

## REPORT ON THE WORKSHOP: THERMAL CHARACTERIZATION OF NON-STOICHIOMETRIC OXIDES AND SIMILAR COMPOUNDS AND THEIR APPLICATION IN ENERGY STORAGE AND CONVERSION

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The workshop moderators (Dr. O. Toft Sørensen and Dr. D. Jakeš) were assisted by a panel scientific board consisting of Prof. V.S. Darshane (India) and Prof. P.D. Ownby (U.S.A.).

After the introduction on non-stoichiometric compounds and their application in the energy field, prepared by the Chairman, a discussion of the question “How useful is a workshop on materials science dealing with a specific class of materials for a thermal analysis conference?” took place. The report of the workshop covers presentations and discussion on three main topics and concluding remarks.

### I. INTRODUCTION

Compounds with large deviations from the stoichiometric composition, i.e., grossly non-stoichiometric compounds as they are also termed, can be formed either by interaction with an atmosphere (oxidation or reduction) or by doping with aliovalent cations. Typical examples of the first type are various compounds (oxides, fluorides, sulphides, etc.) of transition metals, rare earth metals and actinide metals, whereas yttria-doped zirconia is a typical example of the second type of non-stoichiometric compounds. In the latter instance compounds showing a high conductivity for oxygen ions are obtained owing to the oxygen vacancies introduced by the doping.

Non-stoichiometric compounds, especially oxides, have attracted much interest during the last two decades because of their technological applications in both energy conversion and conservation fields. As examples of such applications, there were mentioned:

(1)  $\text{UO}_{2 \pm x}$ ,  $\text{PuO}_{2-x}$ ,  $(\text{U,Pu})\text{O}_{2 \pm x}$

Nuclear energy

- (2) Doped oxides of  $ZrO_2$ ,  $CeO_2$ ,  $ThO_2$ 
  - Fuel cells
  - Electrolysers
  - Semipermeable membranes for  $H_2$  production
  - Oxygen sensors
- (3)  $ZrO_2$ -strengthened ceramics
  - Combustion engines

Finally, it was stressed that in materials research on non-stoichiometric compounds it is necessary to characterize these on three levels, by using supplementary techniques. First, it is, of course, of interest to determine their general or macroscopic properties such as melting point, thermal stability, thermal expansion, heat capacity and phase relationships, and for these measurements thermal analysis is very helpful.

Second, there are the more specific properties of direct interest for specific applications. For applications in the energy field, an important specific property is the electrical conductivity (ionic and electronic), which must be determined by either d.c. or a.c. measurements as a function of temperature and oxygen pressure (for oxides). Conductivity measurements thus comply with the general definition of thermal analysis, and it deserves a much better coverage at ICTA Conferences than has hitherto been the case.

In order to understand fully the real nature of non-stoichiometric compounds, a thorough characterization of their what could be termed microscopic properties is, however, also essential. Among these properties was mentioned the defect structure, which can be determined by structural studies using X-ray, neutron and electron diffraction. For many non-stoichiometric systems the defect structure has been deduced directly from the thermodynamic and transport properties (conductivity, diffusion, etc.). It is important to realize, however, that the defect structure derived in this way can only be a model and, no matter how well it describes the experimental data, it has to be verified by direct structural observations in order to become realistic.

## II. DISCUSSION

Should sessions on materials research play a more dominant role at ICTA conferences than has hitherto been the case?

In previous conferences and at this one, materials research has traditionally been discussed in sessions that were too large and, in the opinion of the authors, rather incoherent. In the case of non-stoichiometric compounds, for instance, these would typically be discussed in sessions on inorganic chemistry where, however, virtually all possible inorganic compounds are dealt with. The audience agreed that this is unsatisfactory and for future conferences it was recommended that the scientific programme be subdivided

into smaller sessions in which contributions dealing with related materials could be presented and thoroughly discussed from a thermal analysis, but certainly also from a materials point of view.

### III. TRENDS IN MATERIALS RESEARCH ON NON-STOICHIOMETRIC COMPOUNDS

Previously it was believed that non-stoichiometric phases were single-phase materials of variable composition. This is probably still true for compounds that exist only within a narrow composition range, but for the so-called grossly non-stoichiometric systems interactions between the defects leading to long-range ordering must be expected. This has been shown to be the case, for instance, for  $\text{CeO}_{2-x}$  [1], which at high temperature ( $1000^\circ\text{C}$ ) exists in the range  $0 \leq x \leq 0.25$ . Another example is wüstite,  $\text{Fe}_{1-y}\text{O}$ , which typically exists as a non-stoichiometric phase in the range  $0.05 \leq y \leq 0.12$  ( $1000^\circ\text{C}$ ), and where the non-stoichiometric phase range has been shown to consist of several subphases, each with a specific type of predominant defect [2]. To illustrate this aspect, the Chairman gave a short review of his thermogravimetric equilibration studies on these two grossly non-stoichiometric oxide systems.

