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Review on Piezoelectric Materials as Thin Films with their Applications

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ABSTRACT

Piezoelectric Materials have played a pivotal role in the progress of Science and Technology since the First World War, being used historically as naturally occurring transducer for precise measurement or to transform energy from one form to the other while currently being used in the MEMS domain for sensing or energy harvesting. Thus this paper reviews piezoelectric materials and their applications in MEMS as thin films by categorizing the known materials in 3 types namely Naturally Occurring Materials, Piezoelectric Ceramics and Piezoelectric Polymers. Piezoelectric constants of the above mentioned materials are also enlisted.

Key words: Ferroelectric, Morphotropic Phase Boundary, Perovskite Structure, Piezoelectric Coefficient.

INTRODUCTION

Piezoelectric materials have been largely used in transducers since the last century[1]. Moreover, many piezoelectric materials have been synthesized by blending two compounds in appropriate proportions to tailor the properties of the so formed materials to suit the application[1]. After the discovery of naturally occurring piezoelectric materials, perovskite structured piezo-ceramics have been synthesized with far better piezoelectric constants and mechanical stability[1]. Currently for MEMS, thin films of compounds like Zinc Oxide, PZT, and Aluminium Nitride are being produced which have an enhanced performance due to the selected process parameters during their manufacturing[2]. Piezoelectric materials also are manufactured as a composite with the help of a synergic effect of a polymer and its ceramic phase to get the best fit of intermediate properties[3]. This paper discusses the trends in piezoelectric materials and their piezoelectric properties used as thin films with their application in MEMS devices.

Naturally occuring materials

The most common naturally occurring materials showing piezoelectricity are Quartz, Berlinite, Sucrose, Rochelle Salt, Cinnabar, Topaz and the Tourmaline group. Quartz is the first piezoelectric material to be found which has a crystalline structure made up of a continuous framework of SiO_4 silicon-oxygen tetrahedral with each oxygen atom being shared by two tetrahedral. The overall Quartz structure is an intermingle of two helices with different handedness with each SiO_4 being a member of the above mentioned helices. Thus overall the structure is not polar unless subjected to a pressure which results in a polarized structure.

The reported values of naturally occurring quartz crystal owing to its piezo-electric coefficients and dielectric properties are given below in Table 1, where ‘K’ refers to coupling constant.

However due to a serious dearth of naturally occurring materials, quartz is also being

Table 1: Piezoelectric Properties of Quartz[1]

Cut	K	Piezo-Constant
X	-0.09	2.3 X 10^{-12} C/N
Y	-0.14	-4.6 X 10^{-12} C/N
AT	-0.08	-3.4 X 10^{-12} C/N
AC	-0.10	-3.7 X 10^{-12} C/N
BC	-0.04	-0.9 X 10^{-12} C/N

Cut described in the above Table:
X (Parallel to YZ Plane),Y (Parallel to XZ Plane),AT(35°15´ with Z axis),AC(31° with Z axis),BC(-59° with Z axis)

synthesized artificially with the same physical, electric and chemical properties but the Quartz wafer is cut at different angles making them suitable for various applications according to the frequencies it can work with as shown in the Table above[1].

Quartz Crystal have also been deposited on silicon substrate as a thin film to be used as FBAR(Film Bulk Acoustic Resonator) working in frequencies close to 200MHz with a coupling factor close to 0.004 and thermal expansion coefficient being equal to 26 ppm /°C[4]. Quartz crystal has also been used as a part of MEMS motion sensing devices like the accelerometer and as a resonator[5]. Quartz has been inculcated in temperature sensor, as the frequency of the resonator is subject to change with temperature and precise calculations are possible with the temperature coefficient of frequency being 75ppm/°C[5]. Quartz is also been seen as an alternative to silicon in MEMS inertial sensors, as an accelerometer using fluoride based chemical etchant and chromium gold thin foil as a masking agent in Quartz (using electrodes to induce vibration) has been fabricated yielding ‘Q’ values of 7000-8000[6].It has also found application as a transducer(a Quartz tuning fork) to be used for photo-acoustic detection of trace gases with the reported sensitivity of 5.4 X 10^{-9} cm^{-1} $W/(Hz)^{1/2}$[7].

