MULTIFERROIC MATERIALS
FOR SENSORS, TRANSDUCERS AND MEMORY DEVICES
(review article)

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Chemical compositions and basic properties of smart materials (ferroics, biferroics, multiferroics) are introduced in this paper. Single phase and composite ferroelectromagnetics are characterized in detail. Multiferroic ferroelectromagnetics are materials which are both ferromagnetic/ferrimagnetic/antiferromagnetic and ferroelectric/ferrielectric, antiferroelectric in the same phase. As a result they have a spontaneous magnetization which can be switched by an applied magnetic field, a spontaneous polarization which can be switched by an applied electric field, and often there is some coupling between those fields. The physical mechanisms of the coupling process were analyzed. In the case of the ferroelectromagnetics in general the transitions method $d$ electrons, which are essential for magnetism, reduce the tendency for off-center ferroelectric distortion. Such materials have all the potential applications of both their parent ferroelectric and ferromagnetic materials.

Keywords: smart materials, ferroics, multiferroics, ferroelectromagnetics, ferroelectroelastics, single-phases, composites, phase transition.

1. Introduction

The development in mainly fields of technique is possible thanks to the search and production of new materials and the investigation of their properties. The investigations of smart materials is particularly important for electronics, informatics, electro-acoustics, optoelectronics etc.

Smart materials are defined broadly as materials that can be altered or controlled by an external stimulus. They can be grouped into several basic categories including piezoelectrics, electrostrictive materials, magnetostrictive materials, shape memory alloys, optical fibers etc. (Fig. 1).

What is smart about them is that, instead of having fixed properties, they can change their properties in a predesigned way in order to serve for a useful purpose [1].
Members of the family of products containing smart materials can be used in a variety of applications and in diverse industries such as automation, process control systems, robotics, material processing, aerospace, and automotive, electronics, defenses and medical technologies and biotechnologies. Adaptive learning can also be incorporated in the device of applications called actively smart structures by the use of fast, real-time, information processing arrangements involving neural networks [2].

Ferroics and multiferroics (biferroics) deserve special attention among the smart materials (Fig. 1).

Ferroic crystals are crystals which involve at least one phase transition which changes the directional symmetry of the crystal. In the science of crystals, study of changes of symmetry as a function of temperature, pressure, etc. is a very developed subject. When a crystal changes its symmetry, it is a process of going from one phase to another one. It is called a phase transition entailing a change of symmetry [3].

The term ferroic materials (ferroics) is a general term covering ferromagnetics, ferrimagnetics / antiferromagnetics, ferroelectrics / ferrielectrics / antiferroelectrics and ferroelastics / ferrielastics / antiferroelastics [3]. These three types of ferroics are called primary ferroics.

Ferroic materials exhibit a hysteresis (Fig. 2).
There are several common features among materials exhibiting the properties of ferromagnetism, ferroelectricity and ferroelasticity, the most notable being the occurrence of a domain structure (a consequence of spontaneous breaking of symmetry), and the resultant hysteresis behaviour. A. Aizu (1969) \[4\] therefore coined the general term ferroics materials (ferroics) for all such materials. Although ferro has been used for coining the word ferroic, it has nothing to do with the presence or absence of iron in a ferroic material.

Apart from the domain structure, a second important feature of ferroics is the high value of certain response functions of the material that can acquire in the vicinity of the ferroic phase transition.

A third significant feature is the very large temperature dependence of certain macroscopic properties in the vicinity of the ferroic phase transition.

Furthermore, if there is a strong coupling between these properties and other properties, then the latter also behave in a similar way \[1\].

These four features form the basis of a large variety of device applications of ferroics (Fig. 3).

In the ferroic materials science, the important notion of prototype symmetry is in the context of ferroic phase transitions. The symmetry of any ferroic phase of a material can be regarded as derived by a small distortion of the prototype symmetry. For example, the symmetry of the cubic phase \((T > T_{CE})\) of the paraelectric BaTiO\(_3\) is the prototype for its tetragonal ferroelectric – ferroelastic phase occurring at room temperature \((T_r < T_{CE})\).

Ferroelastics are the least well-known ones in the family of ferroics. Let us remind therefore the basic properties of these materials.

Ferroelasticity must be a mechanical or elastic analogue of ferromagnetism and ferroelectricity. A ferroelastic material has a spontaneous strain and a concomitant domain structure the consequence of which is the observed hysteresis when the bulk spontaneous strain is plotted as a function of the applied directional stress. A ferroelastic crystal contains two or several stable states of orientation with no mechanical stress. It is possible to change reversibly from one state to another by applying a stress \((\sigma)\) in the defined directions. There exist a strain – stress elastic hysteresis with spontaneous strain \((\eta_s)\) and a coercive stress \((\sigma_c)\). Transition from a ferroelastic phase to a higher
temperature phase, termed \textit{paraelastic}, occurs by an increase in symmetry and a change in the crystalline system \cite{4}.

