$LiIO_3$ 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.

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

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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.

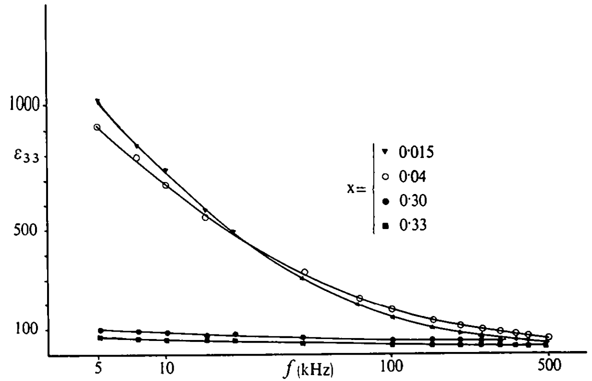

Fig. 1. Frequency dependence of the apparent dielectric constant ε_{33}.

Results and methods of examination

(1) *Dielectric, loss-tangent and piezoelectric constants*

$Li_{1-x}H_xIO_3$ shows anomalous dielectric behaviour in the frequency range 5–500 kHz. This anomalous behaviour becomes less and less pronounced with increasing x. The curves $\varepsilon_{33}=\varepsilon_{33}(f)$ for different values of x are shown in Fig. 1. The dielectric constant ε_{33} for $x \geq 0{\cdot}3$ is about 10 times smaller than for $x \simeq 0{\cdot}015$ at 5 kHz. The same constant of the compound $Li_{0{\cdot}67}H_{0{\cdot}33}IO_3$ is approximately independent of the frequency in the range 5–500 kHz. The loss-tan curve shows broad maxima for $x \leq 0{\cdot}04$ at about 200 kHz. Decrease in loss-tan is observed with increasing frequency and/or increasing x for $x \geq 0{\cdot}3$ (Fig. 2). Warner *et al.* (1969) have also recorded the anomalous dielectric behaviour of $LiIO_3$. According to them, the maximum of tan δ lies in the region of 100 kHz. For $LiIO_3$ Nash *et al.* (1969) had found that the value of ε_{33} was 554 in the region of 1 kHz. This would indicate that the dielectric curves (ε_{33}) in relation to the concentration of H^+ would increase until a critical composition is reached and then begin to fall. The critical composition probably lies near $x=0{\cdot}01$. In Fig. 3 it is found that the dielectric constant ε_{11} for $x \leq 0{\cdot}015$ is nearly independent of the frequency. But for $x \geq 0{\cdot}3$ it is found that ε_{11} is very sensitive to frequency; further, a relaxation spectrum is observed at 15–20 kHz. Single crystals between $x=0{\cdot}04$ and $x=0{\cdot}30$ were too small to carry out dielectric measurements. On the other hand, the lattice constants for compounds between the two above-mentioned compositions correspond to Fig. 2 given by Hamid, Kunze & Reuter (1977). The dielectric constant depends strongly on the amount of H^+ in the formula. Small quantities of H^+ have a large effect on the dielectric behaviour. Curves of $\varepsilon_{11}=\varepsilon_{11}(f)$ and $\varepsilon_{33}=\varepsilon_{33}(f)$ indicate a change in the atomic arrangement caused by polarization changes with increasing x.

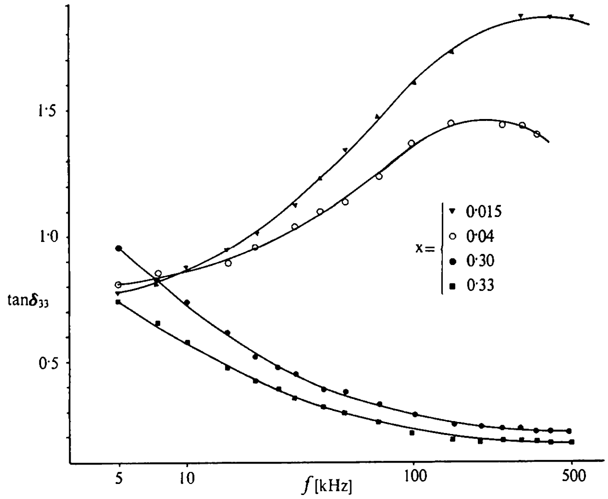

Fig. 2. Frequency dependence of the loss – $\tan\delta_{33}=1/WRC_{33}$.

