Abstract: Flexoelectricity is a gradient electromechanical effect that exists in all solid dielectrics. The effect was first predicted in the late 1950s, but received little interest because it was expected to be small. The experimentally measured large flexoelectric response in ferroelectric ceramics led to the revival of the field in the early 2000s. In this study, the progress made in the flexoelectric field is reviewed. The authors’ focus will be primarily on the experimental studies related to the flexoelectric effect. The techniques employed to measure the flexoelectric coefficients are first summarised. A compilation of the flexoelectric coefficients of different ferroelectric materials reported in the literature will be presented. An unresolved issue in this field is that the measured flexoelectric coefficients in ferroelectric materials are normally much greater than the theoretically predicted values, and the mechanisms proposed to explain this issue are discussed. Finally, the efforts toward the applications of the flexoelectric effect are reviewed.

1 Introduction
The constitutive equation of the electric polarisation in dielectric materials can be expressed as [1]

$$P_i = \chi_{ikl} E_j + e_{ijkl}S_{jk} + \mu_{ijkl} \frac{\partial S_{kl}}{\partial x_j}$$

(1)

where $P_i$, $E_j$, $S_{jk}$, and $\partial S_{kl}/\partial x_j$ are electric polarisation, electric field, elastic strain, and the gradient of elastic strains $S_{kl}$ in the $x_j$-direction, respectively. Parameter $\chi_{ikl}$ is dielectric susceptibility measured under constant elastic strain, $e_{ijkl}$ is the permittivity of free space, and $\mu_{ijkl}$ are the piezoelectric coefficient and flexoelectric coefficient. Piezoelectricity, which is expressed in the second term in (1), is a well-studied electromechanical effect in dielectrics. The last term describes the contribution of another electromechanical effect, flexoelectricity, to polarisation. As shown in (1), $\mu_{ijkl}$ is a fourth-order tensor and $e_{ijkl}$ is a third-order tensor. Therefore, the piezoelectric effect only appears in materials without a centre of symmetry in their crystal structures, but there is no restriction on crystal structures that have a flexoelectric effect.

There are three non-zero components for the flexoelectric coefficient $\mu_{ijkl}$ (or $\mu_{jkl}$ in matrix notation) in a centrosymmetric dielectric material: $\mu_{1111}$ (or $\mu_{11}$), $\mu_{1122}$ (or $\mu_{12}$), and $\mu_{1212}$ (or $\mu_{22}$), which can be expressed in matrix form [1, 2]

$$\mu = \begin{bmatrix}
\mu_{11} & \mu_{12} & 0 & 0 & 0 \\
\mu_{12} & \mu_{11} & 0 & 0 & 0 \\
0 & 0 & \mu_{44} & 0 & 0 \\
0 & 0 & 0 & \mu_{44} & 0 \\
0 & 0 & 0 & 0 & \mu_{44}
\end{bmatrix}$$

(2)

The flexoelectric effect was first predicated in solids in the late 1950s and the first phenomenological framework for the description of this effect was proposed in 1964 [3–5]. Only very few studies were carried out in the following years, primarily because the effect was expected to be weak [2]. In 1981, Indenbom et al. [6] proposed a Landau-type theory for flexoelectricity and the term ‘flexoelectric effect’ was first used to describe the coupling between the electric polarisation and elastic strain gradient as an analogy to the similar charge separation phenomenon in liquid crystals. The initial theoretical calculation of the flexoelectric coefficient in simple dielectrics was estimated to be in the order of $10^{-11}$–$10^{-10}$ C/m, which was small for practical applications [1, 2, 7, 8]. The flexoelectric effect includes four contributors: the bulk static flexoelectricity, the bulk dynamic flexoelectricity, the surface flexoelectricity, and the surface piezoelectricity [1, 9]. Theoretical study by Tagantsev indicated that the flexoelectric coefficient of dielectrics was proportional to the dielectric susceptibility of dielectric materials [9]. Since ferroelectric materials normally have high dielectric properties, the materials are a class of dielectric materials with high flexoelectric response [1, 10]. Inspired by Tagantsev’s theoretical work, Ma and Cross [11–16] measured the flexoelectric coefficients of ferroelectrics of high permittivity. In general, the experimentally measured flexoelectric coefficients in those ferroelectrics are much greater than the theoretical values, and the large flexoelectric response in ferroelectrics can be exploited for practical applications [7, 8, 17]. These experimental findings stimulated continuous interest in research of flexoelectricity in the following years [18–27]. Those studies mainly focused on searching for materials with high flexoelectric coefficients, understanding mechanisms for the larger than theoretically expected flexoelectric response in ferroelectrics, and potential applications of the flexoelectric effect. Although many factors such as defects, local structural distortion, nanopolar regions, built-in polarisation, and residual ferroelectricity have been thought to contribute to the measured flexoelectric effect, the mechanism for the relatively large flexoelectric coefficient in ferroelectrics is not fully understood [8, 23–27]. Additionally, the strain gradient can be enhanced by reducing the material dimensions, which results in a larger flexoelectric response [8, 18, 19]. The size-dependent effect of flexoelectricity has been a topic of great interest [1, 28–32] that can be used to design new electromechanical devices and to understand some nanoscale phenomena such as mechanical writing memory [33], microelectromechanical systems devices [34, 35], the rotation of polarisation in ferroelectric thin films [18], the manipulation of oxygen vacancies in oxides [36], and flexoelectric nanogenerators [17].
In this paper, we will review measurement methods of flexoelectric coefficients, summarise flexoelectric coefficients measured in ferroelectrics, and discuss the mechanisms for the measured large flexoelectric response. The potential applications of flexoelectricity will also be discussed and summarised.