As for  $\text{Fe}_{1-y}\text{O}$ , the phase range for the grossly non-stoichiometric  $\text{CeO}_{2-x}$  was also found to consist of a whole series of subphases bounded by ordered phases whose compositions all could be described by the general formula  $\text{M}_n\text{O}_{2n-2}$  (homologous series). To explain the defect structures of these ordered phases a model was proposed based on the exclusion principle, i.e., when a defect (oxygen vacancy) is formed in a given oxygen site then it requires a higher energy to form another oxygen vacancy in an adjacent site. Each vacancy will thus be surrounded by an exclusion envelope which, however, decreases in size at large defect concentrations where a closer packing of the defects is required. The defect structure of the ordered phases could all be explained by a systematic packing of three types of exclusion envelopes (polyhedra) and, what is considered to be very important, the defect structures obtained in this way all comply very well with the crystal structures determined by X-ray measurements. Further, statistical thermodynamic calculations showed [3] that the proposed packing of exclusion polyhedra gives  $\Delta\bar{H}(\text{O}_2)$  data corresponding to those determined by independent calorimetric measurements. The defect structures obtained in these studies for the  $\text{CeO}_{2-x}$  system are thus considered to be fairly realistic.

As an example of another non-stoichiometric system in which the non-stoichiometric phase range also has been observed to consist of several subphases, Prof. M. Taniguchi (Tokyo Institute of Technology, Japan) reported on some recent results obtained for the  $\text{VS-V}_5\text{S}_8$  system [4,5]. In these studies the samples were equilibrated at high temperatures (923–1174

K) in atmospheres of controlled  $P(S_2)$  (sulphur partial pressures) prepared by the  $H_2S-H_2$  gas mixing method [ $P(S_2) = 10^{-4}-10^{-14}$  atm] and by evaporation of sulphur into a nitrogen carrier gas [ $P(S_2) = 1-10^{-4}$  atm]. After equilibrium was attained at high temperature (3–6 h), the samples were quenched and their composition and structure (X-ray powder diffraction) were determined. From the  $P(S_2)$ -composition isotherms constructed from these data, the  $VS-V_5S_8$  ( $VS_{1.6}$ ) composition range was observed to consist of the following non-stoichiometric subphases (at  $900^\circ C$ ):

$VS_{1+x}$ ;  $x < 1.2$ , hexagonal

$V_3S_{4\pm x}$ ;  $1.22 < x < 1.48$ , monoclinic

$V_3S_4$  exists as an ordered phase at  $x = 1.33$

$V_2S_{3\pm x}$ ;  $1.49 < x < 1.54$

$V_5S_{8-x}$   $1.56 < x < 1.6$ , monoclinic

The defects responsible for the variation in composition observed for these phases have been shown to be vanadium vacancies, which are formed in increasing concentrations with increasing  $P(S_2)$ . In hexagonal  $VS_{1+x}$ , these are believed to be distributed randomly in alternate metal layers of the NiAs structure, whereas they are ordered, although in different ways, in  $V_3S_4$  and  $V_5S_8$ , which becomes distorted to the monoclinic form. Ordering of the defects resulting in phase separations thus also plays an important role in the non-stoichiometric vanadium sulphides.

#### IV. TRENDS IN EXPERIMENTAL TECHNIQUES

An important parameter in measurements on non-stoichiometric compounds is the partial pressure of the anionic component in the atmosphere surrounding the sample, which must be controlled with great precision. In studies on non-stoichiometric oxides, for instance, it is of course important to know precisely the partial pressure of oxygen,  $P(O_2)$ , whereas  $P(S_2)$  must be known in studies of non-stoichiometric sulphides, as demonstrated by Prof. Taniguchi (Section III). In the case of non-stoichiometric oxides,  $P(O_2)$  measurements using galvanic concentration cells based on solid zirconia electrolytes (sensors) have become a very useful and important method. These sensors can either be placed in a separate furnace to determine the  $P(O_2)$  of the incoming or outgoing gas or they can be used for in situ measurements, which gives the most reliable measurements. The main problems with sensors of this type are their size and their need for a continuous supply of a reference gas, usually air. This makes it difficult to instal them in standard equipment, for instance in a thermoanalyser. Therefore, there is a great need for miniature sensors that can work without a supply of reference gas. Such sensors have been developed, but are not yet

commercially available. As examples of how zirconia sensors can be used for  $P(\text{O}_2)$  measurements in studies on oxides, the reader is referred to the contributions by Havlica and Ambruz [6] and Koller et al. [7].