If such a coupling \textit{FE – FES} occurs, the spontaneous strain ($\eta_s$) may be modified by applying an electric field ($E$) and the spontaneous polarization ($P_s$) may be modified applying a mechanical stress ($\sigma$). This leads to a set of four hysteresis cycles: $P(E)$, $\eta(\sigma)$, $\eta(E)$ and $P(\sigma)$ – Fig. 4.

Ferroics are of great importance in the family of smart materials. Among them are the most \textit{smart} multiferroics and biferroics.

The term \textit{multiferroics} has been coined to describe materials in which two or all three of ferromagnetism, ferroelectricity and ferroelasticity occur in the same phase \cite{5}. This means that they have a spontaneous magnetization ($M_s$) which can be reoriented by an applied magnetic field ($H$), a spontaneous polarization ($P_s$) which can be reoriented by an applied electric field ($E$), and a spontaneous deformation ($\eta_s$) which can be reoriented by an applied stress ($\sigma$).

\textit{Biferroics} are materials in which two ferroic states occur in the same phase \cite{6}. Materials with simultaneous ferroelectric and magnetic ordering are called \textit{ferroelec-
Fig. 4. Hysteresis loops for ferroelastoelectric FESE (ferroelectric FE – ferroelastic FES phase with coupling) [4].

tromagnetics, those with simultaneous ferroelectric and those with mechanical ordering – ferroelectroelastics; when and with simultaneous ferromagnetic and mechanical ordering occurs simultaneously they are called ferromagnetoelastics [7].

This work is focused on ferroelectromagnetic multiferroics, which are simultaneously ferroelectrics and ferromagnetics (FE + FM → FEM).

2. Ferroelectromagnetics

2.1. The magnetoelectric (ME) effect

Magnetoelectricity is a property product and needs a biphasic surrounding to exhibit the behavior. The primary magnetoelectric (ME) materials become magnetized when placed in an electric field and electrically polarized when placed in a magnetic field. In the secondary effect, the permeability or permittivity change is expected. The history of the ME effect dates back to as early as 1894, when P. Curie stated that it would be possible for an asymmetric molecular body to polarize directionally under the influence of a magnetic field. Later, L.D. Landau and E. Lifshitz (1958) showed by symmetry considerations that a linear ME can occur in magnetically ordered crystals. Subsequently, I.E. Dzyaloshinskii (1960), on the basis of a theoretical analysis, predicted the existence of the ME effect in antiferromagnetic $\text{Cr}_2\text{O}_3$. This was confirmed by D.W. Astrov (1960) by measuring the electric field induced magnetization and later by G.T. Rado and V.J. Folen (1961) by the detection of the magnetic field-induced polarization.
The primary requirement for the observance of the ME effect is the coexistence of magnetic and electric dipoles.

The magnetoelectric (ME) effect is characterized by a variation of the electrical polarization ($P$) in response to an external magnetic field ($H$), or an induced magnetization ($M$) by an external electric field ($E$) [8]:

$$P = X^E E + X^{EM} H,$$

$$M = X^M H + X^{ME} E,$$

where $X^E$ – electric susceptibility tensor, $X^M$ – magnetic susceptibility tensor, $X^{EM} = X^{ME} = \frac{\delta^2 \varphi}{\delta E_i \delta H_j}$ – mixed magnetoelectric susceptibility tensor;

$$X^{EM} = \frac{\delta P}{\delta H},$$

$$X^{ME} = \frac{\delta M}{\delta E},$$

$\varphi$ – thermodynamic potential.

The following equation in the vicinity of the phase transition point ($T_{CE} = T_{CM} = T_C$) is in force:

$$X^{EM} = X^{ME} \approx (T - T)^{-1/2}.$$  

Since the discovery of the ME effect in the compound Cr$_2$O$_3$ in 1950 s, extensive attention has been drawn to it, in the earlier time to ferroelectromagnetic (FEM) compounds (single-phase FEM) and recently mainly to ferroelectric – ferro-/ferrimagnetic composites [9]. However, the observed ME effect for most of the FEMs is too weak to be applicable, however it has been found that a number of ferroelectric – ferro-/ferrimagnetic composite structures show an significant ME output qualified for potential applications. Generally, for the composite structure, the ME effect originates from a product the magnetostrictive effect from the magnetostrictive phase with the piezoelectric effect from the piezoelectric phase in the composites. It is well established that the ME effect is remarkably dependent on the dc magnetic bias field $H_o$ [7] onto which an ac magnetic signal $H$ is imposed. With increasing the bias $H_o$ magnetoelectric coupling coefficient

$$\alpha_E = \left( \frac{dE}{dH} \right)_{H_o}$$

first increases and ten drops down slowly after reaching its maximum. Nevertheless, the dependence of the ME effect on the bias field $H_o$ is rarely considered in theoretical approaches. For instance, the phenomenological theory proposed recently to explain the ME effect at the microwave frequency for laminate ferroelectric/ferromagnetic composites does not take into account this dependence in a reasonable manner.
Ferroelectromagnetic materials exhibiting the ME effect can be classified into two classes: single phase and composites.

