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Estimating the true piezoelectric properties of $BiFeO_3$ from measurements on $BiFeO_3$-PVDF terpolymer composites

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ABSTRACT

$BiFeO_3$ is an interesting multiferroic material with potential use in sensors and transducers. However, the high coercive field and low dielectric strength of this material make the poling process extremely difficult. Poling becomes a lot easier if the ceramic particles are incorporated in a non-conductive polymer with comparable dielectric properties. In this work, unstructured composites consisting of $BiFeO_3$ particles in a non-piezoactive PVDF terpolymer matrix are made with a ceramic volume fraction ranging from 20% to 60%. The highest piezoelectric charge and voltage constant values (d_{33} = 31 pC/N and g_{33} = 47 mV m/N) are obtained for a $BiFeO_3$-PVDF terpolymer composite with a volume fraction of 60%. The Poon model is chosen to analyse the volume fraction dependence of the dielectric constant while the modified Yamada model is used to analyse the piezoelectric charge constant data. It is concluded that the maximum possible piezoelectric constant for bulk $BiFeO_3$ can be as high as 56 pC/N.

1. Introduction

$BiFeO_3$, also called Bismuth Ferrite or BFO, like many piezoelectrics, crystallises with a distorted rhombohedral perovskite-type structure and was first discovered in the late 1950s by Royen and Swars [1]. However, interest in this material only rose in the early 2000s due to the high Curie temperature (~825 °C [2]) and the high spontaneous polarization: 50–60 $\mu C/cm^2$ in thin films [3], ~100 $\mu C/cm^2$ in single crystals along the $[111]_{pc}$ direction [4] and 45 $\mu C/cm^2$ in bulk ceramics [5]. But studies on the piezoelectric properties of bulk ceramics of $BiFeO_3$ never yielded the high values reported for the thin films (120 pm/V [6])and its true potential was never demonstrated. This is largely due to the problems of electrical leakage and phase purity, which created difficulties in realising the potential maximal properties of bulk $BiFeO_3$. The presence of secondary phases in $BiFeO_3$ leads to large electrical leakage currents, which impose serious restrictions on its industrial use. Furthermore, large leakage currents become increasingly prohibitive at high fields. Thus, due to the high coercive field required to pole $BiFeO_3$, it is important to increase its insulating properties to reduce the leakage currents [7].

One way to prevent leakage and short circuiting is to incorporate $BiFeO_3$ particles into a non-conductive matrix, such as another ceramic [8,9] or a polymer [10–13]. The dielectric properties of different composite films of $BiFeO_3$-PVDF (with $BiFeO_3$ concentrations ranging from 13 to 34 vol%) were found to increase with increasing filler content [14]. Composites of one-dimensional (1D) multiferroic $BiFeO_3$ and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) composites showed coexistence of electric and magnetic hysteresis for the composite materials at room temperature [15].

While the intrinsic piezoelectric properties of granular $BiFeO_3$ can in principle be derived from the volume fraction dependence of the piezoelectric properties of $BiFeO_3$-polymer composites, the analysis is only valid if the dielectric constants of the polymer and the piezoceramic are almost equal. Since $BiFeO_3$ ceramics have a relatively low value for the dielectric constant in comparison to other piezoelectric ceramics, this opens up possibilities for selecting a polymer matrix with a comparable dielectric permittivity. Hence in this work a relaxor polymer, polyvinylidene difluoride with tri-fluoroethylene and chlorofluoroethylene copolymers (P(VDF-TrFE-CFE), or in-short a PVDF terpolymer), with a high dielectric constant and without any piezoelectric properties itself (even cast film 150 µm thick polarized at 35 kV/mm field for 20 min showed no piezoelectric response), is chosen as the matrix material. To minimize the contribution of particle-to-particle connectivity to the properties the work focusses on so-called 0–3 composites where the particles are homogeneously dispersed in the polymer matrix with minimal particle-particle contact. The volumetric dependence of the dielectric and the piezoelectric properties of the composites is then analysed in detail to determine an

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accurate estimate of the intrinsic piezoelectric properties of $BiFeO_3$ in granular form.