2 Characterisation of the flexoelectric coefficient

At present, flexoelectric coefficients have primarily been measured in ferroelectrics, particularly ferroelectric ceramics because of their high flexoelectric response [1, 10]. Non-poled ferroelectric ceramics are centrosymmetric materials, and there are only three non-zero flexoelectric coefficients: \( \mu_{11} \), \( \mu_{12} \), and \( \mu_{44} \) [1, 2]. Of these coefficients, \( \mu_{11} \) and \( \mu_{12} \) have been measured by using materials with special geometries. However, much less work has been devoted to the measurement of \( \mu_{44} \). In this section, we will summarise the test methods for \( \mu_{11} \) and \( \mu_{12} \).

2.1 Measurement of \( \mu_{11} \)

To measure \( \mu_{11} \), the dielectric materials are fabricated into samples with asymmetric shapes such as a truncated pyramid-like shape, as shown in Fig. 1a [1]. During the measurement, a uniaxial sinusoidal compression force \( F \) is applied on the pyramid-like shape sample, as illustrated in Fig. 1b [1]. The strain \( \varepsilon_{33} \) generated by \( F \) varies along the thickness direction because of its asymmetric shape. If we assume that the strain gradient is uniform along the thickness direction, the gradient can be written as [1, 7]

\[
\frac{\partial \varepsilon_{33}}{\partial x_3} = \frac{(F/2Ea^2) - (F/2Eb^2)}{h} = \frac{F(\beta - a^2)}{2Ea^2b^2h} \tag{3}
\]

where \( a \) and \( b \) are the lengths of the sides of the top and bottom square surfaces, respectively, \( E \) is Young's modulus of the materials, and \( h \) is the thickness of the truncated pyramid sample. Owing to the strain gradient, an electrical response can be generated by the flexoelectric effect (or apparent flexoelectric response). The longitudinal flexoelectric coefficient \( \mu_{11} \) can be calculated with the measured electrical response and the strain gradient. For this approach, the estimation of the strain gradient is oversimplified. In reality, when the asymmetric samples are compressed, the strain gradient is non-uniformly distributed in the materials, and the distribution of the strain gradient is complicated [37]. Consequently, it is difficult to express with a simple analytic equation. The exact value of \( \mu_{11} \) cannot be obtained [38]. Nevertheless, the relative magnitude of \( \mu_{11} \) of different materials can be evaluated and compared with this approach. It should be noted that when the flexoelectric coefficients are measured using this method, the ferroelectric materials are not poled and should not have piezoelectric response. However, if piezoelectric effect is produced in the materials due to some non-controllable reasons, the response may have an effect on the measured flexoelectric coefficients [24]. Therefore, caution has to be taken when the experimental results are analysed.

2.2 Measurement of \( \mu_{12} \)

The value of \( \mu_{12} \) is normally measured by bending a long rectangular dielectric material [1]. A strain gradient can be generated by the bending deformation. The bending deformation can be generated via the cantilever method (clamping one end of the beam and applying a force at the other end), three-point-bending (3PB) method (the beam is supported at the two ends and a force is applied in the middle) or 4PB method (the beam is supported at the two ends and a force is applied via two points in the middle of the beam). Here, a survey of the \( \mu_{12} \) measurement methods is presented.