2.2. Single-phase FEM

2.2.1. General characteristics

Single phase materials exhibiting the ME effect have an ordered structure and require the presence of FE / FIE / AFE and FM / FIM / AFM states. These materials should show two phase transitions [9]:

\[
\text{FE/FIE/AFE} \xrightarrow{T_{CE}} \text{PE},
\]

\[
\text{FM/FIM/AFM} \xrightarrow{T_{CM/TN}} \text{PM}.
\]

In single-phase ferroelectromagnetics, the ME effect arises due to the local interaction between the ordered magnetic (FM / FIM / AFM) and ordered electric (FE / FIE / AFE) sublattices. The conditions for the occurrence of ferroelectric and magnetic properties in the same material, often accompanied by ferroelasticity, imply:

- the presence of adequate structural building blocks permitting ferroelectric type ionic movements;
- magnetic interaction pathways, usually of the super exchange type;
- the fulfillment of symmetry conditions.

One simple inference from this is that it is possible to synthesized ferroelectromagnetics by replacing diamagnetic ions by paramagnetic ones on the B-site of oxyoctahedral ferroelectric perovskites ABO\textsubscript{3}. G.A. Smolenskii and V.A. Ioffe in 1958 [8] synthesized the FE – AFM perovskite ceramic Pb(Fe\textsubscript{1/2} Nb\textsubscript{1/2})O\textsubscript{3} (PFN). Later the growing of single crystals of PFN at the presence of a weak spontaneous magnetic moment (W–FM) in ferroelectric phase below \(T = 9\) K was confirmed (D.N. Astrov et al., 1968 [10]).

Ferroelectromagnetic multiferroics are rare materials being both ferromagnetics and ferroelectrics in the same phase. N.A. Hill and A. Filippetti [5] show that their scarcity results from transition metal \(d\) electrons, which are essential for magnetism destabilizing the off-center ferroelectric distortion. By studying some known multiferroics (BiMnO\textsubscript{3}, YMnO\textsubscript{3}) authors [5] identify the unconventional driving forces which can cause ferromagnetism and ferroelectricity to occur simultaneously (identify the chemistry behind the additional electronic or structural driving forces that must be present for FE and FM to occur simultaneously).

In ferroelectrics (e.g. in prototypical perovskite structures such as BaTiO\textsubscript{3}) the spontaneous polarization (\(P_s\)) is achieved by the off-center distortion of small transition metal cations (e.g. Ti\textsuperscript{4+}) at the center of the octahedron of oxygen anions. The existence or absence of such an off-center distortion is determined by a balance between short range repulsions between adjacent electron clouds, which favor the non-ferroelectric symmetric structure, and additional bonding considerations, which might stabilize the ferroelec-
tric phase. It is now widely accepted that the ferroelectricity in conventional perovskite structure oxides is favored because of ligand field stabilization in which the formally filled oxygen $2p$ states donate electron density into the formally empty $d$ states of the transition metal cations as it moves off-center. Clearly, vacant transition metal $d$ states in an appropriate energy range are required for such stabilization to occur [11].

The occurrence of magnetic spin polarization is subject to an opposite requirement – there must be filled transition metal $d$ states. According to the E.C. Stoner model (1933) [5] the fundamental driving force for local spin polarization is the exchange energy, which is minimized if all the electrons have the same spin. Opposing the alignment of spins is the increased band energy involved in transferring electrons from the lowest band states (occupied equally with up-and down-spin electrons) to band states of higher energy. The exchange effect predominates the band energy only in narrow bands, such as those arising from $d$ electrons, which have a high density of states at the Fermi energy.

The existence of ferroelectricity (which requires empty $d$ orbitals) should be inconsistent with the occurrence of spin polarization (which requires filled $d$ orbitals). Spin-polarization means any kind of a local moment, whether ordered ferro- or antiferromagnetically, or not at all.