2. Experimental procedure

2.1. Composite manufacturing

Based on extensive synthesis trials single phase $BiFeO_3$ powder was obtained by solid state synthesis from pre-milled Bi_2O_3 and Fe_2O_3 in equal proportions with 1 at% excess Bi, as described previously [16]. This mixture of oxides was calcined at 750 °C for 1 h The agglomerated powder was then dry-milled using 2 mm yttria stabilized zirconia balls for 5 h by using a planetary ball mill. The particle size distributions of the milled powder in an aqueous solution as measured by a laser diffraction analyser were found to be d(10) = 0.67 µm, d(50) = 1.44 µm, and d(90) = 2.83 µm (d(X) signifies the point in the size distribution, up to and including which X% of the total volume of material in the sample is 'contained'. Therefore, d(50) is the size below which 50% of the particles lie in the distribution). The powder was dried in a circulating air oven at 220 °C for 24 h prior to the experiment to avoid moisture adsorption. Phase purity of the powders was checked by X-ray diffraction analysis using a Rigaku miniflex600 table top diffractometer and Cu Kα radiation.

To produce the $BiFeO_3$-polymer composites, solutions of polyvinylidene difluoride with tri-fluoroethylene and chlorofluoroethylene copolymers (P(VDF-TrFE-CFE)) (obtained from Piezotech Arkema) in dimethylformamide (DMF) were prepared. For low volume fractions of filler particles (< 30 vol%) a solution of 20 wt% P(VDF-TrFE-CFE) in DMF was used while for higher volume fractions a 13 wt% solution was used. The $BiFeO_3$ particles were mixed into this solution using a Hauschild DAC 150 FVZ planetary speed mixer at 750 rpm for 5 min. The mixture formed a viscous liquid that was degassed before casting on a glass substrate for the preparation of the thin films. Cast composites were dried in a vacuum oven at 60 °C for 1 h before annealing at 100 °C for 1 h. The final thickness of the dried samples varied between 120 and 160 µm. Once annealing was completed, a number of discs (12 mm diameter) were cut from the composite for electrical testing. Finally, gold electrodes of 10.9 mm diameter were deposited on both sides of the composite samples with a magnetron sputtering apparatus (Balzers Union, SCD 040).

2.2. Measurement procedures

Scanning Electron Microscope (SEM) images were taken using a Jeol JSM-7500F field emission scanning electron microscope. Prior to SEM measurements a thin (15 nm) layer of gold was deposited on the sample. In order to examine the cross sections of the composites they were first frozen in liquid N_2 to obtain a brittle fracture mode.

Electrical measurements were performed using a Novocontrol Alpha Dielectric Analyzer in the frequency range from 1 Hz to 10 MHz at temperatures from − 50 to 120 °C at a fixed potential difference of 1 V. The piezoelectric constant, d_{33}, measurements were performed with a high precision PM300 Piezometer from Piezotest Piezo Systems, at 110 Hz and a static and dynamic force of 10 and 0.25 N respectively. At least 4 samples of each composite were tested. Inter-sample variability was found to be modest (± 0.5 pC/N).

3. Result and discussion

3.1. Phase purity of $BiFeO_3$

Fig. 1 shows the Rietveld refined XRD patterns of the $BiFeO_3$ ceramic powder. The material crystallises in a rhombohedral perovskite structure type with space group R3c. The refined unit cell parameters of a = 5.57564(7) Å and c = 13.8626(2), are in good agreement with the values reported in the literature [17]. The sample also contains minor amounts of the bismuth-rich phase, $Bi_{25}FeO_{39}$ (0.9 wt%), and the iron-rich phase, $Bi_2Fe_4O_9$ (1.4 wt%) (for more details see Fig. 1S), which are formed due to the addition of extra bismuth and evaporation of bismuth oxide during the calcination process as indicated in the previous work [16].

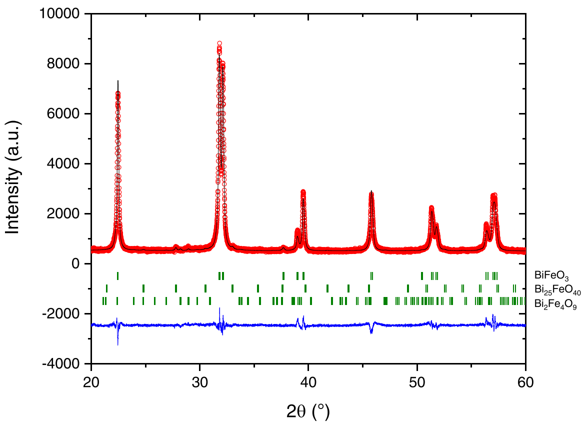

Fig. 1. Rietveld refined XRD patterns of the calcined $BiFeO_3$ ceramic powder. R-Bragg for the main phase is 3.21%.