2.2.1 Cantilever method: In the early 2000s, Ma and Cross [12, 15, 16] measured the transverse flexoelectric coefficient \( \mu_{12} \) of the relaxor \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \) (PMN) in ceramics for the first time using the cantilever method. As illustrated in Fig. 2a, a ceramic bar sample was clamped at one end and driven at the free end by a moving coil loudspeaker [1, 15, 16]. The displacement as a function of position along the beam was measured using a differential variable reluctance transducer. The vibration of the cantilever causes bending deformation of the ceramic beam and induces a strain gradient in the thickness direction. An electric response from the strain gradient due to the flexoelectric effect can then be generated. In their studies, several small circular electrodes were deposited on the surface of the ferroelectric beam along the length direction. Since the strain gradient varies along the length, the electric responses from the different spots with electrodes are also different. The strain gradients for these spots can be expressed by the equation below:

\[
\frac{\partial S_{33}}{\partial x_3} = \frac{\partial W(x_3)}{\partial x_3} \tag{4}
\]

where \( W(x_3) \) is a superposition of different deflection modes of a specific point at \( x_3 \) (the distance from the clamping point). In fact, each mode shape can be written as below:

\[
W(x_3) = A_r \left[ \sin \beta_r L - \sin \beta_r x_3 \right] \tag{5}
\]

In the above equation

\[
A_r = \frac{C_1 r}{\sin \beta L - \sin h \beta L} \tag{6}
\]

where \( r = 1, 2, \ldots \), and \( C_1 \) is determined by the displacement at the electrode position. \( L \) is the length of the sample. Generally, if the fundamental mode \( (r = 1) \) is considered, \( \beta L = 1.875 [16] \).
During the measurement, the electric response from each spot is measured separately. The strain gradient is calculated by (5). A linear relation can be obtained between the polariisation response and strain gradient of these spots. Fig. 2b shows a typical curve measured using this method from (Ba,Sr)TiO$_3$ (BST) ceramics [12]. The flexoelectric coefficient $\mu_{12}$ can be calculated from the slope of the linear fitting curve of the experimental data points.

For materials with weak flexoelectric response such as polymers, the electric response is difficult to measure if a small circular electrode is used. To enhance the electric signal, an electrode with a much larger area can be used. In this case, the relationship between the electric response and the mechanical deformation can be derived. For example, for a cantilever beam with a full electrode, the relationship between the induced electric current $i$ from the flexoelectric effect, which is monitored by a lock-in amplifier, and the deflection $w(x)$ of a specific point at $x$ (the distance from the clamping point) on the cantilever, can be expressed as follows [40]:

$$i = \frac{2\pi f \mu_{12} b L}{x(1-(x/L))^3} w(x)$$

where $f$ is the frequency measurement; $b$ is the width; $h$ is the thickness; $L$ is the length of the ceramic beam; and $x$ is the distance of a specific measurement point from the fixed end of the ceramic beam. The strain gradient in the cantilever can be changed by changing the deflection of the cantilever. A linear relationship between $i$ and $w(x)$ can be obtained and the flexoelectric coefficient can be calculated from the slope of the curve. For example, $i$ versus $w(x)$ curves measured from polyvinylidene fluoride (PVDF) polymers are shown in Fig. 2c [39].

2.2.2 3PB method: The bending deformation can be generated by a 3PB method. A rectangular plate is supported at two ends and a force is applied to the plate in the middle of the plate. In [23], Zubko et al. used a dynamic mechanical analyser (DMA) with an insulating quartz probe to induce oscillatory bending and the amplitude of the vibration can be directly measured by the DMA. The generated current $i$ resulting from the flexoelectric polarisation is measured using a lock-in amplifier and the total electric charge $Q$ is related to the measured electric current $i$ as follows:

$$Q = \frac{i}{2\pi f}$$

For three-point bending, the strain gradient at the centre $\partial S_{11}/\partial x_3$ in the thickness direction ($x_3$) can be expressed as follows:

$$\frac{\partial S_{11}}{\partial x_3} = \frac{12\epsilon_0}{L^3}(L - a)$$

where $L$ is the distance between the two supporting points; $z_0$ is the displacement at the centre of specimen; and $a$ is the half-length of the electrodes. The flexoelectric coefficient $\mu_{12}$ is given by the equation below:

$$\mu_{12} = \frac{L^2}{24\pi f A z_0} \frac{1}{L - a}$$

As a quick measurement of the flexoelectric coefficient, the test can be performed on a commercial $d_{33}$ meter using a custom-made 3PB test fixture [41]. An effective piezoelectric response $d_{33}$ from the flexoelectric response of a rectangular plate under bending can be directly read from the $d_{33}$ meter. The conversion between the effective $d_{33}$ and the flexoelectric coefficient can be expressed as [41]

$$d_{33} = \frac{3\mu_{12}(1 - \lambda)L^2}{2hE}$$

where $d_{33}$ is the measured piezoelectric constant.

It should be noted that there is a requirement for the width-to-length ratio when rectangular plates are used for the flexoelectric measurement. Finite element modelling indicates that the anticlastic effect plays an important role in the measurement of the flexoelectric coefficient [28]. Fig. 3 shows the significant effect of the ratio on the effective $d_{33}$ of a rectangular plate used for the flexoelectric measurement.

To measure the flexoelectric coefficients of nematic liquid crystals, a setup was designed, in which the middle point of the rectangular sample was fixed [42]. The bending of the sample was produced by periodically translating the sidewalls that are attached to the two ends of the sample. This method is suitable for the measurement of the flexoelectric response of soft materials such as liquid crystal thin films.

