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CHARACTERIZATION AND BULK PROPERTIES OF OXIDES\*

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### ABSTRACT

The bulk properties of oxides are divided into two classes, intrinsic properties which depend solely on the identity of the material, and extrinsic ones, which differ for different samples of the same compound. Sources of tabulated numerical values of intrinsic properties are given and modern developments in information storage and retrieval are discussed. Extrinsic properties are shown to depend on defects and trace impurities in the samples. Techniques of trace impurity analysis are discussed and realistic limits of detection and accuracies are given for routine analyses.

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## I. INTRODUCTION

The term characterization, as used in connection with materials, is rather difficult to define; its meaning appears to depend upon the user and the context. One published<sup>1</sup> definition is the following: "Characterization describes those features of the composition and structure that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material." Thus, to characterize a structural steel one would want to know what features influence its mechanical properties, as for example, alloy components and aggregation states. On the other hand, to characterize material for an optical element (e.g., a lens), intrinsic properties of the material, such as band gap and refractive index, are important. When people talk of characterization, the particular "features of the composition and structure" that are relevant to the particular context or use are usually not specified. Moreover, the relationships between "features of composition and structure" and specific properties are poorly understood.

In this lecture I will try to keep the importance of these relationships in mind. I will start with a broad list of properties, in each case describing how, on one hand, values of these properties might be related to composition

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and structure, and on the other, how they might be used as a tool to determine composition and structure. The properties discussed will be divided into two classes, intrinsic and extrinsic. Intrinsic properties will include those that are relatively invariant in different samples of the same material and can be used to identify it. Extrinsic properties are those that vary from sample to sample and depend upon the mode of preparation of the sample and its history.

Table I is a list of properties that will be discussed. The intrinsic properties are appropriate for characterizing, for example, samples of mixed ceramic, where the number, identity and composition of mixed phases is important. We have made an effort to include a reasonably complete list of reference works in which numerical values for the intrinsic properties of many oxides are recorded. As regards extrinsic properties, we will discuss how these properties might be related to the defect and trace impurity content of samples of a given material. A discussion of techniques of trace impurity analysis follows. In a separate presentation<sup>2</sup> the present status of understanding of transport properties in one compound, MgO, will be discussed to show how inadequately we understand the relationship between these properties and the defects and impurities giving rise to them.

## II. INTRINSIC PROPERTIES

### A. Melting Point

The most often quoted identifying property of any material is the melting point. Its measurement is fairly straightforward, either by observation of a melting crystal or by noting the thermal arrest upon cooling. Table II is a typical list of oxides and their melting points. Since we are limiting ourselves to refractory materials, only oxides with melting points above 1700°C are included. It should be pointed out values in Table II and similar tables

in the literature may have uncertainties of 50 or 100°C. More complete data and references on melting points of binary oxide compounds are given in the literature.<sup>3-7</sup> A number of handbooks<sup>8,9</sup> give values but do not include references. Specific recent values and references to work that is not included in the compilations can be obtained from the Molten Salt Data Center.<sup>10</sup>

### B. Structure and Density

A general idea of the symmetry of the structure can sometimes be obtained from observation of the growth facets or cleavage planes of a crystal; whether or not a crystal is cubic can be determined by placing it between crossed polarizers and looking for birefringence. But to obtain detailed knowledge of the structure of a sample, x-ray (or neutron) diffraction data must be carefully Fourier analyzed. There exist excellent collections of x-ray data that include most of the ceramic compounds.<sup>11-13</sup> The data of Ref. 13 are also kept on tape and are updated as new information becomes available. Specific information from these tapes can be obtained from the Crystal Data Center<sup>14</sup> of the National Bureau of Standards (U.S.A.).

The density of a sample of any shape is easily measured by comparing its weight in air with that in an appropriate liquid (water, if the oxide is not hygroscopic). For samples that do not contain voids the density is characteristic of the material and is related to the structure and lattice constant. For example, it is easily shown for a sample with the NaCl structure that the so-called theoretical density (density calculated from crystal structure data) is given by  $d = 4M/a^3A$ , where  $M$  is the molecular weight,  $a$  is the lattice constant and  $A$  is Avogadro's number. Unfortunately, many of the standard tables<sup>8,9</sup> do not state whether the values given are theoretical densities or measured densities of samples that contained voids.