3.2. Microstructure of composites

Fig. 2 shows scanning electron microscope images of the cross-section of $BiFeO_3$-PVDF terpolymer composites. Piezoceramic particles appear to be homogeneously distributed in the polymer matrix and only show minor degrees of agglomeration for composite with 20 and 30 vol%, as shown by the porous agglomerates on Fig. 2b and c. No signs of sedimentation problems were encountered. Although dark fissure-like zones in the micrographs appear due to the uneven height of the cross-section created by inducing brittle fracture, no microcracks were present in the as-produced samples. The average particle size as determined by SEM corresponded well with the results obtained from particle size analysis.

3.3. Dielectric and electrical properties of the constituent materials

Samples of pure polymer and $BiFeO_3$ ceramics were prepared to determine the dielectric constants of the polymer and $BiFeO_3$. PVDF terpolymer films with a thickness of around 200 µm were prepared by the same method as for the composites. $BiFeO_3$ bulk ceramics were sintered at a temperature of 775 °C for 1 h (details in [16]). Fig. 3 shows the temperature dependence of the dielectric constant of the polymer (a) and $BiFeO_3$ (b) at different frequencies. It can be seen in Fig. 3a that, due to its relaxor nature [18], the PVDF terpolymer film demonstrates a strong and clearly non-linear dependence of the dielectric constant on temperature and frequency with a maximum value at around 25 °C. In contrast, the dielectric constant of $BiFeO_3$ (Fig. 3b) increases linearly with temperature due to an increase in the conductivity of the sample. Since measurements of the piezoelectric charge constant of the composites were carried out at 25 °C and a frequency of 100 Hz, we are particularly interested in the difference in dielectric strength of the two materials at this frequency and at this temperature. As can be seen in the Fig. 3 at this temperature and this frequency, the values of the dielectric constant of $BiFeO_3$ and the polymer are 85 and 61 respectively leading to an unusually small mismatch between the polymer matrix and the ceramic filler particles when compared to other piezoelectric ceramic-polymer composites.

Fig. 4 shows the temperature dependence of the DC conductivity for both the polymer and the bulk ceramic. The electrical conductivity of $BiFeO_3$ increases almost linearly with temperature, while the conductivity of the polymer rises sharply over the temperature region of

