Thermodynamic and transport properties of electroceramic oxide systems

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Abstract

Ceramic oxides are finding a wide range of application as materials for electronic systems in the modern world. They are used as electrodes and electrolytes in fuel cells and oxygen sensors, and as magnetic and dielectric materials in control devices, to mention only a few examples. Because of their nature, the fabrication of components incorporating ceramic oxides is usually carried out at high temperatures. The transport properties and redox properties of the constituent ions in these materials therefore play a significant role in determining the ease of fabrication as well as the scope of application of devices.

Examples of the limitations placed on the use of these materials as a result of the chemistry of the systems are summarized for a number of current uses. The possibility of using an assembly of contemporary information to develop new and more useful materials is examined in terms of the oxygen and temperature sensitivity of the desired physical properties of electroceramics. It appears that the field is still open to many new developments, largely because of the wide range of cationic mixtures which can be sustained in the structural and stability properties of these materials.

1. Introduction

Modern electronic equipment from computers to microwave ovens makes use of electroceramic materials as sensors, components of electronic circuitry and industrial control systems. The wide variety of ceramic oxides which is being used for these functions draws cation components from most groups of the periodic table, arranged in diverse crystalline structures with oxygen anions. It is the purpose of this discussion to show the scientific bases on which modern materials are designed, and how the processes for producing them are evolving.

Since these materials are intended for long-term service in each particular application, the thermodynamic stability is of major importance. Kinetic factors such as ionic diffusion and electrical current transport by ions, electrons or positive holes are important considerations in the choice of preparative reactions, and in optimizing the long-term stability and the electrical properties which are to be employed.

Table 1 lists typical applications of ceramic oxides in electrical devices, and it can be seen that the complexity of these materials ranges from the simple oxides for use in oxygen sensors, TiO_2 and SnO_2, to the very complex superconductors, e.g. $Tl_2Ca_2Ba_2Cu_3O_x$, which grow more complex in composition every year. In this respect, the ceramicist has followed the lead of the

TABLE 1. Device potential of ceramic oxides

Semiconducting probes and electrodes
   TiO_{2-x}, SnO_{2-x} (In, Sn)$_2O_3$

Electrochemical oxygen probes
   Y_2O_3–CeO_2, CaO–ZrO_2

Magnetic materials
   Fe_3O_4, $(Mn,Zn)Fe_2O_4$, $M_3Fe_2Fe_3O_{12}$ garnets, $BaO \cdot 6Fe_2O_3$, magneto-plumbite

Dielectric and piezoelectric materials
   $BaTiO_3$, $(Pb,La)(Zr,Ti)O_4$, $LiNbO_3$

Electrode, superconducting and catalytic materials
   $(La,Sr)MO_3$ (M $\equiv$ Cr,Mn,Fe,Co,Ni), $Sr_2Fe_2O_5$,
   $(La,Sr,Ba)CuO_4$, $YBa_2Cu_3O_7$, $(Bi,Pb)_2 Ca_2Sr_2CuO_{10}$

metallurgist in exploiting the development of alloys, or solid solutions, to modify and improve particular properties of materials.

In all of these so-called "electroceramics" there are irregularities in the atomic arrangements of the metal ions which are deliberately introduced to produce a particular physical property. These irregularities can take the form of mixing of cationic species on one or more cation sub-lattices, or the introduction of vacancies either singly on the cation or the anion sublattices, or in agglomerated form to create voids. The resultant materials are normally polycrystalline, with small average grain size, containing a small fraction of porosity

at the grain boundaries. The densities of these materials typically achieve better than 95% of theoretical density.

2. Electroceramic compositions and their functions

2.1. Sensors, thermistors and lasers

The simple metal oxides such as TiO_2 and SnO_2 are used as oxygen sensors in the automotive industry [1]. The response to the oxygen partial pressure in the engine exhaust is detected through the dependence of the n-type electrical conductivity of these oxides on oxygen potential. The conductivity is determined by the electron carrier concentration which is inversely related to the oxygen-to-metal ratio in the oxide. This can be calculated from an application of the mass action law to thermodynamic data providing the deficiency is very small, less than 0.1% of the oxygen ion sites being vacant. It is interesting to note that the electrical conductivity and the departure from stoichiometry vary as a function of oxygen potential in very closely the same manner (Fig. 1). It follows that the electrical mobility of the current-carrying species produced as a result of departure from stoichiometry, is independent of the concentration of these species.

Fig. 1. A comparison of the conductivity and non-stoichiometry of TiO_{2-x} as a function of oxygen pressure.

The limit on the use of these materials as oxygen sensors is determined by a significant departure of the conductivity from the simple mass action prediction at low oxygen pressures. In the case of TiO_{2-x} this is known to be due to the almost complete elimination of the oxygen vacancies, created by departure from stoichiometry, by a shear transformation in the solid. The resulting structure consists of islands of normal TiO_2 separated by shear planes of composition approximating to Ti_2O_3, and as the oxygen pressure is further reduced, the spacing between the shear planes, and hence the volume of the normal TiO_2 regions, decreases. This gives rise to the formation of a series of Magneli phases of general formula Ti_nO_{2n-1} with n decreasing as the oxygen potential decreases. The final member of this series is Ti_2O_3.

A surprising fact is that although SnO_{2-x} has been used as an oxygen sensor in a similar way for many applications over a long period of time, the precise relationship between stoichiometry and oxygen pressure has only recently been elucidated [2]. The lower limit of oxygen potential for the use of this material in an oxygen sensor is that at which there is the appearance of metallic tin.

These two oxygen sensors must be coated with noble metal catalysts in order to respond in a sufficiently short time to changes in the oxygen atmosphere for practical application [3]. In further designs aimed at increasing the speed of response, considerable effort has been expended in producing porous sensors with a stable pore structure at operating temperatures, in order to optimize the gas–solid contact.

