

## EXPERIMENTAL DETERMINATION OF PHASE EQUILIBRIA DIAGRAMS IN CERAMIC SYSTEMS

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A phase equilibria diagram is a pictorial representation of the thermodynamic equilibria between phases in any given chemical system and must obey the Gibbs Phase Rule,  $P+F = C+2$ , where  $P$  = the number of phases,  $F$  = the degrees of freedom and  $C$  = the number of components. However, in practice, the experimental phase equilibria diagram is a compromise between the constraints imposed by the Phase Rule and the observed experimental data, colored by the experimentalist's prejudices. The latter of course are dependent on the type, amount and quality of the experimentalist's education and experience. Furthermore, the results are very strongly dependent on the type of experimental data accumulated, and the sophistication of the instrumentation utilized. For all these reasons, the phase equilibria diagram for a given system tends to change with time. As more and more data are accumulated by more and more workers, the diagram should become more representative of the true equilibrium conditions. However, it is very likely that no diagram is ever completely finished. Nevertheless, even crudely constructed diagrams based on very little experimental data can be of value to the industrial community. Any real information is better than none at all! The discussion of experimental techniques and problems involved in the determination of phase equilibria diagrams will be limited to temperature–composition diagrams at constant pressure. The talk includes specific examples of ceramic oxide systems chosen to illustrate problems associated with phases with possible “ions in motion”.

### 1. Introduction

A phase equilibria diagram is a plot of the phases present under conditions of varying temperature, pressure and chemical composition. Only these three variables can be used to depict a phase equilibria diagram. The simplest diagrams are those in which one of these variables is held constant (most often pressure) and the other two are allowed to vary. Time is never one of the coordinates or variables in a phase equilibria diagram, nor are unit cell dimensions, density, magnetism, conductivity, or any other useful or important physical property.

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The following discussions of experimental techniques and problems involved in the determination of phase equilibria diagrams will therefore be limited to temperature–composition diagrams at ambient pressure ( $\approx 10^5$  Pa or 1 atm), generally air, although occasional reference may be made to problems involving the control of oxygen partial pressure ( $P_{O_2}$ ). The discussion will involve specific examples of ceramic oxide systems, although many of the techniques and problems **are** directly or indirectly applicable to metallic, carbide, nitride, sulfide, etc. systems. Most of the examples are from experimental phase equilibria studies carried out in the Ceramics Division of the National Bureau of Standards (now renamed the National Institute of Standards and Technology) during the last  $\approx 50$  years. Most of the studies were carried out in the Solid State Chemistry Section which was a group comprised of two previously existing smaller entities devoted to experimental research in phase equilibria and crystal growth. Most of these diagrams have been (or will be) reproduced in the reference compilation “*Phase Equilibria Diagrams*”<sup>1</sup>, known prior to 1992 as “*Phase Diagrams for Ceramists*”.

Among the first 92 elements in the periodic table, 59 have oxides which are solids at room temperature. Thus there are 1711 binary oxide systems of possible interest to ceramists. Of these, many have no published diagram and very little published data. The number of ternary and more complex systems quickly become practically impossible to enumerate, so that studies for a given system should be chosen for their possible usefulness.

## 2. Techniques and Methods of Specimen Equilibration

There are two main methodological approaches to the preparation of “equilibrated” specimens: (1) static and (2) dynamic. In the first, specimens are synthesized at high temperature and examined or characterized at room temperature. In dynamic methods, test specimens are characterized in situ during the heat treatment.

### 2.1. Static

Static techniques are both less expensive and easier to use in experimental studies of the phase equilibria in a given system. Therefore, these are the most commonly used methods to prepare specimens and collect data. The synthetic method is often known, not necessarily disparagingly, as the “shake-and-bake”

technique or “cookbook-chemistry”, although “heat-and-grind” may be more applicable.