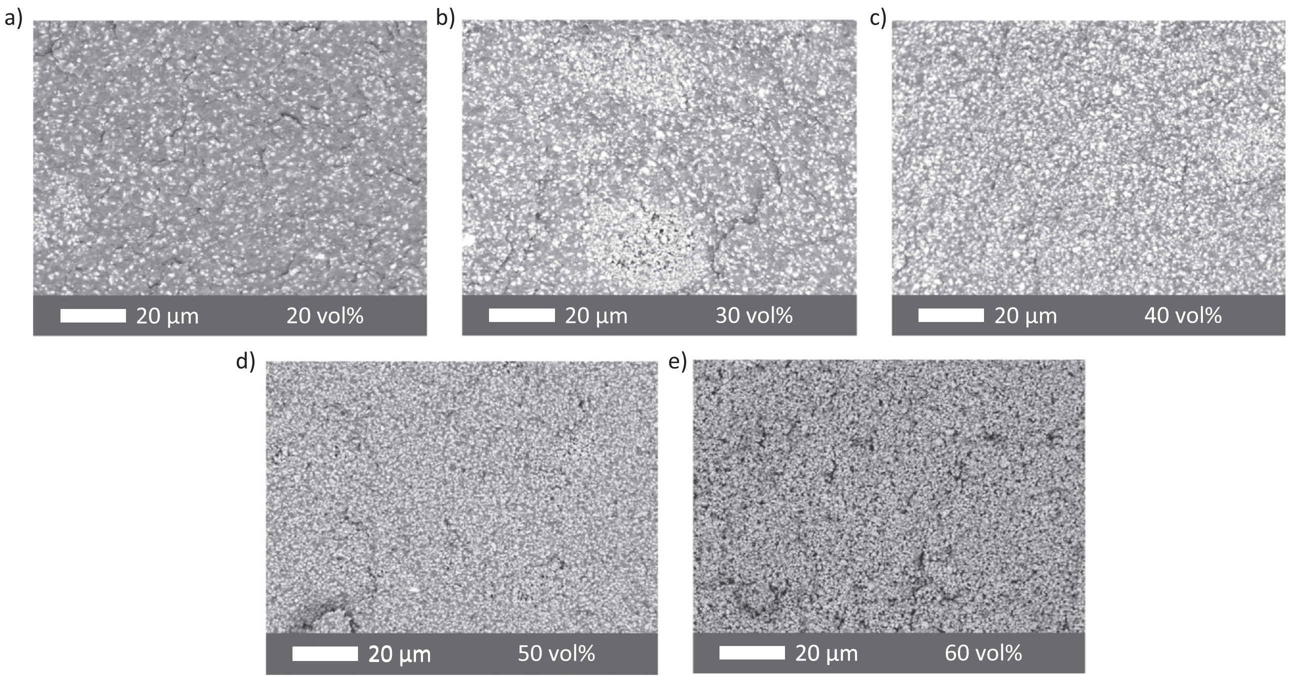

Fig. 2. SEM picture cross-section of $BiFeO_3$-PVDF composites: a) 20 vol%; b) 30 vol%; c) 40 vol%; d) 50 vol%; e) 60 vol%.

10–50 °C and then increases more linearly. Such a sharp increase in conductivity over a limited temperature range can be explained by the relaxor phase transition [19]. The origin of the high dielectric response of this class of terpolymers is its ferroelectric phase and the polar nanodomains. The former is responsible for almost frequency independent dielectric maxima (sharp phase transition), while the latter leads to a strong frequency dependence of dielectric spectra (relaxor phase transition). Such a ferroelectric relaxation is associated with short segmentation mobility in the nanodomains [20]. Considering that there are no free protons in our polymer, the conductivity is most likely associated with the transfer of ions by induced segmental dynamics in the nanodomains, [21].

3.4. Dielectric and electrical properties of the composite materials

Fig. 5 shows the dielectric measurements of the composite with a 50 vol% $BiFeO_3$ (Other samples show similar behavior; this concentration is chosen as to analyse the material behaviour because of its optimal properties and uniform microstructure). It can be seen

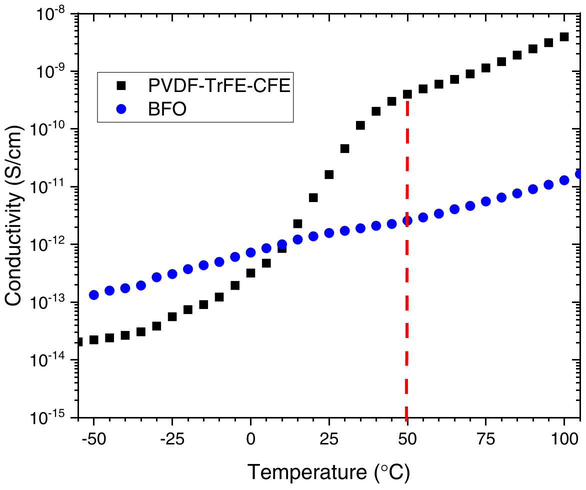

Fig. 4. DC conductivity PVDF-terpolymer film and bulk $BiFeO_3$ ceramic as a function of the temperature.

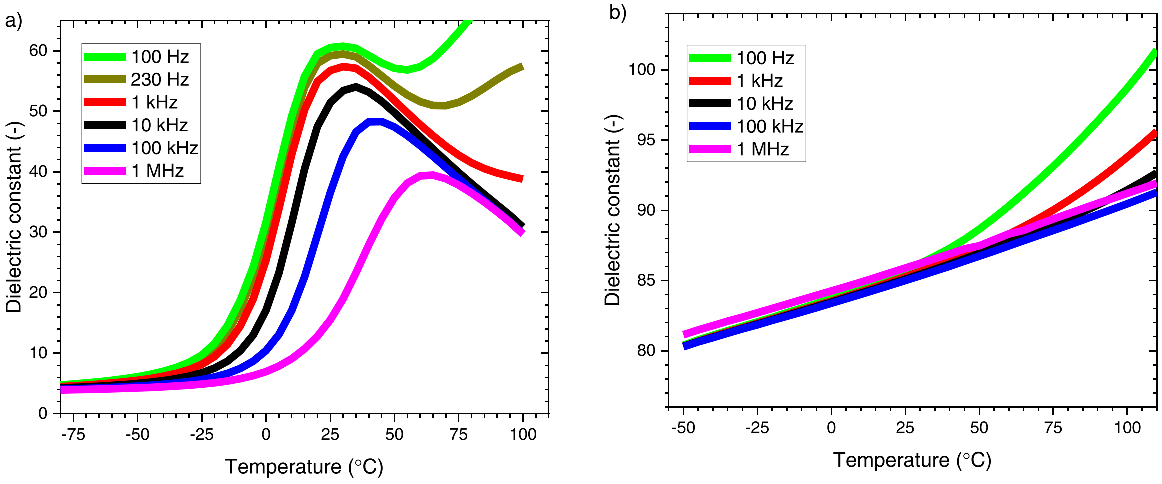

Fig. 3. Dielectric constant as a function of the temperature: a) PVDF terpolymer film and b) sintered $BiFeO_3$ bulk ceramic.