Many of the transition metal and rare earth oxides are ferro-, ferri, or antiferromagnetic, particularly at low temperatures. The magnetic structures of the ordered (non-paramagnetic) phases of many of these compounds have been determined by neutron diffraction methods and are tabulated.<sup>15,16</sup> Moreover since many of these compounds undergo magnetic phase changes at characteristic temperatures, tabulations of Neel and Curie points<sup>15,16,17</sup> are very useful for identifying the compounds.

### C. Phase Diagrams

Phase diagrams are not, themselves, material properties. They provide, however, a convenient way of representing a number of properties of solid materials in a semiquantitative fashion. For example, they contain information on the variety and composition of compounds that will form from two elements or compounds. They provide melting point data, temperatures of phase changes, and information on solubilities.

The complexity of a phase diagram is related to the bonding of the constituents. For example, let us compare the system, magnesium and oxygen, with the one titanium and oxygen. The outer shell of the Mg atom contains only two 3S electrons, whereas Ti has two 3D and two 4S electrons. The only simple way for Mg to bond to oxygen is for the two 3S electrons to fall into the oxygen 2P level. For Ti, however, any two of the 4 outer electrons can fill the oxygen shell, allowing for a variety of bonded configurations. The phase diagrams reflect this difference; the Mg-O phase diagram is extremely simple; there is only one compound MgO existing over an extremely narrow composition range at 50%. That compound has the same structure throughout the temperature range of existence of the solid.

In contrast the phase diagram for the Ti-O system,<sup>18</sup> reproduced in Fig.1, is extremely complex. It shows that numerous combinations of  $Ti_xO_y$  are possible, and that many of these combinations have different structures, not only as a function of relative concentration of Ti and O but also as a function of temperature. The series of combinations  $Ti_nO_{2n-1}$  shown near the right side of the diagram are an example of related structures that can all be thought of as being made up of basic identical blocks of crystals separated by line or planar defects<sup>19</sup> (for example, shear planes). The crystalline orientation or separation of these defects determines the overall composition. Such Magneli phases and related structures also occur in other transition metal oxides. Before it was understood how line and planar defects form ordered arrays, "characterization" of transition metal oxides with respect to structural properties left much to be desired.

There exist excellent compilations of phase diagrams that include binary as well as more complex oxide systems.<sup>20,21</sup> Phase diagrams are occasionally modified as more detailed information becomes available and is incorporated.

#### D. Optical Properties

Since most of the oxides are transparent, the index of refraction can be used to identify a sample. It is particularly useful for glasses and mutually soluble oxide systems for which the refractive index is known as a function of composition. The refractive index along particular symmetry axes has also been used for many years to identify minerals and other single crystal samples of inorganic compounds. Most of the numerical data in handbooks<sup>3,7,8,22</sup> is limited to the wavelength of the yellow sodium lines. There is some data published of index vs wavelength, but for most materials it is necessary to find the original literature. ~~Data on the index of refraction as a function of~~

composition of a number of oxide systems is given, together with phase diagrams.<sup>20</sup>

The transparency range of many of the oxides is large and data on the reststrahlen absorption<sup>23</sup> and the ultraviolet absorption edge<sup>23,24</sup> are compiled for a number of oxide materials. The data are not at all complete and it must be remembered that an experimentally determined absorption edge may depend on impurities in the sample.

#### E. Elastic Properties

Values of the Young's Modulus and Shear Modulus are of great practical importance and measured values are occasionally listed or quoted for polycrystalline ceramics.<sup>25</sup> However, these parameters are of limited use in identifying materials, since their values may vary as much as a factor of 2, depending upon crystallite size, orientation and void volume. The elastic constants, which are more difficult to measure and require large single crystal samples are, however, intrinsic material properties; many of their values are tabulated.<sup>26,27</sup> Elastic moduli, such as the Shear modulus, that one might measure for uniform isotropic polycrystalline samples can be calculated from the elastic constants.<sup>28,29</sup> Values so calculated are also tabulated.<sup>27</sup>

