Chapter 1
Introduction

1.1 Ferroelectric Materials

1.1.1 Basic Concept of Ferroelectric Materials

Solid materials can be divided into conductors, semiconductors, and insulators according to the respective conductive properties. Insulators can also be referred to as dielectric materials [1]. There is no free charge inside the ideal dielectric materials, charged particles are bound around the molecules or atoms. As shown in Fig. 1.1, when the dielectric is under the influence of an external electric field, the internal charge distribution will change: the positive and negative charge centers of non-polar molecules will be separated under the induction of the electric field to generate the electric dipole moment (displacement polarization); the intrinsic dipole moment of the polar molecule rotates until it coincides with the direction of the external electric field (orientated polarization). The phenomenon of the elastic displacement and dipole orientation alignment of the charge inside the dielectric is called the polarization of the dielectric [2, 3]. Polarization causes the dielectric to exhibit electrical
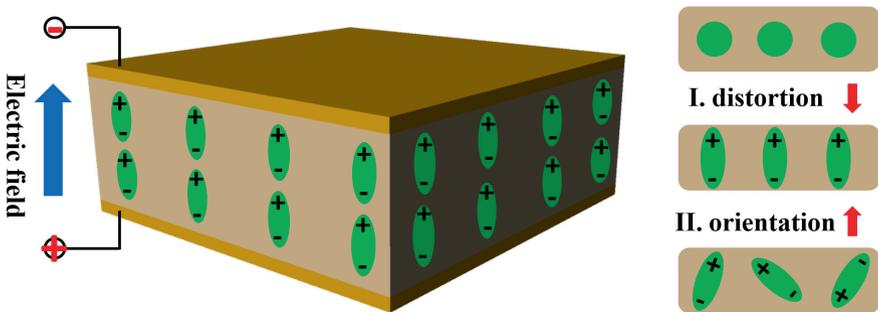

Fig. 1.1 The polarization of dielectric materials

properties at the macroscopic scale. A large amount of charges appear on the surface of the dielectric, which is called polarization charge. The degree of polarization of the dielectric by the external electric field can be expressed by the vector sum of the electric dipole moment per unit volume [4], defined as the polarization intensity. (Polarization, P):

$$P = \frac{\sum \overrightarrow{p_i}}{\Delta V} \tag{1.1}$$

There is a simple linear relationship between the polarization intensity of the common dielectric and the strength of the electric field. Once the external electric field is removed, the polarization of the dielectric immediately disappears. However, there is a special type of dielectric material with non-linear response, which can maintain the polarization state after the external electric field is removed. These ferroelectric materials are a class of materials that have spontaneous polarization and the spontaneous polarization can be switched by an external electric field [5]. A hysteresis loop similar to that depicted in Fig. 1.2 is an important feature of ferroelectric materials [6]. The non-poled ferroelectric material consists of many small regions with different spontaneous polarization directions. The spontaneous polarization directions in each small region is the same. This kind of small region is called the ferroelectric domain, and the boundary of adjacent domains is called the domain wall [7]. When a ferroelectric material is gradually applied to an external electric field, its polarization P increases along the O-A dash line as the electric field E increases. The orientation of almost all of the domains at point A is parallel to the direction of the external electric field such that the polarization is saturated. Increasing the electric field will only cause a linear increase in the displacement polarization of electrons or ions. Extending the linear portion to the longitudinal axis, the intercept is called the saturated polarization (P_{sa}) of the material. In the process of removing the external electric field, the polarization does not return to the

**Fig. 1.2** The P-E loop of a typical ferroelectric material
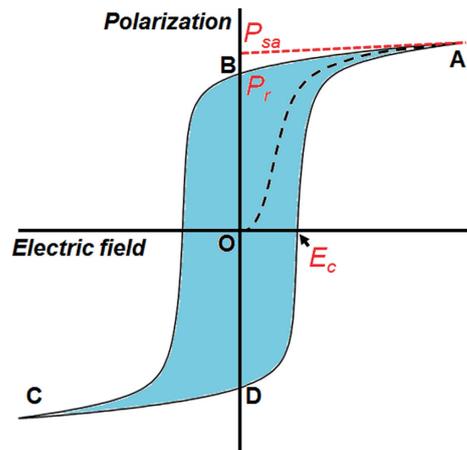
origin, but reaches the point B along the A-B curve. The polarization at this time is an important parameter for characterizing the ferroelectric properties of the material, called remnant polarization (P_r). When the electric field is applied in the opposite direction, the polarization will decrease along the B-C curve to a negative saturation value. The B-C curve intersects with the horizontal axis, and the corresponding absolute value of the electric field strength is called the coercive field (E_c), which can be used to measure the difficulty of poling ferroelectrics.