In the last few decades the FEM effect has been found in numerous single-phase materials (compounds and solid solutions) of various types of crystalline structures:

- perovskites ($ABO_3$), e.g. [12–16];
- bismuth layer perovskite-like oxides ($A_{m-1}Bi_2B_mO_{3m+3}$), e.g. [17–20];
- boracites ($Me_3B_7O_{13}X$), e.g. [8, 10];
- RMnO$_3$-type ($R = Y, Ho, Er, Yb, Tu, Lu, Sc$) hexagonal manganites, e.g. [8, 10, 21];
- Ba Me $F_4$-type ($Me = Mn, Fe, Co, Ni$) hexagonal fluorides, e.g. [8, 10];
- hexagonal BaTiO$_3$-type compounds, [e.g. 8, 10];
- tungsten–bronze-type niobiate compounds (e.g. $Ba_6Nb_9FeO_{30}, Sr_6Nb_9FeO_{30}$), e.g. [19, 20];
- other compounds and solid solutions (e.g. FeS, Cu(HCOO)$_2 \cdot 4H_2O$, $Li(Fe_{1/2}Ta_{1/2})O_2F$), e.g. [8, 10].

### 2.2.2. Phase transitions in single-phase multiferroics

With the rapidly increasing interest in the study of structural phase transitions, the need for a simple representation of the dielectric, elastic, magnetic, and symmetry properties involved becomes acute. K. Aizu [22, 23] and L.A. Shuvalov [24] have recognized and enumerated the various possible phase transitions in terms of their point groups.

For discontinuous (first-order) type of ferroelectric transitions, there is no necessary symmetry for the compatibility between high- and low-temperature phases. However, for all continuous (or quasi-continuous) transitions there are symmetry restrictions which can be probed by the group theory via a Landau free-energy analysis. A concise description of the method is given by R. Blinc and B. Žeks [25] and here it will
suffice to state that all the possible ferroelectric states derivable from a particular higher-symmetry configuration by a quasi-continuous phase transition can be enunciated, together with the number of possible ferroelectric domains (with different but equivalent orientations of spontaneous polarization), for each lower-symmetry phase. All the possible ferroelectric point groups which can result from the 32 paraelectric point groups are given in Table 1. A simplified but more general representation which includes magnetic as well as dielectric and elastic properties of materials has been introduced by E.T. KEEVE and S.C. ABRAHAMS [26]. Its simplicity, and the fact that it can include recognition of coupling between properties, makes the latter particularly suitable for discussion in the context of coupled phase transitions.

Each phase of a crystal is represented by a triplet of symbols followed by the point group of that phase [20].

The first symbol refers to the dielectric state of the crystal as follows:
- F – for actual or potential ferroelectric in which the spontaneous polarization $P_s$ can be reversed or reoriented either experimentally or conceptually (i.e. including pyroelectric);
- A – for antiferroelectric, characterized by the existence of ordered local dipoles in the structure but of a net zero polarization (i.e. including antipolar);
- $\pi$ – for piezoelectric, encompassing all piezoelectric materials except those characterized by F or A;
- P – for paraelectric, characterized by zero net polarization and containing no ordered local dipoles in the structure.

The second symbol refers to the elastic state of the crystal as follows:
- F – for ferroelastic, characterized by the existence of a net spontaneous strain $\eta_s$ which can be reoriented either experimentally or conceptually;
- A – for antiferroelastic, defined by the existence of a single stable mechanical state in which the unit cell contains an equal number of opposite local spontaneous strains with a zero resultant;
- P – for paraelastic, encompassing all other crystals with a single stable mechanical state and zero net strain.

The third symbol refers to the magnetic state in the normally accepted terminology as follows:
- F – for ferromagnetic, characterized as possessing a non-zero net magnetic moment $M_s$ (i.e. including ferrimagnetisms, weak ferromagnetism, etc.);
- A – for antiferromagnetic;
- P – for a lack of magnetic order (i.e. paramagnetic or diamagnetic).

In multiferroic materials the possibility of any pair of ferroelectric, ferroelastic, and ferromagnetic order parameters being coupled always exists. When this occurs, the strongly coupled properties are denoted by a subscript $c$ on both property symbols. The possibility that all three order parameters are strongly coupled in a ferroelectric, ferroelastic, ferromagnetic phase cannot be discounted. The emphasis in this work is obviously on ferroelectric transitions and most of the examples (Table 2) are taken from [26].
Table 1. Place of ferroelectrics in the crystal family.