### *2.1.1. Specimen Preparation*

Specimens are prepared by weighing, to the nearest tenth of a milligram (0.0001 g), appropriate amounts of each chemical in the system on a molar basis. (In studying a phase diagram, crystal chemistry is so important that the compositional coordinates of the diagram should always be in mole fraction (mol%) rather than mass fraction (wt%)). The specimen is then mixed in a manner that will minimize the introduction of impurities while maximizing the degree of homogeneity. This is usually done by wet grinding in an agate mortar and pestle, generally with an acetone or alcohol medium. Ball milling in alumina or zirconia mills (or other hard ceramic mills) is not recommended unless a pre-determined amount of the chemicals in these mills is to be deliberately added to the specimen.

Wet-mixed specimens are allowed to dry in the mortar, then scraped out and pressed into disks in a hardened steel die. The disk size depends on the batch volume, the height of the disk being no more than about half its diameter. The disk is preferable to loose powder as it allows closer contact between particles. Loose powder is used only if pressure caused by internal grain growth inside the pellet is undesirable; it is not used if contamination with the container is undesirable. Loose powder should only be used if the grain size has been minimized and homogeneity has been maximized using better methods than hand wet-mixing as previously described. When pellets are used, contact with the container or setter plate can be eliminated by using a very thin sacrificial pellet of the same composition under the specimen to be heated. Volatility can also be minimized if necessary by imbedding the pellet in (sacrificial) powder of the same composition and/or using tightly closed or even sealed containers. The containers or setters should be made of the “least-likely-to-contaminate” material. This is most often a “noble” metal such as Ag, Au, Ag/Pd, Pt or even Ir, depending on the temperature of calcination.

### *2.1.2. Calcining*

The specimen is calcined at a temperature well below its possible melting point and well below any possible solidus in the chemical system. However, the calcining temperature must be high enough to promote solid-state reaction and

an appreciable increase in chemical homogeneity via diffusion and subsequent grain growth. This temperature is generally called the Tamman temperature and can be estimated as  $2/3$  of the melting point in degrees Kelvin. The specimen is calcined for an appropriate period of time to cause the desired homogeneity, varying from a few hours to a few days depending on the system. It is then removed from the furnace, ground in a mortar and pestle (again avoiding container contamination as much as possible), repressed, and refired at the same or higher temperature. Grinding and reheating are generally both necessary and desirable as new surfaces are exposed and recombined for further reaction; the decrease in particle size also results in shorter diffusion paths and enhanced reaction rates. According to synthesis lore, “A *single grinding is worth 2-3 times the normally utilized time for calcining*”; however, it should be kept in mind that each chemical system is unique! Time, temperature, and furnace-type must vary according to the chemical nature of the system; all must be estimated beforehand and changed if the estimation proves to be incorrect.

Remember the definition of the scientific method: “The method of multiple working hypotheses”. In the field of the experimental determination of a phase equilibria diagram this can be modified to: “The method of multiple working prejudices”. The experimenter must be prepared to change his prejudices with each experiment. More will be said about this later.

The first calcining is generally done at a temperature between 600-1000 °C for almost all ceramic oxide systems depending on the melting point of the lowest melting end member. This heating is therefore most likely to be done in a furnace utilizing nichrome or Kanthol<sup>b</sup> heating elements. The latter are most commonly used today and can be used in either a horizontal (front loading) or vertical (top or bottom loading) furnace for sustained periods at 1000 °C. After the specimens have been calcined at the first temperature for the desired number of times it is sometimes advisable to recalcine at some higher temperature. Higher temperatures are generally achieved in furnaces heated with MoSi<sub>2</sub> heating elements although lanthanum-chromite based elements, SiC, or Pt wire heaters can also be utilized.

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<sup>b</sup> Certain trade names and company products are identified in order to adequately specify the experimental procedures and do not imply recommendation or endorsement by the National Institute of Standards and Technology.

### 2.1.3. Equilibration

Although a calcining-type furnace can obviously be used to equilibrate a specimen, this is definitely not advised for accuracy. Such furnaces can be calibrated, at best, to  $\pm 10$  °C to  $\pm 25$  °C. For acceptable results of precision and accuracy a vertical quench furnace is the best design. In the early days, vertical quench furnaces generally consisted of several  $\text{Al}_2\text{O}_3$  tubes wound with Pt or Pt/Rh wire. However, the prohibitive cost of Pt and especially Rh, and the availability of  $\text{MoSi}_2$  heating elements, have caused a change in design. The geometry of the vertical furnace is illustrated in Figure 1.