1.1.2 Physical Properties of Ferroelectric Materials

Since the discovery of ferroelectricity in 1920s [8], the research on ferroelectric materials can be described as long-lasting. So far, there are thousands of ferroelectric materials that have been discovered, and the physical origins of ferroelectric properties of different materials are not the same [9]. With the continuous emergence of various new types of ferroelectric materials, the theoretical understanding of ferroelectric materials is gradually deepening and improving. As early as 1940, Mueller's theory of Rochelle salt proposed a systematic understanding of the relationship between various properties of materials [10]. In 1945, the first displacement ferroelectric without hydrogen bonds, barium titanate ($BaTiO_3$), was discovered. During this period, the theory of ferroelectric phenomenology began to sprout and grew. The phenomenological theory summarizes some of the phenomena observed in ferroelectric materials with a few parameters and describes the relationship between these phenomena without in-depth explanation of the underlying causes [11, 12]. By the 1960s, many ferroelectric materials such as lead zirconate titanate (PZT) and lithium niobate ($LiNbO_3$), appeared one after another. From the perspective of lattice dynamics, Cochran and Anderson creatively proposed soft mode theory to explain ferroelectric phase transitions. Their viewpoint is that the occurrence of spontaneous polarization corresponds to the softening of an optical transverse mode at the center of the Brillouin zone [13, 14]. After that, the soft mode theory and the Landau phase transition theory caused profound changes in ferroelectric physics. After long-term work in related fields, scientists have gradually clarified the relationship between some physical properties of dielectric materials [15], as shown in Fig. 1.3.

Fig. 1.3 Piezoelectric, pyroelectric and ferroelectric material relationships
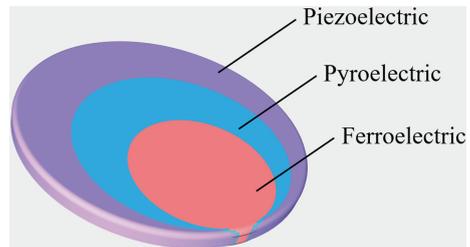
As we can see that a material with ferroelectric properties must have both pyroelectric and piezoelectric properties. Among them, pyroelectric performance describes the relationship between polarization and temperature. When the ferroelectric material is uniformly heated, the intensified thermal vibration tends to disturb the ordered state after poling, so that the polarization is lowered. This change in polarization is manifested macroscopically as the release of charge, which will cause current in an external circuit [16]. The pyroelectric performance can be quantitatively characterized by the pyroelectric coefficient of the material, which is defined as the first derivative of the polarization (P) versus temperature (T) [17]

$$p = \frac{\mathrm{d}P}{\mathrm{d}T} \tag{1.2}$$

The pyroelectric coefficient is not a scalar but a vector with a unit of $\mathrm{C\,m^{-2}\,K^{-1}}$.

Piezoelectric properties refer to the phenomenon of charge accumulation on a surface that is proportional to external force when a material is subjected to mechanical stress (positive piezoelectric effect); or stress and strain generated when the material is subjected to an applied electric field (inverse piezoelectric effect) [18, 19]. The piezoelectric effect bridges the dielectric properties and elastic properties, reflecting the coupling relationship between the polarization and mechanical stress of the material. The piezoelectric constant d_{mj} is usually used to describe this coupling relationship. The physical meaning is the change rate of the electrical displacement component D_m with the stress component X_j when the applied electric field strength is constant [20].

$$d_{mj} = \left(\frac{\partial D_m}{\partial X_j} \right)_E \tag{1.3}$$

The piezoelectric constant is a third-order tensor, and the first-kind piezoelectric constant (piezoelectric strain constant) is expressed with the unit of pC/N. In general, ferroelectric materials have better piezoelectric properties than non-ferroelectric piezoelectric materials, so the most widely used materials in the piezoelectric field are ferroelectric materials. These physical properties of ferroelectric materials determine their broad application areas.

