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The Role of the Lanthanides in the Photonics, Electronics and Related Industries*

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Abstract

Actual applications of the lanthanides (not forgetting their family relation yttrium) in the electronic and photonic industries, in uses such as NPO capacitors, YAG lasers, and PLZT electro-optics, are illustrated. An attempt is made to relate the use to the essential underlying properties of the appropriate lanthanide-containing materials. Also a guide to future commercial potential in electronics and photonics uses is given. Abundant available resources, not only of the light lanthanides but increasingly so of the heavies, will ensure that developing technologies can rely on the supply of these f-elements.

Introduction

The aim here is to bring together many of the varied applications of the lanthanides and yttrium that are often overlooked in reviews. Some of these uses are commercially significant; others less so but are often of interest for the scientific and technological principles involved. As will appear many of these 'orphan' uses are in new fast-developing high-tech areas, particularly those associated with electronics and photonics.

To discuss applications in a logical manner it is helpful to provide a conceptual framework upon which ideas can be placed, a framework whereby one application can be related to another for illustration and for convenience. Materials oriented disciplines such as ceramics, catalysis, or metallurgy are each obvious categories, or frameworks, within which the technology of lanthanide applications can be treated. However, to provide a convenient handle for a very broad range of diverse applications the best approach would seem in terms of function rather than material. For this end ideas derived from the rapidly evolving technology of sensors [1] will be used.

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Transducer Terminology

A sensor is a device for detecting, and ideally quantifying, some property by providing an external signal, usually electrical, in response to that property. For example the yttria-stabilized zirconia (YSZ) sensors in modern vehicles give a voltage output that depends on the oxygen partial pressure of the exhaust gas. A sensor in essence responds to some form of energy and, to extend the concept further, is a type of transducer, converting one form of energy to another. In the extreme even devices that simply modify energy, such as neodymium-colored filter glass, can be considered transducers.

Notation

For any 'sensor/transducer' it is convenient to use a notation that specifies both the nature of the input and the output energy. For example:

	Input	Output
YSZ sensors	chemical	electrical
CRT phosphors	electrical	radiation
Optical filter	radiation	radiation

We can thus envisage a two-dimensional matrix with the axes each labelled with potential energy forms such as: radiation, electrical, magnetic, thermal, mechanical, and chemical.

In addition the 'radiation' label could be subdivided: gamma, X-ray, ultra-violet, visible, infra-red, microwave, and radio.

This 2-D picture is however insufficient. Many transducers utilize an auxiliary source of energy. A gamut of electrical devices, for example, have electrical energy as both input and output forms but the output signal is determined by a third form of energy such as thermal or radiation. Thus the notation needs three identifiers (input, output, auxiliary) if the device is a so-called modulating transducer. (There is an implicit zero if no auxiliary is needed, *i.e.* the transducer is self generating.) The lanthanum-doped barium titanates [2] that display, at a certain temperature, a rapid rise in resistance, for example, are: PTC thermistors (electrical, electrical, thermal).

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The full three-dimensional matrix of transducer possibilities contains, of course, much empty space but within this framework are several regions of particular relevance to applications of the lanthanides, especially in photonics and electronics. The novel spectral and magnetic behavior of the lanthanides are behind many of these uses, some well-known others less so.

Photonics

The technology associated with light and other forms of radiant energy whose quantum unit is called the photon is conveniently termed photonics. Our own eyes process information in the visible portion of the electro-magnetic spectrum and hence transducers that have this radiation as output are widely used. Phosphors are such transducers and luminescence is the phenomenon.

Table I gives luminescence applications by input energy form. This listing includes well-known uses in CRT phosphors and fluorescent lamps plus others less recognized such as temperature measurement.

Not all phosphors have to be self-generating and recent technology makes use of stimulable phosphors, *i.e.* modulating transducers, to delay the output. Some examples are found in Table II. The dose can be read off a film badge, for example, at the end of the working day by making use of thermoluminescence. A thulium-doped calcium sulphate phosphor allows precise measurement of low doses. In photosimulable luminescence (PSL) an X-ray image can be handled digitally by stimulating the exposed phosphor with light in a step separate from the actual exposure. The response of the PSL intensity to the incident X-ray energy shows good linearity over a 10^5 range of X-ray dose.

Radiation Transducers

Turning to the optical field there are many applications in which the lanthanides, through their novel spectral behavior, are converting, or modifying, input energy from the visible or near-visible spectrum. The neodymium ion lasers, based on a variety of host lattices such as yttrium aluminum garnet (YAG) or the newer gadolinium scandium gallium garnet (GSGG), are such uses. In addition a samarium-doped filter glass surrounding such an Nd lasing rod can absorb unwanted UV and IR radiation while reinforcing the wavelengths corresponding to the Nd pumping bands.

Sometimes the transducer requirement is the non-modification of the incoming radiation, *i.e.* transparency. Hence the development of infra-red transparent materials such as yttrium oxide, doped with lanthanum oxide, or ternary sulfides of the calcium lanthanum sulfide family. The reverse phenomenon, the blocking of undesired radiation, is performed by cerium-doped glasses that block the UV in a variety of uses.

