POLAR DIELECTRICS AND THEIR APPLICATIONS

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First published 1979 by
THE MACMILLAN PRESS LTD
London and Basingstoke
Associated companies in Delhi Dublin
Hong Kong Johannesburg Lagos Melbourne
New York Singapore and Tokyo

British Library Cataloguing in Publication Data

Burfoot, Jack C
Polar dielectrics and their applications
1. Dielectrics 2. Polarization (Electricity)
I. Title II. Taylor, George W
537.2′4 QC585

ISBN 0–333–17958–7

Printed in Great Britain by
Unwin Brothers Limited
The Gresham Press
Old Woking, Surrey

Acknowledgements

We have sought the permissions of authors and publishers to use their diagrams or data. We trust that we have made due and full acknowledgement, and we apologise for any accidental omissions. The acknowledgement is usually in the form of a reference number, directing attention to the references at the end of the chapter.

We would like to express our thanks to a number of colleagues, rather too numerous to name, for their critical improvements; to C. E. Land and A. Miller for their patient reading and reviewing; to R. V. Latham for a reading of the whole manuscript; to R. V. Peacock for help with the diagrams; and to our families for their patience and help.

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1

Introduction

Dielectric materials can be divided into 32 crystal classes or point groups. In all of these classes a polarisation or dipole moment can be induced by an applied electric field. Twenty of the 32 classes are piezoelectric and they have the property that a polarisation can also be induced by an applied mechanical stress. Half of the piezoelectric classes of materials, i.e. ten of the original dielectric classes, exhibit the very important property that a finite and permanent value of polarisation, known as spontaneous polarisation, exists in the absence of an applied electric field or stress. Such dielectrics are termed *polar materials* and are the principal subject matter of this book.

The spontaneous polarisation of a polar material results from an inherent asymmetry within the basic crystal cell. This asymmetry gives rise to ionic and/or electronic forces that create elemental dipole moments. Because of co-operative effects the dipole moments add to give a finite and permanent polarisation. The spontaneous polarisation of a polar material cannot be measured directly with an electrometer, since charge compensation rapidly occurs within the crystal. For the same reason, the short circuiting together of electrodes on opposite surfaces of a polar material does not destroy the spontaneous polarisation. By comparison, in non-polar dielectric materials, the induced polarisation can be measured with an electrometer and can be destroyed by shorting the surface electrodes.

A classical method of detecting spontaneous polarisation is to subject the polar material to a change in temperature. An increase or decrease in temperature alters the ionic and electronic forces within the basic crystal cell, and the extent of thermal disorganisation, which results in a change in the values of the dipole moments of the polar material. If the change in temperature is fast enough, then there is not time for charge compensation of the dipoles to occur. The nėt result is that a detectable current, termed the pyroelectric current, will flow out of electrodes placed on opposite surfaces of a polar material. Since all polar materials can, in theory, exhibit pyroelectricity, the adjectives *polar* and *pyroelectric* have been used synonymously by some authors. In practice, pyroelectric effects have only been measured in about a hundred out of a multitude of polar materials. The probable reason for this is the difficulties of measurement together with the lack of interest, until recently, in the pyroelectric effect. The pyroelectric coefficients of the materials that have been measured vary greatly in magnitude[1]. They range from 17 000 $\mu C\ m^{-2}\ K^{-1}$ for barium titanate, $BaTiO_3$, near its transition temperature down to 0·002 $\mu C\ m^{-2}\ K^{-1}$ for animal bone.

As we have seen, a polar material is a dielectric material which possesses a spontaneous polarisation. In certain polar materials, the direction of the spontaneous polarisation can be changed by a suitably applied electric field, subsequently removed. In most of these materials the change is a 180° reversal of the direction of the polar axis, but in some materials the polar axis is reoriented by less than 180°.[2]

Polar materials whose direction of spontaneous polarisation can be changed by an applied electric field are known as *ferroelectrics* or occasionally as *Seignette-electrics*. The term ferroelectric is derived from the analogy with ferromagnetic materials in that both types of materials possess domains, exhibit hysteresis loops and show Curie–Weiss behaviour near their phase transition temperatures. The hysteresis loop of a ferroelectric is obtained by plotting polarisation (P) against applied electric field (E), while in a ferromagnetic it is achieved by plotting magnetisation (B) against the applied magnetic field (H). The term Seignette-electric is derived from the name of the chemist who originally prepared Rochelle salt in the 17th century. This material was subsequently identified by Valasek[3] in 1921 as possessing a field reversible spontaneous polarisation.

