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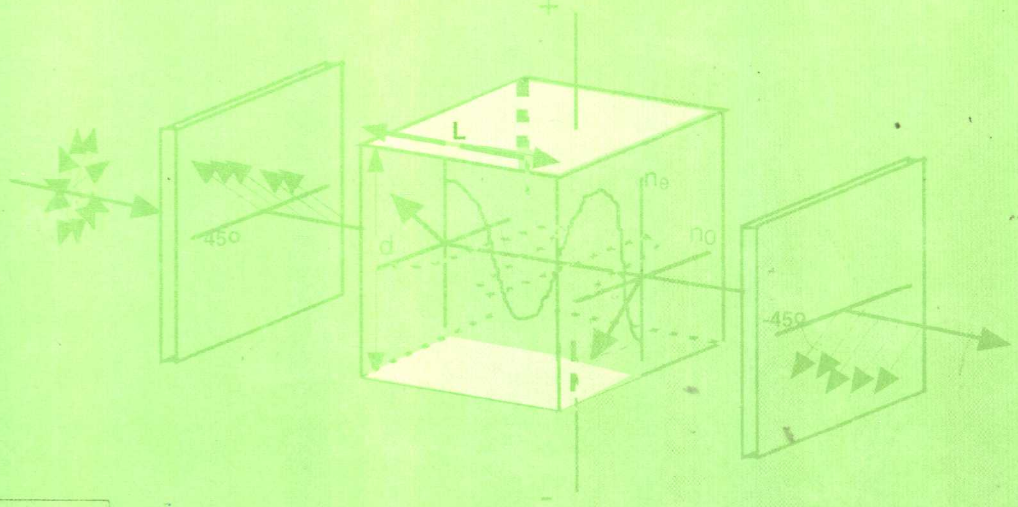

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PREFACE

Ferroelectrics can be utilized in various devices such as high-permittivity dielectrics, pyroelectric sensors, piezoelectric devices, electrooptic devices and PTC components. The industries are producing large amounts of simple devices, e.g. ceramic capacitors, piezoelectric igniters, buzzers and PTC thermistors continuously. But until now ferroelectric devices have failed to reach commercialization in more functional cases. In the light sensor, for example, semiconductive materials are superior to ferroelectrics in response speed and sensitivity. Magnetic devices are much more popular in the memory field, and liquid crystals are typically used for optical displays. Ferroelectric devices often fail to be developed in the cases where competitive materials exist. This is mainly due to a lack of systematic accumulation of fundamental knowledge of the materials and developmental experiences on the devices.

During my 12-year teaching period on "Ferroelectric Devices," I found that no suitable textbook is available in this particular field, except some professional books like multi-author paper collections. Hence, I decided to write a single-authored textbook based on my lecture notes, including my device development philosophy. This textbook introduces the theoretical background of ferroelectric devices, practical materials, device designs, drive/control techniques and typical applications, and looks forward to the future progress in this field. Though the discovery of ferroelectricity is relatively old, since the device development is really new and interdisciplinary, it is probably impossible to cover all the recent studies in a limited-page book. Therefore, I selected only important and basic ideas to understand how to design and develop the ferroelectric devices, putting a particular focus on thin/thick film devices.

Let me introduce the contents. Chapter 1 introduces the overall background, "General view of ferroelectrics," followed by the theoretical background in Chapter 2, "Mathematical treatment of ferroelectrics." Chapter 3, "Device designing and fabrication processes," provides practical designing and manufacturing of the devices. Capacitor applications are described in Chapter 4, "High permittivity devices." Chapters 5 and 6 treat thin/thick film applications, i.e. "Ferroelectric memory devices" and "Pyroelectric devices," respectively. Chapter 7, "Piezoelectric devices" deals with piezoelectric actuators and ultrasonic motors as well as acoustic transducers and piezoelectric sensors. Optical devices such as light valves, displays, wave guides and bulk photovoltaic devices are described in Chapter 8, "Electrooptic devices." In Chapters 9 and 10, we learn basic concepts of "PTC materials" and

"Composite materials," and their device applications. Finally in Chapter 11 we discuss "Future of ferroelectric devices," in which the market size is estimated, and the author's strategy for developing bestseller devices is introduced.

This textbook was written for graduate students and industry engineers studying or working in the fields of electronic materials, optical materials and communications, precision machinery and robotics. Though this text is designed for a course with thirty 75-minute lectures, the reader can learn the content by himself/herself aided by the availability of examples and problems.