<table>
<thead>
<tr>
<th>Symmetry classes</th>
<th>No. class</th>
<th>Symbols</th>
<th>Centrosymmetric crystals</th>
<th>Non-centric crystal classes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Krentz</td>
<td>Schoenflies</td>
</tr>
<tr>
<td>Triclinic</td>
<td>1</td>
<td>( L_1 )</td>
<td>( C_1 )</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>( C )</td>
<td>( C_1 )</td>
<td>1</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>3</td>
<td>( L_2 )</td>
<td>( C_2 )</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>( P_y )</td>
<td>( C_4 )</td>
<td>( m )</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>( L_2 )</td>
<td>( C_{2h} )</td>
<td>( 2/m )</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>6</td>
<td>( L_4 )</td>
<td>( C_{2v} )</td>
<td>( 2mm )</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>( L_4 )</td>
<td>( D_2 )</td>
<td>( 222 )</td>
</tr>
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<td></td>
<td>8</td>
<td>( L_4 )</td>
<td>( D_{2h} )</td>
<td>( mmm )</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>9</td>
<td>( A_4^2 )</td>
<td>( S_4 )</td>
<td>( 4 )</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>( L_4 )</td>
<td>( C_4 )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>( L_4 )</td>
<td>( C_4 )</td>
<td>( 4/m )</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>( A_4^2 )</td>
<td>( D_{2d} )</td>
<td>( 42m )</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>( L_4 )</td>
<td>( C_{4v} )</td>
<td>( 4mm )</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>( L_4 )</td>
<td>( D_4 )</td>
<td>( 422 )</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>( L_4 )</td>
<td>( D_{4h} )</td>
<td>( 4/mmm )</td>
</tr>
<tr>
<td>Trigonal</td>
<td>16</td>
<td>( L_3 )</td>
<td>( C_3 )</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>( L_3 )</td>
<td>( S_6/C_3h )</td>
<td>( \overline{3} )</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>( L_3 )</td>
<td>( C_{3v} )</td>
<td>( 3m )</td>
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<td></td>
<td>19</td>
<td>( L_3 )</td>
<td>( D_3 )</td>
<td>( 322 )</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>( L_3 )</td>
<td>( D_{3d} )</td>
<td>( 3m )</td>
</tr>
<tr>
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<td>21</td>
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<td>( C_{3h} )</td>
<td>( \overline{6} )</td>
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<tr>
<td></td>
<td>22</td>
<td>( L_6 )</td>
<td>( D_{3h} )</td>
<td>( \overline{6}m2 )</td>
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<td></td>
<td>23</td>
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<td>( C_6 )</td>
<td>6</td>
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<tr>
<td></td>
<td>26</td>
<td>( L_6 )</td>
<td>( D_6 )</td>
<td>( 622 )</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>( L_6 )</td>
<td>( D_{6h} )</td>
<td>( 6/mmm )</td>
</tr>
<tr>
<td>Cubic</td>
<td>28</td>
<td>( L_3L_3 )</td>
<td>( T )</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>( L_3L_3 )</td>
<td>( T )</td>
<td>( m3 )</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>( L_4L_4 )</td>
<td>( T )</td>
<td>( 4\overline{3}m )</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>( L_4L_4 )</td>
<td>( O )</td>
<td>432</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>( L_4L_4 )</td>
<td>( O_h )</td>
<td>( m3m )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>The sum total</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

32
Table 2. Characteristic examples of the phase transitions in multiferroics.

<table>
<thead>
<tr>
<th>No</th>
<th>Materials</th>
<th>Phase transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BaTiO₃</td>
<td>PPP (m/3m) - (F, F, P (4mm)) - F, F, P (mm2) - F, F, P (3m)</td>
</tr>
<tr>
<td>2</td>
<td>K₂H₂PO₄</td>
<td>πPP (T₄mm) - F, F, P (mm2)</td>
</tr>
<tr>
<td>3</td>
<td>Cd₂(MoO₄)₃</td>
<td>πPP (T₄mm) - F, F, P (mm2)</td>
</tr>
<tr>
<td>4</td>
<td>K₃Fe₅⁺Fe₃⁺F₁₅</td>
<td>PPP (4/mmm) - F, F, P (mm2)</td>
</tr>
<tr>
<td>5</td>
<td>Na₃W₃O₉F₅</td>
<td>PPP - F, F, P</td>
</tr>
<tr>
<td>6</td>
<td>Ba₄Na₂Nb₁₀O₃₀</td>
<td>PPP (4/mmm) - FPP (4mm) - FPP (mm2)</td>
</tr>
<tr>
<td>7</td>
<td>Ba₅Sr₆₋ₓNb₁₀O₃₀</td>
<td>PPP (4/mmm) - πPP (T₄mm) - FPP (4mm)</td>
</tr>
<tr>
<td>8</td>
<td>Pb₅Cr₃F₁₉</td>
<td>PPP (4/mmm) - FPP (4mm)</td>
</tr>
<tr>
<td>9</td>
<td>Pb₅(Al₃₉Al₀₁₀)₃F₁₉</td>
<td>PPP (4/mmm) - PPP (4/m) - PFP (2/m) - AFP (4/m) - FPP (4mm)</td>
</tr>
<tr>
<td>10</td>
<td>BaCoF₄</td>
<td>PPP (m/mmm) - FPP (mm2) - FFA (2) PPP (mm2) - FPP (mm2) - FAA (mm2)</td>
</tr>
<tr>
<td>11</td>
<td>RbFeF₄</td>
<td>PPP (4/mmm) - PFP (mm2) - PFA (mm2)</td>
</tr>
<tr>
<td>12</td>
<td>K₃NiF₄</td>
<td>PPP (4/mmm) - PFP (mm2) - PFA (mm2)</td>
</tr>
<tr>
<td>13</td>
<td>KFeF₃</td>
<td>PPP (m/mmm) - PFP (3m) - PFA (3m)</td>
</tr>
<tr>
<td>14</td>
<td>Mn₃O₄</td>
<td>PPP (4/mmm) - PFP (m)</td>
</tr>
</tbody>
</table>

