**Title**

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**Publication Date**

1982-04-01

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## Materials & Molecular Research Division

Submitted to the Journal of the American
Ceramic Society

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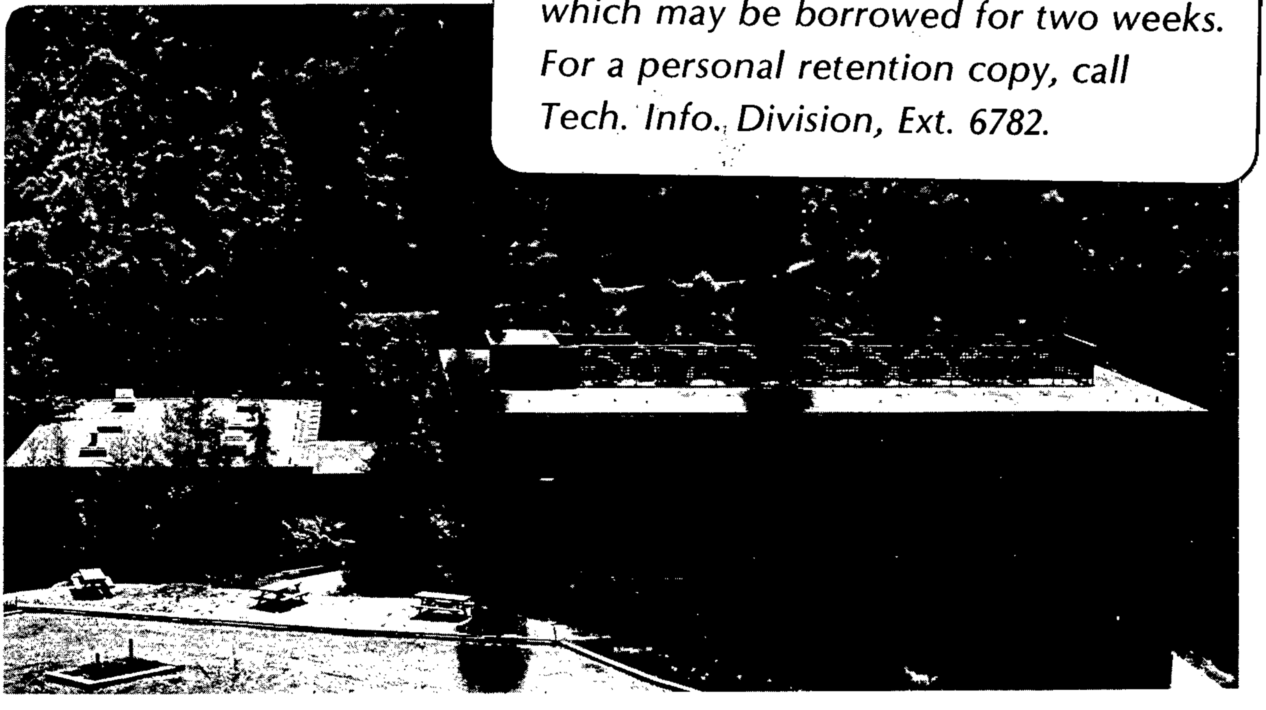
April 1982



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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# Technique for Measuring Grain Boundary Mobility:
# Application to MgO-doped $Al_2O_3$

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## ABSTRACT

An experimental technique employing localized laser heating has been developed to seed abnormal grain growth in Mg-doped $Al_2O_3$, permitting the migration behavior of individual grain boundaries to be investigated. Nonuniform growth of both naturally nucleated and laser nucleated abnormal grains was observed. Calculated boundary mobilities exceeded those characterizing grain growth in both doped and undoped porous $Al_2O_3$.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

## 1. Introduction

An understanding of grain boundary migration, in particular, the development of an ability to predict and control boundary migration rates, is essential to the control of microstructural development. Boundary migration rates can be influenced by interactions between the grain boundary and solutes, pores, precipitates, etc.. In many cases, the magnitude of the driving force for migration (normally assumed to be inversely proportional to the grain size) and the absolute and/or relative magnitudes of the drag forces due to the aforementioned interactions are time dependent, making interpretation and prediction of boundary migration rates in typical ceramics difficult.

To circumvent such complications, it would clearly be desirable to experimentally isolate a specific interaction or a particular variable and systematically investigate its influence on boundary migration behavior. Unfortunately, few available experimental techniques have this capability and their applicability to high temperature oxides is extremely limited. Consequently, the nature of the various interactions and their effects on microstructure development are poorly understood. The present report describes an experimental technique which is being used to investigate the migration behavior of individual grain boundaries in MgO-doped $Al_2O_3$ and should be applicable to a wide variety of oxides.