Thermistors which show a negative temperature coefficient of resistance are usually simple oxide solid solutions which can be designed to give a readily detected change in electrical conductivity for a small change in temperature. They are normally insensitive to oxygen pressure changes in the temperature range 0–200 °C where they are used. (This is because both types of semiconductivity depend on thermally activated conduction by small polaron motion.) Transition metal ions are used in the production of these materials, and both n- and p-type semiconduction has been applied for this purpose. This temperature dependence can be adequately described by the Arrhenius expression

$$\sigma_T = \sigma_0 \exp(-E/RT)$$

The simple solid solutions obey Raoult's law reasonably well and can thus be described by assuming that the random mixing of cations leads to an ideal entropy contribution to the stability.

The practical advantage of using oxides as thermistors is that a relatively low conductivity, dependent on the current carrier concentration, can be blended with a high activation energy E, for polaron migration, to
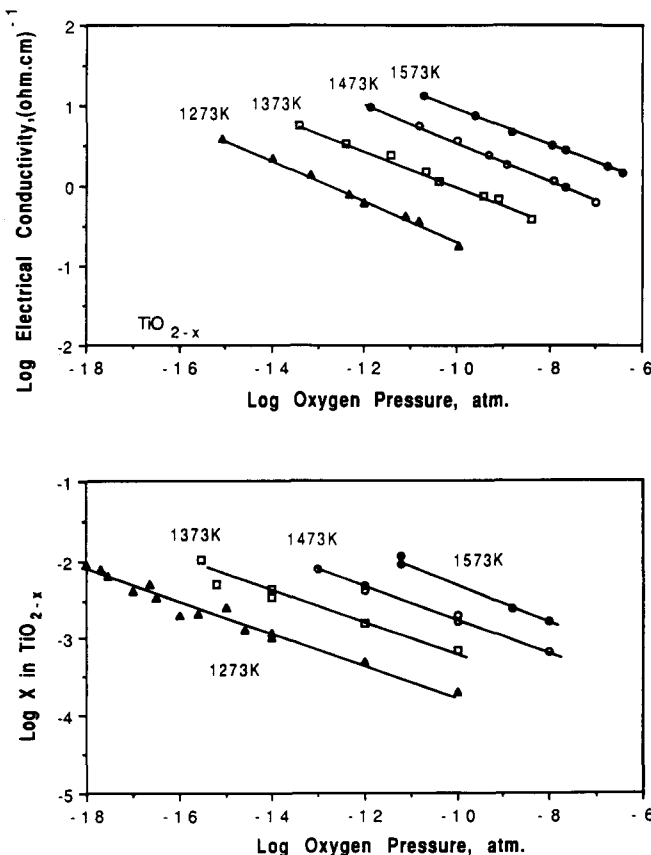
produce a sensitive temperature measuring device. Several commercial materials are based on the spinel Mn_3O_4 in which some substitution is made of nickel, cobalt or copper ions to provide the optimum values of these two parameters. Because of the sensitivity of the valency of these transition metal ionic species to the oxygen potential of the surrounding gaseous phase at the high temperatures used in the fabrication process, great care must be exercised in control of the atmosphere during production.

In the spinel structure of Mn_3O_4 the Mn^{2+} ions occupy tetrahedrally coordinated sites, while the Mn^{3+} ions occupy octahedral sites. When nickel is added to Mn_3O_4, Ni^{2+} ions occupy octahedral sites and some Mn^{3+} ions are oxidized to the Mn^{4+} state to compensate for this loss in cationic charge. Electron "hopping" occurs between the Mn^{3+} ions and Mn^{4+} ions which are formed on nickel substitution to create the semiconductivity. The relative occupancy of these two chemical species in the two different coordinations is important in magnetic spinels which are discussed below.

Solid solutions are also used in laser materials in which transition or rare earth metal ions are placed in an oxide ion environment specifically designed to remove the ground state degeneracy of the d or f electrons. A very familiar example of this is the ruby laser which is a dilute solution of Cr_2O_3 in Al_2O_3. The asymmetry of the Al^{3+} ion site in Al_2O_3 leads to crystal field splitting of the Cr^{3+} d shell. This provides energy levels for the absorption of the pumping radiation, the descent to lower levels by phonon emission, and finally the laser action with stimulated emission before the return to the ground state with or without phonon emission.

2.2. Oxide electrolytes–solid solutions with anion vacancy formation

Oxides which conduct electricity almost exclusively by the migration of oxygen ions have found use as oxygen sensors and as the electrolytes in solid oxide fuel cells. The most successful of these have been based on the fluorite crystal structure and involved elements in Group IV. For zirconia and hafnia, the fluorite structure is only stable at very high temperatures, and it must be "stabilized" at lower temperatures by the addition of oxides of elements of Groups IIA and IIIA. This stabilization is accompanied by the formation of a proportional number of oxygen ion vacancies to the added metal cation, and replaces the stable monoclinic and tetragonal phases which are found in pure ZrO_2 and HfO_2. In the case of thoria, the pure phase already has the fluorite structure. The principle of the addition of lower valency cations to produce oxygen vacancies has also been applied to the solution of alkaline earth oxides in oxides of Group IIIA and the rare earth

metals. These latter materials function well as electrolytes in sensors, but have too high an electrical resistance to be useful as fuel cell electrolytes. In this respect stabilized zirconia is the only solid electrolyte that has so far been used in practical solid oxide fuel cells. It is interesting to note that the electrical conductivity of these Group IV solid electrolytes can vary, at 1000 °C, over two orders of magnitude at approximately the same oxygen ion vacancy concentration (Fig. 2). The zirconia-based electrolytes have a much higher conductivity than the corresponding thoria-based electrolytes.