2.3. Composite ferroelectromagnetics

The choice of single-phase multiferroics exhibiting coexistence of strong ferro- / ferrimagnetisms and ferroelectricity is limited.

The ferroelectric – ferro- / ferrimagnetic composite exhibits responses that are not available in the individual component phases.

If new ferroelectromagnetic composites and the conditions of their production are designed, the researcher should pay attention to the following problems.

No chemical reaction should occur between the ferroelectric and ferro- / ferrimagnetic materials during the high–temperature sintering process. A chemical reaction may reduce the piezoelectric and / or magnetostrictive properties of each phase.

The resistivity of the magnetostrictive phase should be as high as possible. If the resistivity of a magnetostrictive phase is low, the electric poling becomes very difficult due to the leakage current. Furthermore, the leakage current reduces the ME properties of the composites. When the ferrite particles make connected chains, the electric resistivity of the composites is reduced significantly because of the low resistivity of the ferrite. Therefore, good dispersion of the ferrite particles in the ferroelectric matrix is required in order to sustain sufficient electric resistivity of the composite.

Mechanical defects such as pores at the interface between the two phases should not exist in the composite in order to achieve a good mechanical coupling.

The basic ideas underlying composite ferroelectromagnetic ceramics can be classified into three categories: (a) sum properties, (b) product properties and (c) combination properties (Fig. 5).
Depending on the application, the appropriate properties of the individual phases can be invoked to design a composite which will have a sum property or a product property. These concepts are of fundamental importance.

A *sum property* (Fig. 5a) of a composite is a weighted sum of the contributions from the individual component phases proportional to the volume of weight fractions of these phases in the composite (physical quantities like density and resistivity are sum properties).

A *product property* (Fig. 5b) is reflected in the composite structure but is absent in the individual phases. In a biphasic composite material, if one phase exhibits a property \( A \rightarrow B \) (application of an independent variable \( A \) resulting in an effect \( B \)) with a proportionality tensor \( \frac{dB}{dA} = X \) (may be a constant or dependent on \( A \) or \( B \)) and the second phase exhibits a property \( B \rightarrow C \) with a proportionality tensor \( \frac{dC}{dB} = Y \), then...
the composite will exhibit a property $A \to C$ (product property of the composite) which is absent in either of the initial phases. The proportionality tensor $dC/dA$ is the product of the proportionality tensor of the phases, i.e. $dC/dA = (dC/dB) (dB/dA) = YX$.

A combination property (Fig. 5c) of a composite takes place in the following situation. In certain cases, the averaged value of the output, $B^*$, of a composite does exceed the magnitude of end components $B_1$ and $B_2$. This enhanced output refers to an effect $B/C$ which depends on the two parameters $B$ and $C$. Suppose that $A$ and $C$ follow convex and concave type sum effects, respectively. The combination value $B/C$ will exhibit a maximum at an intermediate ratio of the phases.

All these properties (Fig. 5a, b, c) can be exploited to yield the requisite effect for the desired application.

In composite ferroelectromagnetics magnetoelectric (ME) the effect is realized by using the concept of product properties [8]. A suitable combination of two phases can yield the desirable property such as a combination of piezomagnetic and piezoelectric phases or a combination of magnetostrictive and piezoelectric phases. The ME effect can be realized also by coupling the thermal interaction in pyroelectric-pyromagnetic composites. Most ferromagnetic materials show a magnetostrictive effect, however a piezomagnetic effect has not been observed in these materials. This means that in these materials the strain caused by a magnetic field is not linearly proportional to the field strength but is related to the square of the magnetic field strength. This makes the product property, the magnetoelectric effect in the piezoelectric-magnetostrictive composites, a nonlinear effect unlike the single phase materials where the magnetoelectric effect is a linear effect over a wide range of the of the magnetic or electric field values. Also the magnetoelectric effect in these composites shows hysteresis behavior. This makes the applications of such composites difficult in linear devices. Linearity in such composites is achieved by applying a bias magnetic field across them so that the magnetoelectric effect over a short range around this bias can be approximated as a linear effect. The hysteresis nature of this effect can be used in memory devices, for which there is no necessity of a bias magnetic field.