Rochelle Salt ($NaKC_4H_4O_6$-$4H_2O$), is one oldest material showing ferroelectricity between the two Curie temperatures T_{c1}=255K[8] and T_{c2}=297K[8] showing orthorhombic structure in the paraelectric phase and the monoclinic structure in the ferroelectric phase. It has a very low decomposition temperature equal to 55°C[8].Due to its bad behaviour to change in temperature and being water soluble it is not currently being used and also has not been fabricated as a thin film. The known piezoelectric coefficients (‘d’ and ‘g’) of Rochelle Salt obtained with the help of X-ray multiple diffraction are given in Table 2,

Piezoceramics

Piezoceramics first came into being due to high dielectric constant observed in $BaTiO_3$ due to its ferroelectricity (a phenomena in which a polar state exists before the application of pressure).$BaTiO_3$ was the first piezoelectric ceramic developed which namely exists in two basic structures a perovskitic form which is ferroelectric at temperatures below 1460°C and a hexagonal form which is stable above 1460°C [10- Pg 53].

Compounds based originally on $BaTiO_3$ like $BaTi_{0.90}Ga_{0.05}Nb_{0.05}O_3$ (BTGN) and $Ba_{0.60}Sr_{0.40}TiO_3$ (BST) have also found way in microwave applications at desired frequencies[11].Thin films of $BaTiO_3$ have been used for energy conversion after having deposited on a flexible substrate and then used for electrical power generation by bending the corresponding with the nano-generator producing voltage up to 1V[12].Most of the known piezoceramics have a perovskitic structure in which larger cations occupy the corner of the cubic unit cell while smaller cations are at the body centre and oxygen atoms at the centre of each face[10-Pg49].By adding combinations of atoms to $BaTiO_3$ that are oppositely deviating valency, such as K^{+1} or Li^{+1} replacing Ba^{+2}, Fe^{+3} + Nb^{+5} replacing $2Ti^{+4}$, Na^{+1}, Nb^{+5} replacing Ba^{+2} + Ti^{+4} extensive solid solutions are possible with modified ferroelectricty and a decrease in Curie point sharply [10-Pg107-108].Some additives have

Table 2: Piezoelectric Properties of Rochelle Salt[9]

d_{21}	7.0 X 10^{-10} C/N
d_{22}	2.2 X 10^{-9} C/N
d_{23}	2.1 X 10^{-9} C/N
d_{25}	3.7 X 10^{-11} C/N

Along with these naturally occurring materials, organic substances like tendon, silk, wood and dentin are also known to be piezoelectric materials.

also been used to improve the dielectric strength of $BaTiO_3$ like Nb_2O_5 , Ta_2O_5, $NaNbO_3$, $NaTaO_3$, CuO , In_2O_3,La_2O_3 and some larger rare earths like CeO_2,Fe_2O_3 and NiO [10-Pg 104].Aluminium Nitride (AlN) and ZnO are the materials widely used as piezoelectric thin films for MEMS[13-Pg40]. Some of the lead based piezoceramics like PZT (lead zirconium titanate) have also been used as thin films in cantilever beams, diaphragms for optical-MEMS(mirrors, scanners) and have also formed a part of RF-MEMS(Antennas, Resonators, Microwave Switches), Power-MEMS and Bio-MEMS[13-Pg 477-478]. Rare earth substituted thin films of $BiFeO_3$ have also been investigated with adulterations of Nd^{3+} and La^{3+}[14].

