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SUPPLEMENTARY VOLUME 5

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ENCYCLOPAEDIC DICTIONARY OF PHYSICS

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AND RELATED SUBJECTS

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ARTICLES CONTAINED IN THIS VOLUME

Acoustics in the fishing industry	R. E. CRAIG
Advances in oxide materials.	B. COCKAYNE
Applications of reverse osmosis and ultrafiltration	J. R. GROVER
Archaeological dating by physical methods	M. J. AITKEN
Barium clouds for experiments in space	E. RIEGER
Beam-foil spectroscopy	I. MARTINSON
Biochemical fuel cells	R. F. ACKER
Black holes in space	H. I. ELLINGTON
Blocking patterns from crystals	R. S. NELSON
Calculation of thermodynamic properties from spectroscopic data	J. C. LOCKHART
Carbon fibre	W. G. HARLAND
Charge-transfer complexes	R. FOSTER
Circular dichroism	S. F. MASON
Colour transparencies, copying of	R. G. W. HUNT
Counting technology, recent advances in	H. W. WILSON
Critical point	D. AMBROSE
Crystal structure determination, direct methods of.	J. KARLE
Detection and identification of individual atoms and ions in mass spectrometry	G. D. W. SMITH
Digital learning computers	I. ALEKSANDER
Electret transducers	C. W. REEDYK
Electric motors using transverse flux	E. R. LAITHWAITE
Electrogravimetric analysis	J. V. WESTWOOD
Electromagnetic gun	E. R. LAITHWAITE
Enthalpimetry	H. J. V. TYRELL
Ferroelectrics—recent applications of	A. M. GLAZER
Fibre reinforcement of cement and concrete.	R. W. NURSE
Field-ion microscopy and the atom-probe FIM	E. W. MÜLLER
Four-colour problem	J. H. THEWLIS
Fractional horsepower motors	E. R. LAITHWAITE
Geometrostatics	D. BRILL
Helium, negative ion of	I. G. MAIN
Helium dilution refrigeration	D. S. BETTS
High-energy heavy ions	R. H. THOMAS
Holography, engineering applications of	E. ARCHBOLD
Infrared galaxies	N. C. WICKRAMASINGHE
Insulation of electric power cables	B. M. WEEDY
Ion implantation	G. CARTER and W. A. GRANT

Lasers in biology and medicine	D. SMART
Location and reduction of noise	B. J. FIELDING
Mach effect (visual)	W. T. WELFORD
Magnetism, medical applications of	E. H. FREI
Medical ultrasonics	P. N. T. WELLS
Mesonic atoms	Y. N. KIM
Meteorological observations from satellites	R. S. HARWOOD
Microwave phonons	K. W. H. STEVENS
Mirror electron microscope	M. E. BARNETT
Modular electronic equipment	H. BISBY
Modulation spectroscopy	D. E. ASPNES and J. E. FISCHER
Monsoon meteorology	C. S. RAMAGE
Myoelectric control	A. K. GODDEN
Neutron radiography—the present position	H. BERGER
Neutron stars	H. I. ELLINGTON
Neutrons, chemical binding of	H. BRIDGE
Nondestructive testing, automation of	R. S. SHARPE
Optical communication systems	J. E. MIDWINTER
Optical data processing	A. C. MOORE
Optical processing of radar and sonar signals	I. FIRTH
Palaeogeophysics	J. C. BRIDEN
Pattern recognition	A. M. ANDREW
Planets, magnetic fields of	I. WILKINSON
Pollution of the air	W. S. MOORE
Power sources, isotopic	A. W. PENN
Pulsars	F. G. SMITH
Quasars	R. W. HUNSTEAD
Radiation and entry of space vehicles into planetary atmospheres	D. B. OLFE
Radiation and shielding in space	J. W. HAFFNER
Radiation dosimeter, colour	W. L. McLAUGHLIN
Radiation, non-ionizing, hazards of	R. OLIVER
Recent advances in radio and x-ray astronomy	S. MITTON
Reflection spectroscopy	J. CHAMBERLAIN
Regenerative flywheels	S. J. PEERLESS
Regge model of elementary particles	E. J. SQUIRES
Resonance in the orbits of the earth and an asteroid	L. DANIELSSON
Signal detection, statistical theory of	A. D. WHALEN
Spectroscopy, biological applications of	K. R. NAQVI
Spectroscopy, photoelectron	W. C. PRICE
Speech spectrometry	R. E. BOGNER
Superconducting machines	A. D. APPLETON and B. E. MULHALL
Superconductivity, applications of	M. W. WILSON
Super-heavy elements beyond the known periodic table	P. R. FIELDS and J. K. UNIK
Sweep circuits	J. D. WEAVER
Tachyons	T. P. SWETMAN
Technological forecasting	I. C. HENDRY
Thermal desorption spectroscopy	J. YARWOOD
Thermoluminescent dating	M. J. AITKEN
Thermonuclear power—the present position	I. COOK

Thick film technology	R. G. LOASBY
Time, atomic.	B. W. PETLEY
Ultrasonics in medical diagnosis	W. N. McDICKEN
Void formation in fast-reactor materials	R. S. NELSON
Wankel engine	J. A. BARNES and N. WATSON
X-ray interferometry	M. HART

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ACOUSTICS IN THE FISHING INDUSTRY. Since the possibilities were first recognized in the early 1930s, the applications of acoustics in fisheries have developed steadily, and appear to be extending with each year that passes. Among the aspects of current or potential importance may be listed:

- sonar, including echo-sounding;
- passive listening, to locate or identify fish;
- Telemetry, to convey information from gear to ships;
- Silencing of ships and gear to improve catching efficiency;
- Artificial sound sources to attract fish, or drive them in a desired direction.