2.2.3 4PB method: When the flexoelectric response is measured, the bending deformation can also be applied by a 4PB test fixture, as schematically shown in Fig. 4 [11]. A force is applied on the sample at two points in the middle of a rectangular plate while the plate is supported at the two ends. The induced electric charge $Q$ from the flexoelectric response can be detected by an electrometer. The generated flexoelectric polarisation $P$ is given by the equation below:

$$P = \frac{Q}{A}$$

where $A$ is the electrodes area. The strain gradient in the thickness direction $\partial S_{11}/\partial x_3$ is calculated using the following equation:

$$\frac{\partial S_{11}}{\partial x_3} = \frac{12\epsilon_0}{L^3} s$$

where $s$ is the moving crosshead speed and $t$ is the time after the force is applied. The transverse flexoelectric coefficient $\mu_{13}$ is calculated with the equation below:

$$\mu_{13} = \frac{Q L^2}{12 A s t}$$

The electrodes are deposited on opposite surfaces between the two points, where the force is applied. This method is used to study the effect of the movement of ferroelastic domains on the flexoelectric response of the ferroelectric ceramics because a high stress can be applied on the samples.

2.2.4 Point-ring (PR) method: The flexoelectric response can be induced in a disc sample by using the PR method, in which the dielectric disc sample is supported at the edge and a force is applied in the middle of the samples, as shown in Fig. 5 [43, 44].
The test can be performed on a $d_{33}$ meter. The vibration of the probe of the $d_{33}$ meter causes bending deformation of the ceramic wafers and induces an effective $d_{33}$ from the flexoelectric effect of the tested dielectric materials. The strain gradient $\partial S(r)/\partial z$ in the thickness $z$-direction is [43]

$$\frac{\partial S(r)}{\partial z} = -\frac{3F(1-\sigma^3)}{\pi Eh}(\frac{\sigma}{1+\sigma} + \ln\frac{Eh}{R})$$  \hspace{0.5cm} (15)

where $F$ is the point force applied to the centre of the ceramic wafer, $E$ is the elastic modulus, $\sigma$ is Poisson’s ratio, $R$ and $h$ are the radius and the thickness of the wafer, respectively, and $r$ is the distance of the point from the centre of the wafer. The measured apparent PR $d_{33}$ can be expressed as

$$d_{33} = \frac{Q}{F}$$ \hspace{0.5cm} (16)

In the above equation, the generated electric charge $Q$ by the flexoelectricity can be deduced by

$$Q = 2\pi \int_0^\pi r \mu_\rho \frac{\partial S(r)}{\partial z} dr$$ \hspace{0.5cm} (17)

where $\mu_\rho$ is the apparent flexoelectric coefficient, which includes contributions from both $\mu_{12}$ and $\mu_1$. From (15)–(17), the apparent flexoelectric coefficient can be derived as

$$\mu_\rho = \frac{2d_{33}Eh^3}{3(1-\sigma)R}$$ \hspace{0.5cm} (18)

### 2.3 Measurement of the converse effect

The converse flexoelectric effect (CFE) describes the generation of the mechanical response by applying an electric field gradient, which can be expressed in the form of

$$T_{ij} = \mu_{ijkl} \frac{\partial E_k}{\partial l}$$ \hspace{0.5cm} (19)

The flexoelectric coefficients can be measured based on the CFE [45, 46]. To do this, ceramics are fabricated into a truncated pyramid-like structure. Owing to the asymmetric shape, the voltage applied on the top and bottom surfaces of the structure results in an inhomogeneous electric field in the materials. A mechanical deformation can be generated due to the CFE. The flexoelectric coefficient can be calculated from the electric field gradient and the measured strain. The flexoelectric coefficients measured based on the direct effect and the converse effect should be the same, as observed previously [47].

The macroscopic characterisation methods for the flexoelectric effect are straightforward and easy to implement. The flexoelectric coefficients can also be studied using the microscopic approach such as by the measurement of the phonon spectrum [2]. However, the absolute value of the flexoelectric coefficients cannot be directly obtained from phonon data. The microscopic method can be combined with the macroscopic method to obtain the value of the flexoelectric coefficients of different components [48, 49].