There is a limit to the extent to which the formation of oxygen vacancies increases the diffusion coefficient of oxygen. Beyond about 5% of oxygen vacancies, the diffusion coefficient decreases and further addition leads to the formation of complex interoxide compounds. Some of the rare earth oxides such as Dy_2O_3 and those at the higher atomic weight end of the group, adopt the fluorite lattice. Although a quarter of the oxygen sites are empty, formally these oxides can be represented as $MO_{1.5}$, the oxygen vacancies are ordered, and do not contribute to a high oxygen diffusion coefficient as might be expected. In the phase diagrams, the range of solid solutions which show electrolytic behavior is usually limited by a two-phase region which involves an interoxide compound, such as $CaZr_4O_9$ in the
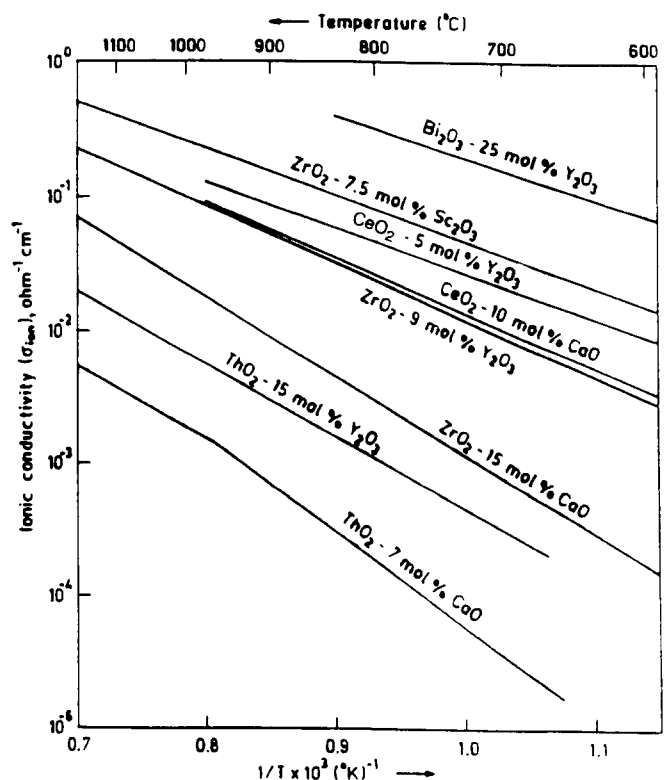

Fig. 2. Ionic conductivities of the substituted Group IVa oxides and Bi_2O_3 as a function of temperature.

CaO–ZrO_2 system or $Zr_3Y_4O_{12}$ in the Y_2O_3–ZrO_2 system [4].

The wide range of conductivity found in the stabilized zirconia solid solutions is clearly related to the ionic radius and charge of the aliovalent cation. Thus the addition of the Sc^{3+}, scandium ion yields an approximately tenfold increase in conductivity over the Y^{3+} ion. Also, either of these additions yields a higher conductivity than the Ca^{2+}, calcium ion addition.

One curious feature of all of these solid solutions, except those based on zirconia, and including some of the relatively highly conducting electrolytes based on the perovskite structure, such as $La_{1-x}Sr_xYO_{3-x/2}$, is the occurrence of p-type semiconduction at oxygen pressures above about 10^{-6} atm [5]. This semiconductivity cannot be ascribed to impurity effects, but may be associated with O^- ion formation. The exception of the zirconia-based electrolytes, even up to 100 atm oxygen pressure, to this behavior is remarkable.

2.3. Defect clusters

In both the simple non-stoichiometric oxides such as TiO_2 and the more complex solid electrolyte ZrO_2–Y_2O_3 for example, the simple mass action relationship between defect (oxygen vacancy) concentration and electrical conductivity only applies over a narrow range of composition. It is reasonable to expect that the departures from mass action behavior come about as a result of defect interaction. Thus in the case of the solid electrolyte, the oxygen vacancies have a net *positive* charge, or absence of negative charge with respect to oxygen ions. The aliovalent ion Y^{3+} has a net *negative* charge with respect to the Zr^{4+} ions on the cation lattice. It is to be anticipated then that there will be a tendency to association between the oxygen vacancies and the aliovalent Y^{3+} ions which will tend to remove the randomness of distribution which is required by the mass action law.

2.4. Magnetic spinels, garnets and magneto-plumbites

These materials show the wide possibilities in device design when two or more cation sub-lattices with differing oxygen coordination numbers can be utilized. The effects of crystal field splitting of orbital degeneracy mentioned earlier in connection with laser action are exploited to a greater extent in the design of magnetic materials with the spinel structure. Here the distribution of cations between the tetrahedrally and octahedrally oxygen-coordinated sites is determined in part by the relative ionic energies in these two sites. A very simple-minded calculation can be made of the distribution of two transition metal cations between these sites in a spinel using the octahedral site preference energies (OSPE). Thus the mass action constant K for the exchange process in the compound $(M,R_{tet})[M,R_{oct}]_2O_4$

has a value

$$K = \frac{C_{M_{oct}}C_{R_{tet}}}{C_{M_{te}}C_{R_{oct}}} = \exp\left[-\frac{\Delta E(OSPE)}{RT}\right]$$

Here the concentration values are ionic fractions, and if m_i are the number of g. ions per formula of the compound

$$C_{M_{tet}} + C_{R_{tet}} = 1 \qquad m_{M_{tet}} + m_{R_{tet}} = 1$$

$$C_{M_{oct}} + C_{R_{oct}} = 1 \qquad m_{M_{oct}} + m_{R_{oct}} = 2$$

This expression is essentially a Boltzmann distribution making use of the energy change $\Delta E(OSPE)$ as a weighting factor. From a thermodynamic point of view, the correct equation would be

$$K_{th} = \frac{\gamma C_{M_{oct}}\gamma' C_{R_{tet}}}{\gamma'' C_{M_{tet}}\gamma''' C_{R_{oct}}} = \exp\left[-\frac{\Delta G°(OSPE)}{RT}\right]$$

where the γ are activity coefficients and $\Delta G°(OSPE)$ is the Gibbs energy change for the site exchange reaction [6].