Since only the first of these is a well-established technique, with a considerable literature and commercial importance, it will be dealt with last, allowing only a few remarks to the other items. It is first necessary to introduce a few definitions and general principles.

Definitions and Principles

The *intensity* I of sound in the sea depends on the square of the sound pressure. The standard unit of intensity is that of a sound field with an r.m.s. pressure of 1 pascal.† (This corresponds to $6.5 \times 10^{-7} \text{ W m}^{-2}$.) Observed sound intensities are described as plus or minus so many decibels with respect to one pascal.

Standard *source level* is such that it gives rise to a sound intensity of 1 pascal r.m.s. at a distance of 1 m, in the direction of greatest intensity. Thus we can describe a source level S in decibels with respect to a standard source. In dealing with sonar we may be effectively radiating energy at a single frequency, and no ambiguity arises. When dealing with a natural source, it will be necessary to specify the frequency range under consideration when describing the source level. In a large homogeneous body of water, the energy spreads uniformly so the intensity at a range R from a source level S would be, in the absence of losses,

$$I = S - 20 \log R \text{ (logarithms to the base 10).}$$

† 1 pascal = 1 newton per square metre.

There is, however, some attenuation due to the conversion of sound energy to heat within the medium. Let this be A decibels per metre, then the more adequate expression becomes

$$I = S - 20 \log R - AR.†$$

This is the most used expression, but it may be in error for signal sin the horizontal direction; (a) where the depth is small compared with the range, so that spreading is limited by the boundaries. In such cases empirical formulae are required, taking account of the nature of the substrate; (b) when refraction is significant, causing the sound to be channelled, and so giving excess energy in some directions, and a deficiency in others. The value of A is frequency dependent (Fig. 1) and the magnitude of the attenuation term is the main factor controlling the usable range of high-frequency equipments.

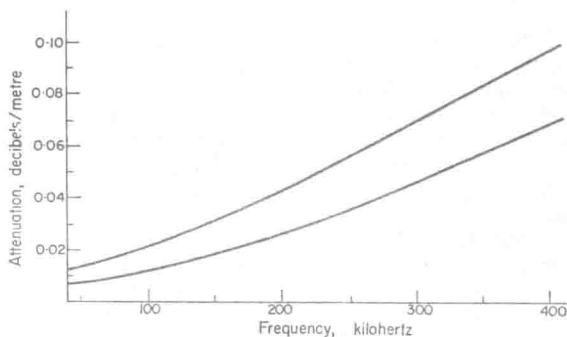


Fig. 1. Attenuation of acoustic energy in sea water. Authorities vary somewhat, and values probably lie between the limits shown.

The velocity of sound in the sea is dependent on the temperature, salinity and hydrostatic pressure (Fig. 2). For a wide range of purposes, however,

† For directness of presentation it is best to adhere to the decibel notation consistently. The reader should note that the above relationship would in arithmetic units merely express an inverse square law of intensity, modified by an exponential term representing the energy conversion losses.

the round figure of 1500 m/sec may be used with confidence. When very accurate soundings are required, some correction is needed, but the most important effect of the small changes that occur is to cause refraction, which is of great importance in echo-ranging over distances in excess of about a kilometre.

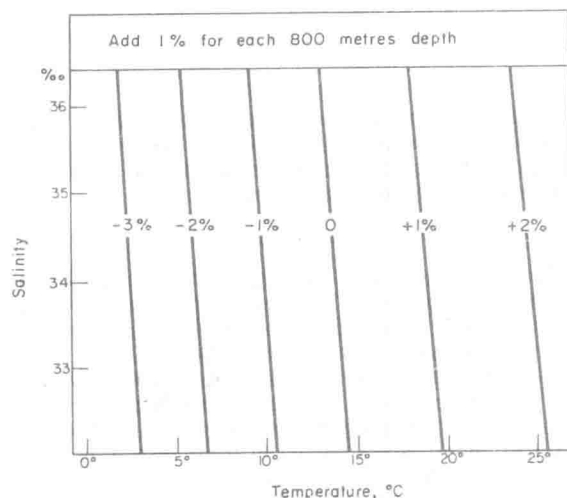


Fig. 2. Velocity of sound in sea water. The figure shows the variation with temperature, salinity, and depth, from the notional value of 1500 m/sec.

The final term to be defined is *Target Level* which again is conveniently expressed in decibels relative to a standard. The incidence of acoustic energy on a target causes the target to act as a secondary source. If the incidence of standard intensity causes the target to act as a standard source, then that target is said to be of standard level, or a "0 db" target.

If the range of the target from the equipment be R , the target strength T , and the intensity incident upon the target I_T , then the intensity of the echo signal at the receiver will be, as discussed,

$$I_R = I_T + T - 20 \log R - AR,$$

we have already noted, however, that

$$I_T = S - 20 \log R - AR$$

and combining these pieces of information we see that

$$I_R = S - 40 \log R - 2AR + T$$

and this equation is in fact the clearest definition of target strength. In ordinary usage the term is applied to small objects, such as might exist wholly within the beamwidth of the search equipment. Where an extended target exists, larger than the equipment beamwidth, a larger and larger section of

the target becomes involved in reflection as the range increase. A useful example is that of a perfectly reflecting plane mirror placed at a range R so as to reflect energy directly back to the equipment. So far as the receiver is concerned, it looks at an image of the transmitter sited at a distance of $2R$. Thus the received intensity is

$$\begin{aligned} I_R &= S - 20 \log 2R - 2AR \\ &= S - 20 \log R - 20 \log 2 - 2AR \\ &= S - 40 \log R - 2AR + (20 \log R - 6). \end{aligned}$$

We recognize the term in brackets as corresponding to the target strength of a small object, and may conclude that the target strength of an extensive plane mirror is represented by $(20 \log R - 6)$ decibels. This expression is useful in the calibration of equipment since a water surface regarded from below is close to being a plane mirror for acoustic energy.