The study of the general classification of polar materials stretches back into antiquity[1] with the detailed qualitative work commencing in the 18th Century[4]. While the study of the ferroelectric subgroup of polar materials began just over 50 years ago with Valasek's work on Rochelle salt, it has since then grown at an exponential rate. This is shown in figure 1.1, which gives the number of papers on ferroelectricity published each year. Other manifestations of this growth are the holding every three or four years of an international

† Strictly speaking, a ferroelectric hysteresis loop is a plot of dielectric displacement (D) versus E where $D = P + \epsilon_0 E$. In practice, for most ferroelectric materials, the product of ϵ_0, the permittivity of free space, and E is very much smaller than P; hence D is essentially equal to P.

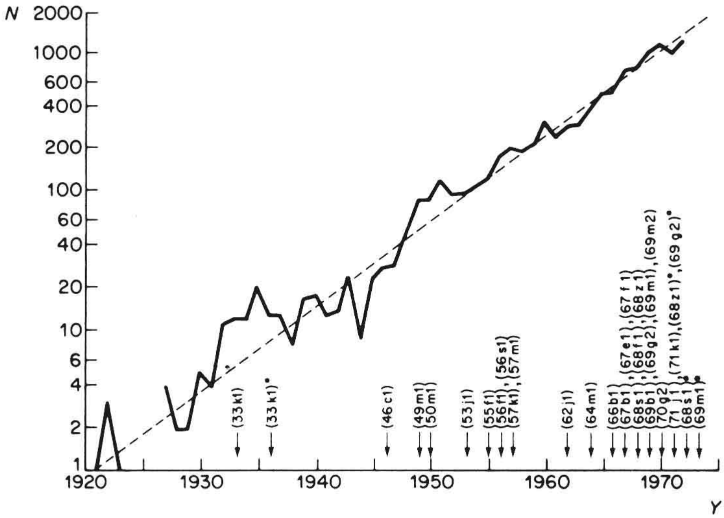

Figure 1.1 Number of research papers, N, on ferroelectrics and antiferroelectrics published in each year. The dashed line corresponds to

$$N = \exp\{0.14\ (Y - 1921)\}$$

Y is the year. Books on ferroelectrics published in each year are also shown. The one marked with asterisks represent a version translated into another language (from Ref. 11, Vol. 9)

meeting[5], a regional European meeting[6], an IEEE Applications Conference[7] and national meetings in the USSR[8] and other countries[9]. There is an international journal *Ferroelectrics*[10] devoted to the subject, the publication of which has increased from, initially one volume per year in 1970, to three volumes per year in 1976. Almost 700 ferroelectric pure compounds and solid solutions have been identified at this date[11]. The reversible spontaneous polarisations in these materials range from $5 \times 10^5\ \mu C\ m^{-2}$ for lithium tantalate, $LiTaO_3$, down to $1.7 \times 10^3\ \mu C\ m^{-2}$ for gadolinium molybdate, $Gd_2(MoO_4)_3$.

Major sources of bibliographic information on polar materials include the Landolt-Börnstein series[11], Lang's Source Book of Pyroelectricity[1] and his annual literature Guide to Pyroelectricity[12], Toyoda's continuing Bibliography of Ferroelectrics[13], an annually published Digest of Literature on Dielectrics[14] and two O.R.N.L. Ferroelectric Literature Indexes[15].

Though ferroelectrics are only a sub-group of polar materials, they include the most significant polar materials, both from a basic viewpoint and from an applications viewpoint. Many of the ferroelectrics possess some of the most interesting piezoelectric, thermal, optical and electrical properties of all the dielectric materials.

Polar materials, in particular the ferroelectrics, can exhibit a large degree of non-linearity in their electrical, optical and piezoelectric properties. Through-out this book the three adjectives *polar*, *ferroelectric* and *non-linear* are used somewhat interchangeably. However, as much as possible, we have striven to use the most suitable term in each instance.