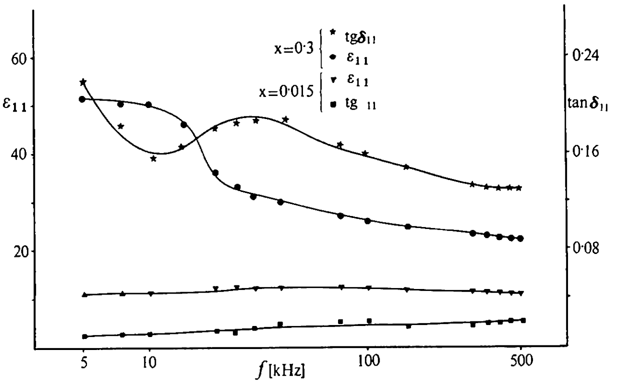

Fig. 3. Frequency dependence of the apparent dielectric constant ε_{11} and loss – $\tan\delta_{11}$.

The dynamical piezoelectric tensor component g_{33} has been measured for $x=0{\cdot}015$, 0·04 and 0·3. The g_{33} values together with ε_{33}, ε_{11}, ϱ_{33}, ϱ_{11} (AC specific resistivity) and the unit-cell parameters are given in Table 1. The polarization P_i can be expressed by the following two well known equations:

$$P_i=\varepsilon\chi_{im}E_m \tag{1}$$

$$P_i=d_{ijk}\sigma_{jk}. \tag{2}$$

By taking account of the further relation:

$$E_m=g_{mjk}\sigma_{jk} \tag{3}$$

combined with (1) and (2) we obtain:

$$g_{mjk}=(\chi^{-1})_{ml}d_{ljk}\frac{1}{\varepsilon_0}. \tag{4}$$

In these equations the concentration x is implicitly contained as parameter. According to Table 1 the series of g_{33} has a maximum at $x \gtrsim 0{\cdot}04$; on the other hand, the critical composition for ε_{33}, as mentioned

Table 1. *Piezoelectric constant* g_{33}, *dielectric constants* ε_{33}, ε_{11} (5 kHz), *specific resistivity* ϱ_{33}, ϱ_{11} (5 kHz) *and cell parameters for various x values*

x	g_{33} (V m kp^{-1}) $\times 10^{-6}$	ε_{33}	ε_{11}	ϱ_{33} (MΩ cm)	ϱ_{11} (MΩ cm)	a_0 (Å)	c_0 (Å)
0·015	155	1035	11	0·43	3033	5·4803 (6)	5·1689 (9)
0·040	424	924	—	0·50	—	5·4822 (2)	5·168 (1)
0·30	368	107	52	3·5	30·7	5·5494 (6)	4·9817 (9)
0·33	310	76	—	6·2	—	5·5544 (4)	4·9626 (8)

above, has been found at $x \simeq 0{\cdot}01$. These two values do not coincide, but this may presumably be because of the differences in the frequencies at which the measurements were carried out.

(2) *IR and Raman spectra*

Free IO_3 ions possess molecular symmetry C_{3v} with four fundamental vibrations, $\Gamma = 2A_1 + 2EA_1$ and E are both Raman and IR active. Inspections of *IR* spectra of LiIO_3 and $\mathrm{Li}_{0\cdot67}\mathrm{H}_{0\cdot33}\mathrm{IO}_3$ (Fig. 4) reveal two absorption maxima at 380 and 800 cm^{-1} for LiIO_3. Dasent & Waddington (1960) reported two absorption maxima at 360 and 780 cm^{-1} for LiIO_3. These maxima correspond to the ν_1, ν_3 and ν_2, ν_4 internal modes of the free iodate ion. The IR spectra of $\mathrm{Li}_{0\cdot67}\mathrm{H}_{0\cdot33}\mathrm{IO}_3$ show absorption bands at 595 cm^{-1} besides the two previously mentioned bands noticed in LiIO_3. Moreover there are two more weak bands which appear at 1700 and 3570 cm^{-1}. These may be due to O–H interaction.