Passive Listening

While for experimental purposes it is perfectly feasible to listen to sounds made by fish in aquaria or in selected situations in nature, and although a considerable body of information exists, no practical application has yet proved possible in advanced fisheries. This is because the source level of most individual fish is of the order of 10 decibels only, and typical background intensities of sound at the low frequencies concerned are about -30 decibels, in the range 200 Hz to 1 kHz, depending of course on sea state and other conditions. Thus the fish noise is lost in the background at a range of about 100 m. In practice the presence of machinery and propeller noise from ships worsens the situation considerably. Future development may exploit listening hydrophones, linked by radio with the skipper or with some central control station, and there are possibilities of exploiting directional hydrophones, listening on selected frequency bands.

Telemetry

Acoustic links to convey information from the net to the ship have found application in research, and are beginning to be accepted commercially. While an acoustic link is in general inferior in reliability to a cable link, the greater convenience of the former tends to make it more acceptable. Multi-channel F.M. systems have been most generally used, the information being modulated to a depth of a few kHz on a carrier of around 50 kHz. Pulse-code systems have also been developed, which are likely to predominate in the future.

A special aspect of telemetry is the use of an F.M. link on one frequency to relay information from a self-contained echo-sounder on the net to a recorder onboard ship.

Silencing of Ships and Gear

Practical experience has shown that ship noises, in particular propeller noise, can be a factor influencing the capture of herring and similar fish by purse seine. Since the low-frequency hearing of fish is acute (being usually limited by the level of background noise), this is not very surprising. Research continues on the identification of the most significant components of ship noise, and on means of reducing these to a minimum.

Use of Artificial Sound Sources

Only the most tentative experiments have so far been carried out on this potentially important subject, and there is good reason to expect progress in the very near future.

Sonar

Sound Navigation and Ranging is a subject on which extensive research and development has been carried out for both civil and military purposes. Echo-sounders for navigation presented fishermen with one type of ready-made tool which found application in finding fish and assessing the nature of the seabed. Similarly, equipment already highly developed for finding submarines was found to be a powerful means of seeking out shoals of pelagic fish, and has made possible the development of new methods of fishing. From these bases of established hardware, interested firms and fishery researchers have sought to develop equipment for the needs of fishermen, and suited to the type of vessels in use by them. The target levels of important fish range from about -20 decibels for a large cod to about -40 decibels for an adult herring. The smallest fish of commercial interest have target levels of perhaps -50 decibels. To detect even herring as individuals in depths of say 200 m, requires more sensitive equipment than is needed for most navigational purposes. The target strength of the sea-bed is about -10 decibels per square metre, and so for a typical beamshape the sea-bed at 200 m has a target level of about +20 decibels. (It has been assumed that effectively 1000 square metres fall within the acoustic beam.) Thus the overall sensitivity needed to detect a single herring at this depth is some 60 decibels greater (a voltage amplification 1000 times greater) than is required simply to detect the seabed. Detection of fish by the earlier low-powered sounders depended on the presence of large shoals of fish, for example 100,000 herring in a mass, which might give an effective target level of -10 decibels or thereabouts. This is only a rough estimate, as the level of such a target depends on the pulse length and beamwidth of the equipment in use.

A typical fishing echo-sounder or sonar in 1974 would consist of a pulse transmitter, giving a 1-msec

pulse with a source level around 110 decibels, and having a beamwidth of the order of 15° measured between the half-power points. (Beamshape is controlled by the size of the transducer face relative to the acoustic wavelength, in the identical way as an optical beam depends on the size of the pinhole or slit forming it.) The carrier frequency would probably be 30 or 50 kHz and the transducers constructed either from nickel laminations (magnetostrictive) or from ceramics (piezo-electric or electrostrictive). The receive transducer would be similar, or commonly would be the same transducer. A target of -40 decibels at 200-m range would give an echo-intensity at the receiver of

$$\begin{aligned} I_R &= S - 40 \log R - 2AR + T \\ &= 110 - 92 - 6 - 40 \\ &= -28 \text{ decibels.} \end{aligned}$$

This signal would give an input of 1 to 2×10^{-11} W to the receiving amplifier input, depending on the efficiency and size of the transducer and the adequacy of matching between the transducer and the input circuits. Thus to give an output of 1 W to the display, a gain of about 110 decibels is required in the receiving amplifier. The same target at a range of only 100 m would give an echo signal higher by 15° decibels, and the gain required to present this to the display as a 1-W signal would be only 95 decibels.

Since it is obviously desirable that the signal at the display should depend on the target level of the fish, and not be influenced by the range, it should be arranged that the gain of the receiving amplifier is low at the instant of transmission, and rises uniformly at a rate which will keep the amplified echo from a given target at the same level regardless of range. Clearly the appropriate law is

$$G = \text{constant} + 40 \log R + 2AR.$$

The value of the constant will depend on the target level which it is required to detect. Two remarks may be made here:

- The time-varied gain must necessarily be limited at a point where noise or volume reverberation become excessive. Beyond this range it is necessary to keep the gain constant, and small targets will not be detected.
- Where fish are present in large numbers, so that one's concern is with measurement of volume reverberation, or if it is for some reason desired to keep the *seabed* echo approximately constant irrespective of range, the appropriate T.V.G. law becomes

$$G = \text{constant} + 20 \log R + 2AR.$$

Sonar Equipments

The principles described above apply to echo-sounding, and with the qualifications made, to all

echo methods. The normal side-search or "search-light sonar" is simply an echo-sounder mounted so as to be trainable in any direction, and usually so that the beam can be tilted downward as required. These functions are controlled from a console in the bridge, and automatic search programmes are frequently incorporated. The skilled operator makes use of an audio presentation of the echoes, as well as of some form of paper recorder. The audio presentation is valuable in using a sense not distracted by other duties, and is helpful in interpretation carrying as it does a certain amount of Doppler information. The direction of the target is found by noting the direction of the sound beam for best signal strength. In a simple searchlight sonar, this is of course the direction from which the signal is *in phase* at all points on the transducer face. This is the only way in which phase relationships are exploited by the simple system. However, by dividing the transducer into sections it is possible to sample the phase of the incoming signal at various points. By suitable processing of the signals it is possible to determine, along with the range, the *direction* of each target relative to the transducer. Equipments using signal processing of this kind are already in use for specialized purposes and, with the advent of integrated circuits, signal processing is made cheaper and more reliable so it is likely that fishing equipments will shortly be available, based on these principles, and giving much enhanced performance.

R. E. CRAIG

ADVANCES IN OXIDE MATERIALS

1. Introduction

Traditionally, oxides have been recognized mainly as refractories, ceramics, glass-forming materials and phosphors. Oxides are also widely distributed in Nature and form the basis of many ores for metal extraction; in somewhat rarer natural deposits, oxides occur as single crystals which find application as gemstones.

During the past decade, important developments in solid state physics, such as the discovery of the crystalline laser, have opened entirely new fields for the use of oxides, particularly in optics and electronics.

Synthetic single crystals possessing a high degree of structural and chemical homogeneity have been required for these new fields of interest, hence, the development of techniques for producing single crystals with properties which can meet stringent device requirements has been one of the most important aspects of the progress made in using oxides and is reviewed in Section 2.

The provision of single-crystal materials and the knowledge gained by measuring the relevant properties has stimulated the demand for improved

materials so, during the past decade, a vast number of existing and previously unknown chemical compounds has been investigated. For a full list of compounds, the reader is referred to the bibliography, but in Section 3 the more important materials are discussed in terms of the properties which make them useful for particular device applications.

Substantial developments in the traditional uses of oxides have also taken place during the past 10 years and these are reviewed in Section 4. Traditional uses often tend to be ignored amongst the excitement of innovating new physical devices and effects but it is as well to realize that, in terms of tonnage and profitability, their importance frequently outweighs that of the newer developments in oxide materials.

The basic feature common to all oxides is that they are compounds of oxygen containing one or more metallic elements. Most oxides possess a substantial degree of ionic bonding and therefore can exhibit properties characteristic of ionic crystals such as optical transparency, high electrical resistivity and low thermal conductivity. They are also refractory, chemically inert, hard, and fracture in a brittle manner. These properties have always formed the framework within which oxide materials can be used. At first sight this framework appears restrictive but, during the past decade, new ways of exploiting the various combinations of these properties have been discovered, thereby accounting for the advances in oxide materials described herein.

Inevitably, exceptions exist to this general framework of properties and these have also promoted the use of oxides. For instance, beryllia (BeO) is a good thermal conductor making it an attractive substrate material whilst β -alumina ($\text{NaAl}_{11}\text{O}_{17}$) is a useful ionic conductor.

2. Single-crystal Growth

The single-crystal growth of oxides has been carried out commercially for many years. The best known examples are ruby and other alumina-based crystals, grown by the Verneuil flame fusion process (Verneuil, 1902; Bauer and Field, 1963) for either watch bearings or synthetic gemstones, and quartz, produced by the hydrothermal technique (Ballman and Laudise, 1963) for piezoelectric applications. On a research scale, a wide range of oxide materials has been produced by crystallization from solution at high temperatures (Laudise, 1963), a technique often referred to as flux growth.

2.1. Czochralski developments

The most significant of the recent developments in oxide single-crystal growth has been the adaptation of the Czochralski technique (Nassau and Broyer, 1962; Cockayne *et al.*, 1967), which crystallizes materials directly from the melt, to the high

temperatures at which oxide materials fuse. The principal features of the process are that a seed crystal is dipped into a crucible containing the melt and then slowly withdrawn. Melt solidifies on to the seed during the withdrawal process and the seed is grown into a crystal of the requisite shape by changing the heat input into the melt in order to control the crystal diameter.

The Czochralski technique has proved capable of producing oxide crystals of a larger size and with a higher degree of chemical and structural uniformity than other processes can provide. There are many reasons for this success. Firstly, the inherent characteristics of the technique which allow the crystal to be extracted conveniently from both crucible and melt and the relatively large thermal masses involved which confer stability upon the growth process. Secondly, the development of suitably shaped crucible and refractory materials which are chemically and mechanically compatible with molten oxides and the inert or slightly oxidizing growth atmosphere; crucibles are usually manufactured from the precious metals platinum (maximum operational temperature 1550°C; m.p. 1773°C) and iridium (maximum operational temperature 2200°C; m.p. 2443°C) whilst alumina, magnesia and zirconia are the commonly used refractories (Cockayne, 1968). Thirdly, the scientific understanding which has been obtained about the nature and formation of crystal defects and thereby has allowed development of methods for controlling defect formation (Cockayne, 1968); the recognition that phenomena occurring in the melt (e.g. convection), at the solid/liquid interface (e.g. segregation of gases and impurities) and in the crystal subsequent to growth (e.g. dislocation generation and propagation, solid state precipitation) are all important, has contributed substantially to the improvements made in the chemically and structurally sensitive properties of oxide single crystals.