Many other lead based compounds were synthesized following structural analogy with $BaTiO_3$ like $PbZrO_3$, $PbTiO_3$, $PbHfO_3$, $PbSnO_3$[10- Pg 115-133].$PbTiO_3$ has a distorted perovskitic structure [10-Pg115].$PbTiO_3$ and $Pb_{1-x}La_xTi_{1-x/4}O_3$(PLT) thin films grown on MgO substrate have been successfully integrated in IR sensors which have shown better pyroelectric, piezoelectric and ferroelectric properties along with good response time[15].Also $BaTiO_3$ is adulterated with isovalent cations like Ca^{+2}, Sr^{+2} and Cd^{+2} to lower the Curie point and to diminish the tetragonal distortion [10-Pg91-96].Similarly when $BaTiO_3$ as poled with Sr^{+2} a linear reduction in Curie point was seen [10-Pg94]. Some of the other known solid solutions of $PbTiO_3$ are $PbTiO_3$-$LaAlO_3$, $PbTiO_3$—$LaFeO_3$,$PbTiO_3$-$Pb(Fe_{0.5}Ta_{0.5})O_3$, $PbTiO_3$-$PbMg_{0.5}W_{0.5}O_3$, $PbTiO_3$-$Pb(Fe_{0.5}Nb_{0.5})O_3$, $PbTiO_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$,$PbTiO_3$-$Pb(Zn_{1/3}Nb_{2/3})O_3$, $PbTiO_3$-$KNbO_3$,$PbTiO_3$-$BiMnO_3$,$PbTiO_3$-$K_{1/2}Bi_{1/2}TiO_3$ [10-Pg151-154].Most of the above mentioned solid solutions operate near the Morphotropic Phase Boundary which is related to percentage composition where two lattice structures co-exist leading to the elevation of piezoelectric properties. Some of the other lead based ternary systems with their characteristics are given in Table 4 below,

With a view to reduce the environmental damage to the earth, bismuth based ternary compounds were synthesized like $(Bi_{1/2}K_{1/2})TiO_3$, $(Bi_{1/2}Li_{1/2})TiO_3$ with properties comparable to lead based ternary compounds[13-Pg130]. Antiferroelectricity is the presence of switchable polar states above Curie temperature which was first seen in Rochelle Salt and later in $PbZrO_3$ [8,10].There are several additives to $PbZrO_3$ that in small quantities stabilize either a rhombohedral ferroelectric phase or a tetragonal antiferroelectric phase below Curie Point[10- Pg127-130].$PbSnO_3$ is also ferroelectric but unstable thus popularly exists in a binary state of (Pb,Ba)SnO_3[10-Pg 131].$PbHfO_3$ is isostructural to $PbZrO_3$ and also anti-ferroelectric for a tetragonal phase between 163°C and 215°C [10-Pg 132].

Table 3: Comparative Piezoelectric Properties of $BaTiO_3$ ceramic and single crystal [10- Pg 74]

	Single Crystal	Ceramic
k_{15}	0.570	0.476
k_{31}	0.315	0.208
k_{33}	0.560	0.493
d_{15}	392 X 10^{-12} C/N	270 X 10^{-12} C/N
d_{33}	85.6 X 10^{-12} C/N	191 X 10^{-12} C/N
d_{31}	-34.5 X 10^{-12} C/N	-79 X 10^{-12} C/N
g_{31}	-23.0 X 10^{-3}Vm/N	-4.7 X 10^{-3}Vm/N
g_{33}	57.5 X 10^{-3}Vm/N	11.4 X 10^{-3}Vm/N
g_{15}	15.2 X 10^{-3}Vm/N	18.8 X 10^{-3}Vm/N

Table 4: Characteristics of ternary systems [13-Pg100]

Pb $(Mn_{1/3}Sb_{2/3})O_3$	High Q_m (Quality factor), Large k
Pb $(Sn_{1/3}Sb_{2/3})O_3$	High Q_m, (Quality factor), Large k
Pb $(Mg_{1/3}Nb_{2/3})O_3$	High Q_m(Quality factor)
Pb $(Nb_{1/2}Sb_{1/2})O_3$	Thermal Stability
Pb $(Ni_{1/3}Nb_{2/3})O_3$	Large d constant
Pb $(Zn_{1/3}Nb_{2/3})O_3$	Large d constant

Table 5: Piezoelectric Constants of $Pb(Ti_{0.48}Zr_{0.52})O_3$ [10-Pg 146]

k_{31}	0.31
k_{33}	0.67
d_{31}	-93 X 10^{-12} C/N
d_{33}	223 X 10^{-12} C/N
d_{15}	494 X 10^{-12} C/N
g_{31}	-11.1 X 10^{-3} Vm/N
g_{33}	26.1 X 10^{-3} Vm/N
g_{15}	39.4 X 10^{-3} Vm/N

