Science and Technology of Ceramics

2. Functional Ceramics

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In Part 1[1] we saw that ceramics could be broadly classified as traditional and advanced ceramics. Traditional ceramics are those made from naturally occurring materials like clays and minerals without requiring much refinement. In this part the second category, namely advanced ceramics will be dealt with.

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Advanced Ceramics

These ceramics are developed by chemical synthesis, in other words, they are man-made. They can also be made from highly refined naturally occurring materials. Advanced ceramics are known by many other names such as engineering, fine, special or technical ceramics. This group can be further divided into functional and structural ceramics depending on the property of the ceramic that is used in the application. Functional ceramics have electrical, magnetic, electronic or optical properties (also include amorphous materials) and are used accordingly whereas the use of structural ceramics depends on mechanical properties. In addition to these two categories, there are advanced glassy ceramics called glass-ceramics.

Functional Ceramics

With the development of automotive and aircraft engine industry, the need for high performance spark plugs motivated the improvement of the traditional clay-feldspar-flint triaxial porcelain which was used for low voltage insulation. Removal of the ionically conducting potassium ions from these porcelains was achieved finally leading to an alumina body. Thus by tailoring the concentration of the alkali ions, various compositions of different performance electronic ceramics were obtained. With the development of new synthesis and sintering techniques[2],

[1] Part 1 appeared in *Resonance*, Vol.4, No.8, 1999.

[2] Solid-state sintering of the raw materials eliminated the glassy grain boundary phase which results from vitrification or liquid phase sintering. In the solid-state sintering it is important to control the purity and size of the starting powders, their size distribution and extent of agglomeration. If these processing parameters are not controlled, the fired ceramic can possess a broad range of grain sizes and porosity, and uncontrolled grain boundary phases which can degrade the physical properties of the ceramic article.

high density sintered compacts could be made. It is important to control the microstructure of the functional ceramics as they are used in corrosive environments and their stability and reliability are put to severe tests.

Electronic and Ionic Conductors

In any material, charge transport leading to electrical conduction could occur either due to the transport of electrons or ions, or both. If the conduction is predominantly due to transport of electrons (as in metals), we call the material an electronic conductor. On the other hand, if the electrical conductivity is due to the transport of ions, as in NaCl crystal, the material is an ionic conductor. There are ionic crystals in which the conduction due to ions is as large as those in liquid electrolytes. These materials are called superionic conductors and can be used as electrolytes in an all solid state battery. There also exist materials in which both electronic and ionic conductivity are significant, example AgS. These materials known as mixed conductors find application as electrode materials in solid state batteries.

Electronic Conductors

The room temperature electrical conductivity of oxides varies by 24 orders of magnitude. The high temperature superconductors (like $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2Ca_2Cu_3O_{10}$, $Tl_2Ba_2Ca_2Cu_3O_{10}$, $HgBa_2Ca_2Cu_3O_8$, etc.) are at one extreme where the conductivity below their T_c is infinitely high and at the other extreme are the high purity Al_2O_3 and SiO_2, where the conductivity is of the order of 10^{-15} (ohm-cm)$^{-1}$. Similarly, wide variation in dielectric, magnetic and optical transmissivity has been observed in ceramics. An important aspect of functional ceramics is the cooperative interaction of electrical, mechanical, optical and magnetic properties. Since these interactions are a consequence of complex crystal structures that have anisotropic characteristics (*Box* 1), they can be varied by replacing the cations and/or anions to suit the function of the device. Here the ceramics used for various functions are considered.

Box 1.

Some crystalline materials exhibit different magnitudes of response to external stimuli (such as electric and magnetic fields) in different crystallographic directions. Such materials are said to be anisotropic. Anisotropy arises because of differences in ionic distribution and/or bonding in the unit cell along different crystallographic axes. For example: In a compound, if the distance between the metallic ions along a- and b-axes is small compared to that along the c-axis, then the conductivity along a- and b-axes will be more than that along the c-axis. Example of such a material is graphite. By introducing spacer ions, it is possible to control the value of a property along a particular axis in a crystalline material.