The extensive application of Czochralski growth is illustrated by the materials and melting points encompassed, ranging from lead molybdate (Pb_2MoO_5 ; m.p. 950°C) to magnesium aluminate spinel (MgAl_2O_4 ; m.p. 2150°C) and including important device materials such as lithium niobate (LiNbO_3 ; m.p. 1260°C), yttrium aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$; m.p. 1970°C) and sapphire (Al_2O_3 ; m.p. 2050°C).

A very recent ingenious development of the Czochralski technique has been the production of continuous lengths of sapphire filament and a variety of other cross-sectional shapes by making use of a shaped die (Chalmers *et al.*, 1971). The liquid pool, from which the crystal is withdrawn, is formed on the top surface of the die and is fed by capillaries in the die which lead down into the bulk melt. Shaping of the crystal is achieved by controlling the geometry of the top surface of the die and maintaining the correct contact angle between the liquid and the die material.

2.2. Crucible-less techniques

The main restrictions on the Czochralski technique at the current stage of development are the limited number and the expense of compatible crucible materials, particularly for materials which melt at temperatures above 2200°C. Hence, some attention has been paid to crucible-less techniques. Direct radio-frequency heating (Montfort *et al.*, 1961), direct arc heating (Abraham *et al.*, 1971) electronbeam heating (Class, 1968) and indirect optical heating (Field and Wagner, 1968, Gasson and Cockayne, 1970) of oxide materials have been attempted.

Direct coupling suffers from the disadvantage of having to preheat the oxide by ancillary means until it becomes sufficiently conducting to couple into the radio-frequency field whilst the radiation flux available for current optical heating, using either arc lamps or CO_2 - N_2 -He gas lasers, restricts the volume of material which can be melted at any one time. Direct-arc heating is normally used to fuse a large mass of material which is slowly cooled to yield large polycrystals.

In principle, heating methods of these types can be applied to Czochralski growth but, in practice, development has been slow, partly because of the difficult high-temperature technology and partly because of the absence of an important device material amongst the higher melting-point compounds. Even so, the floating-zone recrystallization technique of crystal growth, used in conjunction with optical heating, has been developed to produce small single crystals of yttria (Y_2O_3 ; m.p. 2450°C) and other rare-earth oxides whilst direct arc heating has yielded crystals of calcia (CaO ; m.p. 2580°C) zirconia (ZrO_2 ; m.p. 2700°C) and magnesia (MgO ; m.p. 2800°C).

Much more development is needed before these technologies can compete commercially with the current Czochralski technique. The relative stages of development are well illustrated by ruby crystal growth where Czochralski growth from iridium crucibles can yield 60 cm long \times 6.5 cm diameter crystals compared to 5 cm long \times 0.5 cm diameter for material produced by floating-zone recrystallization.

2.3. Epitaxial techniques

A requirement for thin single-crystal films of oxide materials based on the magnetic garnets (Bobeck *et al.*, 1969) has recently stimulated the development of epitaxial growth processes for oxides. These processes can be divided into three basic groups, namely, liquid phase epitaxy (LPE), hydrothermal epitaxy (HE) and chemical vapour deposition (CVD). Growth is produced in LPE and HE by crystallization on to a substrate from a super-

saturated solution and in CVD by similar crystallization from a supersaturated vapour (Laudise, 1972). These processes require a chemically and structurally homogeneous substrate of similar general structure to the material forming the epitaxial layer. Substrates are normally prepared as thin slices from Czochralski-grown materials, an important requirement being the production of a damage-free surface in order to inhibit defect generation at the substrate/thin-film interface and prevent consequent impairment of the thin film properties.

3. Single-crystal Applications

3.1. Crystalline lasers

The expansion of interest in single crystal oxides has been stimulated mainly by the discovery of the solid state laser. Pulsed laser action in the solid state was first observed in ruby, $\text{Al}_2\text{O}_3/\text{Cr}^{3+}$ (Maiman, 1960), and the first continuously emitting room temperature laser was the mixed oxide calcium tungstate, $\text{CaWO}_4/\text{Nd}^{3+}$ (Johnson *et al.*, 1962). Currently, another mixed oxide, yttrium aluminium garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}/\text{Nd}^{3+}$, is the established material for a wide range of laser devices (Geusic *et al.*, 1964).

The key properties of oxides exploited in laser use are optical transparency, hardness, mechanical stability and chemical inertness.

In order to stimulate laser action efficiently it is essential for the host lattice (e.g. Al_2O_3) to be completely transparent at both the absorption and emission wavelengths of the lasing ion (e.g. Cr^{3+}); the wavelength range 0.5–3.0 μm meets the demands of most laser ions and corresponds with the maximum transmissivity of most oxides. Other optical requirements are freedom from scattering particles, absorption centres and changes in refractive index which inhibit laser action; these properties are most readily obtained in Czochralski grown single crystals of the hard stable lattices provided by the strongly-bonded high melting point oxides (Cockayne, 1972).

A laser medium is normally used in the form of a cylindrical rod, typically 0.5 cm diameter \times 7.5 cm long and with accurately polished plane and parallel ends, which has to be machined from a single crystal. Thus, mechanical stability and hardness are important properties during the respective shaping and polishing processes. Good mechanical properties are also required during the broad band optical pumping process used to stimulate laser action, when stresses develop due to the non-uniform absorption of heat energy within the rod; freedom from cleavage for fracture planes is a particularly important characteristic, exhibited by both $\text{Y}_3\text{Al}_5\text{O}_{12}$ and Al_2O_3 .

Chemical stability is a property pertinent to the processes used to deposit reflecting ends on the laser

rod and to the liquid coolants circulated within a laser cavity to assist the removal of excess heat.