Popular PZT solid solutions are $Pb(Ti_{0.48}Zr_{0.52})O_3$ and $(Pb_{0.94}Sr_{0.06})(Ti_{0.47}Zr_{0.53})O_3$ and have properties as tabulated in Table 5 and 6,

PZT is at the heart of various applications due to the attributes given in Table 7 below,

Ultrasonic motors have also been fabricated in MEMS using PZT thin films but however its actuation requires large current compared to electric static motors [16].Due to its ferroelectric nature it has also found use in NVRAMs due to its switchable configurations being used as memory states and in SAW devices and pyroelectric sensors[17]. The other known solid solutions of $Pb(Hf,Sn,Ti,Zr)O_3$ are $(Pb,Ba)(Ti,Sn)O_3$,$Pb(Hf,Ti)O_3$ and $Pb(Hf,Sn,Ti)O_3$[10-Pg 170-175].

$NaNbO_3$, $KNbO_3$, $NaTaO_3$ and $KTaO_3$ also have a perovskitic structure and are reported to be ferroelectric [10-Pg 185].$KNbO_3$ has a great similarity with $BaTiO_3$ having four polymorphic forms namely cubic, tetragonal, orthorhombic and rhombohedral with a Curie temperature of 435°C[10-Pg 186-187]. Solid solutions in niobates and tantalates include $(Na,K)NbO_3$ (with $Na_{0.5}K_{0.5}NbO_3$ showing the highest piezoelectric coupling coefficient)[10-Pg 194], $(Na,Cd)NbO_3$ (with $Na_{0.75}Cd_{0.125}NbO_3$ showing optimum piezoelectric properties)[10-Pg 197], $(Na,Pb)NbO_3$, $NaTaO_3$-$NaNbO_3$, $KTaO_3$-$KNbO_3$, $AgNbO_3$-$AgTaO_3$ [10- Pg 197-200]. $LiNbO_3$ and $LiTaO_3$ are being used extensively as electro-optic, photorefractive, and non-linear optical crystals and being poled ferroelectrics they are also used in memory storage[18]. Some of the other known compounds with their Curie temperatures are given below in Table 8,

$PbNb_2O_6$ was the first ever oxide type non-perovskite ferroelectric discovered (T_c = 570°C) [10-Pg 214] having a potassium tungsten bronze structure. Some other examples showing similar structure are $PbTa_2O_6$ (T_c = 260°C[10-Pg 217]), $BaNb_2O_6$, $SrNb_2O_6$ and $K_{1.2}Li_{0.8}Nb_2O_6$.Solid solutions of the above compounds also do exist like $PbNb_2O_6$-$PbTa_2O_6$, $PbNb_2O_6$- $BaNb_2O_6$, $PbNb_2O_6$-$SrNb_2O_6$[10-Pg 218-220].Some of the ferroelectrics also have a distorted pyrochlore structure like $Cd_2Nb_2O_7$ and $Sr_2Ta_2O_7$ are ferroelectric with Curie points of -88°C [10-Pg226] and -80°C [10-Pg226].The Bismuth Layered Structures are characterized weak piezoelectric effects.The structure consists of layers of Bi_2O_{2+} separating two perovskite structures in one dimension while the structure spreading infinitely in the other two directions [10-Pg226]. The general formula is described by $Bi_2A_{x-1}B_xO_{3x+3}$[10-Pg226]. Known Bismuth layered structured compounds are Bi_3TiNbO_9, $BiTiTaO_9$, $Bi_2PbNb_2O_9$, $Bi_2CaNb_2O_9$, $Bi_2PbTa_2O_9$,$Bi_2CaNb_2O_9$, $Bi_2CaTa_2O_9$, $Bi_2SrNb_2O_9$, $Bi_2SrTa_2O_9$, $Bi_2BaNb_2O_9$, $Bi_2BaTa_2O_9$[10-Pg224]. Relaxor ferroelectrics have a diffuse, frequency dependent permittivity. Some examples of relaxor ferroelectrics are PMN-PT, PZN-PT and PIN-PT[10-Pg206].As the properties of relaxor ferroelectrics can be 'tuned' it is used to sense acoustic waves of various frequencies and depth profiles[19].

