Parameters necessary for the adequate characterization of a SOLID-STATE MATERIAL

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A large number of scientists are caught up in the greatly expanded and accelerated national effort in materials science and technology. The impetus for this push came largely from members of one branch of the field—the solid-state physicists concerned with the properties of a material or the phenomena observable in a particular solid. It is, therefore, understandable that the initial emphasis of "materials science" programs stressed the solid-state physics or "measurement of properties" aspects. Only during the last two or three years has the recognition grown beyond verbal acquiescence that in order to have a flourishing program of measuring and interpreting properties of solids, it was essential to have "good" materials. In other words, the necessity to support and develop the whole science of "materials preparation" became apparent. This note is concerned with the third stage of the development of solid-state materials science and technology. Hardly had the effort in materials preparation been launched that it became apparent that one essential was still lacking —that which can be summarized in the expression "characterization of materials". Some definition is in order: this term is used herein to include the whole spectrum of analyses, tests, measurements, etc., which must be carried out in order to be able to describe both accurately and precisely a particular solid. Another way of putting it is to say that it concerns the specifications necessary in order that another specimen can be established as being sensibly the same as a given model.

It has been assumed for some time that "purity" or the elemental content of a solid phase is its chief significant "characteristic". The fact that the whole of transistor science was uncovered by improvement of the "purity" is, of course, responsible for this great prominence to this particular characterization. Attention to this one characteristic has tended to obscure the importance and necessity for other parameters in providing effective characterization.

Before proceeding to develop a scheme for such other means of characterization, it is necessary to provide some guidelines for their use. A simple way to summarize this is in the Gilbert and Sullivan phrase, "Let the punishment fit the crime". Let the degree of sophistication and detail of characterization match the detail and sophistication of the measurement to be performed. Moreover, it is not only the degree of sophistication which is determined by the measurement or use to which the solid will be put, but the *content* of the characterization procedure. It is quite obvious that for a particular measurement, certain parameters are very much more important than others; e.g., dislocation content is much more important in a strength measurement and can be virtually ignored (today) in a Mössbauer-effect measurement. Likewise, "doping level" is less important than the homogeneity of distribution of the dopant in a solid-state laser crystal. Bearing these caveats in mind, we can turn to the presentation of the scheme for adequate materials characterization.

The solid-state material to be analyzed may fall broadly into the categories presented in Fig. 1. It

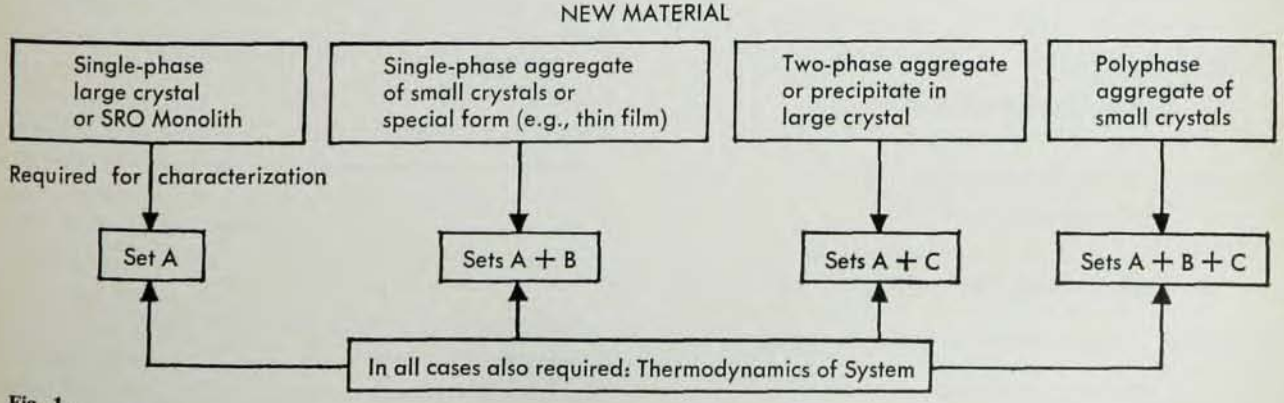

Fig. 1.

is either single phase or polyphasic, and either a single monolith (either crystalline or noncrystalline—short-range order) or an aggregate of small units (called "powders"). Clearly, the most complex task is that of characterizing a polycrystalline polyphasic aggregate, but it is obvious that much of this task is common to the characterization of a single-crystal monolith, and even more of it common to the characterization of a single-phase polycrystalline aggregate. We have, therefore, subdivided the characterizations necessary into those labeled *A*, *B*, and *C*. The *A* list includes those which would thoroughly describe all analyses necessary for the single-crystal case. To these must be

Table 1. Set A Characterizations

I. Elemental Composition

i. Precise ratios of major elements (i.e., exact stoichiometry of phase); controlled synthesis is the best approach.

ii. Concentration of all "foreign" elements with maximum sensitivity.

iii. Characterization of valence state(s) without destroying phase.

iv. Detection of anion impurities, chiefly oxygen and hydroxyl.

v. Distribution of inhomogeneities or impurities in glass or crystal with maximum resolution.