## II. Background

Relatively few experimental techniques are applicable to boundary mobility* experiments in ceramic systems of commercial importance. Discontinuous recrystallization and bicrystal techniques have been used to study grain boundary motion in alkali halides. Measurements of discontinuous recrystallization rates in deformed crystals of NaCl[1], KCl[2], and LiF[3-5], have permitted the influence of dopant concentration and type on grain boundary migration rates to be isolated and studied in these systems. However, application of this technique to oxides is limited by the availability of sufficiently high-purity single crystals and, more importantly, by the high temperature and/or isostatic pressures necessary to permit a deformation (creep) microstructure to be produced without fracture. A number of bicrystal techniques[6-8], applied to boundary mobility studies in alkali halides,[6,9,10] have also permitted solute-boundary interactions to be isolated and in principle, the boundary misorientation to be systematically varied. In practice, growth of oxide bicrystals is difficult and, in non-cubic oxides, fracture due to thermal expansion anisotropy generally occurs.

Due to these problems and limitations, much of the boundary moblity data for oxide systems[11] has instead been extracted from the results of grain growth or sintering studies. The time dependence of the grain size and/or porosity complicates interpretation of the data. Boundary mobility values for a given oxide system, at a particular temperature, inferred in this way, sometimes vary by orders of magnitude.[11]

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*The boundary mobility is defined as the velocity per unit driving force.

As an alternative to conventional grain growth experiments, in which the "average" boundary mobility is deduced from the rate of increase of the average grain size, the boundary mobility may also be determined by monitoring the growth rate of a large "abnormal" grain into a fine-grained matrix. These large grains have a substantially higher growth rate than the matrix grains and thus consume the surrounding fine-grained matrix, a process referred to as abnormal grain growth. By systematically varying each matrix characteristic (such as the grain size, dopant concentration or type, or volume fraction porosity) the effect of driving force, solutes or pores on boundary migration rates can be isolated and studied. In general, when a typical powder compact is annealed, neither the nucleation frequency nor the location at which abnormal grains develop can be controlled, thus complicating the experiment. In order to produce isolated nuclei, it is necessary to artificially stimulate the occurrence of abnormal grain growth at specific locations.

Several studies of the growth of sapphire or alumina single crystals into a doped or undoped polycrystalline alumina matrix have been conducted. In each case, samples were prepared by sintering[12-14] or hot pressing[15] a powder compact containing one or more single crystal seeds, followed by annealing. A major problem with this technique is associated with the growth of the seed crystal(s) during densification. As a result, the migrating interface initially interacts with a higher porosity level than is characteristic of the final microstructure. By analogy to the case of precipitates,[16] pore accumulation at the single crystal-polycrystal interfaces may occur and subsequent migration may be influenced by or controlled by interactions with a "non-equilibrium" pore distribution. Thus, it would clearly be preferable to introduce a single crystal or coarse-grained region (i.e. to "seed" abnormal grain growth) after the desired density has been reached.

## III. Experimental Procedure

Techniques[17] developed by J. S. Haggerty* at A. D. Little Company several years ago permit the growth of single crystal sapphire tubes and rods from a polycrystalline feed rod. A molten zone is created between the feed rod and a single crystal seed by means of laser heating. Coupled motion of the seed crystal and feed rod permit the molten zone to be passed down the entire length of the feed rod, converting it to a single crystal. However if the laser power is reduced at some intermediate point, the molten region will solidify and a grain size gradient from a single crystal to polycrystal is created. During a subsequent anneal, the resulting single crystal-polycrystal interface should migrate and consume the polycrystalline material by abnormal grain growth.

In the present study, this technique has been simplified and used to generate a coarse-grained region in an otherwise fine-grained pore-free polycrystalline material. Commercially available 0.75 wt.% Mg-doped $Al_2O_3$ tubes† (0.9 cm O.D.) were sectioned to produce 0.2 cm thick rings. A small circular region, ~0.35 cm in diameter, was heated in air and melted by a 1 s pulse of the defocussed beam of a $CO_2$ laser operating at a power of 170W. During solidification, a coarse-grained region bounded by

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(unmelted) fine-grained matrix is produced (Figure 1), thus providing conditions suitable for abnormal grain growth. Although cracking of the rings during cooling was common, in general, the cracks were not extensive and extended perpendicular to the coarse grain-fine grain interface and did not impede grain growth during subsequent annealing.

## IV. Results

Coarse grains bounded by a higher than average number of fine grains (the grains most likely to grow abnormally) were selected, and the original coarse grain-fine grain interface position was recorded with respect to reference marks. Samples were annealed at 1600°C for 24-72 hours. The boundary displacements for the selected coarse grains were determined and time-averaged velocities calculated.