Even this simple expression makes it clear that the distribution of ions on the two sites is a function of temperature, thus placing significant constraints on the manufacturing process. This, however, is not the whole story since the correct expression must also include the thermal entropy change in this ionic exchange process, which has been measured in only a very few cases (Table 2). Even when the OSPEs are known, the calculation using the Boltzmann expression above is only an approximation which becomes increasingly worse with increasing temperature owing to the omission of the *thermal* entropy contribution.

Once the cation distribution is fixed, the resultant magnetic properties of the oxide are determined in part by the alignment of the cation unpaired electron spins. In this structure there is a strong superexchange coupling between the cations on the tetrahedral and octahedral sites via the oxygen ions. A similar coupling between cations on the octahedral sites only is relatively weak by comparison. The second factor determining the magnetic properties is related to the magnetization B, through alignment of the magnetic domains, and the ease with which this alignment can be reversed when the applied magnetic field H is reversed. The shape of the hysteresis B–H curve depends upon the nature of the cations in the particular material. Those which show a ready reversal of magnetization are called "soft" materials while the hard materials retain their magnetic structure during significant external magnetic field reversal. The spinel ferrites MFe_2O_4 ($M = Fe^{2+}$, Co^{2+} and Ni^{2+}) are all soft magnetic materials.

The garnets are of general formula $3MO_{1.5}\cdot5FeO_{1.5}$ ($M = Y$ or rare earth) in which ions of valency 2+ and

TABLE 2. Thermodynamic data for some spinels

Species	Fe^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Mn^{2+}	V^{3+}	Cr^{3+}	Fe^{3+}	Al^{3+}
OSPE (kJ)	−16.7	−86.2	−31.0	−63.6	0	−53.6	−157.7	0	−78

Cation distribution in spinels

Spinel (MX_2O_4)	Cation fraction of M^{2+} on tetrahedral sites	
	Calculated (1200 K)	Measured
$FeAl_2O_4$	0.936	0.923 (1423 K)
$NiAl_2O_4$	0.21	0.20 (1300 K)
$CoAl_2O_4$	0.89	0.95 (1123 K)
$MnAl_2O_4$	0.97	0.96 (1272 K)
$CuAl_2O_4$	0.54	0.4 (1100 K)

Entropy of formation $(J\ deg^{-1}\ mol^{-1})$

	Measured total	Configurational	Thermal
Fe_3O_4 (inverse)	6.15	14.31	−8.16
FeV_2O_4	3.05	9.20	−6.15
$FeAl_2O_4$	−3.26	4.35	−7.61
$FeCr_2O_4$ (normal)	−7.24	0.13	−7.35

4 + can be substituted. They have basically three oxygen coordination numbers for cations in which trivalent ions occupy tetrahedral, octahedral and dodecahedral sites conventionally designated d, a and c respectively, in which there is superexchange coupling between the a and d sites and between the c and d sites. When the cations consist of rare earth or Fe^{3+} ions, there is no significant redox equilibrium of the material is fired in air. In more complex materials there remain the site preference energies to decide the distribution of cations. Relatively large divalent ions such as Ca^{2+} and Sr^{2+} prefer dodecahedral coordination, the IIIA ions are split between dodecahedral and octahedral coordination, and the smaller highly charged ions usually take tetrahedral coordination. There will again be an entropy contribution to stability owing to the mixing of cations on the alternative cation coordination sites, and so the cation distribution is, in many circumstances, temperature dependent [7].

In the magneto-plumbites, of which the archetypal member is $BaO \cdot 6Fe_2O_3$, the structure consists of spinel units joined by units containing the alkaline earth ion in hexagonal coordination. Again, there can be considerable substitution for the alkaline earth and Fe^{3+} ions. If a lanthanide ion M^{3+} is substituted for barium, one Fe^{3+} ion is reduced to Fe^{2+} to maintain charge balance. Iron may be totally replaced with aluminium Al^{3+} or gallium Ga^{3+}, but in this case the replacement of $Ba^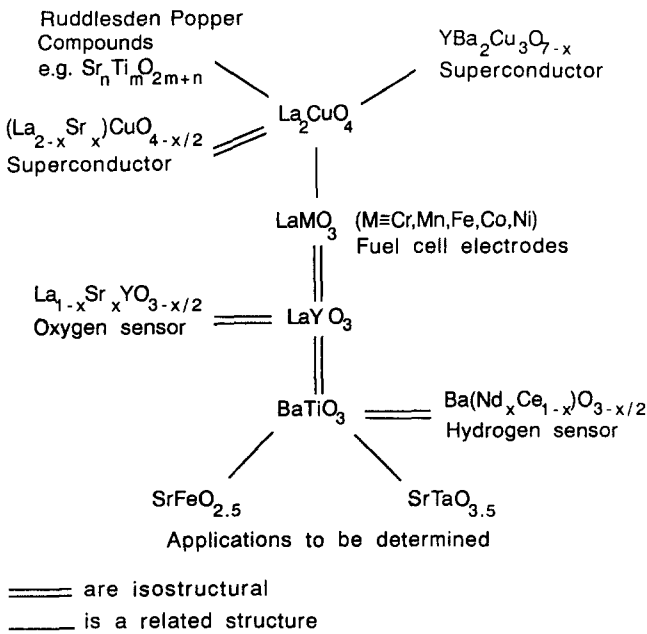{2+}$ by La^{3+} must be charge compensated by replacing Al^{3+}, for instance by Mg^{2+}. The magneto-plumbites are hard magnetic materials.

The variation of the type and charge of the cations on the cation sub-lattices of these magnetic oxide materials makes it possible to produce a wide range of materials, but in all cases where cation substitution is involved, a new source of configurational entropy is introduced which adds further complication to calculation of the cation distribution at any given temperature as well as complicating the manufacturing process. This is because the cation distribution, which determines the magnetic properties, is a function of temperature as well as oxygen potential.