### 3 Magnitude of the flexoelectric coefficient

It has been proposed that the magnitude of the flexoelectric coefficient $\mu$ is roughly proportional to dielectric susceptibility $\chi$, which can be estimated by [10]

$$\mu = \chi C$$ \hspace{0.5cm} (20)

where $e$ is the electron charge and $a$ is the unit cell dimension. The high permittivity of dielectric materials indicates that they are materials with high flexoelectric coefficients [1]. The flexoelectric coefficients of different materials, especially ferroelectric materials, measured mostly using the methods summarised in the last section, are summarised in Table 1. It should be noted that the flexoelectric coefficients shown in this table are effective values. There are two implications of the term ‘effective’. First, the measured flexoelectric response is not merely flexoelectric in origin, but contains contributions from different extrinsic mechanisms [24, 40]. We will discuss this issue in the next section. Second, there are three non-zero components of the flexoelectric coefficients for the ferroelectric ceramics, but it is difficult to separate the three components of the coefficients. For example, the measured $\mu_{11}$, in fact, includes contributions from both $\mu_{11}$ and $\mu_{12}$. Nevertheless, the measured coefficients can still be used to evaluate the strength of the flexoelectric response of materials.

The experimentally measured flexoelectric coefficients are in the range of $10^{-7}$–$10^{-3}$ C/m, which are 3–8 orders of magnitude larger than the theoretically predicted values in simple dielectric materials ($10^{-11}$–$10^{-10}$ C/m) [1].

Studies have shown that the effective flexoelectric coefficient of ferroelectric ceramics can be enhanced by some approaches such as a reduction reaction using graphite as reduction agent or by a thermal treatment [21, 56–58]. For example, the reduced 0.92Na0.5Bi0.5TiO3-0.08BaTiO3 (NBBT8) exhibits a $\mu_\rho$ of more than 1.3 mC/m at room temperature, whereas the $\mu_\rho$ of the unreduced ceramics is $<15$ $\mu$C/m, as shown in Fig. 6 [44]. The large $\mu_\rho$ of the reduced ceramics can be sustained at a high temperature. At 350°C, the $\mu_\rho$ of the reduced ceramics is about 250 $\mu$C/m. The large flexoelectric response in the reduced ferroelectrics is promising for practical applications.

### 4 Mechanism for the measured flexoelectric response

The flexoelectric coefficients of dielectric materials are thought to be associated with their dielectric permittivity. To remove the effect of the permittivity on the flexoelectric response, the flexocoupling coefficient is used to characterise the magnitude of the flexoelectric effect [7]. The flexoelectric effect can then be expressed by
\[ P_i = \chi_{ks} \varepsilon_0 f_{i,jl} \delta S_{kl} \delta x_j \]  

(21)

where \( f_{i,jl} \) is the flexocoupling coefficient. The theoretically predicted value of \( f_{i,jl} \) is typically below 10 V. For materials with

### Table 1

Experimental flexoelectric coefficients of ferroelectric ceramics at room temperature

| Compound                        | Coefficient Value, \( \mu \text{C/m} \) | Method\(^a\) | Reference |
|---------------------------------|----------------------------------------|--------------|-----------|
| \( \text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3 \) | 150                                    | PC           | [1]       |
|                                | 120                                    | CFE          | [45]      |
|                                | 100                                    | CB           | [12]      |
|                                | 124 ± 14                               | CFE          | [46]      |
| \( \text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3 \) | 10.0                                   | PR           | [43]      |
| diffused \( \text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3 \) | 4.2                                    | PR           | [43]      |
| \( \text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3/\text{NiO}_0.8\text{ZnO}_0.2\text{Fe}_2\text{O}_4 \) composite | 128.6                                 | PC           | [50]      |
|                                | 114.7                                  | PC           | [50]      |
|                                | 61.7                                   | PC           | [50]      |
|                                | 16.6                                   | PC           | [50]      |
| \( \text{SrTiO}_3 \) (crystal)       | \( \mu \sim 10^{-2} \)                | 3PB          | [23]      |
| \( \text{Ba(10.87Sn}_{0.13}\text{)}\text{O}_3 \) | 53                                     | CB           | [51]      |
| \( \text{Al}_2\text{O}_3\)-doped \( \text{Ba(Ti}_{0.85}\text{Sn}_{0.15}\text{)}\text{O}_3 \) | 40.5                                   | CB           | [52]      |
| \( \text{BaTiO}_3 \)                | 30.2                                   | PC           | [13]      |
|                                | \( \sim 120 \)                          | PR           | [49]      |
| heat-treated \( \text{BaTiO}_3 \)   | \( \sim 200 \)                         | PR           | [49]      |
| reduced \( \text{BaTiO}_3 \)        | \( \sim 1000 \)                        | 3PB          | [27]      |
| \( \text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3 \) | 20                                     | PC           | [1]       |
| \( \text{PbZrO}_3 \)                | 0.002                                  | 3PB          | [53]      |
| \( \text{AgNbO}_3 \)                | 0.005                                  | 3PB          | [53]      |
| \( \text{Pb(Zr, Ti)}\text{O}_3 \)   | 0.5                                    | 4PB          | [11]      |
|                                | 1.4                                    | CB           | [14]      |
| \( \text{PMN} \)                   | 4                                      | CB           | [16]      |
| \( \text{PMN-PbTiO}_3 \)            | 6–12                                   | PC           | [54]      |
| \( \text{0.3Pb(In}_{1/2}\text{Nb}_{1/2}\text{)}\text{O}_3-0.35\text{PbTiO}_3-0.35\text{PMN} \) | 50                                     | CB           | [55]      |
| \( \text{NBBT6} \)                  | 4.4                                    | PR           | [43]      |
| diffused \( \text{NBBT6} \)        | 2.2                                    | PR           | [43]      |
| \( \text{NBBT8} \)                  | \( \sim 2.1 \)                         | CB           | our work  |
|                                | \( \sim 1.9 \)                         | PR           | our work  |
| reduced \( \text{NBBT8} \)         | \( \sim 1350 \)                        | PR           | [44]      |
| \( \text{NBBT20} \)                | \( \sim 2.8 \)                         | PR           | our work  |
|                                | \( \sim 2.4 \)                         | CB           | [21]      |
|                                | 100                                    | CB           | [21]      |