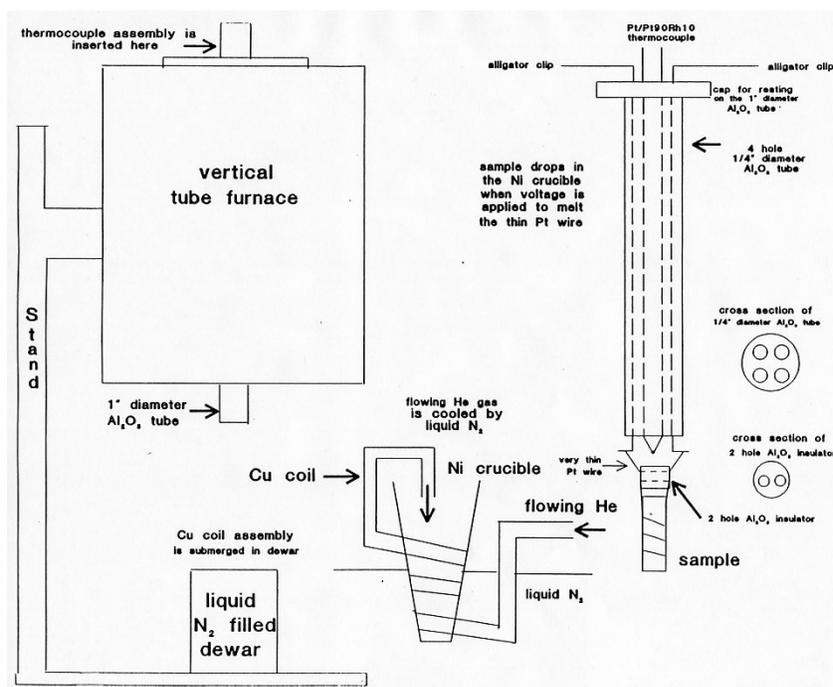


Figure 1. Schematic diagram of a quench furnace arrangement illustrating the liquid-N<sub>2</sub>-cooled He quench cup and the specimen holder assembly.

$\text{MoSi}_2$  "hairpin" elements are arranged around the inside of a cylindrical insulated furnace. Depending on the diameter of the furnace and the size of the heating elements, 4, 6, or 8 hairpin elements may be used. An insulating

cylindrical sleeve of  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$ , about 10 cm to 15 cm (4 in to 6 in) in diameter, separates the heating elements from the working chamber. For the purposes of precision and accuracy a second  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  sleeve,  $\approx 2.5$  cm ( $\approx 1$  in) in diameter forms the actual heating chamber. The specimen holder is a four-hole-bore  $\frac{1}{4}$ -in-diameter  $\text{Al}_2\text{O}_3$  rod. Two thermocouple (Tc) wires ( $\text{Pt}/\text{Pt}_{90}\text{Rh}_{10}$ ) are inserted into two of the holes and the Tc interrogation bead is formed where they exit. Pure Pt wires are inserted in the other two holes; at the exit they are curved into hooks to support the specimen near the Tc bead, and also to provide electrical connectivity to burn through the fine Pt wire used to suspend the sample. The specimen holder-rod is fitted with a larger-diameter ( $> 2.5$  cm) ceramic cap that permits its suspension in the furnace heating sleeve. One or more specimens, each in an Au, Pt, or other container, are tied to a small two-hole  $\text{Al}_2\text{O}_3$  cylinder-bead ( $\approx 4$  mm to 5 mm long, “fishspine”, cut from a two-hole-bore  $\frac{1}{4}$ -in-diameter rod) using Pt wire that is threaded through one of the holes. The entire cylinder-plus-specimen(s) assembly is then attached to the specimen holder-rod with very fine Pt wire which is threaded through the other hole of the fishspine and then wrapped around the supporting Pt wire-hooks on the specimen rod. The specimen should be positioned as close as possible to the Tc bead, without touching it. This entire assembly is then lowered into the furnace so that the specimens are suspended in the predetermined “hot zone” without touching the walls of the heating sleeve. The hot zone is determined prior to conducting experiments using a thermocouple in the heating sleeve, just as for the specimen holder, but sliding it through the vertical length of the heating chamber and recording the measured temperature vs. distance from the top. The “hot-zone” in such a furnace depends on the length of the furnace, but generally is about 5 cm to 8 cm (2 in to 3 in) long and  $\pm 2$  °C near the center of the furnace, dropping off rapidly on either end. After appropriate heat treatment the specimens (with cylinder-bead) are dropped out of the furnace into the quenching medium by applying a voltage to the two Pt “hooks” of the specimen holder-rod, thus burning through the fine Pt suspending wire wrapped around the hooks.