2.5. Dielectric and conducting perovskites

The perovskite structure ABO_3 is very accommodating to a whole range of cationic mixtures on both the A and B sites. In the barium titanate family of dielectric materials, the transformation from ferroelectric to antiferroelectric behavior can be made by substituting zirconium for titanium on the B sites and the order–disorder transformation temperature to paraelectric behavior can be increased by introducing lead in exchange for barium. The dielectric properties of $BaTiO_3$ and $BaZrO_3$ arise from the displacement of the Ti^{4+} or Zr^{4+} ion from the center of the octahedral oxygen coordination shell. In the titanate this leads to ferroelectric behavior where these displacements are lined up in the presence of an external field leading to a

The Perovskite Family Tree

Ruddlesden Popper
Compounds
e.g. $Sr_nTi_mO_{2m+n}$

$YBa_2Cu_3O_{7-x}$
Superconductor

$(La_{2-x}Sr_x)CuO_{4-x/2}$
Superconductor

La_2CuO_4

$LaMO_3$ (M≡Cr,Mn,Fe,Co,Ni)
Fuel cell electrodes

$La_{1-x}Sr_xYO_{3-x/2}$
Oxygen sensor === $LaYO_3$

$BaTiO_3$ === $Ba(Nd_xCe_{1-x})O_{3-x/2}$
Hydrogen sensor

$SrFeO_{2.5}$			$SrTaO_{3.5}$
Applications to be determined

=== are isostructural

_____ is a related structure

high dielectric constant. In the zirconate the effect of the external field is the opposite, leading to alternate planes of Zr^{4+} ions having opposite displacements, and this material is designated as "antiferroelectric". The shape of the hysteresis loop in both the ferromagnetic spinels and the ferroelectric titanates can be affected by substitution of small amounts of aliovalent ions on two cation sublattices. The substitution of lanthanum or neodymium for barium produces a "softer" dielectric material, i.e. one having a smaller coercive field than pure $BaTiO_3$. The exchange of the trivalent La^{3+} ion for divalent Pb^{2+} leads to the formation of vacancies on the cation sublattice, but the major effect is due to the reduction of the p-type semiconduction, and hence a decrease in the electrical conductivity. In this context, the aliovalent ion is termed a "donor", although n-type semiconduction is not introduced with this substitution. The explanation lies in the equation

$$La_2O_3 \longrightarrow 2La^{\cdot}_{Pb} + V''_{Pb} + 3O_O$$

using the Kroger–Vink notation, in which $La^{\cdot}_{Pb}$ indicates the substitution of the trivalent ion for divalent Pb^{2+}, and V''_{Pb} indicates the absence of two positive charges when a vacancy of Pb^{2+} is created. The substitution of trivalent ions for the tetravalent Ti^{4+} or Zr^{4+} ions on the B sites leads to "harder" materials. This is thought to be due to the introduction of vacant oxygen sites which cluster around the trivalent ion, impeding domain wall rotation. This follows according to the equation

$$MnO_{1.5} \longrightarrow Mn'_{Ti,Zr} + 1.5O_O + 0.5V_O^{\cdot\cdot}$$

where the lower valent Mn^{3+} replaces the higher valent Ti^{4+} or Zr^{4+} ions and creates a vacancy $V_O^{\cdot\cdot}$ on the oxygen lattice. Because the oxygen ion has a much higher diffusion coefficient in the perovskites than the corresponding cations, the oxygen vacancy can diffuse more rapidly than the cation vacancy, and forms dipoles with La^{3+} substituted ions. These are thought to impede domain wall rotation and hence to "harden" the ferroelectric behavior. It should be noted that polycrystalline materials, which probably contain pores at the grain boundary, also show a broader hysteresis loop than the corresponding single crystal, probably for the same reason [8].

The perovskite structure has also been used to develop new oxide electrolytes which contain ions which are less reducible than zirconium, and hence can be used in oxygen sensors at low oxygen pressures to replace thorium oxide. Lanthanum yttrium oxide and lanthanum aluminium oxide have been found to function satisfactorily when alkaline earth oxide additions such as SrO on the A sites and CaO or MgO on the B sites are made. The electrolytes show unit transport number for oxygen ions down to the oxygen potential of the $Ta–Ta_2O_5$ system at least and up to a temperature of 1000 °C [9].

These materials have also been shown to be useful catalysts for the coupling reactions of methane such as

$$2CH_4 \longrightarrow C_2H_6 + H_2$$
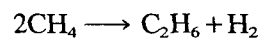
a property which will be considered below.

Perovskites based on Ce^{4+} ions on the B sites have been used to develop hydrogen sensors. For example, if $BaCeO_3$ is doped with Nd_2O_3 to create oxygen vacancies, the resulting material can be used as a solid electrolyte in a hydrogen electrochemical cell [10]

$$pH_2|Ba(Nd,Ce)O_3|p'H_2$$

$$E = \frac{RT}{2F} \ln \frac{p'H_2}{pH_2}$$

It is probable that this class of electrolytes depend for their action on the presence of small partial pressures of water vapor which together with oxygen vacancies in the solid causes the introduction of negatively charged OH^- groups in the solid thus

$$V_O^{\cdot\cdot} + H_2O(g) + O_O \longrightarrow 2(OH^-)_O^{\cdot}$$
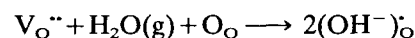
The perovskites which are used as electrode materials in projected solid oxide fuel cells must be both good electrical conductors and have a high oxygen diffusion coefficient. This can be achieved by using mixtures of valencies of transition metals on the B sites to provide the electrical properties, and mixtures of Group II and Group III elements on the A sites to generate oxygen

vacancies. The current carriers are generated by the acquisition of electrons by oxygen atoms which fill the vacant sites, increasingly at increasing oxygen pressure. This unfortunately means that the current carrier concentration *increases* as the oxygen diffusion coefficient *decreases*. Some substituted perovskites such as $La_{0.8}Sr_{0.2}CrO_{3-\delta}$, where δ indicates the departure from stoichiometry, have been found to function very well as oxidation catalysts rivaling platinum for many applications. The addition of Sr^{2+} to lanthanum-based perovskites $LaMO_3$ ($M \equiv Cr$, Mn, Fe, Co, Ni) leads to the formation of oxygen vacancies at low oxygen potentials, and when these are filled at high oxygen potentials there is a marked increase in the p-type semiconduction leading to metallic behavior in some instances. There is a parallel between the electrical conductivity and the departure from stoichiometry [11] which indicates that, similar to the case in the simple oxides, the current carrier mobility appears to be relatively insensitive to concentration (Fig. 3).

