PHASE DIAGRAMS IN ADVANCED CERAMICS

Edited by

Allen M. Alper

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A VOLUME OF THE *TREATISE ON MATERIALS SCIENCE AND TECHNOLOGY*

This book is dedicated to Vincent A. St. Onge who has been a mentor and coach in my business growth and development

Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

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Preface

Since the first four volumes of "Phase Diagrams: Materials Science and Technology"[1] (Alper, Ed.) were published by Academic Press approximately twenty years ago, there has been a revolutionary change in the development and understanding of ceramics materials. Significant advances in the sintering and control of optical properties of ceramics have taken place. An understanding of complex alkali oxides–aluminia–silica phase relations has been gained, and knowledge of multicomponent silicon nitride–metal oxides–nitride–carbide systems has been greatly advanced. The ways in which phase diagrams are used to make unusual composites of refractory oxides and nonoxides have undergone revolutionary changes.

This book is composed of some of the leading work in this field.

ALLEN M. ALPER

[1]Volume I: The Use of Phase Diagrams in Ceramic, Glass, and Metal Technology
Volume II: The Use of Phase Diagrams in Metal, Refractory, Ceramic, and Cement Technology
Volume III: The Use of Phase Diagrams in Electronic Materials and Glass Technology
Volume IV: The Use of Phase Diagrams in Technical Materials
Volume V: Crystal Chemistry, Stoichiometry, Spinodal Decomposition, Properties of Inorganic Phases

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1

Phase Chemistry in the Development of Transparent Polycrystalline Oxides

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I. Introduction

Polycrystalline oxides have been available for optical applications since the early 1960s when Coble [*15*] invented translucent Al_2O_3. Before this, it was thought that porosity, with its inherent light scattering property, was a necessary consequence of the ceramic fabrication process. Translucent Al_2O_3 is a key element in high-pressure sodium lamps manufactured all over the world. Although it is not clear that Coble made extensive use of phase diagrams in his original development, phase relations are important to the success of translucent Al_2O_3, and subsequent researchers seeking to sinter other oxides to transparency have found phase relations important to their success in achieving their ultimate goal in sintering: elimina-

tion of residual porosity. For example, in the La_2O_3–Y_2O_3 system, Rhodes [*54*] used a two-phase field to control grain growth during the pore-removal period of sintering and then shifted to a single-phase field to anneal to transparency.

A number of oxides have been developed for optical applications in which glass, because of refractoriness, chemical compatibility, or limitations on bandwidth, typically cannot compete. These oxides are Al_2O_3, $MgAl_2O_4$, ALON, and Y_2O_3. Although other oxides have been sintered or hot pressed to transparency, these four are considered to be the prime candidates to extend optical applications.

Another important category of optical application uses the electro-optic switching character of perovskites. The system (Pb, La)(Zr, Ti)O_3 has been hot pressed and sintered to transparency by Haertling [*26*] and Snow [*65*], respectively. Phase relations are critical to successful fabrication where Pb volatility makes it difficult to retain compositional limits, and compositional variations make possible memory, linear, or quadratic applications.

II. Yttria

Yttria is of interest for optical applications principally because of its high melting point (2464°C) and capacity for wideband transmittance (0.23 to 9.5 μm). This combination of properties makes possible a material that will perform at high temperatures with low emittance and minimal migration of the phonon edge into the 3- to 5-μm band of interest for many infrared applications. Early development of transparent Y_2O_3 was directed toward the lamp envelope application in competition with Al_2O_3. Interest in this application fell mostly because of the high cost of powder, but it remains viable for applications requiring the thermodynamic properties of Y_2O_3. The infrared window application has received considerable attention throughout the world in the last 10 years. Also, unique x-ray scintillators based on transparent Y_2O_3–Gd_2O_3 developed by Greskovich *et al.* [*25*] are extremely successful commercially.

The early work of Brissette *et al.* [*12*] and Lefever and Matsko [*39*] demonstrated that pure undoped Y_2O_3 could be fabricated to transparency by employing a combination of fine active powders and high-temperature press forging. More recently, Hartnett *et al.* [*34*] and Shibatta *et al.* [*63*] have taken a similar powder approach with hot isostatic pressing to fabricate transparent complex geometries. Success in these approaches relies not only on powder properties and the application of pressure to

enhance densification kinetics, but also on high purity to prevent precipitation of second phases or coloration from transition or rare-earth ions.

Phase relations become critical to success when pressureless sintering is the fabrication mode chosen to attain transparency. A number of sintering mechanism options are available to ceramists in their quest to affect the densification and grain-growth control necessary to eliminate porosity and achieve transparency. These options include liquid-phase sintering, transient second-phase sintering, and doped solid-state sintering. All require accurate knowledge of solid solution limits, eutectics, and other phase relations governing microstructure development.