The thermocouple and entire furnace assembly should all be calibrated together. For lower temperatures, NaCl as the specimen in a Au tube is appropriate (m.p.= 800.5 °C). A small piece of Au foil (m.p.= 1063 °C) bent into a V-shape and placed in fine grained  $\text{Al}_2\text{O}_3$  powder in a Pt tube should be the next calibration point. When quenched from above 1063 °C, the Au-foil will have formed a sphere, whereas below this temperature the V-shape will be

unchanged. Other calibration points can be used depending on the temperatures to be investigated and the degree of accuracy desired.

As mentioned above, the specimen in a vertical quench furnace is contained in a small noble metal tube: Au, Ag, Ag/Pd, Pt, Pt/Rh, etc. These tubes are generally 3 or 5 mm in outside diameter, 0.2 mm in wall thickness, and 2.0 cm to 2.5 cm (3/4 in to 1 in) in length. The tubes should always be sealed on the bottom and filled one-half to three-quarters full with powdered specimen. The tubes may then be sealed at the top or left open to the atmosphere as desired. If sealing by welding is desired, the inner rim of the capsule must be carefully cleaned of specimen, and then most of the air should be squeezed out with flat-surfaced pliers that will not rip the metal. If one or more of the components are relatively volatile, the tube must be sealed. Sealing is generally accomplished with a DC arc welder. The tube is firmly clamped (above the top of the powdered specimen) in a jewelers' vice, which serves as one electrical side of the arc. A spectroscopic grade carbon rod sharpened to a pencil point completes the arc circuit and is used to make the weld. Alternately, a mini-torch can be used with the specimen inserted into some type of heat sink, but the DC arc is preferable. This jewelers' vice arrangement has been used to seal specimens with a weighed amount of H<sub>2</sub>O or other liquid deliberately added to the specimen. Platinum capsules with 0.2 mm wall thickness will easily withstand internal pressures of 10<sup>6</sup> Pa (10 atm) and may withstand as high as 2x10<sup>6</sup> Pa to 3x10<sup>6</sup> Pa (20 atm to 30 atm). If open specimen containers are desired, Au or Pt foil may be used instead of tubes, with the foil folded into an envelope containing the specimen and hung in the furnace in a like manner.

A vertical furnace is used instead of a horizontal geometry in order to obtain the fastest possible cooling short of shooting the specimen from a gun, or "splat" cooling. Simply "turning off" the furnace or opening the front door and removing the specimen with tongs is NOT quenching. If the specimen is completely sealed or known to be unreactive with H<sub>2</sub>O, simply dropping the hot tube into cold water is quite an adequate quench. Dropping into mercury is NOT advised. Dropping into liquid N<sub>2</sub> does not produce a good quench as hot N<sub>2</sub> gas with poor thermal conductivity is formed around the specimen. For open specimens which might react with water, a quench cup may be utilized which consists of a Ni crucible surrounded by a copper coil inserted into an wide-mouthed dewar of liquid N<sub>2</sub>. Helium gas is passed through the copper coil with the coil exit aimed at the inside of the Ni crucible. Specimens dropped out of the furnace into the cup are instantly exposed to He gas cooled to 77 K. Since

helium gas exhibits high thermal conductivity, the quench rate is nearly equivalent to dropping the specimen into H<sub>2</sub>O.

Under certain circumstances it may become necessary to study the phase equilibria in a given system utilizing a carefully controlled atmosphere. This is much easier to accomplish in a horizontal furnace if quenching is not considered necessary. However, the apparatus described above can theoretically be modified to accommodate a controlled atmosphere. It should be remembered that, even with a properly designed controlled-atmosphere quench furnace equipped with an apparatus to carefully measure the P<sub>O<sub>2</sub></sub> at the exit of a gas-flow system, the time required to conduct such experiments is 3 to 5 times longer than ambient-atmosphere experiments.