The use of perovskites as catalysts in methane chemistry can have two principal objectives. In the oxidation of methane, the conversion is usually carried out to completion over Al_2O_3-supported catalysts of platinum or palladium in pure or alloyed form. Figure 4 shows that the p-type perovskites perform nearly as well as platinum, but the noble metal catalyst in this example
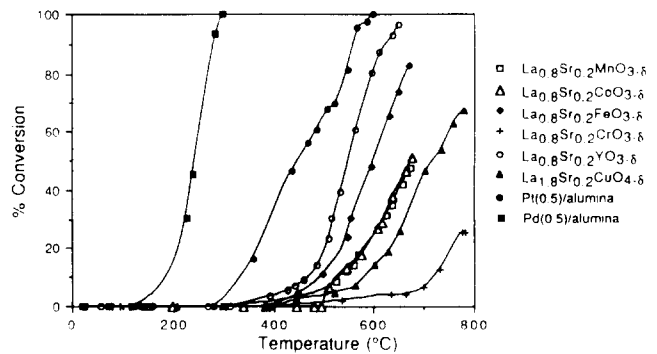

Fig. 4. Methane oxidation by A-site substituted perovskites and noble metal catalysts.

had a very much larger surface area than any of the perovskites [12]. The solid electrolyte $La_{0.8}Sr_{0.2}YO_{2.9}$ performed poorly in this respect, but was significantly better than the others for the methane coupling reaction. Perovskites of predominantly n-type semiconduction such as $LaFe_{0.8}Nb_{0.2}O_{3-x}$ also showed greater catalytic activity for the coupling reaction than for methane oxidation [13].

A survey of phase diagrams of pseudobinary oxide mixtures in which perovskite structures are formed shows that they are frequently very complex. If the M ion in M_2TiO_4 is small, such as zinc for example, a spinel is formed with one zinc ion mixing with Ti^{4+} on the octahedral sites to form an entropy-stabilized compound. When M is a large ion, such as Sr^{2+}, another structure is formed which is the first member of the Ruddlesden–Popper series $M_nTi_mO_{2m+n}$, e.g. Sr_2TiO_4 and $Sr_3Ti_2O_7$ [14]. These structures consist of alternate perovskite and rock salt structures in which one or more perovskite unit cells are found in neighboring positions. Owing to the large difference in size between the cations Sr^{2+} and Ti^{4+}, there is no possibility of entropy stabilization in these structures.

However, there is a source of entropy when zirconia is partially substituted for titania and at high temperatures the oxygen octahedra incorporating these cations are randomly mixed. On cooling there is an ordering tendency, the kinetics of which is very slow since it depends on cation interdiffusion. The annealing times needed to achieve these ordered structures can be very long, thus leading to phase diagrams the complexity of which will depend on the time allowed and the temperature of the anneal [15]. There appears to be very little quantitative information in the literature regarding diffusion coefficients of cations in the perovskite structure, but the few data there are suggest diffusion coefficients of the order of 10^{-14} cm^2 s^{-1} at temperatures around 1000 °C.

The brownmillerite and a perovskite-based slab structures may be derived from the perovskite structure by the complete exchange of trivalent and pentavalent
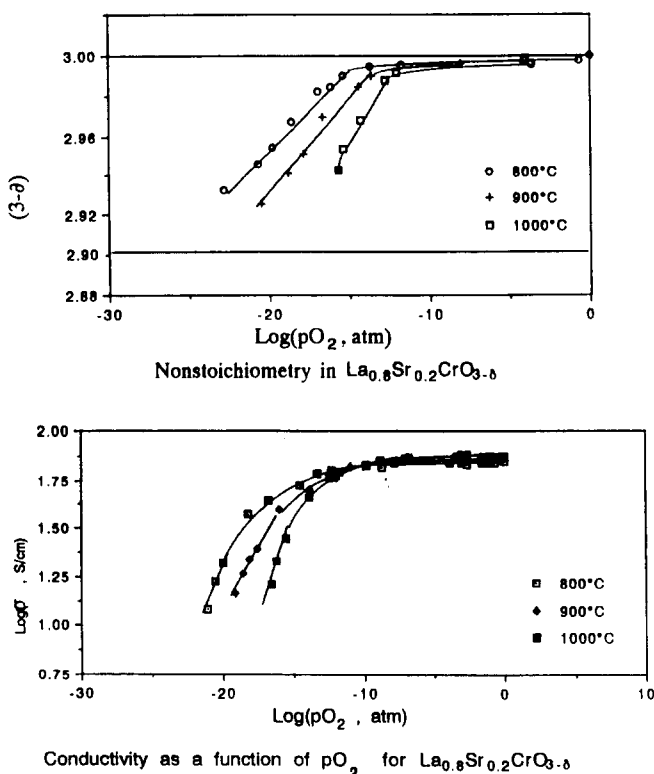

Nonstoichiometry in $La_{0.8}Sr_{0.2}CrO_{3-\delta}$

Conductivity as a function of pO_2 for $La_{0.8}Sr_{0.2}CrO_{3-\delta}$

Fig. 3. A comparison of the oxygen dependence of the nonstoichiometry and conductivity of $La_{0.8}Sr_{0.2}CrO_{3-\delta}$.

ions respectively for Ti^{4+}. These compounds therefore have the typical formulas $Sr_2Fe_2O_5$ and $Sr_2Ta_2O_7$. In the former compound the Fe^{3+} ion is believed to occur in both 4- and 6- coordination. This suggests that only ions with relatively small octahedral site preference energies could be involved in this structure [16].

