Phase Equilibria Diagrams

When the American Ceramic Society celebrated its own centennial review in 1998 [1], the NIST/ACerS publication of phase diagrams was cited as one of the two most important accomplishments of the Society affecting the worldwide development and application of ceramics. Working together, NIST and ACerS have published more than 20 000 phase diagrams. (Fig. 1)

Phase diagrams are graphical representations of the regions of distinct chemical and structural behavior of materials in thermodynamic equilibrium. The regions are defined by the composition of the material and by the measurement conditions. Most importantly for ceramics industries, the diagrams are constructed as a function of composition and temperature. The properties of a material, and thus its functionality, often depend critically on what region is used in the preparation of the material. Often, the processing conditions must be maintained in very narrow regions of temperature and composition in order to achieve a material with a desired property. Phase diagram data were essential, for example, in the development of a durable material now used worldwide in more than 500 million catalytic converters to control emissions from cars and trucks. Thus phase diagrams are not only vital to understanding the behavior of ceramics and metal alloys; they are also essential for manufacturing the materials reproducibly, effectively, and economically.

The NIST/ACerS collaboration on phase diagrams can be traced back to the year 1933 when F. P. Hall (Pass and Seymour, Inc., Syracuse, New York) and Herbert Insley (NBS) published a compilation of 178 diagrams in the *Journal of the American Ceramic Society* [2]. These authors published a supplement to this collection in 1938 [3] and then revised and extended the entire compilation in 1947 [4], at which time the collection contained 507 diagrams. A further supplement was compiled and published by Howard McMurdie (NBS) and Hall in 1949 [5]. By 1964, the need and growing demand for reliable phase equilibria diagrams was abundantly clear, and the collaboration between NIST and ACerS began in earnest with the founding of *Phase Diagrams for Ceramists* as a separate publication series [6]. The first volume, published without a volume number, was prepared by Ernest M. Levin, Carl R. Robbins, and Howard McMurdie as a revision and expansion of the previous compilations. The 1964 edition contained 2066 diagrams. Since that time, the series has expanded to twelve regular volumes, three volume supplements, and three special monographs. In the process of this expansion, the series acquired a much broader scope than was originally anticipated. To reflect that broader scope more accurately, the name of the series was changed to *Phase Equilibria Diagrams.* Also, in keeping with advancing technology, a computerized version of the collection was developed for use on personal computers. Today, the compilations encompass systems containing oxides; salts; semiconductor elements; borides, carbides, and nitrides for structural ceramics; high-temperature superconductors; and systems containing a mix of these compounds. More than 45000 copies of individual volumes have been sold to ceramic industries, research laboratories, and academic libraries.

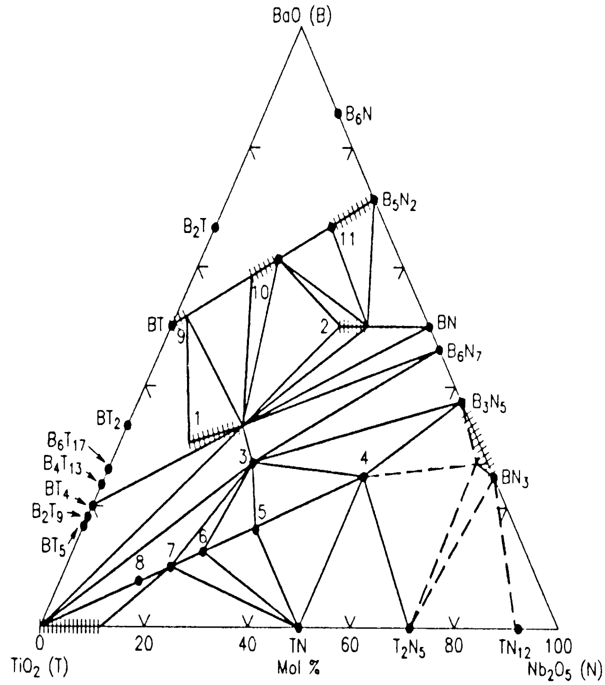

Fig. 1. Diagram #9529 from Volume XI. The phase diagram for the BaO-TiO_2-Nb_2O_5 system determined at NBS by R. S. Roth and his colleagues has provided key data for understanding and processing barium titanate dielectric ceramics important for wireless communications technology.

The sustained success of the series beyond the initial volumes has been due in part to the contributions of numerous distinguished individuals who have served in various editorial capacities. An acknowledgment of the General Editors for the published volumes is given in

Table

Vol.	General Editors
VIII	
I	E. M. Levin, C. R. Robins, and H. F. McMurdie
II	E. M. Levin, C. R. Robins, and H. F. McMurdie
III	E. M. Levin and H. F. McMurdie
IV	R. S. Roth, T. Negas, and L. P. Cook
V	R. S. Roth, T. Negas, and L. P. Cook
VI	R. S. Roth, J. R. Dennis, and H. F. McMurdie
VII	L. P. Cook and H. F. McMurdie
VIII	B. O. Mysen (Geophysical Laboratory)
IX	G. B. Stringfellow (U. Utah)
X	A. E. McHale (Consultant)
XI	R. S. Roth
XII	A. E. McHale and R. S. Roth
A91*	A. E. McHale
A92*	A. E. McHale
A93*	A. E. McHale
M1≠	J. D. Whitler and R. S. Roth
M2≠	T. A. Vanderah, R. S. Roth, and H. F. McMurdie
M3≠	H. M. Ondik and H. F. McMurdie