One approach to reducing experimental time is the use of a horizontal gradient furnace with many specimens, generally all of the same composition, each placed at a pre-determined temperature. This method is not advised as the accuracy, etc., is bound to be very poor. Nevertheless, some pertinent data may be obtained relatively quickly by some suitable modification of such equipment.

## 2.2. *Dynamic*

There are two commonly utilized techniques for dynamic measurements in phase equilibria studies. The first involves recording a change in heat capacity during a heating/cooling cycle due to a change in phase or phases, generally by differential thermal analyses (DTA), and the second involves characterization of the crystal structure of the phase or phases in situ during the heat treatment, usually by high-temperature X-ray diffraction, although optical microscopy can also be used.

### 2.2.1. *Differential Thermal Analysis (DTA)*

Differential Thermal Analysis (DTA) has often been used as the sole method of analyzing a phase equilibrium diagram. The results so obtained, in the absence of other data (especially X-ray diffraction), are usually misleading and result in incorrect or at least incomplete interpretation. Thermogravimetric analysis (TGA) is often used in conjunction with DTA as differential thermogravimetric analysis (DTGA), especially if weight loss or gain is expected during the chemical reactions which may take place during the heat treatment. DTA and DTGA are often useful before or during quench experiments to determine the approximate temperature of a suspected phase transition or to approximate

melting temperatures. It is most valuable when the specimen is known to be single-phase, or if weight changes are expected (or suspected) during equilibration. It should never be used without collaborative X-ray diffraction analyses.

There are many commercial apparatus available for experimental DTA and/or DTGA. All involve use of a thermocouple and careful calibration is advisable. DTGA can also be combined with mass spectrographic analyses of escaping gases. The description and possible uses of such equipment will be left for other expert review.

### 2.2.2. High-Temperature X-Ray Diffraction

The preferred method of dynamic equilibria analyses is in-situ high-temperature X-ray powder diffraction. This method should be utilized when a suspected unquenchable phase transition is encountered. Such a transition may be suspected upon observation of several different phenomena: a specimen cracks or crumbles (“dusts”) after solid-state sintering (e.g.:  $ZrO_2$ ,  $Ca_2SiO_4$ ,  $REBO_3$  (RE= rare earth),  $SrLi_{1/4}Nb_{3/4}O_3$ , etc.); the X-ray powder diffraction pattern becomes broader and more diffuse instead of sharper with increasing quench temperature; optical observation may show fine domain structure ( $SrBi_2O_4$ ); large “single-crystal” grains show considerable “polysynthetic” twinning usually indicative of transformation twinning ( $BaTiO_3$ ,  $PbTiO_3$ ,  $LaNbO_4$ ,  $LaTaO_4$ ). Such transitions may or may not be indicated by a DTA peak, depending on the nature of the transition (first- or lower-order thermodynamic transition) and the amount of heat involved. High-temperature X-ray diffraction may also be useful as a direct synthetic tool to observe, in situ, the actual formation of phases in a given system. This technique may be most valuable in systems requiring a controlled atmosphere as more information can be obtained during one thermal cycle than can be obtained from many (static) quench experiments, thus greatly decreasing the time involved. Obviously, high-temperature X-ray diffraction is not practical in a system where differential volatilization is a significant factor, since the very thin specimen required for X-ray diffraction is completely open to the atmosphere. Several commercial instruments are available for high-temperature X-ray diffraction. However, due to the necessarily open specimen, surface thermal gradients are very severe and careful *in situ* temperature calibration is absolutely necessary. For chemical systems in which only ambient atmosphere is required, either for sealed or unsealed specimens, the quench

technique accompanied by characterization is still the best and most accurate way to determine a phase equilibria diagram.