The ME effect obtained in composites is more than a hundred times larger than that of single-phase ME materials (such as Co$_2$O$_3$).

A strong ME effect in a composite can be observed if the following conditions are fulfilled [9]:

- two individual phases should be in equilibrium;
- mismatching between grains should not be present;
- the magnitude of the magnetostriction coefficient of the piezomagnetic or magnetostrictive phase and the magnitude of the piezoelectric coefficient of the piezoelectric phase must be greater;
- the accumulated charge must not leak through the piezomagnetic or magnetostrictive phases;
- the strategy for poling of the composites must be determined.

At present many various ferroelectromagnetic composites are received, among other things e.g.:
Various ferroelectromagnetic composites are produced by different methods and forms, among other things e.g. [27]:

- bulk ceramics (x [%] ferro- / ferrimagnetic powders in (1-x) [%] ferroelectric matrix);
- multilayer geometry consisting of alternating layers of the ferroelectric phase, e.g. perovskite BaTiO$_3$, and the ferro- / ferrimagnetic phase e.g. spinel CoFe$_2$O$_4$ (a thin film – on – substrate geometry);
- a heterostructure consisting of nanopillars of the ferro- / ferrimagnetic phase embedded in a ferroelectric matrix (a thin film – on – substrate geometry);
- a laminated structure made by using piezoelectric and magnetostrictive materials (by sandwiching and bonding a PZT ceramic disk between two layers of Terfenol–D disks or a ferroelectric single crystal disc e.g. Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ – PbFe$_3$O$_4$ (PMN – PT), Pb (Zn$_{1/3}$ Nb$_{2/3}$)$_3$O$_3$ – PbFe$_3$O$_4$ (PZT – PT)) between two discs of Terfenol–D).

The ferroelectromagnetic composites are manufactured by using various processes, e.g. [28]: a high – advanced ceramic technology (bulk ceramic composites), rf sputtering, the sol-gel process, pulsed laser deposition (thin film and multilayer composites).

The ferroelectromagnetic composites consist of two different phases: the ferroelectric phase and ferro- / ferrimagnetic phase. These phases can not be mutually independent, but they have to be coupled. This coupling is set between order parameters of the electric ($P_s$) and magnetic ($M_s$) systems.

In ferroelectromagnetics, the temperature dependent magnetic measurements illustrate the coupling between two order parameters, which is manifested as a change in the magnetization at the ferroelectric Curie temperature ($T_{CE}$). In case of the multiferroic multilayer (for example ferroelectric BaTiO$_3$ with a perovskite-type structure and ferro-/ ferrimagnetic CoFe$_2$O$_4$ with a spinel-type structure [27]), the thermodynamic analyses show that the magnetoelectric coupling in such a structure can be understood on the basis of the strong elastic interaction between the two phases. In other cases (e.g. in single-phase multiferroics), the problem becomes considerably more complicated and more difficult.

H. ZENG et al. [27] proposed that composite piezoelectric and magnetostrictive phases can be electromagnetically coupled via the mediation of stress. When the magnetoelectric coupling is purely by elastic interaction, the effect in a multilayer structure of a substrate will be negligible due to the clamping effect of the substrate. This system shows a strong coupling of the order parameters trough the heteroepitaxy of the two lattices (e.g. BaTiO$_3$ – CoFe$_2$O$_4$). This approach is general. At the present technologists have been able to create similar structures of other spinel – perovskite systems, such as...
H. Tabata et al. [29] constructed ferroelectric and/or ferromagnetic superlattices by a layer-by-layer successive deposition technique with a laser MBE. An ideal hetero–epitaxy can be obtained due to the similar crystal structure of the perovskite type ferroelectrics (BaTiO$_3$, SrTiO$_3$, Bi-based layered compound) and ferro- or antiferromagnetics (LaFeO$_3$, LaCrO$_3$, (La, Sr)MnO$_3$). In both superlattices, the strain effect plays an important role in deterring their ferroelectromagnetic properties.