1.2   PMN-PT Relaxor Ferroelectric Single Crystals

1.2.1   *PMN-PT Complex Perovskite Structure*

In general, most inorganic ferroelectric materials perform much better than organic ferroelectric materials. Oxygenated compounds are important families in inorganic ferroelectric materials. According to the division of crystal structure, they mainly

Fig. 1.4 Crystal structure of
perovskite compounds
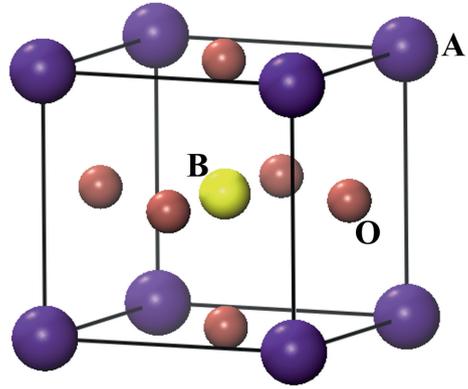
include the following categories: tungsten bronze structure, bismuth layer-structured
compounds, pyrochlore structure, lithium niobate structure and perovskite structure
[21]. Among them, the ferroelectric properties of the materials with perovskite struc-
ture are the best. Figure 1.4 shows a schematic diagram of the crystal structure of
a perovskite material with a chemical formula of ABO_3. The cation at the A site
occupies 8 vertex positions of a single unit cell, and the cation at the B site occupies
the body center of the unit cell accordingly. The oxygen ions are located in the six
face centers and enclose the B-site cations to form the $[BO_6]$ octahedron. When the
vibration equilibrium position of the B-site cation is shifted with respect to the center
of the oxygen octahedron, an electric dipole moment is generated. And the response
of the electric dipole moment to the external electric field is a poling process of
the perovskite-type ferroelectric materials. This special crystal structure allows ions
at each equivalent lattice position to be replaced by other ions with similar radius
and similar properties, which can greatly enrich the types of perovskite structural
materials.

In the perovskite structure, if there is more than one kind of cation in the A or B
position, it is called a composite perovskite structure. The lead magnesium niobate-
lead titanate system $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (hereinafter referred to as
PMN-PT) is in the case of B-site complex. The A site in the PMN-PT crystal struc-
ture is occupied by Pb^{2+} ion with a large radius, while the B site is occupied by
Mg^{2+}, Nb^{5+} or Ti^{4+} ions with a small radius. From the chemical composition analy-
sis, the perovskite composite PMN-PT can be regarded as a complex solid solution
system formed by the perovskite structure of the relaxor ferroelectric PMN and the
ordinary ferroelectric PT [22]. Since the crystal structures of the two compositions
are similar, PMN and PT can be dissolved with each other in any ratio. However, as
the PT composition content increases, the crystal structure of PMN-PT will exhibit
a phase transition from the rhombohedral ferroelectric phase (R) to the tetragonal
ferroelectric phase (T). Figure 1.5 shows the low temperature phase diagram of the
PMN-PT solid solution system [23]. In a certain composition region, the rhombo-
hedral and tetragonal ferroelectric phases in the PMN-PT system will coexist. The

Fig. 1.5 The phase diagram
of PMN-*x*PT solid solution
system [23]
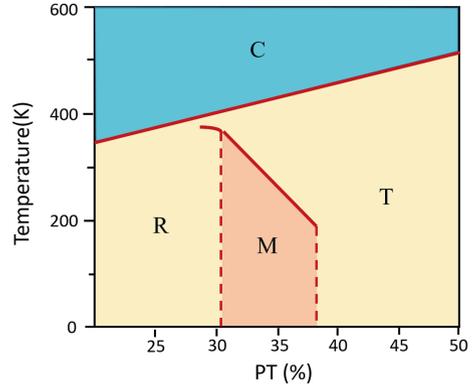
crystal present the optimal piezoelectric performance, and this composition region is
called the morphotropic phase boundary (MPB). It is generally believed that the MPB
of PMN-*x*PT material system at room temperature is between $x = 0.30$–0.35 [24–
26]. The structure and properties of PMN-PT solid solution materials are closely
related to their compositions. Therefore, PMN-PT functional materials with high
piezoelectric, ferroelectric, and pyroelectric properties and specific structures can be
obtained by composition adjustment.