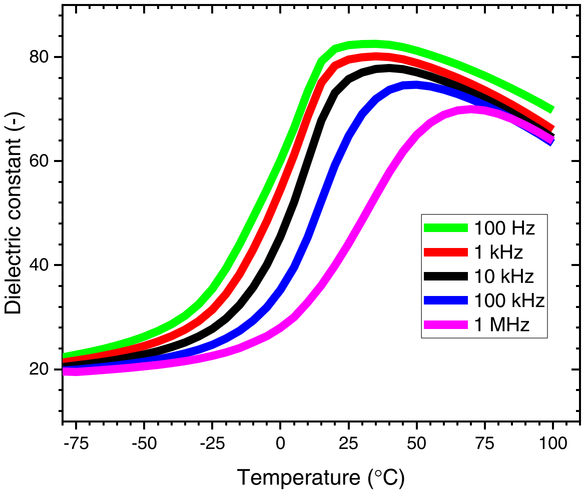

Fig. 5. Dielectric constant of 50 vol% $BiFeO_3$-PVDF terpolymer composite as a function of temperature.

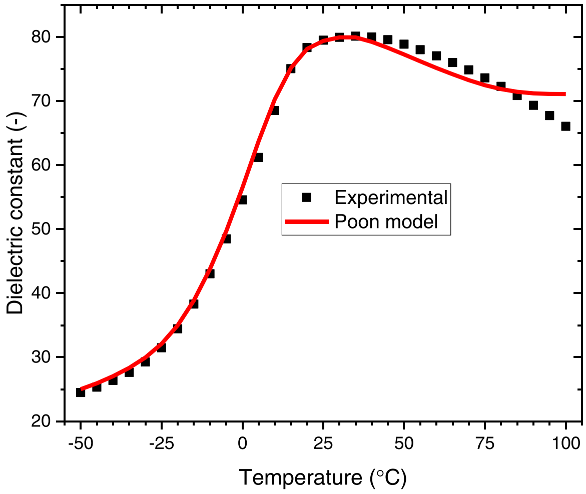

Fig. 7. Fitting of the temperature dependence of the dielectric constant at 1 kHz for the 50 vol% $BiFeO_3$-PVDF composite to the Poon model using the data from Fig. 3.

Table 1

Dielectric constant approximation models for 0–3 composites. The subscript c refers to the ceramic filler particle, the subscript p refers to the polymer matrix and the parameter ν refers to the volume fraction.

Model	Equation
Maxwell-Garnett [22]	$\varepsilon_{eff} = \varepsilon_p \frac{2\varepsilon_p + \varepsilon_c + 2\nu(\varepsilon_c - \varepsilon_p)}{2\varepsilon_p + \varepsilon_c - \nu(\varepsilon_c - \varepsilon_p)}$
Yamada [23]	$\varepsilon_{eff} = \varepsilon_p \left(1 + \frac{n\nu(\varepsilon_c - \varepsilon_p)}{n\varepsilon_p + (1-\nu)(\varepsilon_c - \varepsilon_p)}\right)$
Lichtenecker [24]	$\ln(\varepsilon_{eff}) = (1-\nu)\ln(\varepsilon_p) + \nu\ln(\varepsilon_p)$
Jayasundere [25]	$\varepsilon_{eff} = \frac{\varepsilon_p(1-\nu) + \varepsilon_c\gamma}{(1-\nu)+\gamma}$ $\gamma = \frac{3\varepsilon_p\nu}{2\varepsilon_p + \varepsilon_c}(1 + 3\nu\frac{(\varepsilon_c - \varepsilon_p)}{2\varepsilon_p + \varepsilon_c})$
Poon [26]	$\varepsilon_{eff} = \varepsilon_p + \frac{\nu(\varepsilon_c - \varepsilon_p)}{\nu + (1-\nu)\frac{\varepsilon_c + 2\varepsilon_p - \nu(\varepsilon_c - \varepsilon_p)}{3\varepsilon_p}}$

that the temperature response is similar to that observed for a pure polymer. At low temperatures, the dielectric constant is most notably changed by the ceramic filler which increases the dielectric constant from a value of 5 for the pure polymer to a value of 20 for this composite. The relaxation peak at higher temperatures is less pronounced than for the pure polymer due to the linear temperature behaviour of the dielectric constant of the $BiFeO_3$.