Within this key framework of properties, a search for materials with optimized laser properties has occurred. Solid solubilities for the lasing ion >1 at % are preferred in order to provide reasonable gain. Crystal lattice sites consistent with broad absorption bands, a high quantum efficiency and a narrow output linewidth are also desirable in continuous wave operation; these conditions can be relaxed to a certain extent in pulsed operation where energy storage capability is more important. Crystal structure characteristics related to crystal growth, such as an absence of phase transformation, are of paramount importance.

Inevitably, no material has all the requisite properties and a compromise has to be effected. The materials in current use, namely $\text{Al}_2\text{O}_3/\text{Cr}^{3+}$, $\text{Y}_3\text{Al}_5\text{O}_{12}/\text{Nd}^{3+}$ and some Nd^{3+} doped glass oxides, are the most effective compromises so far obtained in relation to device use.

The predominant use of oxide lasers has been distance measurement but other applications include specialized welding, drilling, material shaping, material removal, plasma research and eye therapy.

3.2. Non-linear optics

The basic properties demanded from non-linear optical materials are very similar to those for laser materials. Thus, single crystals of good optical quality which are hard and stable are required. This is not surprising because readily detectable non-linear-effects are only induced at optical frequencies by laser radiation. Non-linear optical effects can be used in two main ways, either to generate harmonics of the fundamental laser radiation impinging upon a crystal (e.g. second harmonic generation, SHG) or to produce a change of refractive index within the crystal by the application of an electric field (the electro-optic effect). Thus, non-linear optical crystals can be used either to switch or change the frequency of a laser beam (Hulme, 1972).

In applications of this type, the subsidiary properties required strictly limit the number of available materials. Acentricity of the crystal structure is obligatory for SHG and preferred for electro-optic switching materials. In both applications, the ability to withstand high optical power densities without surface or bulk damage is essential and for SHG, adequate birefringence for phase-matching is an additional criterion. Consequently, only two oxides have proved of significant use, lithium niobate LiNbO_3 for SHG and electro-optic Q-switches (Boyd *et al.*, 1964), and barium sodium niobate, $\text{Ba}_2\text{NaNb}_2\text{O}_{15}$, also for SHG (Geusic *et al.*, 1968); SHG has been applied mainly to the generation of 0.53 μm green light from 1.06 μm Nd-based lasers. Both these materials are used in relatively small sections, typically 1 cm cubes, accurately orientated

and polished and cut from Czochralski grown crystals.

Chemical inertness is even more important here than in laser use, compatibility with electrodes being necessary in the Q-switches and stability at the phase matching temperatures (80–200°C) being essential for SHG.

3.3. Acousto-optics

Acousto-optic interactions within solid state materials also offer ways of controlling laser beams for a diversity of applications which include optical stores and laser Q-switches (Hobden, 1972). Stable, durable, optically perfect materials are again demanded. Devices based on acousto-optic interactions use an acoustic strain wave generated within the material to diffract light beams passing through it. Hence, properties which govern the diffracting efficiency and acoustic propagation are also important. Chemical compatibility with the transducer material and stability during the bonding of the transducer are essential.

Suitable properties are often expressed as a figure of merit, which can be confusing as the definition of the merit figure varies according to the application. For modulator applications, the merit figure M_2 , is defined as $n^6 p^2 \rho^{1/2} c^{-3/2}$ (n is refractive index, p is the relevant photo-elastic coefficient, ρ is density and c is the relevant elastic modulus). Thus dense materials with a high refractive index are preferred. Low melting point mixed oxides of the lead molybdate type, Pb_2MoO_5 and $PbMoO_4$, meet these two requirements but, even in single-crystal form, the low acoustic and optical absorptions required for efficient use are not consistently obtained. Hence, more optically perfect materials with lower figures of merit, such as SF4 glass, are used in some circumstances.

3.4. Delay lines

Oxides have recently found considerable application in ultrasonic delay lines both as transducers and delay media (Lewis, 1972). Typical transducer materials are barium titanate ($BaTiO_3$) and zinc oxide (ZnO). The delay lines are of two basic types, those employing bulk waves propagated in either shear or longitudinal modes and those employing surface waves.

For bulk media, the most important properties are compatibility of the acoustic impedance with that of the input and output transducers, mechanical hardness for accurate machining and polishing, and low ultrasonic propagation losses. The acoustic wavelength at the frequencies used is similar to the wavelength of light so many of the properties and tolerances demanded are identical to those for lasers. Large Czochralski grown crystals (typically 5–10 cm long \times 0.5–2.0 cm diameter) of sapphire, spinel and yttrium aluminium garnet have all been

used as bulk delay media. Thus far, spinel in shear wave propagation has proved to have the lowest attenuation.

Surface acoustic wave devices consist of an interdigital metal finger array mounted on a piezoelectric medium. The media in current use are single crystals of the oxide materials lithium niobate and quartz, the former being produced by the Czochralski technique and the latter by the hydrothermal process. The properties required for surface wave media are similar to those for bulk media but because the surface devices generally operate at higher frequencies, it is especially important that acoustic losses are low and surface-wave velocities are high. A zero temperature coefficient for the delay time is also an important operational consideration and quartz is the only known material to have this property.

Magnetoelastic delay lines can be produced in ferrimagnetic insulators by using spin waves to produce delay in a manner analogous to the use of sound waves. Only one suitable material is presently known. This is the mixed oxide, yttrium iron garnet ($Y_3Fe_5O_{12}$) which can be produced as single crystals by flux growth techniques.