1.2.2 Research Progress of PMN-PT Single Crystals

Due to the periodic structure and the anisotropy of physical properties, single crystals
always have the best performances among the materials of the same chemical com-
position. For example, monocrystalline silicon is superior to polycrystalline silicon
and amorphous silicon in both mechanical and electrical properties in the field of
photovoltaic technology. In addition, the structure of single crystal materials is much
simpler than polycrystalline materials, which is more conducive to the study of the
mechanisms of various physical effects [27, 28]. In order to make full use of these
advantages of crystals, people began to explore the growth of relaxor ferroelectric sin-
gle crystals. However, compared with the ceramic preparation process, the growth
of single crystal has more influencing factors and is therefore more complicated.
Fortunately, in the existing relaxor ferroelectric material system, PMN-PT has the
characteristics of quasi-congruent melting [29], and it is easier to grow large single
crystals than the incongruent melting solid solution of other chemical compositions.

For a long time, researchers have carried out a lot of works about the prepara-
tion and performance of PMN-PT relaxor ferroelectric single crystals. For instance,
Shrout et al. [30] has grown a PMN-30PT single crystal with a maximum size of
about 1 cm in 1990, and measured a d_{33} mode piezoelectric coefficient of 1500 pC/N.
Park and Shrout [31] has grown high-performance PMN-PT crystals and studied the
properties of single crystals near the MPB composition. Dong and Ye [32] has grown

PMN-PT single crystals in 2000, and systematically studied the effects of chemical and thermodynamic parameters on the crystal growth process. In China, many research institutions represented by the Shanghai Institute of Ceramics, Tsinghua University, and Xi'an Jiaotong University have also developed the ability to grow large-size PMN-PT single crystals. Nowadays, large-size PMN-PT single crystals with a growth direction along the [001] crystal orientation have been commercialized [33]. The piezoelectric constant of the MPB composition crystal exceeds 2000 pC/N, and the longitudinal electromechanical coupling coefficient k_{33} is as high as 0.9. These properties are far superior to the currently widely used PZT piezoelectric ceramics. Figure 1.6 shows the PMN-PT single crystals and various processed products.

The PMN-PT relaxor ferroelectric single crystal is the most outstanding representative of ferroelectric materials. The emergence of PMN-PT crystal and another
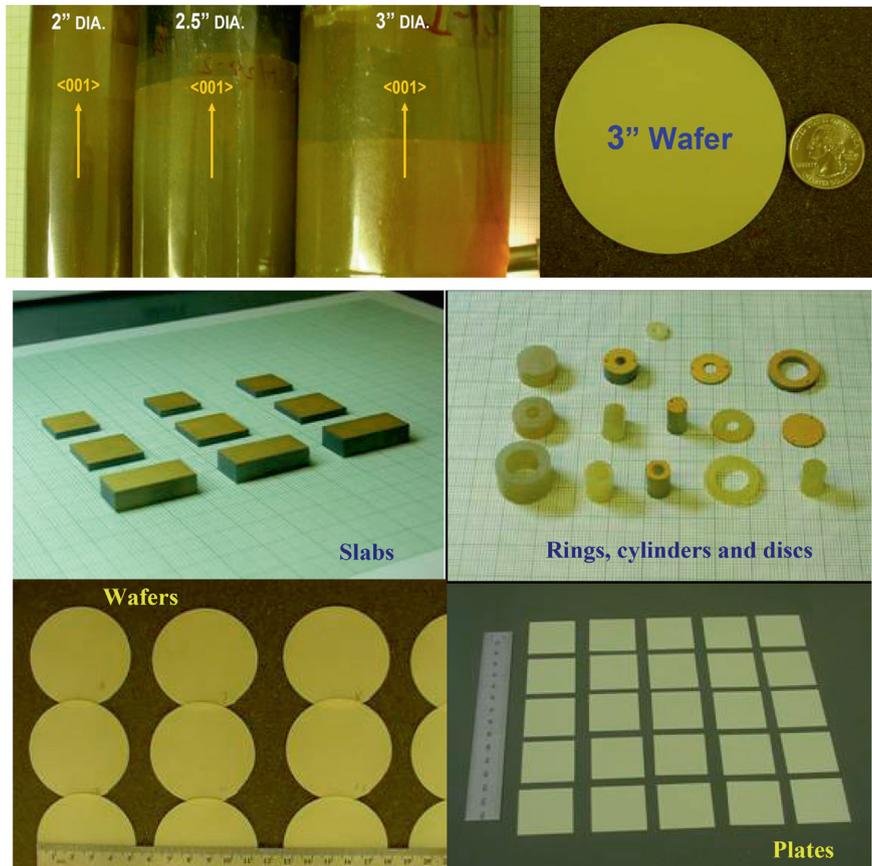