To fit the temperature dependent dielectric constant of the composites multiple models (as presented in Table 1) are available. Fig. 6a shows a comparison of these models with the experimental results. All models lead to a linear behavior up to 35 °C, which corresponds to the dielectric peak temperature for the polymer. Above this temperature, all models show a deviation in the prediction of the dielectric constant. The Poon and Shin model was identified as the most optimal for the current dataset. This model shows good results over the entire temperature and frequency range (Fig. 6b), as well as for different concentrations of ceramic filler (Fig. 6c).

Fig. 7 shows in more detail the approximation of the experimental data for the 50 vol% composite using the Poon model. It can be seen that the predicted behaviour matches the recorded values rather well with only minor deviations above 35 °C which may be attributed either to the polymer matrix behaving marginally different due to the constraining effect of the ceramic filler particles or some inter-particle connectivity not accounted for.

3.5. Poling study

The effect of poling field and temperature on the piezoelectric charge constants of the $BiFeO_3$ –PVDF terpolymer composites is shown in Fig. 8. The electric field was kept constant at 25 kV/mm while investigating the effect of temperature, and temperature was held constant at 60 °C during the electric field magnitude study. All samples were polarized for 20 min. As can be seen in Fig. 8a, as the field increases to 22.5 kV/mm, the piezoelectric charge constant also

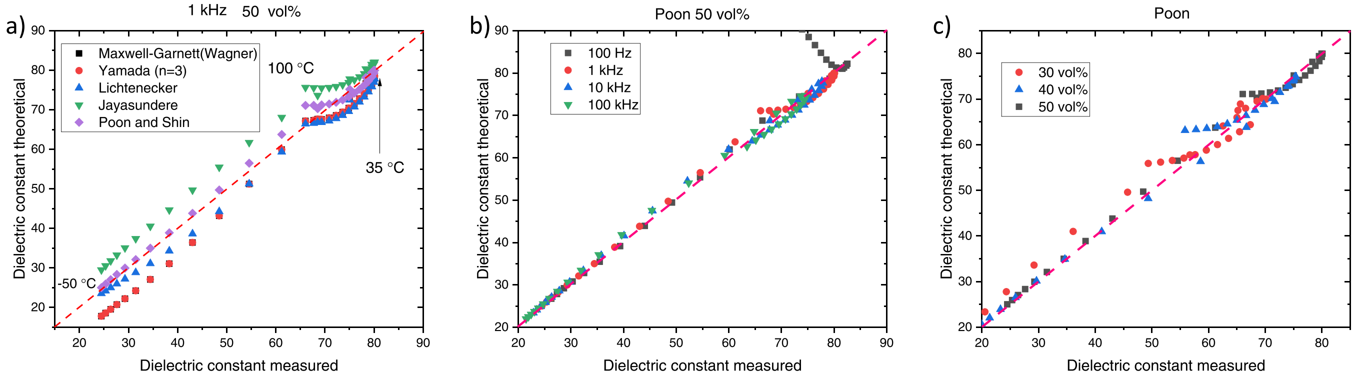

Fig. 6. Comparing different theoretical models for ceramic-polymer composites: a) comparison of the predicted dielectric constant versus the measured value; b) comparison of the predicted dielectric constant against the measure value as a function of the frequency for the Poon model; c) comparison of the predicted dielectric constant against the measure value as a function of the volume fraction for the Poon model.