### ***2.3. Specimen Contamination***

One of the most difficult problems in the determination of a phase equilibria diagram is to avoid or characterize chemical impurities in specimens. Chemical contamination of the specimen can take place during every aspect of the experimental determination of a data point. Very often the amount and nature of the contamination is not reproducible and therefore not easily characterized. Contamination during selection of chemical sources, weighing, grinding, etc., at room temperature are all controllable, with care. Contamination during heat treatment by contact with the specimen container is the most severe problem and sometimes cannot be overcome. Every system has its own problems with various sources of contamination, and each must be carefully understood in order to obtain useful, reliable information.

## **3. Characterization of Results**

In determination of a phase equilibria diagram each experimental data point is composed of a specimen which must be characterized as to the number and nature of the phases present. In the experimental determination of most ceramic phase diagrams the nature of the gaseous species is often ignored and the phase rule degenerates into  $P + F = C + I$ . Characterization then depends on the observation of all solid, solid plus liquid, or all liquid, as well as the total number of solid phases. The most common characterization techniques are therefore physical observation and optical and/or diffraction methods of examination.

### ***3.1. Physical Observation of Melting***

Determination of the solidus and liquidus temperatures for a given composition by static techniques is completely dependent on physical observation of the specimen. When using a horizontal or box furnace, front or top loader, specimens can be prepared in the shape of a cone or pyramid with sharp corners and/or edges. First melting (solidus) is observed by a gentle rounding of the

edges, considerable or complete melting by formation of a rounded button. When using a vertical quench furnace, however, the specimen must be very carefully removed from the tube without crushing in order to observe the geometry resulting from liquid formation. The noble metal tube should be carefully peeled from the specimen like peeling the skin from an orange. The qualitative amount of melting can then be observed directly from the appearance of the specimen as shown in Figure 2.

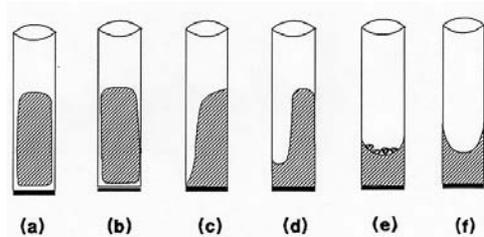


Figure 2. Schematic diagrams of the physical appearance of specimens after quenching; (a) through (f) illustrate increasing degrees of melting.

When quenched from slightly below the solidus (Fig. 2a), the powdered specimen should have sintered into a single mass the exact shape of the inside of the tube. As the flattened bottom of the capsule is a different shape from the cylindrical portion, this shape should be reflected in the sintered specimen. The specimen should be loose inside the tube. The first sign of melting (Fig. 2b) occurs when the specimen sticks at one spot where the liquid wets both the tube and the solid specimen. The degree of melting is then reflected in the specimens by the amount of sticking to the tube (Fig. 2c), and slumping of the specimen (Fig. 2d), as the liquid wets the tube and forms a meniscus (Fig. 2e,f). The last bit of solid will result in crystals growing in the center of the meniscus (Fig. 2e).

The technique illustrated in Figure 2 can be very accurate for determination of the first sign of melting (solidus), but is generally not as accurate for determining the last bit of solid (liquidus). If the system forms a very fluid liquid, there can often be a large amount of solid left in a specimen with a well formed meniscus. Since the tubes (Au, Ag, Pt, etc.) are manufactured by extrusion, their interior surfaces have very fine ridges, somewhat similar to the rifling in a gun barrel. These ridges or striations leave corresponding impressions on the now-solidified liquid formed in the tube before quenching. They are easily observed with a low-power binocular microscope, and have been

labeled “slickensides”, a geological term for the marks left on rocks by the motion of fault planes.

### **3.2. Phase Identification**

#### *3.2.1. Optical Microscopy*

Phase identification by optical microscopy using index of refraction and behavior under polarized light (crossed nicols) is a seldom-used technique in the age of the availability of computerized X-ray diffraction methods. Nevertheless, it can still be of value in identifying a very small amount of a second phase for certain systems. When partial melting has occurred, the shape of the crystallites (euhedral vs. anhedral, etc.) can also be an important clue. The polarizing microscope is a necessity for picking small crystals to mount for single-crystal X-ray diffraction (see below).