Fig. 1.6 PMN-PT crystals and processed products. Reproduced with permission [33] . Copyright 2014, Elsevier

relaxor system $(1 - x)Pb(Zn_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (referred to as PZN-PT) is known as the "exciting breakthrough" in the past 50 years in the entire ferroelectric industry [34]. Researches on the performance and structure of PMN-PT single crystals have attracted much attention. For example, Liu et al. [35] has systematically studied the effects of vibration modes, ferroelectric domain structure, temperature and other factors on the energy dissipation behavior of PMN-PT single crystals. Li and coworkers [36] have studied the surface acoustic wave properties of different cut PMN-PT single crystals and found that the energy flow angle of single crystals is significantly smaller than that of ordinary piezoelectric materials, which is beneficial to increase the working bandwidth and reduce energy loss. Wan et al. [37] has accurately studied the basic electro-optic properties of PMN-PT single crystals according to the method of minimum deflection angle. It was found that the refractive index of PMN-PT single crystal has frequency dispersion phenomenon and the Sellmeier dispersion equation of the crystal is summarized. Yan et al. [38] has analyzed the energy changes in the formation of microdomains, calculated the relationship between potential energy density and microdomain size, and discussed the effect of dual polarization mechanism on the dielectric behavior of PMN-PT single crystal. Zeng et al. [39] has observed the nanoscale ferroelectric domain structure and dynamic behavior of PMN-PT single crystals by piezoresponse force microscope (PFM), and obtained the three-dimensional polarization distribution image of domain structure.

Another research hotspot for PMN-PT crystals is to increase its ferroelectric phase transition temperature (T_{rt}). The dielectric constant of the PMN-PT single crystal near the MPB composition has another significant inflection point before the temperature rises to the Curie temperature. At that temperature, the crystal undergoes a phase transition from the rhombohedral ferroelectric phase to the tetragonal ferroelectric phase [40]. The phase transition of the ferroelectric structure makes the coexistence of two phases disappear, and the original excellent piezoelectric activity and electromechanical coupling performance also deteriorate. In other words, the ferroelectric phase transition temperature is the upper limit of the actual use temperature of the PMN-PT single crystal in the piezoelectric device. Since the T_{rt} of PMN-PT near the MPB composition is only 50–80 °C, their applications in high-power devices is restricted [41]. Recent studies have found that the introduction of the third composition in PMN-PT crystal can effectively break the bottleneck of T_{rt} [42–44]. Yamashita et al. [45] has used a top seed method to grow a 24PIN-43PMN-33PT single crystal with a T_{rt} of about 120 °C. Zhang et al. has used the Bridgman method to grow a larger size PIN-PMN-PT ternary crystal [46], which has a piezoelectric constant of about 1400 pC/N and a T_{rt} between 100 and 125 °C. Xia et al. [47] has successfully grown a PMN-PT-PZ single crystal with a PZ content of 5%, and increased the T_{rt} to 127 °C while maintaining a piezoelectric constant of 1000 pC/N. The research work of introducing the third composition in the crystal lays the foundation for the practical application of the PMN-PT systems single crystal at higher temperature.

1.2.3   The Applications of PMN-PT Single Crystals

The study of functional materials is application-oriented and can contribute to the transformation of scientific and technological achievements. The application of functional materials must be based on some of their physical or chemical properties. It can be seen from Fig. 1.3 that the PMN-PT single crystals as a ferroelectric material have both piezoelectric properties, pyroelectric properties and ferroelectric properties. Below we introduced the current application research progress of PMN-PT single crystals based on different physical properties.

1.2.3.1   Piezoelectric Devices

Due to the elimination of grain boundaries, PMN-PT single crystals exhibit excellent piezoelectric and electromechanical coupling properties at room temperature. They are expected to play an important role in the field of mechanical energy and electrical energy conversion technology. The successful growth of large-size, high-quality PMN-PT relaxor ferroelectric single crystals has also laid a good material foundation for the development of high-performance piezoelectric devices. At present, there are many successful examples for the application of high piezoelectric performance PMN-PT single crystal, and some have even developed into commercial products.

