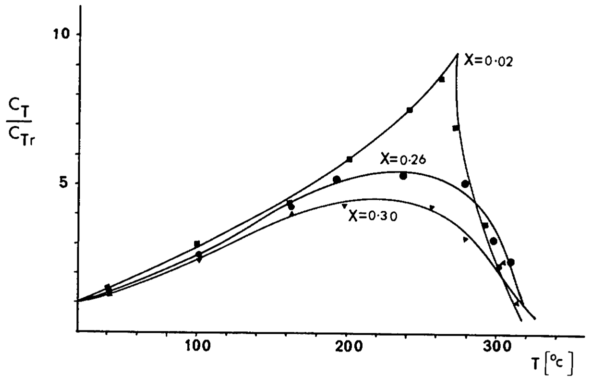

Fig. 6. Relative dielectric constant (C_T/C_{Tr}) *versus* temperature T (Tr = room temperature).

$LiIO_3$ contained small amounts (0·59–0·76%) of HIO_3. The change in the lattice constants for this small amount of HIO_3 ($x \simeq 0{\cdot}005$) cannot be determined by ordinary X-ray methods.

We thank the 'Deutsche Forschungsgemeinschaft' for their support of these investigations.

References

Arend, A., Remoissenet, M. & Staehlin, W. (1972). *Mater. Res. Bull.* **7**, 869–872.

Hamid, S. A. & Kunze, G. (1976). *J. Cryst. Growth*, **32**, 126–128.

Hamid, S. A. & Kunze, G. (1977). *Acta Cryst.* A**33**, 264–267.

Haussühl, S. (1968). *Phys. Stat. Sol.* **29**, 159–161.

Matsumura, S. (1971). *Mater. Res. Bull.* **6**, 469–477.

Nash, F. R., Bergman, J. G., Boyd, G. D. & Turner, E. H. (1969). *J. Appl. Phys.* **40**, 5201–5206.

Nath, G. & Haussühl, S. (1969). *Appl. Phys.* **14**, 154–156.

Rosenzweig, A. & Morosin, B. (1966). *Acta Cryst.* **20**, 758–761.

Volger, J. (1960). *Progr. Semicond.* **4**, 209–213.

Acta Cryst. (1977). A**33**, 264–267

Dielectric Behaviour, Raman and IR Spectra of $Li_{1-x}H_xIO_3$

By S. A. Hamid and G. Kunze

Kristallographische Abteilung am Mineralogischen Institut der Technischen Universität, Welfengarten 1, 3 *Hannover, Germany* (*BRD*)

(*Received* 2 *September* 1976; *accepted* 6 *October* 1976)

The low-frequency dielectric behaviour, the piezoelectric constant g_{33} and Raman and IR spectra of $Li_{1-x}H_xIO_3$ have been measured. The amount of hydrogen, x, in the formula $Li_{1-x}H_xIO_3$ varies from 0·0 to 0·35. The curves $\varepsilon_{33} = \varepsilon_{33}(f)$ and $\tan \delta = \tan \delta(f)$ show anomalous behaviour with respect to frequency and composition. The piezoelectric constant (g_{33}) tends to a maximum at the composition $x \simeq 0{\cdot}04$. A model of the low-frequency relaxation spectra and the high value of ε is discussed.

Introduction

Unlike $NaIO_3$ and KIO_3, $LiIO_3$ does not form stoichiometric compounds with HIO_3. From a saturated solution of $LiIO_3$ with different amounts of HIO_3, crystals of the formula $Li_{1-x}H_xIO_3$ have been obtained (Hamid & Kunze, 1977). The mixed crystals retain the hexagonal symmetry of $LiIO_3$ and show interesting polar properties. Crystal growing conditions, low-frequency resistivity, X-ray diffraction and the temperature dependence of the $\alpha-\beta$ phase transition of $Li_{1-x}H_xIO_3$ have been studied by Hamid, Kunze & Reuter (1977). Because of its striking piezoelectric properties and non-linear optical behaviour, $LiIO_3$ has been studied by many authors (Haussühl, 1968; Warner, Pinnow, Bergman & Crane, 1969; Nath & Haussühl, 1969; Nash, Bergman, Boyd & Turner, 1969). Moreover $LiIO_3$ shows a low-frequency relaxation spectra as reported by Warner *et al.* (1969), Arlt, Puschert & Quadflieg (1970) and Sailer (1971). This anomalous dielectric behaviour remained unexplained. During the present investigation $Li_{1-x}H_xIO_3$ ($0 \le x \le 0{\cdot}15$) is also found to show similar dielectric behaviour and an attempt is made to explain this and to determine the effect of solid solution on the dielectric, symmetry and polar properties.

Experimental

Single crystals of $Li_{1-x}H_xIO_3$ have been grown from aqueous solution (Hamid, Kunze & Reuter, 1977). The crystals were chemically analysed (Li, I) and then X-rayed with Guinier and Buerger precession cameras. The dielectric constants of these substances were determined from single crystals in the form of plates ground parallel to (100) and (001). The thickness of the specimens was small enough that all measurements could be carried out below the mechanical resonance frequency. Silver paste was used as a contact for the probes. The frequencies used ranged between 5 and 500 kHz. The piezoelectric constants were measured by using an AC electromagnetic vibrator at 12 Hz. The piezoelectric voltage was amplified before being screened on the oscillograph. The IR and Raman spectra were measured in the frequency ranges 200–4000 cm^{-1} and 10–900 cm^{-1} respectively.

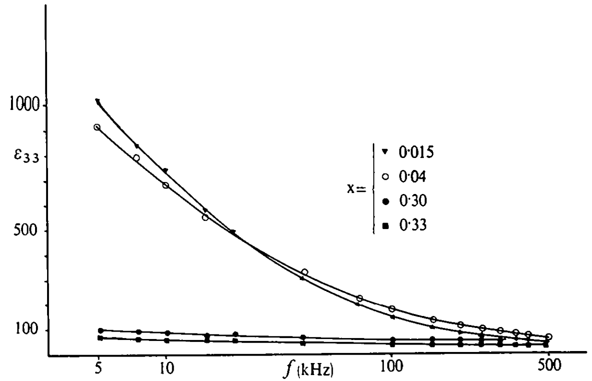

Fig. 1. Frequency dependence of the apparent dielectric constant ε_{33}.