The first ceramic *superconductor* (*Box* 2) was discovered in $La_{2-x}Ba_xCuO_4$ system with a T_c (called the superconducting transition temperature) of 40 K. Then the system Y-Ba-Cu-O was discovered with a T_c of about 90 K. Subsequently, many other combinations were tried out in order to increase the T_c, with a hope to obtain a room temperature superconductor. The highest transition temperature obtained is around 150 K in the Hg system. As mentioned earlier, in a superconducting circuit, if a current is established below its T_c, it can persist for years without much decay because of the zero resistance of the superconductor. Superconducting magnets, which are capable of generating high fields with low power consumption are being used in research equipments and also for magnetic resonance imaging in medicine. Attempts are being made to use these ceramic superconductors in running high-speed magnetically levitated trains (*Box* 2). High T_c ceramic superconductors are technologically very important because by using inexpensive liquid nitrogen, the superconducting state obtained in these materials can

Box 2.

Superconductivity is a phenomenon exhibited by some materials where below a certain temperature the electrical resistivity of the material is zero. In other words, the material does not offer any resistance to the flow of electrical current below the superconducting transition temperature. Besides, superconductors do not allow magnetic lines of force to penetrate into the bulk in the superconducting state (below the T_c). This is the perfect diamagnetism exhibited by superconductors and is known as Meissner effect, named after its discoverer. Meissner effect leads to some dramatic manifestations such as levitation. In the superconducting state, a magnet hangs in air when placed over the superconductor.

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be compared to the current ones that use liquid helium. The thin films of these superconductors can be used in SQUIDs (superconducting quantum interference devices, which are used for measuring very weak magnetic fields) and also in infrared sensors. Another potential application of the ceramic superconductors is in computers. Increasing the speed of the computers and further miniaturization are limited by the generation of heat as also by the charging time of capacitors because of the resistance of interconnecting metal films. Hence the use of superconductors may result in miniaturized chips that could transmit information orders of magnitude more rapidly.

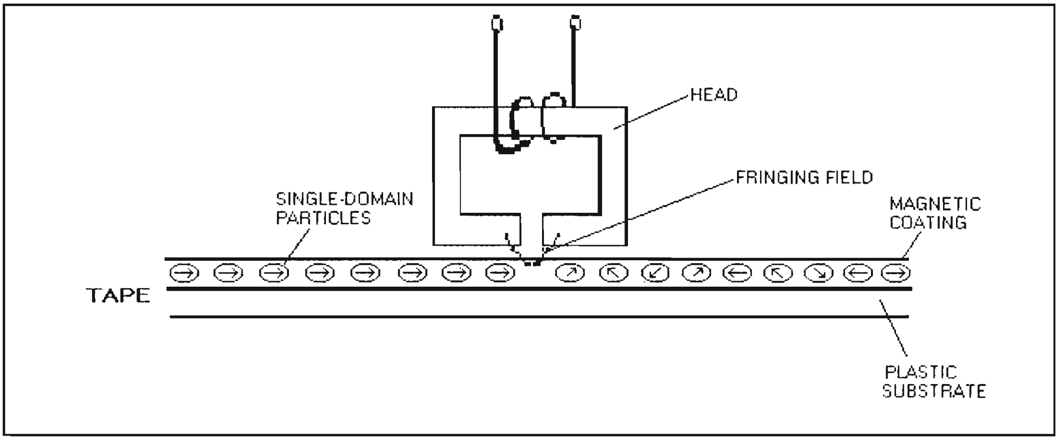
Ionic Conductors

The materials in which the ionic conductivity is high, of the order of 10^{-2} to 10 (ohm-cm^{-1}), are called fast ion conductors or *superionic conductors.* Some of the fast ion conductors are purely cationic conductors while in others the conduction is entirely by the anion. However, some materials, like the ferrites have a mixed ionic and electronic conductivity. Thus, there are halides and chalcogenides of silver and copper (eg. α-AgI, CuS, $RbAg_4I_5$) where the metal ion is mobile. The oxides with β-alumina structure are also cationic conductors with mobile monovalent cation whereas in the oxides with fluorite structure containing large concentrations of defects (eg. $CaO.ZrO_2$, $Y_2O_3.ZrO_2$) the mobile ions are the oxygen anions. There is another class of ionic conductors (eg. sodium superionic conductor, (NASICON) with formula $Na_3Zr_2PSi_2O_{12}$) which contains intersecting tunnels in three dimensions. In β-alumina, the Na^+ conduction is along two dimensions whereas in $LiAlSiO_4$ the transport of Li^+ ions is along one direction. In polycrystalline fast ion conductors, the grain boundaries impede the conduction and give rise to AC frequency effects. An important consequence of the high resistance due to the presence of grain boundaries is that a large fraction of the applied voltage of an electrochemical device appears across the grain boundaries which can lead to electrochemical deterioration of grain boundary phases leading to dielectric breakdown.