1. Medical ultrasonic imaging

Ultrasonic imaging is currently one of the most effective medical diagnostic techniques, and ultrasonic transducers are a core component in the entire imaging system [48]. The electromechanical conversion properties of the piezoelectric material used in the transducer will ultimately determine the resolution of the ultrasonic imaging. The electromechanical coupling coefficient of PMN-PT single crystal is higher than 0.9, and it has a small attenuation and velocity dispersion in the frequency range of 20–100 MHz [49]. These excellent material properties make it shine in the field of ultrasonic transducers. For example, Peng et al. [50] has prepared a single-element ultrasonic transducer based on PMN-PT single crystal as a transcranial Doppler probe. The high-frequency focusing transducer can be prepared on PMN-PT single crystal by using a dimpling grinder [51]. It exhibits better sensitivity and bandwidth than a single-element transducer of planar configuration. Based on the Krimholz-Leedom-Mattaei (KLM) model, array type transducers fabricated from PMN-PT single crystals can theoretically achieve 130% bandwidth, and experiment bandwidth values as high as 114% have also been reported [52]. IBULE Company (South Korea) has successfully developed a 64-channel ultrasonic transducer array using PMN-33PT single crystal, and its imaging quality is significantly better than the commercially available lead zirconate titanate ceramic transducer [53]. Philips Company began research on the production of single crystal transducers in 1997. The first broadband phase array transducer was named "PureWave" and was launched in 2004. Figure 1.7 shows heart image obtained by the phase array transducers [54].
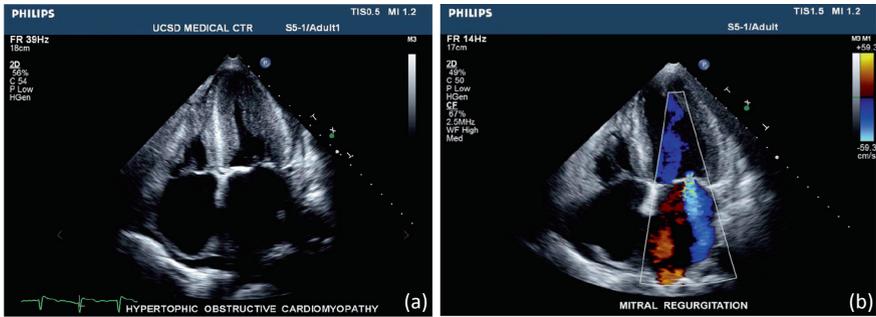
Fig. 1.7 Apical 4 chamber view of cardiac harmonic and color flow images obtained using a single crystal transducer. Reproduced with permission [54]. Copyright 2005, IEEE

The annular array transducer [55] shown in Fig. 1.8 can also be fabricated using PMN-PT single crystal and its 1-3 composites. It can be applied to an endoscopic ultrasonic imaging system to get information about human organs and tissues fast and clearly without mechanical rotation.

2. Hydroacoustic transducer

Sound waves are the most effective telematics carrier under water, so submarine, subsea oil exploration and underwater exploration equipment need to transmit information by means of sound waves [56]. The underwater acoustic transducer is an energy conversion element that realizes underwater acoustic emission and reception. In the early 1990s, the research on relaxor ferroelectric single crystals was promoted by the urgent application need for underwater acoustic transducers and medical ultrasonic imaging. The US Naval Undersea Warfare Center (NUWC) developed the underwater acoustic transducers based on PMN-PT single crystal and PZN-PT single crystal [57], and explored their application in underwater unmanned vehicles and torpedoes. Researchers in Penn State University have conducted researches on low-noise Tonpilz hydrophones. Figure 1.9a depicts the cross-sectional structure of a typical Tonpilz hydrophone. It is reported that PMN-PT single crystal can reduce the
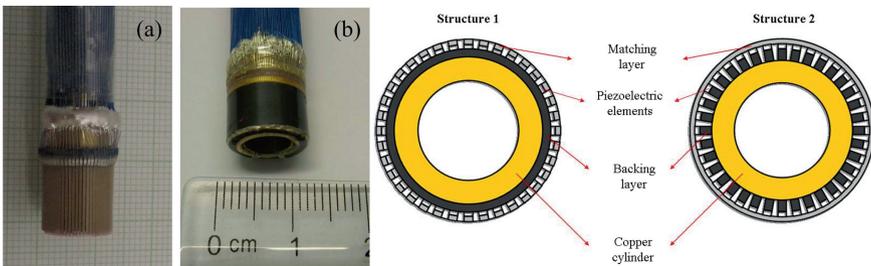

Fig. 1.8 The annular array transducers based on PMN-PT crystals. Reproduced with permission [55]. Copyright 2010, IEEE