The Raman spectra of LiIO_3, $\mathrm{Li}_{0\cdot74}\mathrm{H}_{0\cdot26}\mathrm{IO}_3$ and $\mathrm{Li}_{0\cdot67}\mathrm{H}_{0\cdot33}\mathrm{IO}_3$ are given in Fig. 5. It is clearly evident that the Raman signals in the case of the two latter compounds are broadened compared with those of the first compound, but they show two new signals, one of them at 595 cm^{-1} and the other, less pronounced, at about 700 cm^{-1}.

Discussion

The relation between the lattice constant and the Li content in the compound $\mathrm{Li}_{1-x}\mathrm{H}_x\mathrm{IO}_3$ was found to be linear (Hamid, Kunze & Reuter, 1977). In this case, it could be concluded that the change in the atomic arrangement in the crystal is continuously correlated with the dielectric constant. The relaxation spectra for the electronic, atomic, and dipole parts occur in the UV, IR and decimeter wavelength to radio-frequency ranges respectively. On the other hand, the piezoelectric crystals show dielectric absorption at low-frequency owing to vibrations of the crystal as a whole. In this case, the frequency at which absorption spectra occur depends on the crystal direction and dimension. The observed anomalous dielectric behaviour of LiIO_3 and $\mathrm{Li}_{1-x}\mathrm{H}_x\mathrm{IO}_3$ cannot be explained through the reciprocal piezoelectric effect because the specimens were thin enough to eliminate this effect. In polar dielectric materials the total polarizability consists of four components: the electronic, ionic, orientational and space-charge polarizabilities. This can be represented as follows:

$$\alpha_{\text{total}} = \alpha_e + \alpha_a + \alpha_o + \alpha_s\,.$$

The polarization $\mathbf{P}$, depends on α as

$$\mathbf{P} = \sum_{\nu} [N_\nu \alpha_\nu (\mathbf{E} + \sum_{\mu} \gamma_{\nu\mu} \mathbf{P}_\mu)] \qquad (5)$$

where N_ν = number of particles, $\mathbf{E}$ = electric field, $\gamma_{\nu\mu}$ = form factor, $\mathbf{P}_\mu$ = polarization of the particles of type μ, α_ν = polarizability of the particle ν.

However, the magnitude of P, and also of ε, changes if any of the four component polarizabilities change. When charge carriers are impeded in their motion, space charges and a macroscopic field distortion result. Such a distortion increases the capacitance of the crystals and is indistinguishable from a real rise in the dielectric permittivity. Space charges or interfacial and dipolar polarizations have a large damping effect. This leads to relaxation spectra at low frequency. The high value of dielectric constant at low frequency is probably also due to space charges, independent of dipolar polarizability in LiIO_3 and $\mathrm{Li}_{1-x}\mathrm{H}_x\mathrm{IO}_3$ caused by the polar IO_3 groups. Nägerl & Haussühl (1970), who reported the influence of injected current carriers on the electric conductivity in LiIO_3, explained these observed currents as 'space-charge limited' currents. In the case of $0 \leq x \leq 0{\cdot}015$ in $\mathrm{Li}_{1-x}\mathrm{H}_x\mathrm{IO}_3$ the dielectric constant ε_{33} increases owing to the increased formation of the space charges. However, an increase in the amount of x to $x \geq 0{\cdot}04$ caused an increase in the lattice constant a_0 accompanied by a decrease in c_0. In this case, the angle of the IO_3 pyramid (O–I–O) increased. This latter effect lead to a decrease in the total dipole moment per unit cell and a recombination of the space charges (with increasing x) and ac-