#### *3.2.2. X-Ray Powder Diffraction*

The standard technique for phase identification is X-ray powder diffraction. The most modern equipment available, with the best peak-to-background ratio, is highly recommended. Every specimen should be examined carefully by X-ray powder diffraction, and ***every peak in the powder pattern must be accounted for***. This should be done by computerized least-squares analyses of the unit cell parameters and indexing of each observed peak. In practice this must be done for all single-phase compositions, if not for all specimens. The reason for this should be obvious: if any peak cannot be accounted for by an assigned ( $hkl$ ) index, then there is a very good chance it belongs to a previously unidentified phase in the system. Such unaccounted-for peaks could belong to a stable phase in temperature/pressure/composition space which is present because the specimen was not heated enough to overcome the effects of adverse kinetics. Unaccounted-for peaks may also arise from some phase which is only metastable under the experimental conditions of the study. They may also arise from an impurity not originally recognized or accounted for. Unaccounted-for peaks may actually belong to one of the known phases which has been incorrectly or incompletely characterized crystallographically.

These ideas result in a basic principle for the experimental determination of phase equilibria diagrams: Every effort must be made to prepare a small single crystal of every phase in the system so that single-crystal X-ray diffraction can be used to determine the true unit cell, symmetry, etc., so that, in turn, their X-ray diffraction powder patterns can be completely accounted for. It is not enough to just look at an X-ray diffraction powder pattern and say these peaks are about in the right place for such-and-such a phase. *Every observed peak must be mathematically accounted for!*

### 3.2.3. Single-Crystal X-Ray Diffraction:

As stated above, it is very important to obtain a small single crystal of each previously uncharacterized phase in the system under study in order to unambiguously index the X-ray diffraction powder pattern of the phase. At a minimum, the unit cell, symmetry, and possible space groups should be obtained by single-crystal diffraction techniques. The simplest and least expensive technique is the Buerger precession camera method (Polaroid film makes this a much less time-consuming task). If the expertise is available, the crystal structure analysis of a new phase should be attempted. There are often crystallographers in other locations eager to obtain crystals of previously unreported structures. The importance of the knowledge of the structure cannot be overemphasized. Knowledge of the structure of phases leads to an understanding of the crystal chemistry, which can lead to the prediction of new phases with interesting and useful physical properties.

The crystals needed to obtain the desired data should be  $\approx 0.2$  mm to 0.5 mm in the largest dimensions. This is quite small for any crystal grower accustomed to growing crystals to exploit their desired physical properties. Nevertheless, it is larger than can be formed by strictly solid-state techniques, and therefore the crystals must be grown from a liquid. This can often be accomplished by slow-cooling an appropriate composition from the melt. Occasionally, slow-cooling the single-phase composition will result in suitable crystals if the phase either melts congruently or incongruently to a liquid composition close to the original. More often, truly incongruent phases need to be slow-cooled from an off-stoichiometric region where the desired crystal has a primary phase field in which it is in equilibrium with liquid. This may be either one solid plus liquid or even two or more solids plus liquid. It is not necessary that all crystals from a given crystal growth experiment belong to the same phase. For the purpose under discussion only one crystal of each phase is really needed.

If the desired phase dissociates below the solidus, undergoes a solid phase transition, or has a melting point too high for practical liquid/solid experiments, it may become necessary to use a flux. A flux is a substance that is mixed with the phase of interest (i.e, of which the crystals are to be grown); the mixture forms a melt in which the compound of interest dissolves, thereby forming the liquid phase required to grow single crystals. Although this technique is well known to professional crystal growers, it is not often appreciated by those who are only interested in studying a given phase diagram. In oxide systems, lithium molybdate may be the universal solvent. Other alkali molybdates are also useful, as are alkali vanadates and some tungstates. Other useful fluxes for oxide systems include alkali or alkaline earth borates or phosphates, bismuth and/or lead oxides, alkali halides, or any chemicals with melting points lower than the maximum stability of the desired phase<sup>2</sup>. Care must be taken to chemically characterize the crystals grown from a flux for possible contamination which could modify the crystallographic properties.