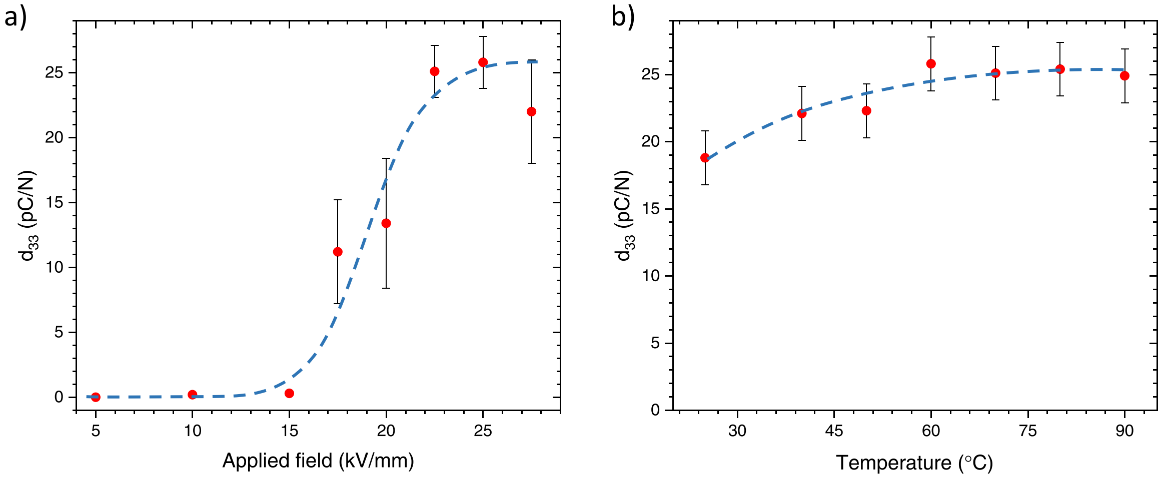

Fig. 8. Poling study of the $BiFeO_3$-PVDF 50 vol% composite. a) as function of applied field at 60 °C and b) as a function of the poling temperature at 25 kV/mm. The fit lines are to guide the eye and are not based on model predictions.

increases and then stabilizes abruptly. This is a clear indication that the sample is optimally polarized at a field of 22.5 kV/mm. The decrease in the piezoelectric constant at a field of 27.5 kV/mm is attributed to damage to the electrodes during polarization. As shown in Fig. 8b, a modest increase in d_{33} with poling temperature is observed.

The observed optimal poling temperature can be explained on the basis of the competing temperature dependences of the DC conductivity [27] and that of the dielectric constant of the polymer matrix.

3.6. Piezoelectric properties

The piezoelectric charge constant (d_{33}) of the composites as a function of the $BiFeO_3$ volume fraction is shown in Fig. 9a. As expected, with an increase in the volume fraction of $BiFeO_3$, the piezoelectric constant also increases. The maximum value of d_{33} at 60 vol % is 31 pC/N. Since the dielectric constant of the matrix material (about 61 at room temperature) is very similar to that of $BiFeO_3$ (about 85), the field distribution in the composite should be rather uniform and the piezoelectric constant should grow almost linearly with increasing ceramic loading. The piezoelectric voltage constant (g_{33}) is proportional to the piezoelectric charge constant and inversely proportional to the dielectric constant, and because the dielectric constants of the matrix and the filler differ insignificantly, g_{33} should also grow almost linearly with increasing ceramic content. The maximum value of the piezoelectric voltage constant experimentally measured at 60 vol% is 47 mV m/N. Table 2 presents the ceramic volume fraction, permittivity, piezoelectric charge and piezoelectric voltage constants of our composite compared with composites and ceramics reported by others. As the value of the dielectric constant is low compared to that of PZT or different composites, the measured piezoelectric voltage constants of the present composites are quite high and compare favorably with those of other composites. Due to the fact that the dielectric constant is higher than that of other composites, devices based on this family of composites will have a higher capacitance, which expands the frequency range (Reducing the cutoff frequency at low frequencies) of applications and makes the $BiFeO_3$-PVDF terpolymer composite a promising material for sensor applications.

3.7. Determining the true piezoelectric constant of granular $BiFeO_3$ material

Since incorporation of $BiFeO_3$ particles in the polymer matrix selected allowed us to increase the electric field for poling, it opened up the possibility to indirectly measure the maximum or intrinsic piezoelectric properties of the granular $BiFeO_3$ particles. In order to