The brownmillerite structure has channels of vacant sites through the oxygen sublattice as a result of the transition from $SrTiO_4$ to $SrFeO_{1.5}$, as this compound might be described. There are also intermediate "compounds" between these two extremes, belonging to a series of general formula $A_nB_nO_{3n-1}$ in which the distance between these channels increases as n increases, i.e. the thickness of the perovskite slabs which connect the channels increases.

The $ABO_{2.5}$ structure consists of slightly distorted perovskite slabs, separated by cleavage planes. The extra oxygen atoms required to neutralize the change in cation charge from 4^+ to 5^+, terminate the perovskite slabs to leave two-dimensional cleavage planes. Intermediate substitutions are again possible leading to the series. $A_nB_nO_{3n+2}$ in which the perovskite slab thickness increases as n increases.

Both of these structures offer new possibilities for high ionic mobilities, through the vacant channels of the brownmillerite structure, and the cleavage planes of the $A_2B_2O_7$ structure which could play a part in the development of new materials.

Finally, the perovskite structure appears in the generic superconducting structure La_2CuO_4. This consists of alternate blocks of perovskite and rock salt structure. The partially strontium-substituted compound was the first high T_c superconductor, and the superconducting compounds such as $YBa_2Cu_3O_{7-x}$ which have been subsequently developed have crystal structures related to the perovskite lattice [17].

3. Themes for the development of new materials

This review of the major features of oxide electroceramics contains most of the experimental and theoretical repertoire presently available to the materials engineer for the production of useful devices. While these tools of thought are adequate and will most probably be used successfully in the development of further materials, there are many avenues for further exploration in this field. Table 3 depicts five aspects of development which show that many new approaches to device design and construction await the engineer of the future. These will now be considered seriatim.

3.1. High temperature vs. solution preparation techniques

A change has come about in preparative methods for ceramic oxide materials in the recent past. The

TABLE 3. Themes for the development of new materials

Solution methods to replace solid state preparative methods
Exploitation of anion substitution, F^- or OH^- for the preparation of new materials
The use of composite materials to produce enhanced transport and strengthening mechanisms
The preparation of metastable materials with new properties
Exploration of ionicity of bonds by first principle calculation

TABLE 4. Preparation of ceramic oxide materials

Classical procedure
Mix individual oxide powders, sinter to high temperature 1000–1600 °C, regrind and sinter until material is homogeneous by X-ray diffraction (usually 3–4 days)

Modern sol–gel method (Pechini)
Mix appropriate nitrates and add citric acid, mix with ethylene glycol at 80–100 °C, heat to 400–450 °C to char and oxidize resin, pelletize and sinter at an appropriate temperature for required grain size

Alkaline gelation method
Mix appropriate nitrates, hydroxides or alkoxides and gel with ammonia, wash and then dry in air, sinter to appropriate temperature

traditional mixing of separate oxides followed by sintering, grinding and pelletizing processes usually requires the use of high temperatures. In most of the systems discussed here, the conditions for achieving homogeneity in the product are determined by interdiffusion of cationic species to bring about the proper mixing, but then the achievement of the desired crystallographic structure would either require rapid cooling, which leads to thermal shock problems, or cooling to an annealing temperature where an ordered cationic arrangement which is more stable than a random distribution of cations, could be achieved.

The major difficulties associated with this high temperature procedure, which leads to grain growth through sintering, are potential depletion of the original mixture of a volatile component, such as PbO, and the risk of significant interaction with container materials.

These hazards can be avoided if solution techniques such as sol–gel are used, and fine grained products can be obtained from low temperature operations, typically less than 500 °C (Table 4). In the solution techniques either aqueous solutions are mixed with an organic phase to form a gel, or metal organic compounds, such as the alkoxides, are mixed and then hydrolyzed. In both cases, the final product is heated to about 400 °C to decompose the organic compounds and to oxidize the remaining carbon-containing char. These products must still be annealed, as in the high temperature process, to achieve a required ordered structure of

cations, since the solution methods will produce initial structures having a random distribution of cations. In favorable cases, however, the fine-grained materials can be retained in the final product with many advantages in device fabrication where grain boundary contributions should be optimized. Another advantage of the low temperature techniques over high temperature synthesis, is that thermodynamically metastable structures could be exploited. Besides these solution methods, there are many other techniques which can be used for assembling metastable structures, especially when the required application can be achieved in the thin film state.

Chemical vapor deposition and Knudsen cell evaporation allows the formation of thin films of metallic alloys of a widely variable composition, and these alloys can be oxidized subsequently to form the electroceramic film. Care must be exercised in the oxidation step to avoid rupture of the film due to the exothermic nature of metal oxidation processes. This can be avoided by the use of a suitably low oxygen potential gaseous phase or preferably by coulometric oxidation using a solid electrolyte [18].

When surface modification only is required, the surface composition can be modified by ion implantation, but the material so formed requires careful annealing to remove radiation damage. The presence of significant amounts of radiation damage can affect the electrical properties in the surface layer significantly.

Techniques which avoid the necessity for subsequent oxidation include freeze and spray drying, in which aqueous solutions containing mixed cations can be preserved in the solid state, and the "splat" cooling of melts in which the random mixing of fused salts can be mainly conserved in a solid product [19]. These processes open a potentially large area for exploitation since kinetic factors would impede cation redistribution at low temperatures and might lead to cation site occupancies which have been unattainable through the conventional route. It should be remembered in this context that practically the whole of the vast body of organic materials are thermodynamically unstable at very moderately elevated temperatures, and yet many valuable applications of these molecules depend upon kinetic factors for their successful long-term use.