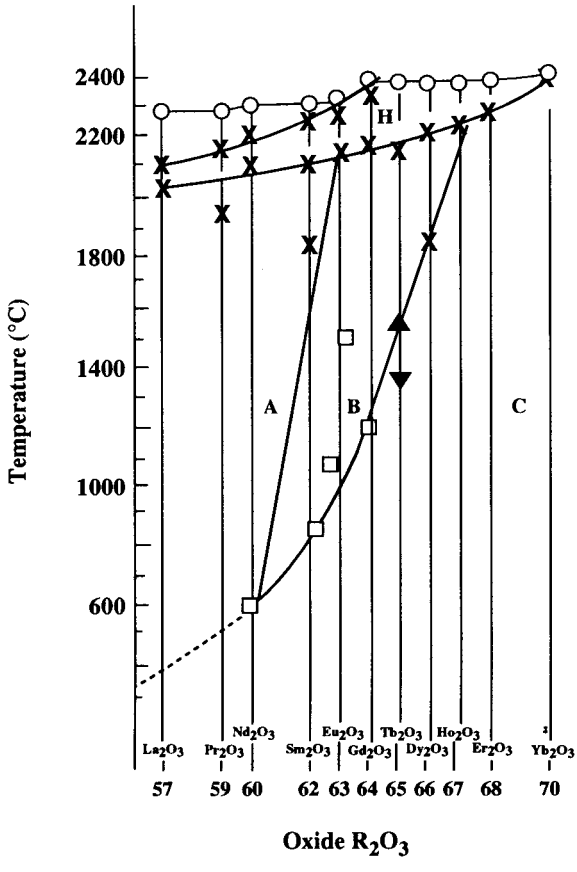

FIG. 1. Phase field diagram for the rare-earth oxides. After Foex and Traverse [*18*]. Reprinted by permission of Societie Francaise de Mineralogie et al Crystallographie.

The phase field diagram of Foex and Traverse [*18*] is useful in evaluating possible sintering aids for Y_2O_3. Figure 1 shows that the rare-earth oxides are generally found in one of three structures, depending on cation size. The cubic, or C, structure is a distorted fluorite structure having octahedral cation coordination with 32 $MO_{1.5}$ groups per unit cell and a large vacancy in the center. Y_2O_3 has this structure since it has the same ionic radius (0.892 Å) as Ho (0.894), atomic number 67. The lower atomic numbers have larger ionic radii, which result in a monoclinic, or B, structure having either six or seven cationic coordination. Still larger ions form the seven coordinated hexagonal, or A, structure. One can see that additions of larger cations to Y_2O_3 would develop extremely complex, interesting, and potentially useful phase diagrams.

A. Y_2O_3–Lanthanide Additives

Rhodes [*54*] was looking for a noncoloring aliovalent sintering aid for Y_2O_3. Among the rare-earth ions, this restricts additions to La or Gd, because these ions have no electronic transitions in the visible or infrared frequencies. Rhodes's early sintering experiments were compared with the

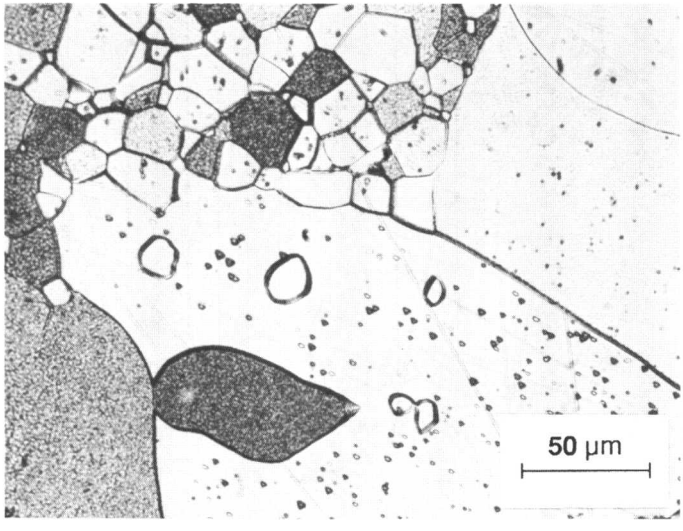

FIG. 2. Uncontrolled La_2O_3-Y_2O_3 microstructure resulting from lack of phase diagram knowledge.