Critical review and content corrections on this book are highly appreciated. Send the information directed to Kenji Uchino at 134 Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802-4800. Fax: 814-865-2326, E-mail: KenjiUchino@PSU.EDU

For the reader who needs detailed information on smart piezoelectric actuators and sensors, "Piezoelectric Actuators and Ultrasonic Motors" (349 pages) authored by K. Uchino, (Kluwer Adademic Publishers 1997) is recommended.

Even though I am the sole author of this book, it nevertheless includes the contributions of many others. I express my gratitude to my ICAT center faculty who have generously given me their advice and help during the writing, particularly to Dr. Uma Belegundu, who worked out all the problems. Dr. Yukio Ito (now in Rutgers University) allowed me to use some paragraphs and figures from our coauthored papers. Specific acknowledgement is given to Professor Jayne Giniewicz, Indiana University of Pennsylvania, who reviewed and criticized the entire manuscript and provided linguistic corrections.

Kenji Uchino

LIST OF SYMBOLS

D	Electric displacement
E	Electric field
P	Dielectric polarization
P_s	Spontaneous polarization
P_r	Remanent polarization
p	Pyroelectric coefficient
α	Ionic polarizability
γ	Lorentz factor
μ	Dipole moment
ε_0	Vacuum permittivity
ε	Relative permittivity, dielectric constant
C	Curie-Weiss constant
T_0	Curie-Weiss temperature
T_C	Curie temperature (phase transition temperature)
G_1	Gibbs elastic energy
x	Strain
x_s	Spontaneous strain
X	Stress
s	Elastic compliance
c	Elastic stiffness
v	Sound velocity
d,g	Piezoelectric coefficients
M,Q	Electrostrictive coefficients
k	Electromechanical coupling factor
η	Energy transmission coefficient
n	Refractive index
r	Primary electrooptic coefficient
g	Secondary electrooptic coefficient
Γ	Phase retardation

SUGGESTED TEACHING SCHEDULE

(75 min x 30 times per semester)

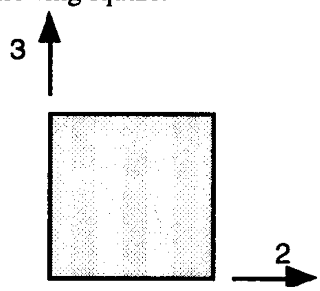
0.	Course Explanation & Prerequisite Knowledge Check	1 Time
1.	General View of Ferroelectrics	4 Times
2.	Mathematical Treatment of Ferroelectrics	4 Times
3.	Device Designing and Fabrication Processes	3 Times
4.	High Permittivity Dielectrics	2 Times
5.	Ferroelectric Memory Devices	1 Time
6.	Pyroelectric Devices	1 Time
7.	Piezoelectric Devices	7 Times
8.	Electrooptic Devices	2 Times
9.	PTC Materials	1 Time:
10.	Composite Materials	2 Times
11.	Future of Ferroelectric Devices	1 Time
	Review/Q&A	1 Time

PREREQUISITE KNOWLEDGE

In order to understand ferroelectric devices, some prerequisite knowledge is expected. Try to solve the following questions without seeing the answers on the next page.

Q1 Describe the definitions of elastic *stiffness* c and *compliance* s, using a stress X - strain x relation.

Q2 Indicate a *shear stress* X_4 on the following square.



Q3 Describe the *sound velocity* v in a material with mass density ρ and elastic compliance s^E.

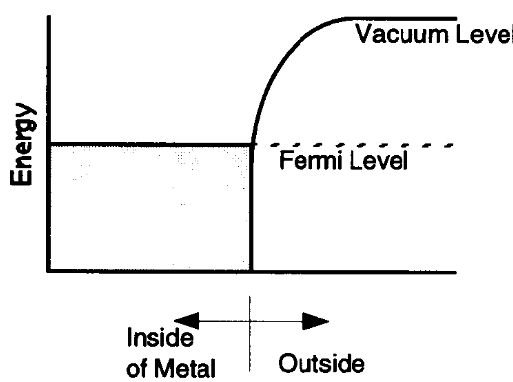
Q4 Calculate the capacitance C of a capacitor with area S and electrode gap t filled with a material of *relative permittivity* ε.

Q5 Calculate the *polarization* P of a material with dipole density N (m^{-3}) of dipole moment qu (C·m).