* A: Annual Supplements
≠ M: Monographs of Special Topics
1: Phase Diagrams for High Tc Superconductors
2: Superconductors II
3: Phase Diagrams for Zirconium and Zirconia Systems

the table. In addition to the General Editors, the production of a single volume also involves associate editors, managing editors, text editors, and editorial assistants. Among the outstanding efforts of the individuals who have served in these capacities are the exceptional contributions of McMurdie (since the inception of the series) and Robert S. Roth (for both editorial and experimental work since Vol. IV). Helen M. Ondik (since Vol. VI) has been especially noted for her meticulous attention to details. She was awarded the Department of Commerce Silver Medal in 1971 and was appointed to a Department of Commerce Science and Technology Fellowship for 1976–1977. Mary A. Clevinger (since Vol. IV) has been a mainstay in numerous aspects of the project, including editing, coordination, and layout. The project is now under the general management of Terrell A. Vanderah, under whose leadership the project staff is undertaking a complete modernization to a computerized desktop publishing system and an internet-ready electronic database.

No list of individuals who have made outstanding contributions to this work is complete without naming Peter K. Schenck and Carla G. Messina. These two individuals were responsible for creating the computer-controlled operations that produced Volume VI and all the succeeding volumes. Peter Schenk's programs for digitizing and plotting phase diagrams (both on-screen and for hard copy) have been compared to other graphics programs by outside graphics experts and have been found to be unequaled. For his outstanding work, he received the Department of Commerce Bronze Medal in 1981.

Fig. 2. Howard McMurdie, 1961.

Howard McMurdie has been involved with the series since its inception. McMurdie began his long association with NIST/NBS when he accepted a position in the Lime and Gypsum Section of the Clay and Mineral Products Division of NBS in April 1928. During the early years in this position, he took a course, taught by Herbert Insley, on the use of the petrographic microscope. That contact proved important later when Insley established the Petrographic Laboratory in the Glass Section of NBS in 1935 and selected McMurdie as his assistant. Insley left NBS about 1944 to take a position at the Pennsylvania State University, but their paths were to cross again about 1947 when Insley returned to NBS as director of the Ceramic Division. Insley selected McMurdie as Chief of the Constitution and Microstructure Section, which later became the Crystallographic Section. McMurdie pursued the study of phase diagrams in that position up to his official retirement in 1966, at which time he became a research associate at NBS; he has been associated with the phase diagram program continuously since that time, a career spanning more than 70 years!

Fig. 3. Robert Roth, 1961.

Robert Roth received his Ph.D. in geology from the University of Illinois in 1951, whereupon he joined the staff at NBS. From the beginning, his work has been dedicated to the discovery of new materials, revealing the existence of phase relations and investigating the structural nature of ceramic compounds. His second publication, of approximately 200 over his career, was entitled "Piezoelectric Properties of Lead Zirconate-Lead Titanate Solid Solution Ceramics." That material, now commonly known as PZT, is one of the most important advanced electronic ceramic materials known to this day, with applications as diverse as providing the spark in charcoal grills and gas stoves to positioning mirrors in giant telescopes. His particular interest in the phase equilibria relations of the oxides of titanium, niobium, and tantalum has resulted in his outstanding contributions to the field of dielectric ceramics. His work in the 1970s on the exploration of the barium titanate systems, and his phase diagrams of those systems, played a critical role in their subsequent commercialization in cellular base stations. He also played a large role in the development of barium neodymium titanate and zirconium tin titanate. All of these ceramics are still the materials of choice as low-loss dielectric resonators at microwave frequencies. In recent years, his effort to elaborate the complex phase diagrams of ceramic copper oxide superconductors is credited with providing the standards upon which many research groups base their processing of the important superconducting material $Ba_2YCu_3O_7$. For his exceptional research activities and his tireless efforts as senior editor of numerous volumes of *Phase Diagrams for Ceramists and Phase Equilibria Diagrams,* he has received numerous awards, including the Department of Commerce Silver Medal, NBS Special Service Award for Meritorious Publication, the Department of Commerce Gold Medal, the Sosman Memorial Lecturer Award (American Ceramic Society), and the John Jeppson Award (American Ceramic Society). He has been elected Fellow of the Mineralogical Society of America, the Geological Society of America, and the American Ceramic Society. He retired from NIST in 1991.

Outside support for the phase equilibria program has been strong, with respect to both technical contributions to the work and the financial commitment necessary to maintain the program. Indeed, the American Ceramic Society made an appeal to its industrial members to contribute to a fund, which ACerS administers yet today, specifically to support the program. Industry and individuals responded with contributions that have amounted to nearly 2.5 million dollars [1]. Those funds are used to support ACerS staff who work at the NIST Gaithersburg facility directly in collaboration with NIST staff.

An independent assessment of the NIST/ACerS phase equilibria program was conducted by TASC, Inc. in 1997 [7]. Their assessment concluded that without the dedicated NIST/ACerS program, the ceramics industry would incur substantial costs for internal research and experimentation and would experience significant delays in introducing innovative ceramic materials to their markets. In their conservative estimate, TASC, Inc. found that the NIST/ACerS program has a remarkable benefit-to-cost ratio of approximately 10 to 1.

Today, the phase diagrams published by the NIST/ ACerS program are proving to be vital to the development of emerging technologies. For example, carefully determined phase stability regions are essential for improving the manufacture of bulk superconducting-wires and tapes. Advanced ceramics with high dielectric constant, low dielectric loss, and reliable temperature stability are needed to improve the performance and to lower the cost of the components of cellular communications circuits. To meet these needs and others, current work includes studies of materials used in a variety of areas such as high temperature superconductors, wireless communications, electronic packaging, fuel cells, and sensors.

Prepared by Ronald Munro, Howard McMurdie, Helen Ondik, and Terrell Vanderah.

Bibliography

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