J.L. Prieto et al. [30] presented a new working configuration for magnetostrictive–piezoelectric magnetic sensors. Magnetostrictive–piezoelectric sensors are very interesting because of their good characteristics such as their high sensitivity, great frequency response, easy construction, low cost, etc. The sensor, like the traditional magnetostrictive–piezoelectric sensor, was made by interfacing a highly magnetostrictive ferromagnetic material with a piezoelectric support through a viscous fluid. In this operating mode, the excitation was caused using a current flowing through the ferromagnetic sample, and the piezoelectric support detects the size of changes of the ferromagnetic material. The sensitivity of this magnetic sensor is really good, but it can be easily increased taking into account the following points:

- the mechanical coupling between the ferromagnetic and piezoelectric materials must be improved;
- the size of the ferromagnetic material compared to the piezoelectric support must increase to a comparable size (or even larger) to obtain a larger effect;
- alternative configurations can improve the characteristics.

Despite the very good characteristics of the actual sensor, it would be very interesting to develop a magnetic sensor without a coil in order to open up the possibility of a planar or integrated device. The more promising planar or integrated technologies could be (1) the magnetotransistor, (2) a bimetallic compound, (3) magnetoresistance or magnetoimpedance, (4) other interesting devices of the Lorentz force, (5) Hall sensors, and even flux-gate in the planar technology. J.L. Prieto et al. [31] presented a new planar technology of magnetic sensors.

T. Ueno et al. [32] described the principle of a magnetic force control by an inverse magnetostrictive effect of the magnetostrictive material and a device, which is a combination of a giant magnetostrictive rod and a stack piezoelectric actuator fabricated to realize the principle practically. The magnetic force control is based on the inverse magnetostrictive effect of Terfenol-D coupled via strain with the piezoelectric actuator and the variation of the voltage applied to the piezoelectric actuator is converted to the variation of the magnetic force via a magnetic circuit in the device. The advantage of zero power consumption and heat generation of the device in a steady-state operation was also confirmed by the comparison of the device with the electromagnet.

In the paper of Y.X. Lin et al. [33], the significant effect of a dc magnetic bias field on the magnetoelectric coupling in a magnetoelectric composite structure has been studied using the finite-element method. It has been demonstrated that the dc bias effect of
the magnetoelectric coupling is ascribed to the nonlinear response of the magnetostress coupling in the magnetostrictive materials to the applied dc bias field. A numerical calculation of the Terfenol-D (Tb$_{0.3}$ Dy$_{0.7}$ Fe$_{1.9}$)–epoxy / Pb (Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT)–epoxy composite structure has revealed that the magnetostress coupling coefficient first increases rapidly and then fall slowly down with an increasing bias field. A significant effect of the bias field on the magnetoelectric yield has been demonstrated too. A rough consistency between the numerical calculation and the experiments has been given.

Composite ferroelectromagnetics, which display simultaneous magnetic and electric ordering, have recently stimulated much scientific and technological interest [29]. The coexistence of magnetic and electric subsystems engenders the material with the product property, thus allowing an additional degree of freedom in the design of actuators, transducers and storage devices.

3. Conclusions

Ferroics form an essential subgroup of smart (or functional) materials whose physical properties are sensitive to changes at external conditions such as temperature, pressure, electric and magnetic field. Ferroelectric, ferromagnetic and ferroelastic materials are the best-known examples of ferroics that are principally distinguished by two main characteristics:

- Firstly, their property specific order parameters (e.g. polarization, magnetization, or self-strain, for ferroelectrics, ferromagnetics and ferroelastics, respectively), spontaneously assume nonzero values below a threshold temperature even in the absence of an applied stimulus. Thus these substances are usually high-energy – density materials that can be configured to store and release energy (electrical, magnetic and mechanical) in well-regulated manners, making them highly useful as sensor and actuators.
- Secondly, ferroics (as a general class of materials) exhibit hysteresis in their stimulus – response behaviour: e.g. polarization versus the applied electric field, magnetization versus the applied magnetic field and strain versus the applied stress.

By definition, for a material to be ferroelectromagnetic multiferroic it must be simultaneously ferromagnetic and ferroelectric. Therefore, its allowed physical, structural and electronic properties are restricted to those which occur both in ferromagnetic and in ferroelectric materials.

The first ferroelectromagnetic material to be discovered (E. ASCHER et al., 1966 [34]) was a weakly ferromagnetic nickel iodine boracite Ni$_3$B$_7$O$_{13}$I. The latter was followed by the synthesis of many more ferroic, biferroic and multiferroic single-phase compounds and by the production of magnetoelectric composites.

Specific device applications which have been suggested for such materials include multiple state memory elements, electric field controlled ferromagnetic resonance devices, and transducers with magnetically modulated piezoelectricity.
Exciting developments can be expected in the area of smart materials and structures in the near future. Investigations of ferroic and multiferroic materials can thus pay rich dividends.

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