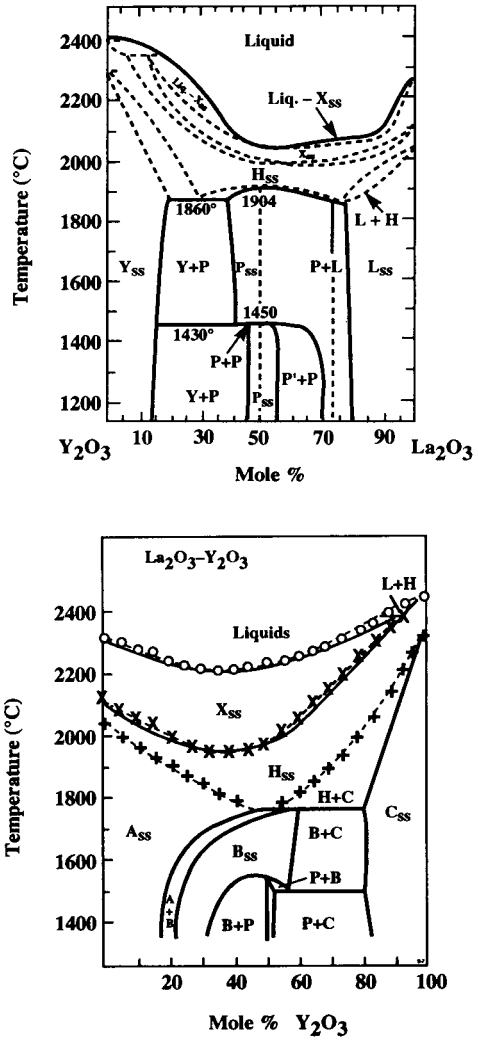

FIG. 3. Phase diagrams for the La_2O_3-Y_2O_3 system by (top) Coutures and Foex [*17*] and (bottom) Mizuno *et al.* [*47*]. Reprinted by permission of Academic Press and the Ceramic Society of Japan.

incorrect phase diagram of Cassedanne and Forestier [*13*]. This greatly retarded progress, because early experiments with 10 mole % La_2O_3 additions did not show evidence for the predicted liquid phase, but exhibited highly unusual microstructures (such as the one shown in Fig. 2) that were difficult to understand. Finally, a model emerged that can be explained with the aid of the phase diagram of Contures and Foex [*17*], shown in Fig. 3 (top), which coincidentally was being established at the same time. Mizuno *et al.* [*47*] were also working on the La_2O_3–Y_2O_3 system, and they found some differences (Fig. 3, bottom).

A composition of 9 mole % La_2O_3 was typically prepared by coprecipitating the oxalates. After calcining to form the oxides and milling to reduce agglomerate size, isostatic pressing was used to form near-net-shape

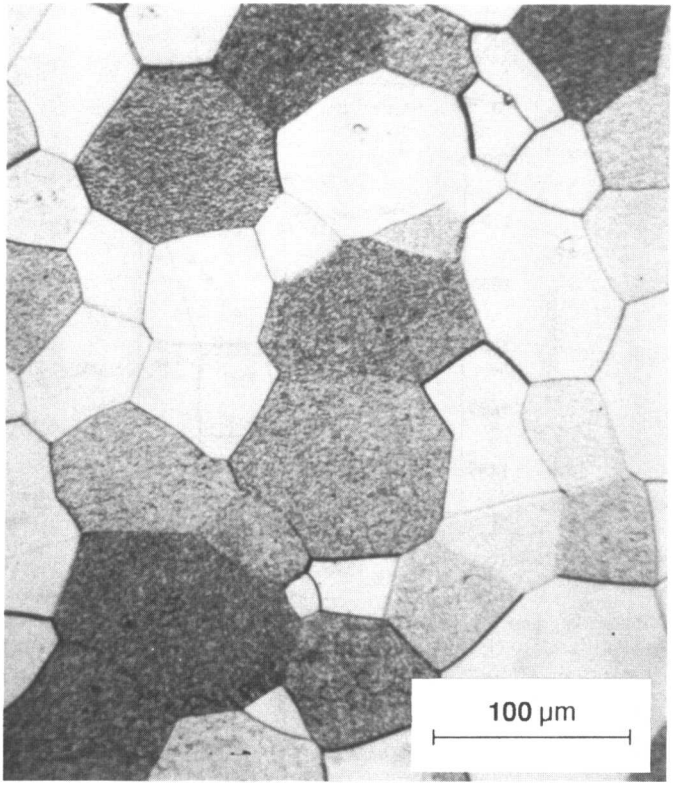

FIG. 4. A 0.09 La_2O_3 · 0.91 Y_2O_3 pore-free microstructure achieved by sintering in the two-phase (2150°C) and annealing in the single-phase (1900°C) region of the phase diagram.

compacts. The compacts were heated at a rate that was rapid enough to prevent pore entrapment into the two-phase C solid solution plus H solid solution field. A sintering temperature, typically 2150°C, was chosen to assure approximately 25 vol % H phase. Grain growth was markedly retarded by the second phase and followed a one-third time constant kinetics predicted for grain growth limited by particles of a second phase coalescing by lattice diffusion. Pores were thought to remain attached to the slow-moving grain boundaries and annihilate by a classic vacancy solid-state diffusion process. The temperature was lowered to approximately 1900°C, which is well inside the C solid solution field. Holding at this temperature dissolved the H phase by a slow diffusion process. Fortunately, the phase change was not displacive nor accompanied by a volume change that generated porosity. Instead, the pore-free microstructure shown in Fig. 4 was achieved.

