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Electroaccustic Transducers
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MATERIALS FOR ELECTROACOUSTIC TRANSDUCERS

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Piezoelectric Materials for Transducers.

Piezoelectricity

Piezoelectricity[1] is observed in materials whose structures are non-centrosymmetric, which subdivide into polar crystals with permanent dipoles and non-polar crystals, in which dipoles are created by an external stress. Polar crystals are subdivided into 2 classes dependent on the effect on their dipoles by an external field; if the dipoles can be reversed the crystal is called ferroelectric. (Figs 1, 2, 3).

Materials (Table 1)

Materials may be divided into 3 groups (a) available commerically in bulk, Rochelle salt, quartz, ADP, barium titanate and lead zirconate titanate (LZT) (b) available in small quantities and made by special techniques, lithium niobate, cadmium sulphide and lithium sulphate (c) reported but not available.

The development of piezoelectric materials has stemmed from known materials. From Rochelle salt (sodium potassium tartrate) have come tartrates, phosphates, arsenates and sulphates of sodium, potassium, lithium and ammonium, all grown from solution as single crystals (Fig. 4). Lithium sulphate, guanidinium aluminium sulphate (GASH), potassium dihydrogen phosphate and tri-glycine sulphate (TGS) are the most interesting of this group but the Curie temperatures of most of the others are below room temperature.

From barium titanate have come titanates, zirconates, niobates and tantolates of lead, strontium, lithium, sodium and potassium (Figs. 5, 6, 7, 8), which have been prepared either as ceramics or, in a few cases, grown from the melt as single crystals, Substitution for barium and titanium in the perovskite structure of barium titanate has led to the discovery that other structures, tungsten bronze, pyrochlore and layer structure can also exhibit piezoelectricity.

Cadmium sulphide, zinc sulphide and zinc oxide have the Wurtzite structure and are polar piezoelectrics but are not ferroelectric (Fig. 9). They are being developed for high frequency transducers, 100 MHz to 10Ghz; the necessary thin films are achieved by sputtering[2].

Ceramics v single crystals

A comparison between the properties of single crystals and ceramics is not easy since few materials have been made in both forms but it may be assumed that the piezoelectric activity is higher in single crystals.

The main advantages of ceramics are (a) their lower cost. (b) the fabrication of certain shapes, not possible with single crystals, such as tubes and hemispheres, (c) the ready adjustment of their electrical properties by variation of their chemical compositions e.g. it is possible in the case of barium titanate to add cobalt oxide to reduce dielectric loss, calcium carbonate to lower the room temperature phase transition and lead oxide to reduce ageing[3]. Ceramics have the main limitation that only ferroelectric materials can be considered since poling is involved.

High power transducer materials

(a) The ceramics BT and LZT operate by the oscillations of dipoles and the strain is small e.g. 2kV applied across a 1cm thick LZT ceramic element causes an extension of 4×10^{-5}cm. The extension is directly proportional to the field but this is limited by the dielectric loss factor, tan S, which also increases with the field. Improvements in LZT ceramics are being made and it may prove possible to operate with fields as high as 10kV/cm.

(b) Fig. 10. The strain in poling, or orientating, an unpoled LZT ceramic can be a hundred times greater than the strain from driving an already poled element. A single shot, large strain, transducer could employ the poling of an unpoled LZT element but the ceramic would then have to be restored to its zero state by thermal depoling. Conversely, a very much larger amount of electrical energy, 1 Joule/cm^3, can be obtained by allowing a poled ceramic element to be completely depoled by a large mechanical force. This again would be a single shot transducer since the element would have to be restored to its original state by repoling.. Transient currents of several hundred amps may be released by this means[4]

(c) The higher strains which occur in poling and depoling can also be obtained in phase transitions from a ferroelectric state F to an anti-ferroelectric state AF, which in some LZT compositions have a small energy difference (An AF state may be considered as opposing adjacent dipoles). In Fig. 11 an outline is given of a transition transducer. When a sufficiently large electric field E_F is applied there is a transition from AF to F, accompanied by a large volume strain and when the field is reduced there is a return to AF at a lower field E_{AF}. However, when this type of transducer is used to drive a mechanical load the pressure acts to prevent the change from AF to F. Consequently, a higher field is necessary to change from AF to F and the dielectric loss per cycle rises. Such transducers are likely to have very low efficiency(5).