Q6 Describe the *Curie-Weiss law* of relative permittivity ε, using a Curie-Weiss temperature T_0 and a Curie-Weiss constant C.

Q7 Describe the light velocity in a material with a refractive index n (c: light velocity in vacuum).

Q8 Indicate the work function in the following energy band of a metal.



Q9 There is a voltage supply with an internal impedance Z_0. Indicate the external impedance Z_1 to obtain the maximum output power.

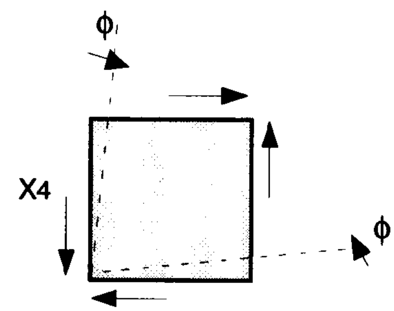
Q10 Calculate the induced polarization P under an external stress X in a *piezoelectric* with a piezoelectric constant d.

Answer

(Correct rate more than 70% of full score is expected)

Q1 $X = c\,x,\ \ x = s\,X$

Q2 $x_4 = 2\,x_{23} = 2\,\phi$ (radian)



Q3 $v = 1/\sqrt{\rho\, s^E}$ [0.5 point for $v = 1/\rho\, s^E$]

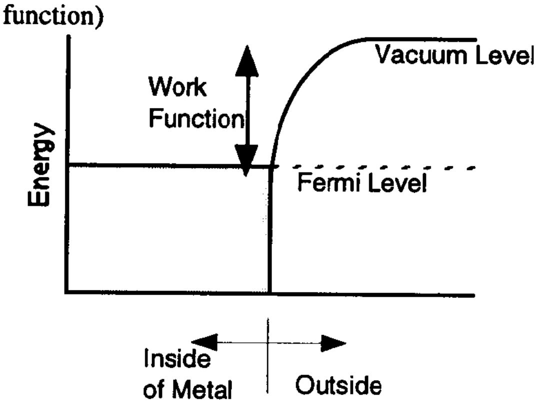
Q4 $C = \varepsilon_0 \varepsilon\, (S / t)$ [0.5 point for $C = \varepsilon\, (S / t)$]

Q5 $P = Nqu$

Q6 $\varepsilon = C / (T - T_0)$ [0.5 point for $\varepsilon = C / T$]

Q7 $c' = c / n$

Q8 (Work function)

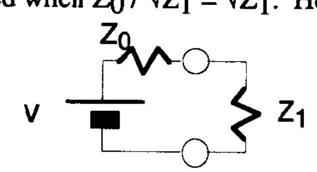


Q9 $Z_1 = Z_0$

On Z_1, current and voltage are given as $V/(Z_0 + Z_1)$ and $[Z_1/(Z_0 + Z_1)]V$, leading to the power:

Power $= V^2 \cdot Z_1/(Z_0 + Z_1)^2 = V^2/(Z_0/\sqrt{Z_1} + \sqrt{Z_1})^2 \le (1/4)\, V^2/Z_0$

The maximum is obtained when $Z_0 / \sqrt{Z_1} = \sqrt{Z_1}$. Hence, $Z_1 = Z_0$.



Q10 $P = d\,X$ (refer to $x = d\,E$)

CONTENTS

1

GENERAL VIEW OF FERROELECTRICS

Let us start with the "smartness" of a material. Table 1.1 lists the various effects relating the input (electric field, magnetic field, stress, heat and light) with the output (charge/current, magnetization, strain, temperature and light). Conducting and elastic materials, which generate current and strain outputs, respectively, for the input, voltage or stress (well-known phenomena!), are sometimes called "trivial" materials. On the other hand, pyroelectric and piezoelectric materials, which generate an electric field with the input of heat and stress (unexpected phenomena!), respectively, are called "smart" materials. These off-diagonal couplings have corresponding converse effects, the electrocaloric and converse-piezoelectric effects, and both "sensing" and "actuating" functions can be realized in the same materials. "Intelligent" materials must possess a "drive/control" or "processing" function which is adaptive to changes in environmental conditions, in addition to actuator and sensing functions. Ferroelectric materials exhibit most of these effects with the exception of the magnetic phenomena. Thus, ferroelectrics are said to be very "smart" materials.

Table 1.1 Various effects in materials.

