Precision Determination of Stoichiometry and Disorder in Multicomponent Compounds by Vibrational Spectroscopy*

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This paper describes the use of vibrational spectroscopy to determine with high precision (.001 %) the stoichiometry and defect structures of multicomponent compounds.

For the first time, measurements have been made of the intrinsic compositional disorder that are more than two orders of magnitude more precise than currently available. These data are essential for the establishment of a scientific base upon which to design specific materials involving multicomponent compounds. Current analytical techniques have left undetected large amounts (0.3 % minimum) of disorder that have significant effects on the properties of materials.

These measurements establish vibrational spectroscopy as a sensitive tool for the determination of defect structures of all types and result in an experimental technique that will allow the study, *in situ*, of degradation and failure mechanisms in multicomponent compounds.

I. Introduction

Significant progress has been made in the determination and utilization of very small amounts of impurities in materials. This progress has depended upon the realization that extremely small amounts of impurity can result in very large changes in material properties. This success can best be illustrated by referring to the semiconductor industry where impurity (dopant) concentrations as low as ten parts per billion (0.000,001 %) are routinely used in commercial devices.

The importance of such small amounts of specific foreign ions in determining the properties of nonmetallics depends upon their being of a different valence than the ion they replace in the host lattice. This difference in valence results in the possibility of an accessible donor or acceptor state and the resultant change in the electrical neutrality condition. Similar alterations in the electrical neutrality condition of nonmetallic compounds occur when the stoichiometry is varied.

For the case of variable stoichiometry in nonmetallic compounds, metal deficiency corresponds to the introduction of an acceptor while excess metal corresponds to the introduction of a donor. Considerable success has been achieved in defining such donor and acceptor states in *binary* nonmetallic compounds where the activity of one of the components is varied (usually the anion) at thermodynamic equilibrium. In some binary compounds (e.g., Al_2O_3, ZrO_2) where the deviation from stoichiometry is small (<0.1 %), a high degree of purity is required to detect this intrinsic compositional disorder, while in others the deviation from stoichiometry is large enough (e.g., FeO, TiO_2) for the intrinsic compositional disorder to easily dominate any impurities that may be present.

The case of *multicomponent* nonmetallic compounds, however, presents a formidable problem in the determination of intrinsic compositional disorder. This problem arises from the introduction of further compositional variables which must be defined in order to characterize the intrinsic compositional disorder. In this case, however, one faces one of

the unsolved problems in analytical chemistry: the precise determination of the concentrations of the major constituents. If one considers one of the optimum examples, $BaTiO_3$, where repeated chemical analyses are performed by a laboratory with exceptional experience in the particular analytical procedure, on samples that are inherently single phase, and of high purity, the Ba/Ti ratio may be determined to a few thousand parts per million precision (0.2–0.5%). Even for the optimum case, therefore, there exist substantial amounts of undetermined built-in intrinsic compositional disorder that is undetectable by chemical analysis-disorder that will have a significant effect on particular properties of the compound.

The development of better techniques to determine the built-in intrinsic compositional disorder in multicomponent compounds should also lead to a new sensitive method to determine the particular defects responsible for disorder in crystals.

Before any quantitative analytical procedure can be developed to answer the important question of stoichiometry of the major constituents, analytical standards must be available. If thermodynamically defined single phase samples of multicomponent compounds can be prepared, then it will be possible to have the analytical standards required to quantitatively determine major constituent stoichiometry.

II. Preparation of Thermodynamically Defined Samples

In a single phase binary oxide the compound is unambiguously defined if the activity of one of the components, oxygen partial pressure, is known and the temperature is sufficiently high to establish thermodynamic equilibrium with the oxygen containing atmosphere. For oxides with more than two components, additional independent variables must be determined in order to unambiguously define the system. For a ternary oxide, two independent variables in addition to temperature and total pressure must be taken into account. In addition to the oxygen

activity one could fix the activity of one of the cations or the ratio of the two cations. If the additional variable is not fixed, the thermodynamic state of the ternary oxide is not defined and measurements of disorder phenomena are generally meaningless (1).

When the cations are not volatile, one may equilibrate the ternary compound under investigation with an excess of either cation at the two respective phase boundaries. This technique only allows the study of the edges of the single-phase region and limits the experimental techniques to those that are not restricted by the existence of a two-phase mixture. A technique has been established (2–4) by which it is possible to know the nonvolatile cationic stoichiometries of the major and minor constituents to within a few parts per million precision (.001%), and thereby thermodynamically define the system in question to this precision.