Like life itself, the writing of this book has been both pleasure and pain. The pleasure has stemmed from the satisfaction of covering, in an age of scientific specialisation, a subject as broad as polar materials. The chemist, the crystallographer, the ceramicist, the physicist and the mechanical and electrical engineer all have a vital interest in polar materials. The interest covers the gamut from theory through experiment to application. The pain has been the challenge of writing within a reasonable number of pages a meaningful book for a diverse readership.

In a rapidly growing field there is always the necessity to be quite selective about what to include in a book. This problem is compounded, in the present instance, because of the interdisciplinary nature of study of polar materials. Hopefully the future will reveal that our use of the hatchet for selection has been more perceptive than arbitrary.

Wherever feasible, principles have been emphasised so as to make the book most valuable to students and newcomers to the field. The examples of single crystal and ceramic materials used to illustrate the principles involved have been selected, as much as possible, from recent publications. Thus the book should be useful for experienced scientists working with or familiar with polar materials. The examples of devices have been selected on the basis of their currentness, as well as the scientific and economic significance-criteria which are most meaningful to engineers utilising or wishing to utilise polar materials.

We begin Part I, 'Basic Properties', with chapter 2 giving outlines of the methods by which the materials of interest may be prepared, either for specific applications or for study and understanding of the physical properties of the materials, with a view to their attempted exploitation. Often the material preparation will consist of crystal growing or ceramic manufacture; ceramic materials are polycrystalline structures. For study of the properties, crystals will usually be preferred as being likely to give results more easily interpretable in terms of reasonably simple models. If the crystals contain imperfections or impurities this may be unavoidable or it may have resulted from deliberate attempts to modify the properties in some way—as for example in bringing the transition temperature, or Curie point, T_c, into some more convenient temperature range. For applications, the more complicated structures of ceramic materials may well be the price we pay for their ease of fabrication and relative cheapness. It is also a test of our ability to understand these materials if we can satisfactorily extend our models to include ceramic structures. Very interesting and prominent examples are the PZT ceramics, which have replaced crystal materials in many piezoelectric devices; more recently it became possible to grow PZT compositions as crystals. In this chapter we discuss also the technique of annealing, and the processes of poling, cutting, electroding, and several methods of making thin films.

Chapters 3–6 give introductions to various aspects of the physical properties—electrical, optical, mechanical and thermal. In each case a prominent effect is the anomaly (or *peak*) which occurs in nearly every physical property in the neighbourhood of T_c. In chapter 3 we describe the dielectric anomaly and the non-linearities, reversal of the spontaneous polarisation P_s by means of electric fields (*switching*), and the techniques for observing it, the relationship of switching behaviour to the parameters of the driving impulses, and various ways in which these effects are observed to decay or 'age'. In principle the perfect ferroelectric is an insulator, but some rather interesting possibilities arise when doping has added semiconduction to its properties. Brief reference is also made to some photoconductive properties.

In chapter 4 we consider the optical properties, and their variation with frequency (mostly within the visible region), with temperature, with applied mechanical and electrical stress, and with incident light. Many of these properties form the basis of applications which are to be discussed. The variation of refractive index, or of birefringence, with electric field (electro-optics) is of particular interest in these materials, where the field involved may well not be an exterior applied field, but may follow the development of internal fields when the material undergoes the transition into its polar state. Non-linear optical effects are also important. An important application of this effect is second harmonic generation. Some absorption-edge, photo-luminescent, electroluminescent and luminescent effects are described.

Chapter 5 includes not only the elastic anomalies, but also the piezoelectric coefficients, since these link the mechanical and electrical parameters. Mechanical loss effects are considered, just as were the electrical loss effects in the chapter 4. Above T_c, in a ferroelectric-to-non-ferroelectric transition, P_s is zero, and there may or may not be 'ordinary' piezoelectricity, unrelated to P_s of course. Nevertheless interest does attach to the differences between those materials which do or do not possess that 'ordinary' piezoelectricity. The quadratic effect, conventionally called *electrostriction*, is also discussed. The effect of applied stress on various properties is considered in section 5.5, and improper and ferroelastic materials are covered in section 5.6. Surface acoustic waves are also briefly mentioned.