Boundary motion was observed to be nonuniform; some portions of the boundary moved by undetectable amounts whereas along other portions boundary displacements constituted several (matrix) grain diameters. Although some of the observed variability may reflect spatial nonuniformity of the driving force, it may also be due to variability of the boundary mobility, i.e. the boundary velocity due to a particular driving force may not be single valued. A computer simulation of grain growth[18] has indicated that nonuniformity of the boundary mobility may play a key role in the nucleation of abnormal grains.

Non uniform boundary motion has been observed in discontinuous recrystallization of NaCl[1,19] and LiF[3-5] and may be inferred from the highly irregular morphologies of some abnormally growing grains in KCl[2,20].

In the case of LiF the nonuniformity was interpreted as indicating that more than one solute was influencing the boundary migration rate. In view of the limited solubility of MgO in $Al_2O_3$[21] at 1600°C, precipitate drag may also influence the migration behavior, possibly pinning certain boundary segments. Experiments using material with lower Mg levels but the same driving force should indicate the degree to which precipitates affect the migration behavior.

During anneals at 1600°C, isolated abnormally growing grains occasionally develop in the fine-grained matrix. Thus, in this particular case, it was possible to measure the growth rates of both the naturally occurring and laser introduced abnormal grains, as well as the matrix grains. The growth rates of both types of abnormal grains were spatially nonuniform; minimum boundary velocities (and hence, minimum boundary mobilities) could not be measured. However, the maximum mobilities and other aspects of the migration behavior of the two types of abnormal grains were similar, suggesting little if any effect of the laser melting on the subsequent behavior.

The "average" mobility of the matrix grains was estimated from the matrix grain growth rate and is comparable in magnitude to the maximum mobilities observed for abnormal grains (Table 1). A comparison of the results to date with those of other investigations is somewhat unsatisfying. Of six previous studies[12-15,22,23] of grain boundary migration in doped and undoped $Al_2O_3$, only one[23] provides data at temperatures as low as 1600°C and in all cases the material was porous. Extrapolation of boundary mobilites extracted from some of these studies[11] suggests that the "expected" boundary mobility at 1600°C should lie between $2 \times 10^{-15}$ and $10^{-13}$ $m^3/N \cdot s$. The higher mobilities observed in the present study may be due to absence of porosity and the consequent elimination of pore drag. However, large differences in boundary mobility may also be the result of subtle differences in the solute concentration or type.

## V. Summary

An experimental technique employing localized laser heating has been developed to seed abnormal grain growth in Mg-doped $Al_2O_3$, permitting the migration behavior of individual grain boundaries to be investigated. Nonuniform growth of both naturally nucleated and laser nucleated abnormal grains was observed. Calculated boundary mobilities exceeded those characterizing grain growth in both doped and undoped porous $Al_2O_3$.

## ACKNOWLEDGMENTS

This work was suppported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The assistance of J. S. Haggerty, T. R. Gattuso, and R. Marra is gratefully acknowledged.

## References

1. H. G. Müller, "Zur Natur der Rekristallisationsvorgänge I. Einkornrekristallisation an verformten Einkristallen," Zeitschrift für Physik, 96, 279-306 (1935).
2. M. F. Yan, "Grain Boundary Mobility of KCl," Ph.D. Thesis, Massachusetts Institute of Technology. Cambridge, MA, June 1975.
3. A. M. Glaeser, "Grain Boundary Migration in Lithium Fluoride," Sc.D. Thesis, Massachusetts Institute of Technology. Cambridge, MA, June 1981.
4. A. M. Glaeser, H. K. Bowen and R. M. Cannon, "Grain Boundary Migration In LiF: I. Mobility Measurements," to be submitted.
5. A. M. Glaeser, R. M. Cannon and H. K. Bowen, "Grain Boundary Migration in LiF: II. Microstructural Characteristics," to be submitted.
6. C. F. Gibbon, "Technique for Measuring Grain Boundary Mobility and Its Application to Potassium Chloride," J. Am. Ceram. Soc., 51 [5] 273-76 (1968).
7. W. E. Bron and E. S. Machlin, "Grain Boundary Mobilities in High Purity Silver," Trans. A.I.M.E., 206 [5] 513-514 (1956).
8. R. C. Sun and C. L. Bauer, "Measurement of Grain Boundary Mobilities Through Magnification of Capillary Forces," Acta Metall., 18 [6] 635-38 (1970).
9. R. C. Sun and C. L. Bauer, "Tilt Boundary Migration in NaCl Bicrystals," ibid., pp. 639-47.
10. K. Kitazawa, T. Arima, N. Bessha, Y. Saito, K. Fueki and T. Mukaiba, "Effect of Solutes on Grain Boundary Migration Kinetics in KCl Bicrystals," Science of Sintering, 10 [1] 27-33 (1978).