Ceramic scintillators developed by Greskovich *et al.* [25] contained large concentrations of lanthanides based on Y_2O_3–Gd_2O_3 solid solutions

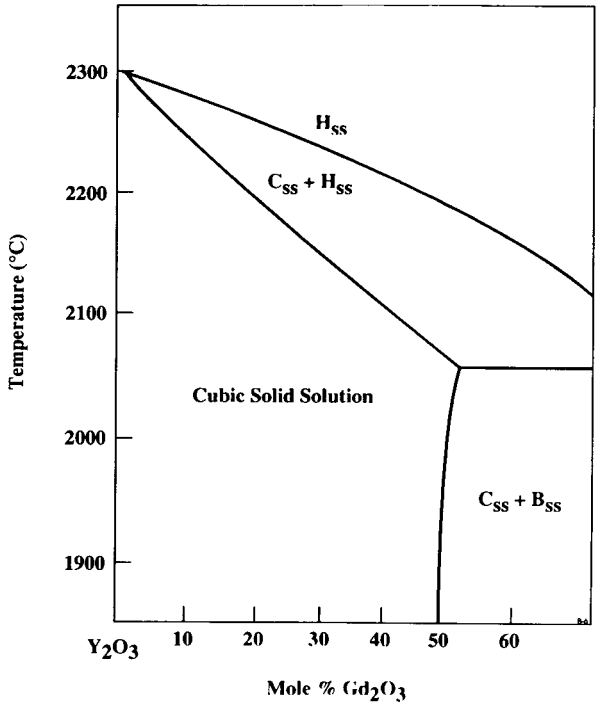

FIG. 5. Tentative Y_2O_3-Gd_2O_3 phase diagram.

and one or more rare-earth activator oxides, such as Eu_2O_3, Nb_2O_3, Yb_2O_3, Dy_2O_3, Pr_2O_3, and Tb_2O_3. The Gd_2O_3 is essential in absorbing the x rays, while the activators undergo electronic transitions that convert the energy to visible wavelengths for photodiode detection. This polycrystalline ceramic may also contain a group-four sintering aid, which is discussed in the next section. The concentrations of lanthanides added to Y_2O_3 appear to adhere deliberately to the general trends suggested by Fig. 1 for C solid solution limits. In previously unpublished work, Rhodes defined the Y_2O_3-rich end of the Y_2O_3–Gd_2O_3 diagram (Fig. 5). The work of Greskovich *et al.* [*25*] shows a cubic/monoclinic phase boundary at 50 mole % Gd_2O_3, in agreement with Figure 5. It is interesting to note, based on similar phase diagrams, that the transient second solid-phase sintering mechanism discussed for La_2O_3 might also be applicable for Gd_2O_3 additions. Greskovich [*23*] reported that the heavy doping in scintillator compositions can act as grain-growth retardants, allowing transparency to be achieved without group-four sintering aids. The sintering mechanism operative in this case must be solute drag, since these aliovalent substitutions would not create defects affecting diffusion rates.

B. Y_2O_3–Group-Four Additives

The classic work of Anderson [*2*] in developing Yttralox (General Electric, Schenectady, N.Y.) originated from research in the Y_2O_3–ZrO_2 system to develop better ionic conductors for fuel cells. After exploring the ZrO_2-rich end of the system that resulted in the good O^{-2} conductors of the fluorite structure, he decided to check the fluorite structure at the Y_2O_3-rich end. Quite unexpectedly, a number of the very first samples in this series sintered to transparency. This led to a research concentration in transparent Y_2O_3, and to the discovery that group-four oxides, HfO_2 and ThO_2, also behaved as effective sintering aids. ThO_2 was the most fully studied and characterized additive.

The ThO_2–Y_2O_3 phase diagram after Sibieude and Foex [*64*], of Fig. 6 shows a solid solution range up to 15.5 mole % at 2000°C. Jorgensen and Anderson [*37*] performed precision lattice parameter measurements in this system in an attempt to elucidate the sintering mechanism. Their results, shown in Fig. 7, agree quite well with the published phase diagram at 2000°C. The lower temperature results suggest a less steep temperature dependence on the solubility limit. A new line has been added to Fig. 6, incorporating the Jorgensen and Anderson measurements and the results of Greskovich and Chernoch [*24*]. Transparent ceramics were obtained with as little as 5 mole % ThO_2; additions of 7 to 10 mole % were