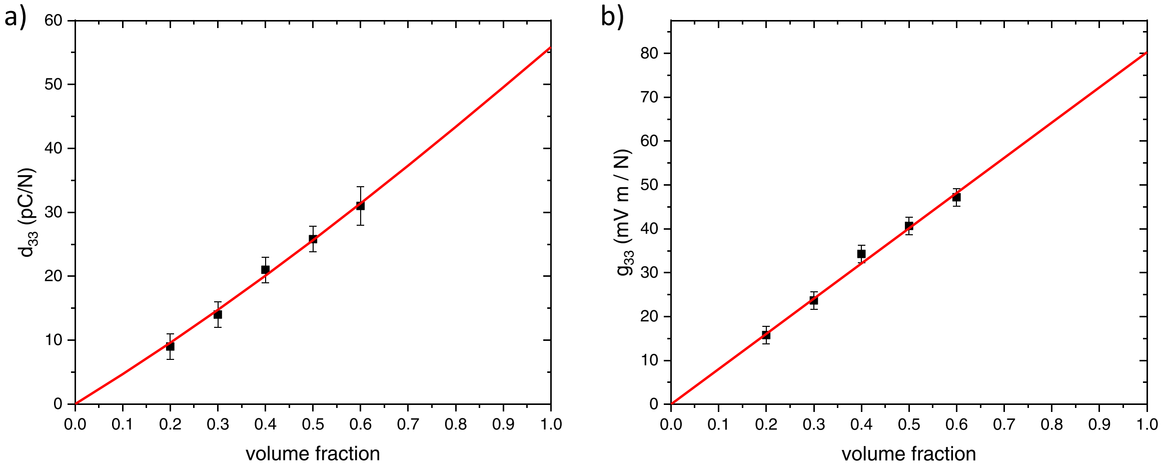

Fig. 9. d_{33}(a) and g_{33}(b) values for $BiFeO_3$–PVDF terpolymer composites with fitted theoretical model predictions according to the Yamada model.

Table 2
Comparing piezoelectric properties of 0–3 ceramic-polymer composites. A volume percent of 100 indicates the pure material.

Material	Volume (%)	ε_r (-)	d_{33} (pC/N)	g_{33} (mV m/N)
$BiFeO_3$ ceramic [5]	100	–	45	–
PZT507 [28]	100	3950	875	25
PVDF [29]	100	12	23	220
PT-PEO [27]	30	21	7.5	40
KNLN-Epoxy [30]	60	48	32	75
PZT-Epoxy [30]	60	48	18	42
BT-Epoxy [30]	60	47	10	24
KNLN-PU [30]	60	65	29	50
PZT-PU [30]	60	50	12	27
BT-PU [30]	60	40	4	11
PT-PEI [31]	30	10	4	45
$BiFeO_3$-PVDF [this work]	60	80	31	47

extract the piezoelectric constant of ceramics from the effective piezoelectric constant of the 0–3 $BiFeO_3$-PVDF terpolymer composites measured, we used Yamada's model:

$$d_{33} = \frac{n\nu\alpha\varepsilon_{eff} d_{33c}}{n\varepsilon_{eff} + \varepsilon_c - \varepsilon_{eff}} \tag{1}$$

Where ν is again the filler volume fraction, α is the poling efficiency and ε_{eff} is the effective dielectric constant. The Yamada model also incorporates shape anisotropy effects of the particles by the parameter n. If n = 3, the particles are spherical while n > 3 reflects elongated particles. The Yamada model has been modified in part to account for changes in the effective dielectric constant as described by the Poon model.

Based on the poling results obtained the poling efficiency, α, was chosen as 1. Since, in our model, the actual value of n does not matter much, and almost equal final results of the piezoelectric constant (with a deviation of 3 pC/N) are obtained for 3 < n < 10 the value for the shape factor, n, was chosen as 3, since this corresponds to a spherical shape of the particles, which is the closest to the morphology of our particles.

If we assume that this model is valid up to 100 vol% loading, we predict that the piezoelectric charge constant of ideally poled granular $BiFeO_3$ could be as high as 56 pC/N, which is 25% higher than highest observed bulk value shown (~ 45 pC/N) in recent studies [32]. Assuming that routes for non-leaking $BiFeO_3$ bulk ceramics will be found in future, the combination of the predicted high value for the piezoelectric voltage constant g_{33} of about 80 mV m/N, and a high Curie temperature (~ 825 °C [2]), would make $BiFeO_3$ a truly attractive material for high-temperature sensors.

4. Conclusions

Embedding $BiFeO_3$ granular material in a non-conducting PVDF terpolymer having a comparable dielectric constant allowed for proper poling of the $BiFeO_3$ particles and a correct interpretation of the volume fraction dependence of the dielectric and piezoelectric properties of the composites made. By combining the Poon model for the dielectric properties and the Yamada model for the piezoelectric properties, the piezoelectric charge and voltage constants of granular $BiFeO_3$ could be determined and were found to be as high as 56 pC/N for d_{33} and 80 mV m/N for g_{33}. These values, in combination with the high Curie temperature, reconfirm the great potential of $BiFeO_3$ as a high temperature sensor material.

CRediT authorship contribution statement

Anton Tuluk: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. **Tadhg Mahon:** Formal analysis, Writing - review & editing. **Sybrand van der Zwaag:** Writing - review & editing, Supervision. **Pim Groen:** Funding acquisition, Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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During the preparation of this manuscript, Prof. Groen tragically passed away. The remaining authors would like to thank him for his contribution in this and many other works. He was a valued colleague and friend and he will be greatly missed.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.159186.

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