#### 3.2.4. Other Diffraction Techniques

In order to account for every peak observed in an X-ray powder diffraction pattern the unit cell and crystallographic symmetry, at a minimum, must be known. Unindexed powder patterns can only lead to incorrect interpretation of the data! However, in practice, one is frequently not able to obtain a new phase as a single crystal. Various methods of indexing unknown powder patterns have been published, with some significant progress in the last decade<sup>3</sup>, but with limited success for complex structures with low symmetry and large unit cells. One of the earliest approaches was the Visser method<sup>4</sup>, which required very accurate d-spacings at low  $2\theta$ -angles; a triclinic cell was initially assigned based on these lowest-angle peaks, and then a search is made for higher symmetry by mathematical manipulations. The only way to be certain that the given technique has resulted in the correct unit cell is to refine the structure via X-ray or neutron Rietveld<sup>5</sup> techniques, in which whole-pattern, least-squares profile fittings are used to refine the crystal structures from powder diffraction data. Of course, the unit cell dimensions must have first been precisely refined by least-squares techniques using the indexed powder diffraction data. If any observed peaks occur at  $2\theta$ -values that deviate more than  $0.03^\circ$  from the calculated values, the proposed unit cell is probably incorrect. Any published indexed powder pattern *must* state specifically how the trial unit cell was obtained. Frequently, such patterns which are not based on single-crystal data are incorrect.

Another approach to structurally characterize phases for which single crystals are unavailable is to utilize electron diffraction methods using a transmission electron microscope (TEM). The unit cell of a phase can be obtained by single-crystal electron diffraction which can interrogate a single small grain from ordinary polycrystalline solid-state preparations. Furthermore, convergent beam electron diffraction (CBED) yields symmetry information. Diffraction-contrast imaging in TEM reveals crystallographic domains and inter-domain boundaries which provide information on the growth and/or phase transition history. Another powerful tool is high resolution electron microscope (HREM) lattice imaging combined with phase contrast simulations. In this technique, important information can be obtained about the crystal structure and/or defects within phases, and/or mechanisms of solid solution. All of these can be important to the interpretation of the phase diagram data and/or the prediction of mechanisms to moderate or improve physical properties.

Neutron powder diffraction, especially with Rietveld analyses<sup>5</sup>, is also a very useful tool for proper interpretation of phase equilibria data. Unfortunately, a relatively large amount of specimen is needed, at least 1-2 cm<sup>3</sup>, preferably 5 cm<sup>3</sup>. The biggest drawback, of course, is the need of a source – either an atomic reactor or a pulsed neutron source. Very few such sources are available, although most institutions with these facilities are very willing to collaborate in useful scientific endeavors. The National Institute of Standards and Technology (NIST), Oak Ridge, Brookhaven, Argonne, and Los Alamos National Laboratories, host most such experiments in the USA, with Grenoble, France the major European contributor. Brookhaven also has useful programs for Rietveld analyses using synchrotron data. Programs are also now available for Rietveld analyses using X-ray powder diffraction data, which is more readily obtained. The different scattering phenomena underlying X-ray and neutron diffraction result in the highly useful combination of these methods in certain cases where one type of data alone will not suffice.

#### 4. Examples of Determination of Phase Diagrams

Phase equilibria information obtained for the following systems is used in the oral presentation to illustrate the results obtained for various examples of phases of possible interest for “ions in motion”.

- (1) Oxide Systems Containing Li<sup>+</sup> Ions
  - (A) Li<sub>2</sub>O-SrO-Nb<sub>2</sub>O<sub>5</sub>

- (B)  $\text{Li}_2\text{O-TiO}_2\text{-Nb}_2\text{O}_5$
- (2) Oxide Systems Containing Variable Oxygen Ions
  - (A) Fluorite Related Systems
    - (a)  $\text{Bi}_2\text{O}_3\text{-CaO}$
    - (b)  $\text{Bi}_2\text{O}_3\text{-SrO}$
  - (B) Perovskite Related Systems
    - (a)  $\text{BaTiO}_3\text{-BaFeO}_{3-x}$

Problems encountered in the generation of phase equilibria diagrams are usually the result of a mismatch between the complexities of the real chemical system and the techniques used to study and characterize the results. Some of the pitfalls which might be expected are best illustrated by discussion of such mismatches which have been found in some real systems. In many cases, the new information leading to a more correct interpretation was crystallographic in nature.

## References

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