3.5. Substrates for semiconductors

Single crystal oxides are useful substrate materials for the epitaxial deposition of some single crystal thin films of semiconductor materials (Filby, 1972). In the field of microelectronics, the insulating properties of oxide substrates allow complete electrical isolation of adjacent regions of semiconducting material to be obtained. This eliminates the parasitic capacitance associated with the back-biasing techniques devised to produce electrical isolation when a semiconducting substrate is used and permits the operational speed of the circuit to be increased. The principal oxide substrates for semiconductors are sapphire and magnesium aluminate spinel; both have been used in conjunction with thin films of silicon but spinel has also been employed in the production of gallium arsenide layers. The substrate materials must exhibit other properties in addition to low electrical conductivity. For instance, a reasonable atomic fit at the substrate/film interface is necessary for epitaxy, so similar lattice spacings for the semiconductor and substrate are essential. As the deposition temperature is approximately 1000°C, similar expansion coefficients are also an advantage, if films are to be obtained stress-free at room temperature. Other important features are chemical stability during deposition and the ability to provide a smooth damage-free surface for deposition.

3.6. Magnetic devices

Certain single-crystal magnetic oxides such as the rare-earth orthoferrites ($RFeO_3$) and gallium-doped yttrium iron garnet, often containing additional rare earth substitutions, can be used to support bubble

domains when prepared as thin films (Bobeck *et al.*, 1969). These domains can be manipulated under the influence of a magnetic field and can thus be applied to a number of logic and storage devices. The ability of a material to form magnetic bubbles depends upon the presence of magnetic anisotropy. This is intrinsic in the anisotropic crystal structure of the orthoferrites but is normally strain-induced in the garnets by depositing the magnetic film on to a substrate with a slight lattice mismatch. Currently, the use of garnets is favoured because of the smaller bubble diameters (5–10 μm , cf. 25–100 μm for the orthoferrites) which facilitate higher packing densities. The substrates used must be non-magnetic, have the necessary mismatch and be available as structurally and chemically homogeneous single crystals. Some of the Czochralski-grown rare-earth garnets meet these requirements. Thus far, gadolinium gallium garnet ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$) has been the substrate material used most extensively.

3.7. Pyroelectric detection

A number of oxide single crystals are of current interest for the detection of infra-red radiation using the pyroelectric effect (Putley, 1971). Important property requirements are a high pyroelectric coefficient, and a low relative permittivity and dielectric loss. Strontium barium niobate, $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$, (Glass, 1969), and lead germanate, $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, (Jones *et al.*, 1972), both exhibit useful properties in single crystal and ceramic form. The chemical and thermal stability of these materials combined with reasonable mechanical properties are of practical importance for device manufacture, which can involve high-temperature vacuum treatment, and stability under a range of operational conditions.

3.8. Gemstones

Several of the higher-melting-point oxide single crystals are sufficiently hard, transparent and dispersive to be attractive as gemstones. Ruby has been available as a synthetic gemstone since the early part of this century, but other materials such as strontium titanate (SrTiO_3) and yttrium aluminium garnet have become fashionable more recently, the latter only because of its primary development as a laser material. The use of the garnet structure opens a wide selection of possible colours for synthetic gemstones because of the substitutions which can be made on both the Y^{3+} and Al^{3+} lattice sites by deliberately added impurity ions.

3.9. Composites

Oxides have a number of useful mechanical properties such as high strength and high rigidity in addition to thermal and chemical stability but from an engineering viewpoint, their use is limited by marked brittleness. However, by combining brittle

oxides with more ductile materials in the form of composites, more favourable engineering properties can be realized (Harris, 1972). The most widely investigated oxide single-crystal system used in this manner has been sapphire whiskers embedded in an aluminium matrix.

4. Developments in Traditional Uses

4.1. Polycrystalline oxide materials

The developments are almost limitless and all the basic properties such as hardness, optical transparency, chemical stability, electrical insulation and refractoriness have been exploited in addition to ferroelectric, piezoelectric, pyroelectric and magnetic characteristics.

The traditional method for making ceramics has been to cold form the material as a powder with subsequent high-temperature sintering to yield a high density product. In recent years, this process has been extended to larger sized articles, for instance $35 \times 45 \times 250$ cm alumina blocks are now available. The use of plastic additives in conjunction with extrusion techniques has permitted complex shapes to be produced. Hot-forming and melt-fusion processes have also been developed; the former is a combined pressing and sintering process whilst the latter involves deposition of oxide coatings from molten oxides produced in a flame or plasma torch. Many of these processes are commercially confidential because of the marked relationship between the properties of the final product and the fine detail of the manufacturing method. Hence, properties are more in evidence in the literature than processes. However, the evolution of ceramic technology has undoubtedly continued with better understanding of the relationship between microstructure and properties, particularly with respect to chemical purity, grain size, bonding across grain boundaries and porosity (Matkin, 1972).

It is now realized that translucent or even transparent ceramics can be obtained when the porosity approaches zero and, as a consequence, ceramics with these optical properties based on magnesia, yttria and alumina (lucalox) are now available. Transparent ferroelectric materials, with useful optical switching properties, based on compounds such as lead zirconate-titanate ($\text{PbTiO}_3\text{--PbZrO}_3$) have also been developed (Ainger, 1972). The piezoelectric and pyroelectric properties of this material are also respectively exploited in electromechanical transducer and radiation detector applications.

Polycrystalline ceramics based on alumina and quartz have been used as substrates for some thin- and thick-film semiconductor circuits where the electrical insulation properties are exploited in a manner similar to that described for single crystal substrates (Filby, 1972). Some polycrystalline oxides are electrically conducting due to a high degree of

ionic mobility (e.g. β -alumina) and are beginning to find application as electrolytes in batteries and fuel cells (Greene, 1972).