#### F. Thermal Properties

According to simplest theory the normal vibrations of the crystal may be considered as independent oscillators, and the resultant molar heat capacity at constant volume approaches the value  $3nR$  at high temperatures. In that expression  $n$  is the number of atoms per molecule and  $R$  is the molar gas constant. More accurate, empirical values of the heat capacity at constant

pressure are tabulated.<sup>4,30,31</sup> For temperatures near and below room temperature measured values are usually given in tabular or graph form. For high temperatures it is often possible to fit an expression

$$C_p = a + bT - cT^{-2}$$

so that only three constants, a, b, and c have to be tabulated.

Data on the thermal conductivity and thermal expansion of ceramic materials is of interest for engineering applications; measured values for many oxide materials are tabulated or given in graphic form.<sup>4,32,33</sup>

### III. SOURCES OF NUMERICAL DATA AND REFERENCES

In the foregoing discussion I have made reference to the most useful compilations of data. However, no tabulation is complete; moreover, any published compendium has a cutoff date, and work completed after that date is not included. There have been a number of developments in information storage and handling with which scientists are only vaguely familiar. I would like to describe two such developments which might be of help to the researcher requiring information not available in published compilations.

#### A. Computerized Bibliographies

Abstracts of scientific papers, which in the past were indexed and could be found in abstract journals such as Chemistry Abstracts, are now recorded on computer accessible magnetic tape.<sup>34</sup> These tapes can be used for producing specialized literature searches, not only according to subject or author but also according to descriptive words in titles (and in some cases abstracts). Moreover, the computers<sup>35</sup> containing these tape data bases are in many cases accessible by phone link, allowing individual researchers rapid access to

the tapes. In practice it turns out to be quite an art to use "correct" descriptive words, and efficient combinations of descriptions using Boolean logic to obtain the desired references without being deluged with irrelevant material.

### B. Information Centers

These centers are stores of bibliographic and numerical information on highly specialized and limited topics.<sup>36</sup> They differ in the services they perform. Most will supply literature references to answer questions posed in a mail request. Some centers publish specialized bibliographies regularly and others use their stored information to produce compendiums of data. For the scientist working in the precise area covered by an information center, its services can be of immense help. However, it is essential that the researcher ask the right question. For example, a letter to a center might request information on "the optical and electrical properties" of a specific compound, when in fact what is needed is a material of, say, optical transmission in a certain range and a high electrical resistivity. Neither of these properties might be properties of the compound inquired after. The question, if answered as given, would generate a large volume of useless information. A good information center would require that the inquiry be more specific and that the intended use of the material be given. The response might then be the suggestion of a more appropriate compound. In brief, inquiries have to be both specific and complete.

## IV. EXTRINSIC PROPERTIES

### A. Optical

Most of the refractory oxides, in particular the stoichiometric compounds of low atomic number cations, have a wide window of transparency between the

vacuum ultraviolet range ( $\sim 1500 \text{ \AA}$ ) and the infrared ( $\sim 10$  microns). Small concentrations of impurities or defects can give rise to absorption bands within that transparent range. Chromium in  $\text{Al}_2\text{O}_3$ ,<sup>37</sup> for example, is well known as the source of the red color of ruby; iron in  $\text{MgO}$  produces a yellow or greenish tint, depending on the concentration and valence state of the iron; and cation vacancy related defects (V centers) give rise to a violet color in  $\text{MgO}$ .<sup>38</sup>

The colors produced in oxides by transition metals (or rare earths), are due to transitions in the partially filled d (or f) subshells. In the normal atom such transitions are forbidden; however, the crystal field splits the levels of the subshells and mixes in non-d-like (or non-f-like) character from excited states, making transitions partly allowed. The effects of crystal fields on d and f level ions has been treated in the literature.<sup>39</sup> Many of the absorptions due to transition metal ions occur in the visible or near infrared.