As the mass of the anionic species of non-stoichiometric compounds is typically small, such as oxygen ions, a high sensitivity is required in measurements of compositional change by thermogravimetry. With  $\text{CeO}_{2-x}$  a sensitivity of  $\pm 0.003$  can be obtained. This appears to be fairly good, but nevertheless it corresponds to an uncertainty in the vacancy concentration (expressed as number per  $\text{cm}^3$ ) of about  $10^{20}$ . In order to perform detailed studies of the phase relationship of non-stoichiometric oxide systems by this technique, thermobalances with improved sensitivity would therefore be very helpful.

For studies on non-stoichiometric oxides, coulometric titration has proved to be very sensitive and accurate. Teske and Nebelung [8] accurately measured the amount of oxygen exchanged with the sample by coulometrically titrating the effluent gas to a pre-determined  $P(\text{O}_2)$ . The galvanic cell used for this titration, which was placed in a separate furnace, was based on a solid zirconia electrolyte. In studies of various non-stoichiometric oxide systems ( $\text{UO}_{2\pm x}$ ,  $\text{UO}_{2-x}$  and other oxides), a standard deviation of  $x = 0.0007$  was achieved, which is a considerable improvement.

Coulometric titration can also be performed directly on a non-stoichiometric sample, which then has to be sealed in a small crucible made of YSZ (yttria-stabilized zirconia). The most important problem in using this technique has been to find suitable sealing materials, which can withstand high temperatures and a high  $P(\text{O}_2)$  differences between the closed compartment and ambient atmosphere. Dr. D. Jakes (Nuclear Research Institute, Rez, Czechoslovakia) described the cell he had developed for studies on non-stoichiometric Sr, Ba and Mg uranates, in which a good seal between the YSZ crucible and an alumina lid was obtained by gold or palladium gold rings. With this cell measurements could be extended up to  $1200^\circ\text{C}$  and, as a remarkable feature, its independence from the ambient conditions and even the quality of the cover gas was mentioned.

Non-stoichiometric oxide systems are typically studied in a coulometric titration cell in the following way. After a stationary temperature has been reached, the composition of the sample is changed by electrochemically pumping oxygen into or out of the closed compartment. The number of oxygen molecules transferred and thus the change in the composition of the sample can therefore be determined from the magnitude of the current passed and the time of titration. As the coulometric titration cell can also be used as a galvanic concentration cell, it is also possible by intermittent e.m.f. measurements to determine the equilibrium oxygen pressure as a function of composition. From the data obtained it is possible to construct a whole  $\log P(\text{O}_2)$ —composition diagram from which the phase relationships can easily be derived. This method is indeed very sensitive, but also very time

consuming if an extended composition range has to be examined. Dr. Jakes mentioned that some of his measurements had lasted for about a year which requires the galvanic cells used to be very stable thermally.

Finally, two other examples of studies on non-stoichiometric oxide systems using the coulometric titration technique were presented. First Dr. T. Maruyama (Tokyo Institute of Technology, Japan) described his and Prof. Y. Saito's (same Institute) cell, which is also based on YSZ, but which was sealed with a glass. With this cell the phase relationships in  $\text{BaBiO}_{3-x}$  and  $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_{3-x}$  (superconductor at 15 K) had been established. These studies also suggested the existence of a new phase of  $\text{BaBiO}_{2.75}$  below 1050 K. Secondly, Prof. Y. Watanabe (National Defence Academy, Yokosuka, Japan) presented some recent results obtained on the  $\text{PrO}_{2-x}$  system. By using a cell similar to that described by Dr. Maruyama, the phase diagram for this non-stoichiometric system [ $\text{PrO}_{1.67}$ – $\text{PrO}_x$  ( $x = 1.6$  at 1200 K and  $x = 1.56$  at 1300 K)] was established by these measurements.

## V. OTHER NON-STOICHIOMETRIC COMPOUNDS DISCUSSED

The workshop was completed by a presentation of recent results obtained in studies on other non-stoichiometric compounds of interest to the energy field, as follows:

- (1) Ferrites (stoichiometric and non-stoichiometric)

Presented by Prof. V.S. Darshane, Institute of Science, Bombay, India.