This preparation technique is based upon having the individual cations complexed in separate weak organic acid solutions or available in salts that are soluble in the weak organic acid solution. The individual solutions or soluble salts are gravimetrically analyzed for the respective cation concentration to a precision of better than ten parts per million. In this way it is possible to precisely control all of the cation concentrations and to mix the ions on an atomic scale in the liquid state. There is no precipitation in the mixed solutions as they are evaporated to the rigid polymeric state in the form of a uniformly colored transparent glass. The glass retains homogeneity on an atomic scale, and may be calcined at a relatively low temperature of only a few hundred degrees Celsius to the homogeneous single phase oxide of precise cationic stoichiometry and particle size of a few hundred angstroms.

This technique of "liquid mix" is quite distinct from processes involving precipitation from precursors (5, 6). Pyrolysis of these precipitates is a distinct improvement over solid state reaction of the simple oxides or salts of the various cations at high temperatures; however, the precipitation from a precursor suffers from a restriction imposed by stoichiometric requirements of the complex salt with

several cations and lack of homogeneity during the precipitation process (*4*).

By using the technique of "liquid mix" one may prepare single phase multicomponent oxides with as high a purity as the starting materials (no subsequent milling is required), homogeneity on the atomic scale, and with a very small particle size of a few hundred angstroms.

III. Vibrational Spectroscopy

Laser Raman spectroscopy is a well established method for investigating the vibrational spectra of crystals. Structural studies from the lattice dynamics approach attempt to determine the nature and magnitude of the forces between atoms and molecules in a crystal and, then, to show how the experimentally measurable properties of crystals may be calculated if those forces are known. Experiments are typically carried out using ir, Raman, and neutron scattering spectroscopy. In order for this approach to be fruitful for multicomponent compounds, well characterized, thermodynamically defined samples must be used, which hitherto have not been available.

Several publications have appeared which incorporate the theories of lattice dynamics and vibrational spectroscopy of perovskite crystals and, in particular, $BaTiO_3$ (*8–11*).

DiDomenico et al. (*8*) have assigned the 18 Raman-active optical phonons in the tetragonal phase of $BaTiO_3$ by a consideration of both long-range electrostatic forces as well as short-range force constant anisotropies. Interference between the one-phonon process (ir and R allowed, 175 cm^{-1}) and the broad two-phonon (acoustic) processes (second-order, 0–300 cm^{-1}) was demonstrated by Rousseau and Porto (*9*). In contrast, Fontana and Lambert (*10*) conclude that the spectrum arises from two different contributions: one from the first-order phonon scattering of the perfect crystal and the second from intrinsic disorder in all phases of the crystal. It should be noted that our new preparative technique results in purely single-phase material and a temperature dependent investigation will be of considerable interest. Fontana and Lambert rule out impurity-induced

first-order results as well as ordinary two-phonon scattering from the temperature dependence of the observed $BaTiO_3$ spectrum; cubic symmetry is reached at ca. 300°C when the intensity vanishes suggesting that the observed spectrum must arise from intrinsic disorder.

Dvorak (*11*) has calculated that a static field of the order of 1 kV/cm is sufficient to induce in cubic $BaTiO_3$ first-order Raman lines; studies of changes in the Raman spectra due to such morphic effects will greatly aid the analysis of the lattice dynamics.

A valuable observation contributed by Scott and Burns (*12–14*) reveals that all of the essential features of single crystal spectra, even when the crystal is quite anisotropic, is contained in the spectra obtained from polycrystalline solids. Single crystals of precisely defined composition are at best difficult to grow, whereas the powder method permits investigation of materials with any desired composition by Raman scattering techniques, as described below.

IV. Experimental

As an aid in developing general defect structure models, a perovskite type oxide multicomponent compound, $BaTiO_3$, was investigated because of its simple structure, well defined large and small cation sites, and ease of establishing anion activity. It might also be noted that the perovskites are among the most technologically interesting and useful groups of materials because of their ferroelectric, piezoelectric, electrooptic, and cata‑lytic properties.

Thermodynamically defined samples were prepared by the previously discussed "liquid mix" technique.