Future materials (Table 2)

The physical and electrical properties in which improvements would be useful are:- (a) dielectric loss (b) sensitivity (c) density (d) frequency constant (e) temperature coefficients (f) pressure coefficients (g) mechanical shock resistance (h) mechanical Q.

Some properties will be improved by new materials but it is still possible to improve existing materials by changes in their chemical compositions or variations in processing; hence, with LZT it is possible to reduce dielectric loss, increase sensitivity, decrease temperature and pressure effects by chemical changes and to increase coupling coefficient by either sintering in oxygen or by hot pressing.

Methods of strengthening ceramics are still in their infancy but experiments have been made with glasses and alumina ceramics to stress the skin by forcing in larger atoms at the surface, e.g. a soda glass can be heat treated in a bath of molten potassium salt causing some larger potassium ions to replace sodium ions and create a compressive stress in the surface. In a similar way larger chromium ions can be made to replace aluminium ions in alumina(6).

Some methods of making materials are shown in Table 3.

Conclusions

Piezoelectric materials used at present satisfy many requirements of transducers and LZT ceramic materials are superior for most purposes. Further research on piezoelectrics is justified and the emphasis should probably be given to ceramics since these have a wider use.

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Table 1 Piezoelectric Materials

Material	Curie Temp °C	Coupling Kd	Coeff. K_{33}	Dielectric Constant	d Coul/N.	Stress
Rochelle salt	30	-	·68	350	550×10^{-12}	SHEAR
Quartz	550	-	·10	5	2 × "	COMPRESS.
ADP	120	-	·29	16	24 × "	SHEAR
BT (Bariumtitanate)	120	·25	·45	1000-2000	190 × "	COMPRESS
LZT (Lead Zirconate Titanate)	150-360	·55	·75	500-3000	250 × "	"
Lead niobate	560	·10	·40	500	120×10^{-12}	COMPRESS
Lithium niobate	1200	-	-	-	-	-
Lithium sulphate	75	-	·38	10	16 × "	-
Cadmium sulphide	-	-	·26	10	-	-
TGS-Tri-glycine sulphate	49	-	-	-	-	-
LZT/leadmagnesium niobate	-	·62	-	1000-2000	-	-
Sodium cadmium niobate	200	·40	-	2000	130×10^{-12}	-
Sodium potassium niobate	400	·43	-	300	40 × "	-
BT/calcium zirconate	20	-	-	10,000	-	-
BT/barium zirconate	-	-	·39	1800-6000	-	-
Lithium hydrogen selenite	-	K_y ·17	-	20 – 12000 (2.5 kV/cm)		
- Tartrates"						-
- Phosphates	110	-	-	-	-	-
- Arsenates						

Table 2 **Future** Piezoelectrics - Requirements:

(a) Lower dielectric loss
(b) Lower change of capacitance with pressure
(c) Lower change of capacitance with temperature
(d) Higher sensitivity
(e) Lower frequency constant
(f) Lower density
(g) Higher shock resistance
(h) Lower mechanical Q for NDT transducers.

Table 3 Material Preparation

1. CERAMICS - polycrystalline, sintering of pressed compacts.
2. SOLUTION SINGLE CRYSTALS - growth of seeds by slow cooling.
3. MELT SINGLE CRYSTALS - growth of seeds by pulling from melt.
4. FLUX SINGLE CRYSTALS - growth of crystals in a molten flux.
5. EPITAXIAL FILMS - (a) vapour deposition (chemical) (b) sputtered.
6. COMPOSITES - (a) plastic and powder (b) glass and powder (c) devitrified glass.
7. THICK FILMS - (a) painted layer (b) screen printed layer (c) electrophoretic layer (films are then fired)
8. HYDROTHERMAL SINGLE CRYSTALS - pressure and temperature gradient solutions.
9. REACTIVE HOT PRESSING - formation of either single crystals or ceramics.