Pressed magnetic oxides based on ferrites can be used in permanent magnets in addition to their uses in communication components, as toroids for computer main stores and magnetic recording tape (Marshall, 1972).

The largest application of oxide ceramics is still for refractories in the iron and steel and glass-making industries, where new production processes have stimulated the development of high-performance materials with increased refractories and better mechanical and chemical stability. Purer materials and improved bonding techniques have been developed to meet the demanded properties (Matkin, 1972).

The high-temperature mechanical stability of oxides has been further utilized in the provision of ceramic cutting tools, based on alumina, and in ceramic dies and cones used in the wire drawing of metals. Room temperature uses in items such as textile thread guides and ceramic bearings also make use of the wear-resistant properties of oxides.

The low density of oxides such as alumina, silica and beryllia has been coupled with good mechanical strength in a number of applications such as radomes, missile noses and transparent window armour.

4.2. Amorphous oxide materials

The most important amorphous materials are glasses and those made in greatest quantities, namely soda-lime-silica, pyrex and lead silicate, are all made from oxide components and are used to manufacture most of the commonplace glass articles. These materials have been further developed to produce a whole range of glasses for technical purposes such as the low dielectric loss materials used in the electrical industry and sealing glasses with specific expansion properties for electronic applications (Savage, 1972).

A number of entirely new oxide glasses have also been developed. Some, based on boric oxide, cerous oxide and ferrous oxide, have semiconducting properties and can be used in channel plate multipliers whilst others, based on alkali/alkaline earth silicate compositions and doped with neodymium, have found application in laser systems. Fibre optical applications are a further new use for glasses. Glass fibres are also potentially useful in laser communication systems and for reinforcing composite materials.

Other innovations for oxide glasses include the production of phase-separated materials, photo-sensitive compositions and glass ceramics; the latter exhibit a wide range of properties including low and high expansion characteristics, low dielectric loss and high strength.

Other amorphous oxide materials with novel uses are boric oxide and the oxides of silicon. Boric

oxide is used as a liquid encapsulant in the Czochralski growth of some compound semiconductors, such as gallium arsenide and indium phosphide, in order to restrict loss of the volatile species at the melting point of the compound (Mullin *et al.*, 1964). Extensive use is made of silicon oxides as masks in the fabrication of microelectric devices (Filby, 1972).

4.3. Crystalline oxide powders

The principal uses of oxides in the form of crystalline powders are as phosphors and basic chemicals.

Phosphor technology is very empirical and is not confined to oxides. Both the literature and the number of recipes are vast. Recent developments where oxides have played an important part (Taylor, 1972) have been concerned with improving efficiency, colour and temperature stability. The main applications have remained cathode-ray tubes and lamps. The most significant development involving an oxide is probably the production of the europium-doped yttrium orthovanadate phosphor for emitting red light in colour-television applications.

The role of oxides as basic chemicals is an area which is frequently overlooked. Very few oxides occur in Nature with either a purity or form directly suitable for device application but, until recently, many industrial chemicals were also insufficiently pure to meet the demands of many of the new applications described here. However, as devices based on oxides developed, the dependence of properties upon chemical purity became much more evident. Chemical manufacturers have responded well to this challenge and by employing solvent extraction, ion-exchange, zone-refining and other fractional crystallization procedures, have produced much purer grades of material, in some cases with a 99.9999% specification. As a consequence, a wide range of high purity oxide chemicals are now available for the single crystal and polycrystalline materials used in both new and traditional applications.

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APPLICATIONS OF REVERSE OSMOSIS AND ULTRAFILTRATION. Reverse osmosis and ultrafiltration are membrane separation processes

which can be applied to both aqueous and non-aqueous systems. A specific membrane is normally characterized by the molecular weight and size of the molecules or the percentage of salts which are retained by the membrane. The name reverse osmosis or hyperfiltration is given to the technique when molecular weights up to 1000 are involved, whereas for the separation of larger organic molecules with molecular weights above 1000, the name ultrafiltration is normally used. However, there are many applications which come at this arbitrary boundary. Reverse osmosis membranes are normally characterized by the percentage salt rejection under standard conditions.

From a given feed, these membrane processes produce two streams:

- (1) Normally the larger fraction that permeates the membrane. In aqueous solutions this is substantially purified water, practically free of colloidal, particulate and microbiological species and relatively low in dissolved organic and inorganic species.
- (2) A stream of reduced volume in which are concentrated all the various species retained by the filtration properties of the membrane.

In many applications it is the purified water stream which is of prime importance and the concentrate is a waste stream. Where one is interested in concentration as a means of recovering valuable materials, or to dewater heat sensitive materials, or to reduce waste disposal costs by volume reduction, it is the second stream that is of importance. In some applications, the ability to reclaim relatively pure water is accompanied by the simultaneous concentration of a useful product or waste. In general membrane properties can be chosen to satisfy these widely differing requirements. The main areas of application of reverse osmosis will be considered in turn, with some examples.

(a) Brackish Water Demineralization

Reverse osmosis has been very successfully applied to the demineralization of brackish water containing up to, but not necessarily limited to, 5000 mg/l total dissolved solids (TDS). This is not a fixed upper limit as there are many cases where high water recovery is not essential and the composition of the water is such that acceptable water quality can be obtained. This is generally dependent upon the mono- and divalent ion concentrations and ion inter-relationships. Three examples are given in Tables 1-3 to illustrate typical results for three widely differing feed streams. The applications are generally purified water for industrial, commercial or potable purposes.

Tables 1 and 2 show feed, product and concentrate analyses from tests on water from two boreholes at Appleby Parva, Leicestershire. Table 1 is for a carbonate rich water, whereas Table 2 is for