\(^a\)Test methods: CB – cantilever bending method; PC – pyramid compression method; CFE – converse flexoelectric effect method; 4PB – four-point-bending method; 3PB – three-point-bending method; PR – point-ring method.

**Fig. 6** Temperature dependence of the effective piezoelectric coefficient \( d_{33} \) and the calculated flexoelectric coefficients of the reduced and unreduced NBBT8 ceramics [44]
the perovskite structure, $f_{ij}$ should be lower than 15 V [7]. Otherwise, the structure will be unstable and an incommensurate phase can be produced. However, the experimentally measured $f_{ij}$ of ferroelectric materials are often several orders of magnitudes greater than the theoretically predicted values. For example, the $f_{ij}$ of BST ceramics is >850 V [12], and our study suggests the $f_{ij}$ of the heat-treated BaTiO$_3$ (BTO) can be higher than 6000 V [56].

Theoretical study indicates that there are four contributors to the flexoelectric effect of a dielectric material [1]. When the flexoelectric coefficients are measured using the above-mentioned methods, all except dynamic flexoelectricity may contribute to the measured coefficients [1]. Typically, the magnitude of $f_{ij}$ of the surface piezoelectricity and surface flexoelectricity is comparable with that of the bulk flexoelectric response from the crystal lattice, which is typically below 10 V [1]. Consequently, there is a large discrepancy between the experimental and theoretical flexoelectric coefficients in ferroelectric ceramics, but the mechanisms for the discrepancy are still not fully understood [24, 26, 27, 56, 59]. Results have shown that other extrinsic mechanisms contribute to the large measured flexoelectric coefficients in addition to the above-mentioned mechanisms. Progress has been made in recent years to understand this issue, and in this section, we summarise several important mechanisms proposed for the issue.

In relaxor ferroelectrics, there exist nanodomains or nanopolar regions, which are easily re-oriented by external perturbation [15, 60]. Under inhomogeneous deformation, the re-orientation of the nanodomains or nanopolar regions can contribute to the measured flexoelectric response, and this is thought to be one mechanism for the large measured flexoelectric response, as schematically shown in Fig. 7. The model in Fig. 7 is based on PMN ceramics, which have a perovskite structure. In the relaxors, the nanodomains or nanopolar regions have eight equivalent <111> polarisation orientations (Figs. 7a and b), and overall, the materials are non-polar because of lack of preferable orientations (Fig. 7c). Under a strain gradient, the orientations become non-equivalent, leading to preferable orientations and polarisation response (Fig. 7d).

It was also found that high-temperature processing of the ferroelectric ceramics could produce an inhomogeneity in the materials, resulting in a symmetry breaking and built-in polarisation [24]. The built-in polarisation develops during the ceramic densification, and the direction of the built-in polarisation depends strongly on the processing conditions. The piezoelectric response from the built-in polarisation is thought to be a mechanism for the large flexoelectric coefficients in ferroelectric ceramics. On the basis of this mechanism, the flexoelectric coefficient of a material should depend, to a great extent, on the symmetry-breaking effect of the sample surface, may arise at surface-adjacent layers even in centrosymmetric materials, and the piezoelectric response is thought to be a mechanism for the measured flexoelectric response [20, 32, 61]. The surface piezoelectricity can generate a flexoelectric-like response, and this response was found to be the same order of magnitude as the intrinsic lattice flexoelectric response [1]. Recently, a barrier-layer mechanism was proposed to explain the anomalously large flexoelectric coefficient of semi-conductive BTO ceramics, which were doped by oxygen vacancies [27]. The doped BTO (BTO$_{0.9}$) can be treated as a sandwich structure, in which two insulating barrier (surface) layers are separated by a semi-conducting (bulk) region, as is schematically illustrated in Fig. 8. The conductive bulk region responds to the bending deformation by allowing free charges to move and accumulate near the interface between the bulk and the surface, which compensates the charge generated by the surface piezoelectricity. This results in a large flexoelectric-like response. Since ferroelectric oxides are normally insulators, the barrier-layer mechanism cannot be applicable to normal ferroelectrics.