INPUT → MATERIAL DEVICE → OUTPUT

INPUT \ OUTPUT	CHARGE CURRENT	MAGNET-IZATION	STRAIN	TEMPERATURE	LIGHT
ELEC. FIELD	Permittivity Conductivity	Elect.-mag. effect	Converse piezo-effect	Elec. caloric effect	Elec.-optic effect
MAG. FIELD	Mag.-elect. effect	Permeability	Magneto-striction	Mag.caloric effect	Mag.optic effect
STRESS	Piezoelectric effect	Piezomag. effect	Elastic constant	—	Photoelastic effect
HEAT	Pyroelectric effect	—	Thermal expansion	Specific heat	—
LIGHT	Photovoltaic effect	—	Photostriction	—	Refractive index

Diagonal Coupling (solid box)
Off-diagonal Coupling = **Smart Material**
Sensor (dashed box)
Actuator (solid box)

Ferroelectrics are utilized in various devices such as high-permittivity dielectrics, pyroelectric sensors, piezoelectric devices, electrooptic devices, and PTC (positive temperature coefficient of resistivity) components. However, ferroelectric devices often fail to be commercialized in areas of application where competitive materials exist. Light sensors, for example, typically are manufactured from semiconductive materials which are superior to ferroelectrics in response speed and sensitivity. Magnetic devices are much more popular for memory applications, and liquid crystals are typically used for optical displays. One reason for this is due to the lack of systematic and comprehensive compilation of knowledge on ferroelectric materials. In this chapter, we will learn fundamental knowledge on ferroelectricity.

1.1 CRYSTAL STRUCTURE AND FERROELECTRICITY

In the so-called *dielectric* materials, the constituent atoms are considered to be ionized to a certain degree and are either positively or negatively charged. In such ionic crystals, when an electric field is applied, cations are attracted to the cathode and anions to the anode due to electrostatic interaction. The electron clouds also deform, causing electric dipoles. This phenomenon is known as *electric polarization* of the dielectric, and the polarization is expressed quantitatively as the sum of the electric dipoles per unit volume [C/m^2]. Figure 1.1 shows schematically the origin of the electric polarization. There are three primary contributions: *electronic, ionic* and *dipole reorientation-related.* The degree to which each mechanism contributes to the overall polarization of the material depends on the frequency of the applied field. Electronic polarization can follow alternating fields with frequencies up to THz-PHz (10^{12}-10^{15} cycle/second, higher than visible light wave) and ionic polarization responds up to GHz-THz (10^{9}-10^{12} cycle/sec, microwave region). Thus, you should understand that a famous relation between the relative permittivity ε and the refractive index n:

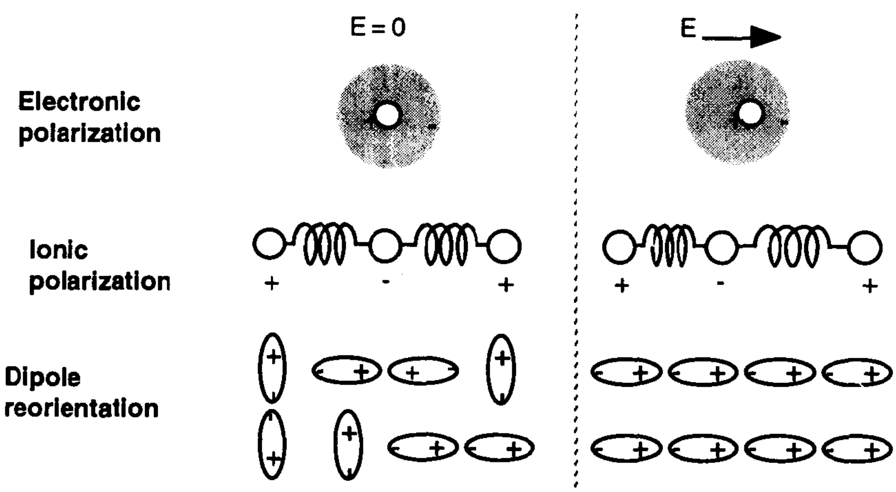


Fig. 1.1 Microscopic origins of the electric polarization.

$$\varepsilon = n^2 \tag{1.1}$$

is valid only when the applied electric field has a frequency on the order of THz or higher. Permanent dipole reorientation can follow only up to MHz-GHz (10^6-10^9 cycle/sec). This is why ferroelectric materials with permanent dipoles cannot be used for microwave dielectric materials; their permittivities are typically high at low frequencies (kHz), but decrease significantly with increasing applied electric field frequency.