Another class of electronic transitions, which is allowed and, therefore, may be caused by quite small traces of impurities is that for which an oxygen p electron is transferred to an empty transition metal d level. The absorption bands corresponding to these transitions are called charge transfer bands, because an electron is transferred from an oxygen ion to the impurity. Lattice defects also give rise to absorption bands in the forbidden gap of oxides.  $\text{V}^-$  centers in  $\text{MgO}$ <sup>40,41</sup> which consist of missing cations with an adjacent trapped hole give rise to an absorption band in the visible (2. eV). F and  $\text{F}^+$  centers which involve oxygen vacancies yield absorption bands in the ultraviolet.<sup>42-45</sup> These defect centers have been identified with varying degrees of certainty in a number of refractory oxides and have been described in the literature.<sup>46</sup>

In addition to producing absorption bands that correspond to electronic

transitions, impurities give rise to absorption corresponding to localized vibrational modes. These bands occur in the infrared and are often hidden within the reststrahlen absorption unless the vibrating impurity ions are lighter than the host ions. Quite a bit of detailed information about light impurities and defects, mostly in halides, has been obtained from studies of infrared vibrational absorption.<sup>47,48</sup>

Light scattering may be caused by certain impurities and defects. Classical scattering occurs if impurities and defects form aggregates. Raman scattering is a process by which incident light is scattered with a change in energy corresponding to a difference in energy of two (usually) vibrational states of the impurity system. Raman scattering techniques are coming into more frequent use for detecting and learning about localized vibrations of light impurities in oxide crystals.<sup>49</sup>

When energy is absorbed in a crystal some of the energy may be remitted as light. Such luminescence can be detected with great sensitivity; fewer than  $10^{11}$  luminescing ions can give rise to detectable emission. Luminescence is of practical as well as great basic interest.<sup>50</sup> The phenomenon is exploited in such diverse products as fluorescent lights, television tubes, and particle counters. In its barest essentials, luminescence requires 1) absorption of energy and resultant excitation or, 2) transfer of this excitation to a site where it may be emitted, and 3) emission of light. The energy transfer process is unnecessary when the absorbing and emitting entity is the same, as is the case for many defects in halides and oxides. Although both absorption and emission of energy may occur by ions of a pure crystal, (e.g.,  $\text{CaWO}_4$ ,  $\text{YVO}_4$ ,  $\text{NdP}_5\text{O}_{14}$ ), most luminescent systems involve a defect or impurity either as absorber (sensitizer) or emitter (activator), or both. Many commercial

phosphors contain dopants in the percent range. However, impurities in the parts per million range have significant effects on the luminescence of some systems, as does, for example, thallium in alkali halides.

### B. Magnetic Properties

The contribution of paramagnetic centers to the susceptibility can be written<sup>51</sup> as

$$\chi = \frac{1}{H} N g j \mu B_j (g j \mu H / kT) \approx N g^2 j(j+1) \mu^2 / 3kT$$

where  $N$  is the density of paramagnetic centers,  $j$  is the total spin of an ion,  $\mu$  is the Bohr Magneton and  $B_j$  is the Brillouin function. The right side of the equation is valid for small  $g j \mu H / kT$ . At room temperature and above, the total susceptibility is made up predominantly of the diamagnetic contribution of the host crystal. However, since the paramagnetic contribution of defects and impurities increases inversely with the temperature, it may dominate, or become a significant contribution below liquid nitrogen temperature. By making measurements at liquid helium temperature the contribution of  $10^{16}$  paramagnetic ions per  $\text{cm}^3$  (.3 ppm) can be measured.

Moreover, as the right side of the equation shows, the temperature dependence of the susceptibility gives a direct measure of the product  $N g^2 \mu j(j+1)$ . If the identity of the paramagnetic center is known, so that  $g$  and  $j$  are specified, the density of centers is determined. However, that the susceptibility reflects the sum of the contributions of all paramagnetic centers, impurities, and defects alike.

A much more specific property which allows identification of paramagnetic centers is electron paramagnetic resonance. Its use will be discussed by other

speakers at this conference.