- (2) Application of transition metal oxides in photoelectrolysis.

Presented by Dr. E. Pollert, Institute of Physics, Praha, Czechoslovakia.

- (3) Defect structure and transport mechanisms in stoichiometric and non-stoichiometric fluorides.

Presented by Dr. V. Trnovcová, Institute of Physics, Bratislava, Czechoslovakia.

- (4) Importance of oxygen activity in the gaseous environment of non-oxide substrates ( $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$ ) on their wetting behaviour and chemical interaction with a molten metal (Si). Presented by Prof. P.D. Ownby, University of Missouri, Rolla, MO, U.S.A.

Although the audience of the workshop was very interested in these contributions, unfortunately they cannot be discussed in detail in this report. For further information the reader should contact the speakers directly.

## VI. CONCLUSION

In addition to discussions of some very interesting non-stoichiometric systems, two important points emerged from this workshop. One, which is addressed to the organizers of future thermal analysis conferences, was a

strong recommendation that the scientific programme be subdivided into smaller sessions to allow a thorough discussion of contributions dealing with related types of materials not only from a thermal analysis, but also from a material point of view. The second concerns experimental techniques and is addressed directly to producers of thermal analysis equipment. As shown in the previous sections, in studies on non-stoichiometric compounds it is very important to be able to measure precisely the partial pressure of an active component in the atmosphere surrounding the sample. With oxygen this can be elegantly achieved by using oxygen sensors based on zirconia electrolytes, and it would be very helpful if sensors suitable for thermal analysis equipment were commercially available. For studies of non-stoichiometric systems, sensors of this type could also be very useful in other studies and routine measurements in controlled atmospheres, such as coal analysis and high-temperature corrosion. Finally, it was also clear that thermobalances with improved sensitivity would be very useful for the field of research discussed in this workshop.

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## NOTE ON THE OCCURRENCE OF OXIDES, SULPHIDES AND/OR OTHER OXYGEN-CONTAINING SUBSTANCES IN THE CONVERSION AND ACCUMULATION OF ENERGY

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For the sake of maintaining the original purpose of this workshop, which was also directed to the conversion and accumulation of energy, we attempt in this note to review briefly the role of oxygen-(and partly sulphur)-containing materials. First we recall that oxides and oxygen-containing substances are the most abundant compounds in nature as a whole. Refractory oxides such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are indispensable supporting materials in microelectronic devices and they also serve as important masking, passivating, antireflective and anticorrosive layers, etc. For solid-state photovoltaic devices oxides, however, do not play a decisive role as active semiconductor materials although for inexpensive conductor-insulator-semiconductor solar cells oxide semiconductor films of  $\text{ZnO}$  and  $\text{SnO}_2$  have been extensively investigated. In thin-film solar cells some sulphides show some promise, particularly heterojunctions of  $\text{Cu}_2\text{S}/\text{CdS}$  or cheaper  $\text{Cu}_2\text{S}/\text{Cd}_x\text{Zn}_{1-x}\text{S}$ , which exhibit as high as 10% efficiency with production costs ten times lower than those of silicon.

There are also promising photochemical devices that can be considered in two classes: (i) Devices where optical energy is converted into electrical energy, as in the previously mentioned devices except that the internal potential barrier producing a charge separation is created by a semiconductor-electrolyte junction. Examples are the redox potential of  $\text{H}_2\text{O}/\text{O}_2$  for polycrystalline thin films of  $\text{TiO}_2$  in  $\text{NaOH}/\text{HClO}_4$  electrolyte,  $\text{TiO}_2$  single crystals in  $\text{HCl}$ , the redox potential of  $\text{S}^{2-}/\text{S}$  for polycrystalline films and single crystals of  $\text{CdS}$  in the  $\text{NaOH}/\text{Na}_2\text{S}/\text{S}$  system. (ii) Devices where optical energy is converted into chemical energy by decomposing water into hydrogen and oxygen using platinum electrodes combined with oxides such as  $\text{WO}_3$ ,  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$  or  $\text{TiO}_2$ , with the titanides  $\text{MTiO}_3$  ( $\text{M} = \text{Sr}, \text{Ba}, \text{Ca}$  or  $\text{Fe}$ ), with tungsten bronzes of the type  $\text{K}_x\text{Me}_v^{5+}\text{W}_{x-v}^{5+}\text{W}_{1-x}^{6+}\text{O}_3$  or with perovskites,  $\text{Na}_x\text{Nd}_{1-x}\text{Ti}_x\text{Nb}_{1-x}\text{O}_3$ .