Our recent study suggested the surfaces of ferroelectrics are spontaneously polarised [56]. The thickness of the surface is approximately several μm, which is much larger than that of the theoretically predicted surface piezoelectricity. Furthermore, the piezoelectric response of the polarised surface is much greater than that of the surface piezoelectricity. Since the signs of the piezoelectric response of the opposite surfaces are different, the surfaces will generate a flexoelectric-like response under bending deformation, as shown in Fig. 9. Our results indicate that the unexpectedly large flexoelectric coefficient measured in ferroelectric ceramics mainly originates from a spontaneously polarised surface. The effect of the polarised surface is greatly affected by the thermal history.

In addition to the mechanisms summarised above, other mechanisms such as local strains induced by interfaces, grain
boundaries, the residual ferroelectricity, and defects were also thought to be the mechanisms for the flexoelectric response measured in ferroelectrics [23, 26, 55, 62, 63]. For the insulating ferroelectrics, one key mechanism, the spontaneously polarised surface, has been identified for the large flexoelectric response in ferroelectric ceramics. However, even if the contribution of this mechanism is excluded, the flexoelectric response of the ferroelectric ceramics is still greater than the theoretical value, indicating the existence of other mechanisms producing the large flexoelectric response [56]. Further work is required to completely understand the large discrepancy between the experimental and theoretical flexoelectric coefficients in ferroelectric ceramics.

5 Potential applications of flexoelectricity

The large flexoelectric coefficients measured in ferroelectrics inspired the exploration of applications of the flexoelectric effect [64]. In this section, progress in the applications of the flexoelectricity will be summarised and discussed.

5.1 Flexoelectric piezoelectric composites

Traditional piezoelectric composites contain at least one piezoelectric component to obtain piezoelectric response [65]. By exploiting flexoelectricity, a composite without a piezoelectric component can exhibit a piezoelectric-like response if the material has special geometries or structures to convert the applied stress into a strain gradient [41, 65]. Studies suggest that the so-called flexoelectric piezoelectric composites can generate large effective piezoelectric response. Several types of flexoelectric piezoelectric composites have been realised experimentally [21, 28, 41, 58, 66–69]. The first type is the composite with the truncated pyramid structure, as shown in Fig. 10a [66]. The asymmetric structure converts the stress into strain gradient, and a flexoelectric response can be generated, mainly from the $d_{11}$ of the ceramic. Although the BST ceramics used to fabricate the structure are in the paraelectric phase, the composite exhibits a piezoelectric response of about 6 pC/N when the size of the structure is several mm.

The flexoelectric piezoelectric composites can also be designed by exploiting the $\mu_{12}$ of ferroelectric ceramics. An example is the flexure mode composites, in which several pieces of BST ferroelectric ceramic sheets are separated by fine tungsten wires, as illustrated in Fig. 10b [41]. The stress applied on the two metal platens for stress distribution can be transferred to the ceramic sheets by the tungsten wires, causing the bending of the ceramics. Composites with this design can generate an effective $d_{33}$ higher than 4300 pC/N at a temperature around the Curie temperature of BST and the effective $d_{33}$ still maintains very high value in the paraelectric phase above the Curie temperature. Similarly, if a piece of ceramic wafer is supported on a metal ring and a force is applied at the centre of the wafer, the bending of the ceramic wafer can also generate a piezoelectric-like response (Fig. 10c) [43]. To simplify the design, a dome-like structure (Fig. 10d) can be produced by the diffusion method or the asymmetrical reduction reaction using graphite as reduction agent [21, 43]. For this design, the metal ring is not necessary, and the structure can generate a bending deformation on a flat surface. Our recent work demonstrated that via the asymmetrical reduction using graphite as reduction agent, a piece of NBBT8 ceramic wafer can function such as a piezoelectric material, and a very high effective $d_{33}$ of ~8900 pC/N can be obtained in reduced ceramics due to the enhanced apparent flexoelectric response. The value of this effective $d_{33}$ is about 60 times larger than the piezoelectric coefficient (~142 pC/N) of the poled Na$_{1/2}$Bi$_{1/2}$TiO$_3$ based ceramics of the same composition, and is also higher than that of piezoelectric single crystals [44].

It should be noted that because the strain gradient can be increased by reducing the size of the materials, the piezoelectric response of flexoelectric piezoelectric composites is size dependent [21, 66]. The apparent piezoelectric response of the composites can be enhanced by reducing the size of the composites.

For flexoelectric piezoelectric composites, it is often observed that the variation in effective $d_{33}$ with temperature follows a similar trend to that of dielectric constant [41, 43], as shown in Fig. 11. The observation can be explained by the surface mechanism of the flexoelectric-like response proposed recently [56, 70].