Magnetic Materials

Magnetic materials have been known to man for a long time. The word magnet is derived from a Greek word to indicate magnetite (Fe_3O_4, an ore of iron) deposits in the district of Magnesia. Every day we use a number of devices whose functioning depend completely on the magnetic ceramics: AC or DC motors (magnetic fields are produced by means of electrical currents which are in turn converted into mechanical energy), power transformers which deliver energy to homes and industries, video and audio applications (tapes and reading or writing heads which contain magnetic materials, *Figure* 1), telephones and telecommunication systems, computer data storage systems, loud speakers, etc.. The most used magnetic ceramics (which are generally called ferrites) can be classified into three groups depending on their structure. These are spinel (with general formula MFe_2O_4 where M is any divalent transition metal ion), garnet (with general formula $3M_2O_3.5Fe_2O_3$ where M is a rare-earth or transition metal ion) and hexagonal ferrites. Cubic spinel ferrites are used as soft magnetic materials because of their low coercive force and high saturation magnetization. Hexagonal ferrites are hard magnetic materials with high coercive force and a large resistance to demagnetization, making them difficult to demagnetize. A wide range of substitutions make it possible to vary the magnetic properties of these ceramics over a wide range of curie points, remnant polarization,

Figure 1. Schematic representation of the digital recording head. The head is an electromagnet and has a small gap. For writing, the electric current in the coil representing the information to be stored induces a magnetic field in the head which appears in the gap. This field produces a magnetization pattern on the tape. While reading, this process is reversed. The signal activates a speaker or a TV system or a processing unit depending on the device.



saturation polarization and coercive fields (*Box* 3). This way, magnetic ceramics can be designed and processed for specific applications. For example, saturation magnetization can be widely varied by cation substitution (like rare earth or transition metal ions in place of yttrium) in the basic garnet (yttrium iron garnet). For specialized applications like floppy-disc drives, printers and other computer peripherals, stepping motors are used. These motors rotate a fraction of a revolution upon application of an electric pulse; in other words, an accurate step angle under a high output torque is required. To obtain this, barium hexaferrite is specially processed such that it is radially magnetized. Magnetic ceramics are also used in VCR tapes and they consist of a polymer that is impregnated with γ-Fe_2O_3 or CrO_2.

Magnetic garnets are isostructural with naturally occurring semiprecious mineral $Ca_3Al_2(SiO_4)_3$. In place of Ca a magnetic rare-earth ion is substituted and Al and Si are replaced by iron ions. Hence the formula is $Ln_3Fe_2Fe_3O_{12}$ (where Ln = a rare-earth ion) or $3Ln_2O_3.5Fe_2O_3$ and these compounds are called rare-earth garnets. The manner in which the magnetic dipoles are arranged in these compounds is interesting. The magnetization of Ln^{3+} is opposite to the net magnetization of the Fe^{3+} ions. At low temperatures the magnetization of the rare-earth garnet is due to the Ln^{3+} ions and with increasing temperature this magnetization decreases rapidly going to zero at the compensation point. With further increase in temperature the polarity of magnetization changes. At temperatures higher than the compensation point the magnetization is due to the Fe^{3+} ions. The presence of a compensation point is a unique property exhibited by the rare-earth iron garnets, which are suited for high frequency microwave (frequencies of 1–300 GHz) applications.

Barium hexaferrites with cobalt and titanium substitutions are used as wide-band absorbers of electromagnetic waves in the GHz (10^9 Hz) range. The aircraft structure that is highly reflecting disturbs the radar navigation near an airport or a harbour. This radar frequency can be attenuated by the use of hexaferrites.

Box 3.

Curie temperature: In ferromagnets and ferrimagnets the magnetic dipoles are oriented in such a way that there is net magnetization up to a certain temperature called the curie temperature. Above the curie temperature, the magnetic dipoles are randomly oriented with no net magnetization and this state is called the paramagnetic state.

Remnant polarization: The magnitude of the residual polarization that remains in a ferro- or a ferri-magnetic material when the magnetic field is removed.

Saturation polarization: The maximum polarization (magnetization) attained by a ferro- or a ferri-magnetic material in a magnetic field.