The idea of a modulating transducer, introduced earlier also applies here. Transducer output can be controlled by external energy such as a magnetic field or an electrical impulse; several examples are given in Table III. Devices based on lead lanthanum zirconate titanate (PLZT) using polarized light can be switched from transparent to opaque in microseconds. Aircraft windows, welding goggles can protect the observer from sudden flashes of intense light. The same

TABLE I. Lanthanides in Luminescence Transducers (???, visible radiation)

Input energy	Material	Application	Reference
Gamma, neutron	Ce-doped glass	particle detection	3
X-ray	Tb; Gd_2O_2S, etc.	screen phosphors	4
UV	several	fluorescent lamps	5
IR	Yb, Er; LnF_3	laser monitoring	6
Electron	Eu: Y_2O_2S, etc.	CRT-TV red, etc.	7
Electrical	Ce, Sm, Tb; etc.	flat-panel displays	8
Mechanical	Eu salts	???	9

TABLE II. Lanthanides in Luminescence Transducers (???, visible radiation, ???)

Input energy	Auxiliary	Material	Application	Reference
Gamma, etc.	thermal	Tm, Dy; $CaSO_4$	dosimetry	10
Visible	thermal	Eu; etc.	temperature measurement	11
X-ray	visible	Eu; BaFCl	computer X-ray	12

TABLE III. Lanthanides in Radiation Uses Transducers (radiation, radiation, ???)

Input/Output	Auxiliary	Material	Application	Reference
Visible	electrical	PLZT	displays, protection	13
Infra-red	magnetic	Ce, Tb, glass	Faraday rotators	14
Visible	magnetic	Ln/GIG	displays, printers	15
Micro, radio	magnetic	YIG/GIG	communications	16

TABLE IV. Lanthanides in Magnetic Devices as Transducers

Magneto-technology	Notation	Material	Application	Reference
Optic	(radiation, magnetic)	Gd/Tb/Fe	data recording	17
Optic	(magnetic, magnetic)	Ln/GGG	bubble memory	18
Strictive	(magnetic, mechanical)	Terfenol	sonar	19
Caloric	(magnetic, thermal)	Gd alloys	refrigeration	20

material can form the basis for display devices that operate over a wide temperature range.

Protection of a different kind is provided by cerium or terbium containing fluorophosphate glasses used in laser-based fusion research. The lasers must be protected from back-reflected light and this optical isolation is obtained using the Faraday effect. A glass with a high-loading of ions with magnetic moments provides this necessary Faraday rotation in an applied magnetic field. This Faraday effect can be used for magnetic field sensing using a long suitably-doped fiber and detecting the polarization light rotation.

Modulating transducers are used in optical information processing. Faster, and smarter, devices are needed to control displays, printers and communications equipment. Thin garnet films, with individual pixels that can be addressed independently and be switched from transparent to opaque, can form the basis of such technology. Light switching arrays (LISA) have been demonstrated with bismuth-substituted GIGs, that is gadolinium iron garnets.

Electronics

The region of the transducer matrix for electrical properties covers many devices, some of which contain lanthanides. For example, the ubiquitous capacitor has been miniaturized and new dielectric compositions formulated to meet stringent performance specifications. One desired property is that the value of the capacitance does not change with temperature. Such NPO (negative–positive–zero) materials are often based on neodymium/barium titanate compositions. In order to fine-tune behavior several of the other lanthanide oxides are also incorporated into similar dielectric compositions. The multi-layer ceramic capacitor is now a significant market for lanthanide oxides, or oxide precursors such as carbonates.

Magnetic properties are important in the function of some electronic devices. The use of YIG, yttrium iron garnets, in microwave equipment is an example. An applied external magnetic field to a disc of this material enables input to be selectively passed, say energy of one particular frequency, to the output. Recent technology in this area is relying on thin film materials based on YIG within which magnetic waves can pass.

In applications related to magnetic properties the lanthanides are well represented. Table IV summarizes in the transducer notation some of these technologies. The non-volatile bubble memories used for data storage are based on the formation of magnetic domains in thin films grown on a gadolinium gallium garnet crystal substrate. The art of molecular engineering is carried to a fine art in creating the precise film compositions for optimum performance.

Another technique under development for data storage is relying on the magnetic behavior of thin magnetizable Ln-alloy films. Here the fact that gadolinium has a Curie point near room temperature and can be driven above this value by local heating is essential.

The conversion of magnetic energy to mechanical is possible with magnetostrictive alloys of which Terfenol is the prime example. This Tb/Dy/Fe material forms the heart of new sonar transducers which have a much greater sound–power output than previously possible, 25 times greater than ceramic transducers. Magnetostrictive alloys will also have potential value in vibration control, for 'infinitely soft' structures that damp any vibration or 'infinitely hard' structures that are perfectly rigid e.g. for exact positioning of tools.

The three dimensional transducer matrix is of course symmetrical, input and output could be interchanged. This principle is illustrated by the technique of magnetic refrigeration. The interchange from (thermal, magnetic) to (magnetic, thermal) can be used to power a refrigeration device. The operating temperature range determines the choice of working material, Gd metal is suitable around ambient.

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