11. M. F. Yan, R. M. Cannon, and H. K. Bowen, "Grain Boundary Migration in Ceramics," pp. 276-307 in Ceramic Microstructures '76. Edited by R. M. Fulrath and J. A. Pask, Westview Press, Boulder, CO, 1977.
12. R. E. Mistler, "Grain Boundary Diffusion, Widths and Migration Kinetics in $Al_2O_3$, NaCl, and Ag," Sc.D. Thesis, Massachusetts Institute of Technology. Cambridge, MA, June 1967.
13. M. Kinoshita, "Boundary Migration of Single Crystal in Polycrystalline Alumina," Yogyo Kyokai Shi, 82 [5] 295-96 (1974).
14. W. S. Patrick and I. B. Cutler, "Grain Growth in Sintered Alumina," J. Am. Ceram. Soc., 48 [10] 541-42 (1965).
15. R. D. Monahan and J. W. Halloran, "Single-Crystal Boundary Migration in Hot-Pressed Aluminum Oxide," ibid., 62 [11-12] 564-67 (1979).
16. M. F. Ashby and R. M. A. Centamore, "The Dragging of Small Oxide Particles by Migrating Grain Boundaries in Copper," Acta Metall., 16 [3] 1081-92 (1968).
17. J. S. Haggerty, W. P. Menashi, and J. P. Wenckus, "Method for Forming Refractory Fibers by Laser Energy," U.S. Patent 3,944,640, March 16, 1976.
18. M. F. Yan, "Microstructural Control in the Processing of Electronic Ceramics," Mat. Sci. and Eng., 48 [1] 53-72 (1981).
19. K. Przibram, "Über die Rekristallisation des Steinsalzes," Zeitschrift für Physik, 67, 89-105 (1931).
20. B. G. Koepke, R. H. Anderson, E. Bernal G., and R. J. Stokes, "Room Temperature Grain Growth in Potassium Chloride," J. Appl. Phys., 45 [2] 969-70 (1974).

21. S. K. Roy and R. L. Coble, "Solubilities of Magnesia, Titania and Magnesium Titanate in Aluminum Oxide," J. Am. Ceram. Soc., 51 [1] 1-6 (1968).

22. A. Mocellin and W. D. Kingery, "Microstructural Changes During Heat Treatment of Sintered $Al_2O_3$," ibid., 56 [6] 309-14 (1973).

23. R. L. Coble, "Sintering Crystalline Solids. II. Experimental Test of Diffusion Models in Powder Compacts," J. Appl. Phys., 32 [5] 793-799 (1961).

Table 1

Grain Boundary Mobility ($m^3/N \cdot s$) at 1600°C

| | | Remarks |
|---|---|---|
| <u>Abnormal Grains</u> | | |
| Laser nucleated | $7 \times 10^{-13}$ | Maximum |
| Naturally nucleated | $4 \times 10^{-13}$ | Maximum |
| <u>Normal Grains</u> | | |
| Matrix | $\sim 2 \times 10^{-13}$ | Average |
| Calculated intrinsic mobility | $\sim 10^{-10}$ | Ref. 11 |

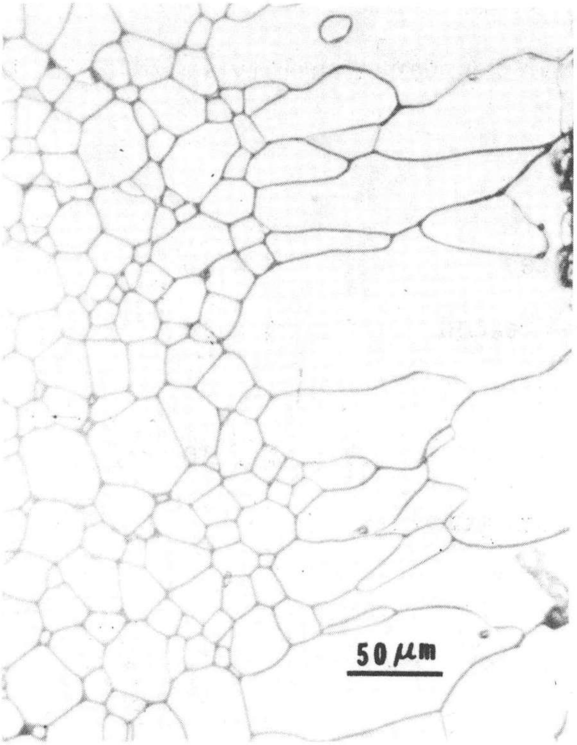

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Figure 1. Typical grain size discontinuity produced by laser melting.

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