Compared with air-filled capacitors, dielectric capacitors can store more electric charge due to the dielectric polarization **P** as shown in Fig. 1.2. The physical quantity corresponding to the stored electric charge per unit area is called the *electric displacement* **D**, and is related to the electric field E by the following expression:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon \varepsilon_0 \mathbf{E}. \tag{1.2}$$

Here, ε_0 is the vacuum permittivity (= 8.854×10^{-12} F/m), ε is the material's *relative permittivity* (also simply called permittivity or *dielectric constant*, and in general is a tensor property).

Depending on the crystal structure, the centers of the positive and negative charges may not coincide even without the application of an external electric field. Such crystals are said to possess a *spontaneous polarization*. When the spontaneous polarization of the dielectric can be reversed by an electric field, it is called *ferroelectric*.

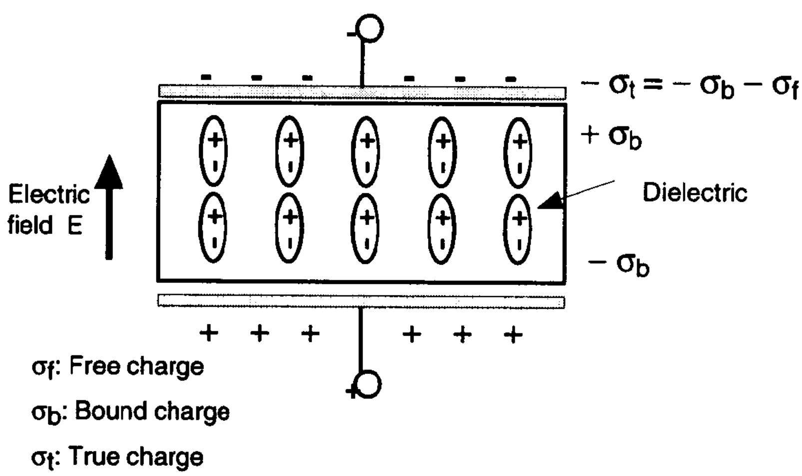


Fig. 1.2 Charge accumulation in a dielectric capacitor.

Table 1.2 Crystallographic classification according to crystal centro-symmetry and polarity.

Polarity	Symmetry	Crystal system										
		Cubic		Hexagonal		Tetragonal		Rhombohedral		Orthorhombic	Monoclinic	Triclinic
Non-polar (22)	Centro (11)	m3m	m3	6/mmm	6/m	4/mmm	4/m	$\bar{3}m$	$\bar{3}$	mmm	2/m	
	Non-centro (21)	432, $\bar{4}3m$	23	622, $\bar{6}m2$	$\bar{6}$	422, $\bar{4}2m$	$\bar{4}$	32		222		
Polar (Pyro-electric) (10)				6mm	6	4mm	4	3m	3	mm2	2, m	1

Inside the bold line are piezoelectrics.

Not every dielectric is a ferroelectric. Crystals can be classified into 32 point groups according to their crystallographic symmetry, and these point groups can be divided into two classes, one with a center of symmetry and the other without as indicated in Table 1.2. There are 21 point groups which do not have a center of symmetry. In crystals belonging to 20 of these point groups [point group (432) being the sole exception], positive and negative charges are generated on the crystal surfaces when appropriate stresses are applied. These materials are known as *piezoelectrics.*

Pyroelectricity is the phenomenon whereby, due to the temperature dependence of the spontaneous polarization, as the temperature of the crystal is changed, electric charges corresponding to the change of the spontaneous polarization appear on the surface of the crystal. Among the pyroelectric crystals, those whose spontaneous polarization can be reversed by an electric field (not exceeding the breakdown limit of the crystal) are called *ferroelectrics*. There is some experimental ambiguity in this definition. In establishing ferroelectricity, it is necessary to apply an electric field to a pyroelectric material and experimentally ascertain the polarization reversal.

1.2 ORIGIN OF SPONTANEOUS POLARIZATION

Why is it that crystals which, from a consideration of elastic energy, should be stable by being non-polar, still experience the shifting of cations and anions and become spontaneously polarized? The reason is briefly explained below. For simplicity, let us assume that dipole moments result from the displacement of one type of ion A