The requirements for this preparation technique to be successful are that the particular cation solutions be stable with respect to time at room temperature and stable when mixed together and heated near the boiling point of the solvent. Solutions of cations complexed in an ethylene glycol–citric acid solvent have been found to satisfy these requirements—they do not precipitate or disproportionate either on storage or when

evaporated to the state of a rigid polymeric glass.

The $BaTiO_3$ powders were lightly pressed into pellets (5 mm diam, 1 mm thick) and supported by a brass sample holder inclined ca. 20° from the vertical. Radiation (5145 Å) from a Coherent Radiation Laboratories Model 52 argon ion laser served as the excitation wavelength. Scattered light was analyzed by a Jarrell–Ash 25-300 Raman spectrophotometer equipped with an ITT FW-130 photomultiplier and Hamner photon counting electronics. Spectra were recorded (100–1100 cm^{-1}) in ratio mode to eliminate intensity variations due to any laser power drift. Spectra were obtained at ambient sample temperature and an incident power of approx 600 mw. Precision of the width measurements at half-maximum intensities, $W_{1/2}$, is better than 0.5 cm^{-1}. Accuracy of sample composition is estimated at 100 ppm but the relative precision between samples is better than 10 ppm.

V. Results and Discussion

The results reported here are for the ternary compound $BaTiO_3$ because of the known defect structure type and previous experience and success in reproducibly preparing samples of precise cation stoichiometry. For example, when a cation deficiency is built into one of the cation sublattices in barium titanate, an equivalent anion (oxygen) deficiency is also built in (3). For this specific example the intrinsic compositional disorder that is built into the compound is a neutral cation–anion vacancy complex (7). These neutral vacancy complexes do not enter the electrical neutrality condition and are not therefore detected by standard techniques to determine nonstoichiometric disorder. This significant but undetermined amount of built-in lattice disorder in conventionally prepared multicomponent compounds enhances mass transport and the eventual degradation and failure from electrical or mechanical stress.

The introduction of this disorder in the $BaTiO_3$ lattice by very small deviations from the stoichiometric cationic ratio would be expected to broaden the Raman-active modes.

In Fig. 1, we illustrate the behavior of the width at half-maximum intensity of the strong, asymmetric band at ca. 520 cm^{-1} with compositional variation. It should be noted that $B/A < 1.0$ corresponds to the removal of Ti. The disruption of such TiO_6-octahedra would be expected to give rise to a marked crystal structure change that would be more significant than a Ba deficiency at $A/B < 1.0$, and hence readily accounts for the asymmetry of the peak half width vs composition curve. Within the limits of the absolute accuracy in composition (100 ppm), the minimum of the curve lies at the ideal 1:1 stoichiometry.

This investigation has provided, for the first time, measurements of the intrinsic compositional disorder in multicomponent compounds that are more than two orders of magnitude more precise than currently available. These data are essential for the establishment of a scientific base upon which to design specific materials involving multicomponent compounds.

Until now, one has had to accept substantial (0.3% minimum) amounts of undetermined built-in intrinsic compositional disorder in multicomponent compounds. Current analytical techniques have left undetected these large amounts of disorder that have significant effects on particular properties of the compound. It is not surprising, therefore, that understanding of the degradation phenomena, that are common and operationally limiting in the use of multicomponent compounds,
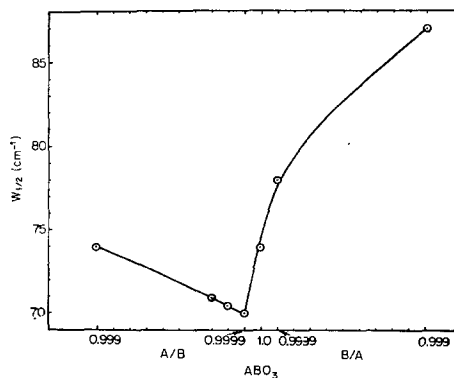

FIG. 1. The width of half-maximum intensity of the ~520 cm^{-1} Raman mode vs composition of $BaTiO_3$ (A = Ba, B = Ti). See text for limits of accuracies.

has not been forthcoming. Using the perovskites as an example, these degradation phenomena occur when the particular compound is under electrical or mechanical stress and lead to dielectric breakdown, as well as "fatigue" and mechanical failure of piezoelectric and electrooptical devices.

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