### C. Mechanical Properties

Most of the work on the effect of impurities and point defects on plastic flow has been done with metals; however, it has been shown that hard oxides, as for instance MgO, also deform plastically and that plastic flow ultimately gives rise to fracture.<sup>52</sup> The onset of plastic flow in MgO has been shown to occur for greater stresses when MgO contains transition metal ions.<sup>53</sup> Impurities such as Li also produce significant increases in the flow stress.<sup>54</sup>

### D. Thermal Properties

The thermal conductivity of solids is limited by scattering of phonons carrying the thermal energy. At room temperature and above, thermal vibrations are the most important source of scattering. However, at low temperature defects and impurities contribute significantly to the scattering of phonons, so that the thermal conductivity is a function of the concentration and the state of aggregation of impurities and lattice defects. Interpretation of the measurements are difficult and the theory is complex; however, much of the actual data is tabulated.<sup>55</sup>

### F. Transport Properties

In the following paper<sup>2</sup> the present status of our understanding of ion transport in MgO is discussed and shown to be very limited. Our understanding

of transport properties in other insulating oxides is similarly unsatisfactory. There has been a significant amount of progress in understanding electron transport in conducting transition metal oxides.<sup>56</sup>

## V. ANALYSIS OF IMPURITIES

From the previous discussion it should be clear that small amounts of impurity can have a very large influence on extrinsic properties of refractory oxides. The elucidation of mechanisms by which impurities influence these properties is a major goal of much of present day basic materials research. It follows that the determination of the impurity content of experimental samples should have high priority as part of any study of these properties. Yet in much of the literature samples are labeled as "pure," "very pure," or "doped," and usually no quantitative information is given on the amount of dopant or the presence of trace impurities. In the remainder of this talk, I will describe the more common techniques for impurity analysis, particularly those techniques appropriate for commercial analytical laboratories. I will try to indicate what can and cannot be accomplished under conditions where analyses are made by someone other than the researcher.

### A. Multiple Element Technique

We include here techniques that have sensitive detection limits for a large number of elements and in which one measurement produces data for determining the presence (or concentration) of a number of elements.

1. Atomic Emission Spectroscopy. A sample of approximately 10 mg is crushed or dissolved and placed in a depression in one of the graphite electrodes of an electric arc. When the arc is struck the sample is vaporized and broken up into atoms. The atomic emission lines of the various elements are identified

from a photograph of the emission spectrum. This is a simple, inexpensive technique for qualitative analysis of almost any sample. However, detection limits are not very low; specific line intensities differ greatly for different elements and because of atomic absorption within the arc, emission intensities are not proportional to concentration.

2. Spark Source Mass Spectrometry. About 10 mg of sample, preferably in solution, but otherwise in powder form is incorporated as part of an electrode of a spark source. The spark vaporizes a small amount of the electrode. The vaporized ions are then accelerated and analyzed in a mass spectrometer. Even though the spark source is not reproducible in an absolute sense, the relative efficiency of ionization of elements of slightly different atomic mass is reproducible, so that "spiking" of the electrode with an isotope not normally present in the sample allows quantitative measurement.

3. Neutron Activation Analysis. A sample is irradiated in a reactor, in a location where predominantly thermal neutrons are present. Since the decay rate of different radioactive isotopes varies greatly, making measurements after different doses and different decay periods allows separation of groups of isotopes. The routine procedure used at ORNL is to make three irradiation-count cycles. The sample is first irradiated 10 s and counted immediately, then reirradiated 120 s and counted after 10 min when short lived isotopes have decayed. The final irradiation is for 20 min with a decay of 2 days or longer. The gamma rays are counted with a Si:Li detector, and their energy spectra are analyzed with the help of a computer. For accurate quantitative measurements it is sometimes necessary to dissolve the sample or do a chemical separation of either an element sought or an interfering element.

4. X-ray Fluorescence. For this technique relatively large samples in the form of thin solid discs are used. If the original sample is unsuitable,

it is incorporated into a pressed disc of an organic (low atomic number) material. Irradiation is with monochromatic x-rays, for example, from a silver target diffracted off a monochromator crystal to remove all but the Ag  $K_{\alpha}$  line. The fluorescence of the elements in the sample is then counted with a Si:Li detector, and from the energy spectrum of the emission the presence and concentration of elements within the sample are determined. Another method of analyzing the x-ray fluorescence is with a dispersing crystal and photographic detection. Since the exciting x-ray source can be made very reproducible, comparison of the sample with standards allows quantitative measurements to be made.