Coercive field: The ferro- and ferri-magnets attain magnetization in presence of a magnetic field. By reversing the direction of the applied field the magnetization can be reduced. Thus, the magnetic field required to bring down the magnetization of a ferro- or a ferri-magnet to zero is called the coercive field.

For these applications, a ferrite powder is dispersed in a resin and the mixture is painted on the structure of the aircraft. War and spy planes are covered with such paints in order to avoid being spotted by radar.

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A large decrease in electrical resistivity is observed in response to a magnetic field in some perovskite rare-earth manganese oxides below 150 K. This *colossal magnetoresistance* is technologically important. In the magneto-resistive reading head, the electrical resistance of a thin film of the magnetic material is changed as a result of magnetic field changes when the read head passes by the tape or the disk. These magneto-resistive reading heads have higher sensitivity and data transfer rates.

Dielectric Materials

A dielectric ceramic is an electrically insulating material in which a separation of positively and negatively charged entities could be achieved by the application of an electric field. The polarization actually accounts for the ability of the dielectrics to increase the charge storing capacity of the capacitors and the dielectric constant is the measure of this efficiency. For electronic applications of ceramics as capacitive components, their dielectric properties are important. The dielectric constant, dielectric loss factor and dielectric strength normally determine the suitability of a particular material for these applications. There is also another aspect of dielectric materials, which is important, i.e. the dielectric breakdown. In electrical industry, the material that is used for insulation must withstand the voltage gradient for the operating life of the system. But failures occur when an electric short circuit develops across the material and this failure is called dielectric breakdown. The breakdown strengths in ceramics depend on many factors like temperature, ambient atmosphere; material finish, porosity, composition, shape and thickness; the voltage gradient applied, the field frequency and the wave form. Thus, by changing sample geometry, the field distribution and heat dissipation patterns can be controlled considerably. Microstructure of the material also

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affects the breakdown strength. A number of ceramics are used in electrical industry for insulation and encapsulation, and as capacitors. Examples of dielectrics are quartz, Al_2O_3, mica, diamond, Mg_2SiO_4, barium lanthanum zirconates, bismuth vanadates, etc.

The group of dielectric materials which exhibit spontaneous polarization is called *ferroelectrics*. These materials contain permanent electric dipoles which is because of the presence of a noncentrosymmetric polar lattice. The common ferroelectric materials are barium titanate, Rochelle salt ($NaKC_4H_4O_6.4H_2O$), potassium dihydrogen phosphate and potassium niobate. In barium titanate, in the ferroelectric phase titanium ion moves away from the center of the TiO_6 octahedra. The other type of dielectrics where the polarization is induced by the imposition of external stress are called *piezoelectrics*. Examples of piezoelectrics are lead zirconate, titanates of barium and lead, quartz and ammonium dihydrogen phosphate. Piezoelectric materials are used in transducers where electrical energy is converted into mechanical energy or vice versa. Most common applications are in gas lighters, microphones, ultrasonic generators, strain gauges, phonograph pickups, actuators and sonar detectors. *Figure* 2 shows the usage of piezoelectric actuator in a dot matrix printer head.

Optical Materials

Optical materials are another class of important functional materials. When electromagnetic radiation impinges on a solid, it is transmitted, absorbed or scattered by the solid depending on the property of the material (mainly the electronic structure). A material can be transparent to a band of wavelengths of radiation while absorbing or scattering the other wavelengths. For instance, CdS has a band gap[3] of about 2.4 eV and hence it absorbs all radiation having energy greater than its band gap. Thus, there are materials that can be used as windows for a particular range of wavelength radiation, like the IR, visible, UV, etc. Even in the visible region, windows can be made to

[3] Band gap is the energy gap between the valence and conduction bands.