Other important groups of oxide materials, also exhibiting a high degree of non-stoichiometry, are solid-state ionic and/or mixed conductors, which are useful for converting chemical energy into electrical current in batteries or fuel cells. The anionic type of conductivity is exhibited by the group of oxides with high coordination numbers such as  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{HfO}_2$  and



ThO<sub>2</sub>, usually heterovalently substituted by Y<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, etc. For example, the most common material based on ZrO<sub>2</sub> can bear the metastable tetragonal phase (if it contains less than 4 mol-% of Y<sub>2</sub>O<sub>3</sub>) or is stabilized with a fluorite structure for more than 8 mol-% of Y<sub>2</sub>O<sub>3</sub>, or is partly stabilized by a fine monoclinic phase precipitated from the originally metastable ZrO<sub>2</sub> + 5 mol-% of Y<sub>2</sub>O<sub>3</sub>. The last material has become very important owing to its high resistance against fracture, necessary for ensuring the desired thin-wall geometry. Materials based on the pseudo-ternary system ZrO<sub>2</sub>-CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> are now used in, e.g., water vapour pyrolysis at high temperatures where dissociated oxygen migrates across the electrolyte wall in the direction of lower partial pressure of oxygen, electroneutrality being maintained by short-cutting of electrons through the solid.

The most important electrolytes with the cation type of conductivity so far used for sulphur/sodium batteries are those based on  $\beta$ -NaAl<sub>11</sub>O<sub>17</sub>, which, however, is difficult to prepare pure using the ordinary powder-ceramic technology. The necessary excess of sodium must be stabilized by introducing Li<sub>2</sub>O or MgO to form associated defects. The most promising materials seem to be solid solutions of composition Na<sub>3</sub>Zr<sub>2</sub>PSi<sub>2</sub>O<sub>12</sub>, which belong to the group of materials called NASICON based on the system SiO<sub>2</sub>-Na<sub>2</sub>ZrO<sub>3</sub>-ZrP<sub>2</sub>O<sub>7</sub>. Silver-type cation conductivity is exhibited by the complex crystalline compounds Ag<sub>7</sub>I<sub>4</sub>PO<sub>4</sub> or Ag<sub>6</sub>I<sub>4</sub>WO<sub>4</sub> and by the recently introduced glassy mixtures of AgI with Ag<sub>2</sub>SeO<sub>4</sub>, Ag<sub>2</sub>MoO<sub>4</sub>, Ag<sub>3</sub>AsO<sub>4</sub>, Ag<sub>2</sub>CrO<sub>4</sub> or Ag<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.

No less important is the selection of electrode materials. An anodic reduction potential makes it possible to employ oxide mixtures of LaCoO<sub>3</sub> or PrCoO<sub>3</sub> doped with SrO or better In<sub>2</sub>O<sub>3</sub> + 4 mol-% of SnO<sub>2</sub> in addition to the ordinary metals Co and Ni. For connecting cells in series, an electron-conductive material is necessary such as doped spinels of the CoCr<sub>2</sub>O<sub>4</sub> type or doped TiO<sub>2</sub>.

Many oxygen-containing compounds are used for solar or thermal energy storage in various types of systems using several principles, as follows.

Thermal energy storage (TES) using reversible hydration-dehydration reactions has been developed for a wide range of working temperatures. Zeolites or silica gel as adsorbents and also sodium sulphide (Na<sub>2</sub>S · 5H<sub>2</sub>O) (in Sweden the commercially successful TEPIDUS system) are the best examples of low- and medium-temperature TES systems. For changes in chemical potential associated with the drying of zeolites, CaO may be used in heat pumps or heat transformers. A heat pump may be based on the reaction of CaCl<sub>2</sub> with methanol. Drying and dilution of sulphuric acid has also been tested. For higher temperatures the hydration-dehydration cycle of CaO-Ca(OH)<sub>2</sub> was also tested. Many common inorganic salts such as nitrates, sulphates, sulphites and carbonates are the main components in systems utilizing the latent heat of phase changes; they may use a one-component system such as Glauber's salt encapsulated in a soluble envelope of