Polymers

Piezoelectricity was first seen in PVDF in 1969[20] and later was discovered in copolymers of vinylidene fluoride, trifluoroethylene, vinyl-cyanide, vinylacetate and nylons along with various bio-polymers[20]. Piezoelectric constants (in the shear direction) of various bio-polymers have been given below in Table 9,

Table 6: Piezoelectric Constants of $(Pb_{0.94}Sr_{0.06})(Ti_{0.47}Zr_{0.53})O_3$ [10-Pg 146]

k_{31}	0.33
k_{33}	0.70
d_{31}	-123 X 10^{-12} C/N
d_{33}	289 X 10^{-12} C/N
d_{15}	494 X 10^{-12} C/N
g_{31}	-14.5 X 10^{-3} Vm/N
g_{33}	34.5 X 10^{-3} Vm/N
g_{15}	47.2 X 10^{-3} Vm/N

Table 7: Applications and Properties [13-Pg95]

Application	Attributes
Injet Actuator	Large d constant;Stability
Fuel Injector	Large d constant
Buzzer	Large d constant
Shock Sensor	Large d & g constant
Ultrasonic Motor	High Q_m(Quality factor)
Gyroscope	High Q_m(Quality factor)
Filter	Thermal Stability

Table 8: Compounds and their Curie Temperatures [10-Pg200-201]

Compound	Curie Temperature
$CsGeCl_3$	155°C
WO_3	-50°C
$CdTiO_3$	-183°C
$BiNaTi_2O_6$	320°C
$BiKTi_2O_6$	380°C
Pb_2FeNbO_6	112°C
Pb_2FeTaO_6	-30°C
Pb_2YbNbO_6	300°C
Pb_2YbTaO_6	285°C
Pb_2LuNbO_6	270°C
Pb_2LuTaO_6	278°C
Pb_2ScNbO_6	90°C
Pb_2ScTaO_6	26°C
Pb_2MgWO_6	39°C
$Pb_3MgNb_2O_9$	-10°C
$Pb_3MgTa_2O_9$	-98°C
$Pb_3CoNb_2O_9$	-70°C
$Pb_3CoTa_2O_9$	-140°C
$Pb_3NiNb_2O_9$	-120°C
$Pb_3NiTa_2O_9$	-196°C
$Pb_3ZnNb_2O_9$	140°C
$Pb_3Fe_2WO_9$	-90°C
Pb_2CdWO_6	130°C -240°C
$BiFeO_3$	850°C

Similarly poled films of PVDF were tested for their piezoelectric constants and large piezoelectricity was seen (d_{31}=20pC/N;d_{32}=1.5pC/N;d_{33}=32pC/N;d_{15}=-27pC/N and d_{24}=-23pC/N)[21].A film of copolymer vinylidene cyanide and vinyl acetate was poled at 150°C and a piezoelectric constant of 5pC/N was observed[22]. PVDF has a glass transition temperature of -35°C and is found to be partially crystalline. Thin films of PVDF also have shown superior piezoelectric constant of 6-7pC/N [13-Pg14].Thin films of P(VDF/TrFE) with a molar ratio (75/25) have also been synthesized with thickness ranging 5-100 micrometers[20]. Thin films of polyurethane have also been synthesized using vapour deposition methods[20]. PVDF has been used extensively in ultrasonic imaging as a transducer with operating frequencies of 60-85kHz[23].Piezoelectric polymers like PVDF having low permittivity, low thermal conductivity and flexibility with low acoustic loss are used extensively in shock sensors, vibration control and tactile sensors[24].

Table 9: Piezoelectric Properties of Natural Biopolymers [20]

Wood	0.1 pC/N
Ramie	0.2 pC/N
Crab Shell	0.2 pC/N
Lobster apoderme	1.5 pC/N
Starch	2.0 pC/N
Bone	0.2 pC/N
Tendon	2.0 pC/N
Skin	0.2 pC/N
Wool	0.1 pC/N
Horn	1.8 pC/N
Salmon DNA	0.07 pC/N

CONCLUSION

From literature a categorization of natural and artificial piezoelectric materials was done and their piezoelectric properties and constants were enlisted. Similarly it was shown that they could also be used for thin film applications in MEMS devices.

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