In discussing the thermal properties in chapter 6 the well-known and very useful Devonshire form of thermodynamic function is introduced. Its purpose is to summarise and interrelate a vast range of experimental information. The thermal-electrical and the thermal-mechanical properties are listed in table 6.1, which includes also the interesting anomalies. The properties discussed here include the pyroelectric and electrocaloric effects, as well as the anomalous behaviours in specific heat and in thermal conductivity.

Chapter 7 links the classical description of the co-operative transition, and the anomalies which occur there, to a more recent viewpoint available from studies of lattice vibrations; the soft-mode concept is in the first place only a change of terminology, though later it will be seen to be capable of many new extensions. The antiferroelectric transition is considered in section 7.4. In section 7.5 is given a brief indication of some recent attempts to clarify the classification of the increasingly complicated phenomena under study. Anharmonic effects require more elaborate mathematical treatment than we are able to give in this book, but an introduction to some of those studies is included. The materials in this book are distinguished experimentally by their extreme non-linearities and by the anomalies. Conceptually, the application of the principles of symmetry to them is very significant, and this is dealt with in chapter 8, not in detail, but in a manner which we hope will enable interested readers to follow up in more detailed studies elsewhere.

In Chapter 9 we give, for reference, a brief summary of aspects of the transition in some of the materials which have been used for illustration elsewhere in the book. There are hundreds of materials in our sphere of interest, and reference is made to places where more complete listings are available.

Chapters 10 and 11 carry some of the previous ideas into the region of spectroscopy, and show how the dispersion phenomena may be used to elucidate the underlying microscopic mechanisms involved in these polar transitions. Attention is paid to the importance of fluctuation phenomena when the transition is approached, and to the *central peak* which has in recent years become distinguishable from the soft mode. Section 11.5 deals with KDP-type materials and the 'pseudospin' descriptions. An appendix to chapter 10 provides a convenient summary of the related optical and dielectric parameters.

Almost all the properties of polar materials are modified considerably by the presence and mobility of domains. The methods of studying them, and the models which seem to be successful, are described in chapter 12.

Part II of this book, chapter 13–18, 'Applications', is concerned with devices and systems that have been or can be built with polar and ferroelectric materials. The applications covered range from those that already have a well established commercial market to those that are still at a developmental stage. Such a detailed treatment of the applications of polar materials is well overdue, since earlier books on polar and ferroelectric materials have only given a cursory treatment of this economically very significant subject.

Chapter 13 details some fundamental aspects of memories and displays, two of the major components in computers and communication systems. The basic parameters of memories and displays, including addressing techniques, are analysed. This analysis is then applied to the properties of polar materials. As is described in the succeeding chapters, polar materials are being used or actively considered for use in a variety of memory and display applications.

The next three chapters, 14–16, contain a description of a wide range of devices that utilise the reversible spontaneous polarisation property, i.e. the switching, of ferroelectric, polar materials. For convenience, this material is divided between three chapters. Chapter 14 deals with devices that involve only the reversal of the spontaneous polarisation of the polar material. Chapter 15 is concerned with polar material devices in which use is made of changes in the piezoelectric, optical and thermal properties that are associated with the reversal of the spontaneous polarisation. In chapter 16 the devices have a complex structure in that the reversible polar material is combined with another electrically active material, such as an electroluminescent material, a photoconductor or a semiconductor material.

Chapter 17 describes a large number of polar material devices in which the common factor is that no large signal switching, or reversal, of spontaneous polarisation is involved. Instead, the devices utilise the anomalously high values of dielectric permittivity, linear and non-linear optic and electro-optic coefficients or photo-refractive, pyroelectric, piezoelectric and elasto-optic constants of polar materials. Some of the devices in this chapter, such as capacitors and piezoelectric transducers, are of great commercial importance. Others, such as optical holographic storage media and colour projection TV systems, are still at a developmental stage but may prove to be economically very significant in the future.

This book concludes with a short treatment in chapter 18 of the basic physics and the electro-optic and thermo-optic applications of an important group of *liquid* materials having polar molecules. These materials are generally referred to as *liquid crystals*, since they simultaneously exhibit the physical properties of liquids and the electrical and optical characteristics of an ordered, polar crystalline structure.

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