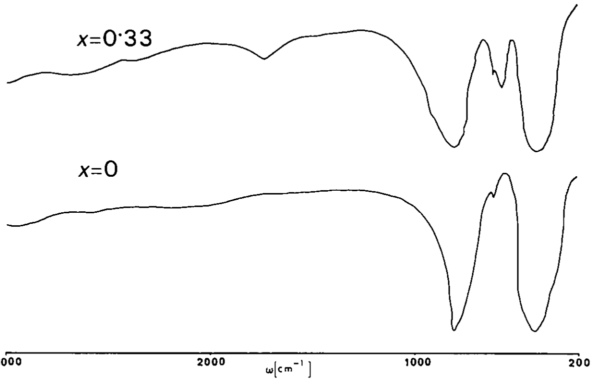

Fig. 4. IR spectra of LiIO_3 and $\mathrm{Li}_{0\cdot67}\mathrm{H}_{0\cdot33}\mathrm{IO}_3$.

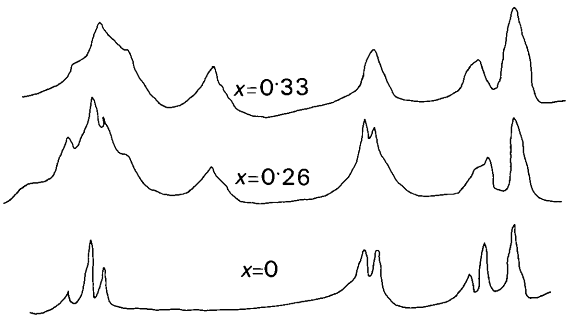

Fig. 5. Raman spectra of LiIO_3, $\mathrm{Li}_{0\cdot74}\mathrm{H}_{0\cdot26}\mathrm{IO}_3$ and $\mathrm{Li}_{0\cdot67}\mathrm{H}_{0\cdot33}\mathrm{IO}_3$.

cordingly a decrease in the dielectric constant ε_{33} occurred. The increase of the dielectric constant ε_{11} (with increasing x) is correlated to the increase of the O–I–O angle and the lattice parameter a_0. Preliminary X-ray measurements have shown that the intensities from $LiIO_3$ and $Li_{1-x}H_xIO_3$ differ a small amount. The change in the X-ray intensity from the compound $Li_{1-x}H_xIO_3$ when compared with the intensity from $LiIO_3$ cannot be explained by a replacement of Li^+ by H^+ (Hamid, Kunze & Reuter, 1977). This indicates that a change in the atomic arrangement in the IO_3 pyramids must take place. It is well known that lowering the symmetry, in general, will be followed by removal of the degeneracy of the IR and Raman vibrations. For a given space group, the number of vibrations can be represented by the factor group analysis. Table 2 shows the correlation between the unit cell, site, and free molecular symmetry for the IO_3 complex. The observed line group at 700–800 cm^{-1} and 300–400 cm^{-1} of the IR and Raman spectra are typical for iodate compounds (Salje, 1976). The Raman and IR signal at 595 cm^{-1} does not exist in the spectra of other iodates. This can be interpreted as a considerable change in the lattice dynamics from inserting protons in the $LiIO_3$ structure. The two flattened IO_3 pyramids and the distribution of protons are the main effects which change the dynamical properties, a phenomenon which cannot be determined by considering the factor group analysis alone.

Table 2. *Correlation diagram for insulated-molecule, site and unit-cell symmetry*

$$\begin{tikzcd}
\text{Insulated molecule} & \text{Site} & \text{Unit cell} \\
C_{3v} & C_3 & C_6 \\
2A_1 \arrow[r] & 2A \arrow[r] & 2A \\
 & & 2B \\
2E \arrow[r] & 2E \arrow[r] & 2E_1 \\
 & & 2E_2
\end{tikzcd}$$

The frequency independence of ε_{33} for this new solid solution, when $x \geq 0{\cdot}3$, may be a reason for new electro-acoustic and electro-optic applications.

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