II. Structural Characteristics

Short-Range Order	*Long-Range Order (Crystalline)*
i. Infrared, NMR, ESR, and light scattering.	i. Structural family if known, and location of atoms to 0.001-0.01 angstrom.
ii. Radial distribution curves.	ii. Precise lattice parameters.
	iii. Order-disorder of ions whenever possible, including ordering of vacancies and other defects.
	iv. Clustering of ions (substitutional, or interstitial, defects) or vacancies.

III. Point-Defect Nature and Concentration

i. Specific gravity.

ii. Precise lattice parameters from above give precise x-ray density.

iii. More general methods for independent characterization of concentration of vacancies and interstitials, especially when mixtures of both are present.

IV. Line-Defect Nature and Concentration

i. Dislocation density and nature.

V. Surface Nature

i. Chemical nature of the surface; are impurities concentrated or diluted?

ii. Structural nature—lattice parameter, point defects, line defects; which ions stand up out of the layers?

iii. How deep does the "surface layer" go?

iv. How fast does it respond to environment?

VI. Volume

i. Residual mechanical strain.

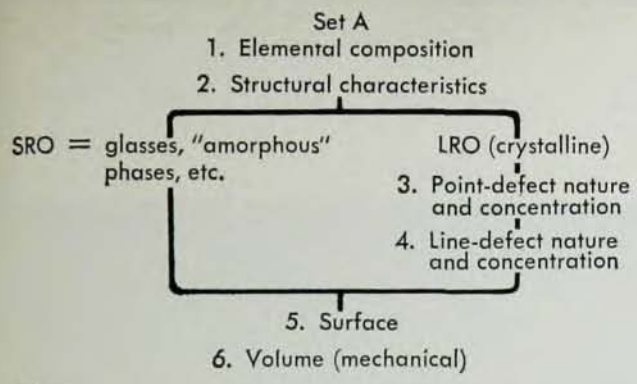

Fig. 2.

added the analyses grouped under *B* for the case of single-phase polycrystalline aggregates. If, instead of a single-phase aggregate, we have a monolith which consists of more than one phase, we add to the set *A* a third set of characterization procedures—*C*. For the polycrystalline polyphasic case, one would require *A*, *B*, and *C* characterizations. Finally, it is our contention that unless the thermodynamics of the system are known no material has really been adequately described. The reason for this is simple. If we do not know the *p-t-x* variables which can change the material being studied, we cannot safely make measurements with varying temperature or pressure, etc., since the material may be changed by its new environment. We certainly cannot claim a high degree of reproducibility without an understanding of the stable and metastable equilibria involved.

Figure 2 lists the whole assembly of different types of characterizations which are required for a single crystal, and we can see that elemental analysis is only a small part of the whole. Table 1 then gives the detailed breakdown of the meaning of elemental analysis, and it will be seen, for instance, that determining the ratio of major constituent elements in a compound is a very difficult and unsolved problem. Our proposal to rely on the synthetic approach is, in fact, the one that is unconsciously adopted by the semiconductor workers.

Two areas for research can be seen in trace-element analysis: first is the development of more and more sensitive tools for detecting impurities below the ppm range; second is study on absolutizing the numbers obtained by different techniques such as solid state mass spectrometry, activation analysis, etc.

The accompanying tables are all more or less self-explanatory. When one surveys them, however, there are areas in which there are very prominent deficiencies which need an immediate concentration of research. A few such selected areas are discussed below:

1. Structure of noncrystalline solids. While more and more use is being made of such materials in solid state science and engineering, we seem to be left without any tools for the analysis of the atomic positions and environments.
2. Point defect, content and nature. Especially in ionic solids the direct determination of the point defects has been neglected to an astonishing degree. Increase in precision of existing methods as well as totally new methods seem to be required.
3. Nature of the equilibrium surface in laboratory ambients. There is no lack of appreciation of the importance of surfaces but a study of the equilibrium nature of the surface in "air", the depth of the "contamination", the kinetics of the reactions, etc., need to be studied. The structural distortions on a surface have recently received prominence, and similar attention must be given to the compositional changes.

Table 2. Set B Characterizations

i. Bulk density and thence porosity.
ii. Distribution of pore size and pore geometry.
iii. Distribution of particle size and particle orientation.
iv. Interaction of surfaces; interfacial energies as a function of orientation.

Table 3. Set C Characterizations

i. Detection of smallest amount of second phase.
ii. Chemical analysis of second phase.
iii. Structure of second phase and any relation to host.
iv. Interaction of phases due to differences of *physical* properties; e.g., difference and/or anisotropy of thermal expansion.

Table 4. Thermodynamics of System

i. Is the phase stable in range of "p" and "t" where it was
   a. Prepared? (This requires phase diagram with appropriate variables)
   b. Studied? (Is it in equilibrium with air at 25° C?)
   If not, what is known about kinetics, to judge ability to freeze equilibrium reproducibly?
ii. Is it at equilibrium with respect to
   a. Other polymorphs?
   b. Order-disorder of crystalline solutes?
   c. Vacancy and interstitial clustering?
iii. If an aggregate, is it in mechanical equilibrium (no strain energy) or in a reproducibly strained state?
iv. What is the nature of the surface layer at equilibrium between, say, O_2 and LiF, or H_2O and MgO when the pH_2O is lower than equilibrium value for reaction?