5.2 Manipulation of the ferroelectric polarisation

Owing to the size effect of the strain gradient, flexoelectricity has a more important impact on the physical properties of materials when the size of the materials is reduced [8, 18, 19, 33]. At nanoscale dimensions, the flexoelectric effect can be large enough to orient the ferroelectric polarisation [18, 71]. For example, in a ferroelectric thin film, the lattice mismatch between the thin film and substrate can generate a high strain gradient of the order of $10^6$ m$^{-3}$, which is much larger than that in bulk materials [23]. One example is that the flexoelectricity in thin films has a significant effect on the orientation of the ferroelectric polarisation [18]. Another example is that by varying oxygen partial pressure during film growth to generate strain gradient in HoMnO$_3$ thin films, the polarisation orientation and domain distributions are influenced by...
the flexoelectricity [19]. The strain gradient can also be applied to ferroelectric nanomaterials in a controllable way. It was demonstrated that the strain gradients generated near the tip of an atomic force microscope can mechanically switch the ferroelectric polarisation of the thin film [33, 72]. This result implies that new memory devices, in which information is written mechanically and read electrically, can be designed.

5.3 Energy-related applications

The reduced ferroelectrics exhibit an enhanced apparent flexoelectric response and a large apparent piezoelectric response, which can be exploited for mechanical energy harvesting applications. The energy harvesting performance of reduced NBBT8 ceramics was investigated [44]. Our recent results show that though the reduction reaction can significantly enhance the apparent flexoelectric response, the energy harvesting properties are inferior to the conventional piezoelectric energy harvesters. The noteworthy advantage of the flexoelectric energy harvesters is that the energy harvesting performance can be sustained at a temperature higher than the depolarisation temperature of the piezoelectric ceramics.

The flexoelectric effect can also be used to convert thermal energy into electrical energy. Our recent work discovered that under a 3PB deformation, the paraelectric ferroelectric plate exhibited a thermal–electrical response even under a uniform temperature environment [73]. The thermal–electrical response originates from the coupling effect of the bending induced flexoelectric effect, which is equivalent to an electric field, and the conduction of the ceramics. In this case, the generation of strain gradient does not require a thermal input, but to generate carriers for conduction, the thermal excitation is needed. The observed thermal–electrical response can be exploited for thermal energy harvesting.

It was found that the bulk photovoltaic effect can be realised in semiconductors by the mediation of the flexoelectric effect [74]. Large photovoltaic currents induced by strain gradient and due to the flexoelectric effect were created from centrosymmetric single crystals of strontium titanate, titanium dioxide, and silicon [75]. Furthermore, an anomalous photovoltaic effect in centrosymmetric ferroelastic BiVO$_4$ was observed, and the phenomenon was also attributed to the flexoelectric effect.

5.4 Sensors and actuators

Applications of the flexoelectric effect in sensor and actuator applications were also explored [17, 76]. An accelerometer was fabricated with a trapezoidal shape BST-steel unimorph structure [77]. The accelerometer exhibits a sensitivity of 0.84 pC/g.

The flexoelectric piezoelectric composites fabricated by the reduction approach exhibit a high apparent direct piezoelectric response. Conversely, as shown in Fig. 12, a relatively large displacement can be generated in asymmetrically reduced NBBT ceramics under a small electric field [67]. The reduced ceramics are promising for actuator applications.

In recent work, we demonstrated that the magnetoelectric response could be achieved through the coupling between flexoelectricity and ferromagnetism. In conventional magnetoelectric materials, the response originates from the coupling between ferroelectricity and ferromagnetism [78].

6 Summary and future prospects

Significant progress has been made in flexoelectric research in the last 15 years. The flexoelectric coefficients of a variety of ferroelectric materials have been measured. One fundamental issue in this field is that the measured flexoelectric coefficients in ferroelectrics are often much larger than theoretically predicted values. Different mechanisms have been proposed to explain this issue, and the spontaneously polarised surface was identified as one key mechanism for the large flexoelectric response. Applications of the flexoelectric effect have been explored. The uniqueness of flexoelectric materials and devices is that their performance is size-dependent and high-temperature stable, which is promising for applications at nanoscale dimensions.

Despite the significant progress made in this field, one important issue is still not completely resolved: the mechanisms for the unexpectedly large flexoelectric effect measured in many ferroelectric materials. The understanding of the issue is not only important for the fundamental study of flexoelectricity, but also important for the design of new materials with large flexoelectric response. Also, though different novel applications of flexoelectricity have been proposed, continuous work is needed to achieve materials or devices for real applications.

7 Acknowledgments

This research was supported by the National Natural Science Foundation of China (Nos. 51672261 and 51373161), the National Key Research and Development Program of China (No. 2017YFA0701301), and the 1000 Young Talents Program.

8 References

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