$\text{Sr}(\text{NO}_3)_2$ , or multi-component systems such as eutectic mixtures of  $\text{H}_3\text{BO}_3$  in  $\text{LiNO}_3$ - $\text{LiOH}$  or  $\text{KNO}_3$ - $\text{NaNO}_3$ - $\text{NaNO}_2$ . Carbon dioxide has been utilized in an energy storage cycle in which  $\text{CO}_2$  is electrochemically reduced to formic acid, which is catalytically decomposed to hydrogen and/or, in the SOLCHEM process,  $\text{CO}_2$  is reduced to methane and the latter is further converted by the EVA-ADAM process into hydrogen and carbon monoxide as a fuel. The large-scale chemical storage of heat based on the decarbonization of calcite at  $850^\circ\text{C}$  should also be mentioned here. So far, all tested large-scale TES systems in solar ponds, caves or systems using huge amounts of sand and/or rock have employed the cheapest natural materials such as water and natural silicates.

The same holds for old systems for energy storage and conversion by using compressed air, overheated steam and water with transfer basins in hydroelectric power stations.

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## **SOME APPLICATIONS OF EPITAXIAL FILMS BASED ON TRANSITION METAL MIXED OXIDES**

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The purpose of this note is to present a partial survey of the possible employment of single crystal films based on mixed oxides of transition metals. These films are grown on non-magnetic single crystal substrates by isothermal liquid phase epitaxy.

The most important and most thoroughly examined direction of industrial employment of these materials is magnetic bubble domain applications. Magnetic bubble devices are constructed using a thin film of an appropriate magnetic material. The dimensions, magnetization and magnetic anisotropy of this film must fulfil the conditions for the creation of magnetic bubbles, the presence or absence of which represents information. The magnetic bubble is a magnetic cylindrical domain, the vector of magnetization of which lies in the direction of an easy axis of magnetization of the material, but this is oriented perpendicular to the plane of the film and antiparallel to the magnetization in the film outside the bubble. Bubbles can be created, propagated, guided, switched, sensed and annihilated by a configuration of magnetic bars and/or electrical conductors deposited on the surface of the bubble film.

The appropriate magnetic properties can be achieved in three classes of crystalline materials: orthoferrites, hexaferrites and garnets.

Orthoferrites were the first materials to be investigated for magnetic bubbles. The orthoferrites have the formula  $RFeO_3$ , where R is a rare earth or yttrium. They have a high anisotropy and they are suitable for bubbles  $25 \mu\text{m}$  or larger. The study of these materials led to the conclusion that they could only support bubbles much larger than is useful for practical devices.

Hexaferrites have many varieties. They have the formula  $RFe_{12-x}A_xO_{19}$ , where R is Ba, Ca, Sr or Pb and A represents trivalent cations of Ga, Al, etc. The hexaferrites offer possibilities for bubbles smaller than  $1 \mu\text{m}$ , but their main disadvantage is the difficulty of growing good single crystal films.

The third class of materials are garnets of general formula  $\{M_{3-x}R_x\} [Fe_{2-y}A_y](Fe_{3-z}B_z)O_{12}$ . Different types of brackets are traditionally used to indicate the three different types of sites:  $\{ \}$  indicates dodecahedral sites, usually occupied by trivalent cations of the rare earths Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu, or cations of large diameter as Y, La, Bi, Ca or Pb; octahedral sites represented by  $[ \ ]$  and tetrahedral sites  $( \ )$  are occupied by smaller cations of Fe, Ga, Al, Ge, Si, etc. Garnet films are widely used in current device technology because they can be tailored to produce high-quality films and a wide variety of properties to support bubbles of size from  $0.1 \mu\text{m}$  to a very large diameter.

Garnets continue to find new applications. First there are magneto-optic applications, which can be roughly divided into two groups. The first group employs a high value of the Faraday rotation for the construction of devices, where the rotation of the polarization plane can be controlled by outside magnetic field, e.g., optical isolators, transfer of information, etc. The important measure of the usefulness of the material is the ratio of the Faraday rotation to the optical absorption. Thin films of  $(Y, Gd, Bi)_3Fe_5O_{12}$  with a Bi content of 1.1–1.2 atoms per formula unit of garnet appear as the most readily available. The second group of applications takes advantage of the garnet material for the temperature writing of information, e.g., printers and displays. Such applications require ferrimagnetic material with a compensation point near to room temperature. Yttrium iron garnets substituted Gd and Bi are acceptable.

Another very important application of ferrimagnetic garnets is in microwave techniques. Extremely narrow ferromagnetic resonance (FMR) curves make garnets of  $(Y, Bi)_3Fe_5O_{12}$  suitable for the construction of microwave filters and resonators.