#### B. Techniques for Quantitative Analysis of Single Elements

Multiple analysis techniques are not always adequate. Mistakes in identification can occur, and there are limits of resolution so that elements may be hidden by other contaminants. For that reason the following single element techniques are often necessary for quantitative analyses:

1. Atomic Absorption Spectrometry. Samples of approximately 1 g are dissolved and injected as a liquid into a flame, furnace, or plasma. In that environment the sample is quickly dried, vaporized, and broken up into its atomic constituents. The sample is illuminated by light from a <sup>one element</sup> single emission lamp. This light is absorbed in proportion to the amount of the element present in the vapor. Atomic absorption analysis is highly specific for a given element. It is reliable and gives excellent quantitative values with low detection limits for a number of elements that are difficult to detect by other means (e.g., Li, Cd, K, Mg).

2. Chemical Methods. These methods have become less popular in recent years because each analytical problem requires the development of a method and

technique. Nevertheless, when the general methods mentioned above fail, classical chemistry can often provide very accurate results. In general, dissolution and treatment of the sample to separate the desired element from others is required, so that the possibility of contamination is present. The concentration of the elements sought is determined by methods such as titration, electrochemistry (polarography and related methods) or by complexing with an agent that produces intense absorption of light.

### C. Accuracy and Limits of Detection

For more detailed discussion of analysis techniques, there are a number of texts and reviews.<sup>57</sup> In Table III is a summary of the techniques explained above, giving advantages and disadvantages, accuracy and detection limit ranges. The parameters given in Table III are estimates for a researcher who requests a routine analysis but has no direct control over the analytical procedures. In the literature,<sup>57</sup> where development of specific techniques is discussed, detection limits may be two orders of magnitude lower and accuracies may be much better than those shown in Table III. This is not surprising, when one realizes that for a routine analysis done on a production line basis, conditions are rarely optimum, and time is rarely available to do as careful a job of sample handling as would be done during the developmental phase of an analytical technique. <sup>A<sub>v</sub></sup> Two examples of what detection limits and accuracies are to be expected in real life are indicated in Table IV where we show results, ~~on one hand,~~ of analyses of transition metals in MgO obtained by a variety of techniques, ~~and on the other,~~ two sets of quantitative neutron activation analyses, ~~performed on identical samples~~ by two different laboratories. Let me repeat, there is a big difference between the theoretical precision of an analytical technique and that obtained when analyses are done according to a general routine that is not necessarily optimum for the purposes of the researcher.

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TABLE I. PROPERTIES OF REFRACTORY OXIDES

Intrinsic Properties

Melting Points

Structure: Crystal structure; density; magnetic structure,  
structure transitions

Optical: Index of refraction; band gap

Elastic Properties

Thermal Properties: Heat Capacity, Thermal Expansion

Extrinsic Properties

Optical: Absorption, scattering, emission

Magnetic: Susceptibility; electron paramagnetic resonance

Mechanical: Elastic limit

Thermal Conductivity

Transport: Ion diffusion; electrical conductivity, reaction rates

TABLE II. MELTING TEMPERATURES OF REFRACTORY OXIDES

<u>Binary Compounds</u>		
<u>Compound</u>	<u>Temperature</u> (deg C)	<u>Comments</u> *
BeO	2570	Toxic
MgO	2800	Vaporizes T > 1700 OA; T > 1900 RA
Al <sub>2</sub> O <sub>3</sub>	2030	
SiO <sub>2</sub>	1720	
CaO	2600	Hygroscopic at R.T.
Sc <sub>2</sub> O <sub>3</sub>	2400	
TiO <sub>2</sub>	1850	URA
Y <sub>2</sub> O <sub>3</sub>	2400	
Cr <sub>2</sub> O <sub>3</sub>	2300	URA
MnO	1780	UOA
Fe <sub>2</sub> O <sub>3</sub>	1560	
CoO	1800	URA
NiO	1950	URA, reacts with oxygen 400 < T < 600
ZnO	1975	URA, volatile T > 1700
Ga <sub>2</sub> O <sub>3</sub>	1740	URA
V <sub>2</sub> O <sub>3</sub>	1977	Uncertain
ZrO <sub>2</sub>	2690	
MoO <sub>2</sub>	1930	
BaO	2000	UOA
La <sub>2</sub> O <sub>3</sub>	2300	Hygroscopic RT
CeO <sub>2</sub>	2650	URA
Other Re <sub>2</sub> O <sub>3</sub>	2000-2460	
HfO <sub>2</sub>	2900	