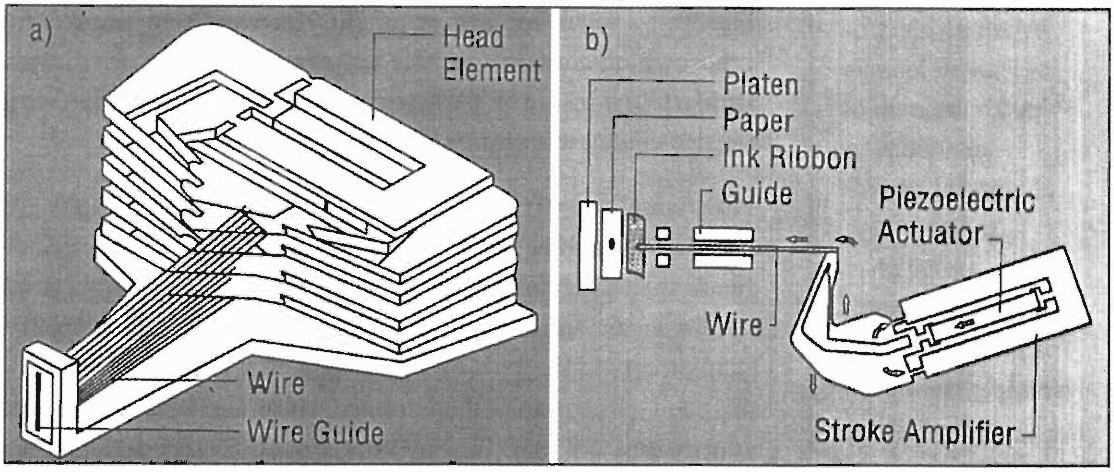

Figure 2. (a) Construction of a dot matrix printer head. Movement of each of the wires is controlled by the signal sent out by the piezoelectric ceramic actuator shown in (b). The printer head element consists of a multilayer piezoelectric device where 100 thin ceramic sheets (about 100 micron in thickness) are stacked. The signal from the device is magnified. Each character that is printed is formed by 24 × 24 dot matrix and the printing ribbon is impacted in accordance with the magnified signal that is received from the device by a multiwire array.

transmit very specific colours by tuning the material band structure. For example, sapphire (which is Al_2O_3) is transparent over the whole visible range but when a small amount of Cr^{3+} ions is substituted for Al^{3+}, the crystal becomes red in colour (called ruby). Similarly other ions like Co^{2+}(blue-violet), Cu^{2+}(blue-green) and Mn^{3+}(purple) can be used to bring about different colours. These crystals are cut to give brilliant reflection and used for making jewellery. Infrared window materials are CaF_2, SrF_2 and other alkali or alkaline earth halides while the windows in the visible range are silica based glasses, sapphire and quartz. Then there are translucent materials that are also chemically inert, like MgO and Al_2O_3, which are used for sodium lamps. Some materials absorb radiation and reemit in visible wavelength range and this phenomenon is called luminescence. The radiation emitted with a delay after absorption is termed phosphorescence and if the emission occurs 'soon' after absorption, then it is fluorescence. A number of materials like sulfides, oxides and tungstates can be made to fluoresce or phosphoresce by introducing impurities in controlled amounts.

When an electro-optical material is put in the path of an incoming polarized beam of radiation, the radiation is transmitted as the material is optically isotropic and this is the off-state.

The well-known application of fluorescence is in fluorescent lamps, which contain specially prepared tungstates or silicates. Similarly the inside of TV screens, the x-ray and γ-ray detectors are also coated with fluorescent materials.

The optical properties of ceramics can be changed by applying electric field and is called the *electro-optical* effect. This effect is due to the change in the spatial distribution of electrons, which results in an anisotropic change in electronic polarizability. Lead-zirconate-titanate (PZT) or lanthanum doped PZT (PLZT) are good electro-optical materials. Here the optically stored information can be erased by applying an electric field as in a memory oscilloscope where the image is stored and erased by the application of an electric field. They can also be used as optical switches. When an electro-optical material is put in the path of an incoming polarized beam of radiation, the radiation is transmitted as the material is optically isotropic and this is the off-state. If an electric field is applied, the grains in the material orient themselves along a particular direction (in other words the material is polarized) and the radiation cannot pass through the material. This is on-state. Again if the electric field is switched off, the material relaxes to its original state. There are also *photochromic* materials in which shining light changes the colour of the material. The energy gap between the valence and the conduction band is in the visible range of the optical spectrum. Hence when white light (in the form of sunlight) falls on these materials, electrons in the valence band absorb the energy from the radiation and are excited to the conduction band. When these electrons relax to the valence band, they give out radiation that is visible to the human eye. Tungsten oxide is an example.

This way one can list many examples and still not exhaust all the functional ceramics that are being used by us. Therefore, only some typical examples were covered here. In the next part of this article, other advanced ceramics namely the structural ceramics and glasses will be discussed.

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