3.2. Fluoride ion substitution in magnetic materials

Extensive studies have been made of the substitution of fluoride for oxide anions in magnetic materials [20]. The introduction of fluorine reduces the charge on the anion sublattice, and thus alters the charge requirements of the cation sublattice. The reduction in cationic charge can be brought about by the substitution of divalent ions to replace the trivalent ions found on the octahedral sites in the normal spinel or of monovalent ions for

divalent ions on the tetrahedral sites. Alternatively, the ions occupying the tetrahedral site can be transferred to octahedral coordination. Substitutions of this kind have been made in spinels such as the ferrites $Zn_xFe_{3-x}O_{4-x}F_x$ ($0 \leqslant x \leqslant 0.50$) and $Co_{1-x}Li_xFe_2O_{4-x}F_x$ which led to new magnetic materials, in some cases having higher Curie temperatures than the corresponding pure oxide systems.

Substitution has also been achieved in magnetoplumbites such as $SrFe_{10}Co_2O_{17}F_2$. In these substituted systems it was found that the divalent alkaline earth ions tended to occupy tetrahedral sites as a result of fluorine substitution instead of the dodecahedral sites occupied in the corresponding oxides. The result was an altered magnetic spin balance between the tetrahedral and octahedral sites, and a larger saturation magnetization.

The substitution of fluoride ion for oxide ion may, in some cases, lead to the formation of compensating vacancies on the cation sublattices, and interaction between the fluoride ions and the cationic vacancies might lead to an increase in the magnetic "hardness" of the products through limitations imposed on domain wall rotation. This is analogous to the $M^{3+}-V_O^{..}$ complex effect in M^{3+} substituted titanates.

3.3. Composite materials

In the development of new electrolyte systems for sensor materials, two applications have been found for dispersed phase systems. In one application it has been found that dispersions of inert oxides such as Al_2O_3 in CaF_2 lead to an enhanced electrical conductivity, by fluoride ion migration [21]. Speculations are that the use of a dispersed phase which takes no part in the conduction process, increases the grain boundary area of the electrolytic material, and hence enhances anionic migration. The precise mechanism for enhancement cannot be quite so simple since there are some dispersions such as [$CaF_2(Al_2O_3)$] in which enhanced conductivity is observed, and others, such as [$CSZ(CaZrO_3)$] in which the perovskite phase does not lead to enhanced conductivity in the fluorite, calcia-stabilized phase.

A composite in which one phase toughens the matrix phase is known in many examples in the field of glass ceramics, where the introduction of phases having nearly zero expansion coefficient has led to significant increases in thermal shock resistance. Similarly, Al_2O_3 may be transformation toughened by the inclusion of a second phase such as zirconia which undergoes a monoclinic–tetragonal transformation in the unstabilized state [22]. Experiments with oxygen probes for steelmaking containing MgO and CaO in solution in zirconia were found to combine the thermal shock resistance arising from MgO inclusion and tetragonal phase separation,

with sealing capability, through CaO inclusion, to silica tubes by stable silicate formation [23]. Conventional glass-blowing techniques using a hydrogen–oxygen torch could then be used on a production basis to produce the steelmaking oxygen probes.

A quite different use of composite materials is the development of electrochemical sensors which respond to different ions from the main current carriers in the electrolyte phase. As an example of this, the incorporation of an oxide dispersed phase having a common cation with a host fluoride electrolyte produces a material which responds in a Nernstian manner to an oxygen chemical potential gradient. Because of the higher mobility of the fluoride ion in the fluoride electrolyte than that of the oxygen ion in any of the proven oxide electrolytes, these composite sensors function to lower temperatures than oxide electrolyte sensors, which usually fail below 400 °C [24].

Sensors for other species such as sulfur, carbon and hydrogen which also function at low temperatures can be made by substituting the appropriate sulfide, carbide or hydride as the dispersed phase in the alkaline earth electrolyte host.

3.4. Ionic or covalent?

The advent of supercomputers has made realistic calculations from near-first principles possible for inorganic systems. It would appear that considerable progress could be made if it can be assumed that all bonding is ionic and therefore stability can be quantitatively assessed by means of a sophisticated extension of the Born–Haber cycle. To the practical scientist, memories of Pauling's use of his electronegativity scale [25] and Fajans concept of polarizability of ions [26] raise the question of covalent contribution to bonding. The Shannon and Prewitt radii [27] reflect the variability of cationic ion radii as a function of coordination number, but one is still uncertain what values to use, and what tolerances to allow for in considering cation substitution. These problems can probably be addressed by the use of a range of advanced structure techniques, but very little guidance appears to be available, or if available to be seldom applied by scientists involved in materials preparation.

When these issues have been successfully resolved, it will be possible to consider the significance of defect association in non-stoichiometric systems. It is usually assumed that departures from the mass action law are due to defect clustering and that such clusters can agglomerate to form units covering more than one unit cell. It was suggested many years ago [28] that these clusters resemble the compound which is formed at the next level of oxidation, and that the range of non-stoichiometry which can be achieved depends on the "saturation" level at which the neighboring oxide ap-

pears as a separate phase. Certainly the clustering of defects in the non-stoichiometric transition metal monoxides, MnO, FeO and CoO, suggests the formation of nuclei of the spinel phases Mn_3O_4, Fe_3O_4 and Co_3O_4. In these systems the range of non-stoichiometry in the monoxide is in the sequence FeO > MnO > CoO > NiO. Of course in the case of NiO, the phase Ni_3O_4 cannot be formed under atmospheric pressure of oxygen.

Finally, the important role of site preference energies in deciding the distribution of cations, and hence physical properties of electroceramics is evident from this discussion. Fundamental calculations would be of considerable help in guiding the materials designer in his choice of coordination numbers and cationic species. When it becomes possible to obtain accurate thermal entropies for a number of possible arrangements, this knowledge could be utilized in the search for new materials.

4. Conclusion

Apart from the obvious physical properties of electroceramic oxides and their relation to the cationic species, the thermodynamic and transport properties of all ionic species are important to materials science. We have come a long way in developing a large body of industrial materials, but demands for more and more options in both properties and conditions of service are bound to present themselves. The techniques, both theoretical and experimental, to meet these demands seem to be at hand, but the industrial prizes will, as always, follow the advance of basic knowledge.

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