TABLE II (Cont'd)

Binary Compounds

<u>Compound</u>	<u>(deg C)</u>	<u>Temperature</u>	<u>Comments</u> *
Ta <sub>2</sub> O <sub>3</sub>	1880		
ThO <sub>2</sub>	3300		
UO <sub>2</sub>	2800	UOA	

Complex Oxides

<u>Compound</u>	<u>Name</u>	<u>Temperature</u>	<u>Comments</u>
BeAl <sub>2</sub> O <sub>4</sub>	Chrysoberyl	1870	
BeSiO <sub>3</sub>		1750	
Be <sub>2</sub> SiO <sub>3</sub>	Phenacite	1800	Incongruent Melting
MgAl <sub>2</sub> O <sub>4</sub>	Spinel	2150	
MgFe <sub>2</sub> O <sub>4</sub>	Magnesioferrite	1750	
Mg <sub>2</sub> SiO <sub>4</sub>	Forsterite	1900	
3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	Mullite	1800	Incongruent Melting
CaTiO <sub>3</sub>	Perovskite	1950	
CaZrO <sub>3</sub>		2350	
ZrSiO <sub>4</sub>	Zircon	2420	Dissociated T > 1750
ThZrO <sub>4</sub>		>2800	

\* URA = unstable in reducing atmosphere at temperatures below the melting point.  
 UOA = unstable in oxidizing atmosphere at temperatures below the melting point.  
 RT = room temperature

TABLE III. ANALYTICAL TECHNIQUES

Technique	Sample Size (mg)	Typical Detection Limit (ppm)	Typical Accuracy	Advantages	Disadvantages	Variations
Atomic Emission	10	0.1-1000	$\times 3$	Cheap, simple, detect almost all elements	Intensity not a concentration; arc conditions difficult to reproduce for comparisons; sample is destroyed	Other types of excitation of sample, e.g. r.f. plasma, flame
Spark Source	10	1-10	$\times 3$ $\pm 20\%$ (with isotope spiking)	Commercial equipment available; useful for most elements; intensity concentration; sample can be used repeatedly	Spark source not reproducible; requires adding known isotope for quantitative use; appropriate comparison isotope not available for all elements	
Neutron Activation	25	.001-1	$\pm 10\%$	can be done without sample preparation; does not destroy sample; good for more than 80 elements with very sensitive detection limits	requires nuclear reactor; computer necessary for general analysis	greater accuracy if sample is dissolved
X-Ray Fluorescence	3000	10-100	$\pm 20\%$ (minor) $\pm 10\%$ (major)	useful for all elements $Z \geq 10$ ; solid sample can be used; does not de-sample	Large sample necessary; still developmental	different monochromatic sources of x-rays

TABLE III. ANALYTICAL TECHNIQUES (Cont'd)

Technique	Sample Size (mg)	Typical Detection Limit (ppm)	Typical Accuracy	Advantages	Disadvantages	Variations
Atomic Absorption	1000	1-1000	±20% (minor) 10% (major)	Specific for given element; well developed, reliable technique	sample is destroyed; requires solution; insensitive with small sample; measures only one element	various methods of atomizing sample, e.g., furnace, plasma light sources for simultaneous measurement of 3 elements available; atomic fluorescence can also be measured
Electro-	100	0.1-100	10% (minor) 5% (major)	can be used simultaneously for a small number of constituents; can be set up by researcher	requires solution; useful chiefly for transition metals and middle of periodic table	
Molecular Complexing	1000	0.1-10	10%	cheap, requires only inexpensive equipment; can be set up by researcher	requires chemical separation	can also detect fluorescence