Title:

MECHANICAL PROPERTIES OF MELT-DERIVED ERBIUM OXIDE

CONF-980110--

Author(s):

A. D. Neuman, B. M. Platero, R. S. Romero,
K. J. McClellan, J. J. Petrovic

RECEIVED

MAY 28 1998

OSTI

Submitted to:

American Ceramic Society
22nd Annual Cocoa Beach Conference and Exposition
Cocoa Beach, FL
January 20-24, 1998

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MECHANICAL PROPERTIES OF MELT-DERIVED ERBIUM OXIDE

A. D. Neuman, Group NMT-9, M.J. Blacic, M. Platero, R.S. Romero, K.J. McClellan, J.J. Petrovic, LANL, Group MST-8, Los Alamos National Laboratory, Los Alamos, NM 87544

Abstract

Erbium oxide (Er_2O_3) is a rare earth oxide that is chemically and thermally stable and has a melting point of 2430 °C. There is relatively little information available regarding single crystal growth of erbia or the properties of erbia. In this study, erbia single crystals have been grown in a Xenon Optical Floating Zone Unit (XeOFZ) capable of melting materials at temperatures up to 3000 °C. Erbium was melt synthesized in the XeOFZ unit in a containerless fashion, proving for little chance of contamination. Crystals were grown in compressed air and in reducing atmospheres. A recurring problem with melt synthesis of erbia is the appearance of "flakes" at the edges of the melt zone during growth; these flakes disrupt the growth process. The processing details and an initial survey of the physical properties of erbia single crystals is discussed.

INTRODUCTION

Erbium oxide is a rare earth oxide with a melting temperature of 2430 °C¹. Polycrystalline erbia has shown low hardness and toughness², but very little is known about single crystal erbia. The main reason for this lack of information is due to the fact that, since erbia has such a high melting point, it is difficult to find a container that is not affected at such a high temperature for crystal growth.

There are various methods in existence for growing single crystals, but the optical floating zone technique is well suited for growing rare earth oxides, such as erbia, because of its containerless method³. The optical floating zone technique went through multiple variations before reaching its current geometry. The first crucible free melting was introduced by Keck and Golay⁴. The

general zone melting method of Kapitza⁵ was developed by Pfann⁶ into the

forefather of the floating zone techniques used today. The basic geometry of the current OFZ unit is based on the Costello method^{7,8}.

The XeOFZ operates by means of a Xenon lamp that is at one foci of an ellipsoidal mirror as can be seen schematically in Figure 1. The other focal point of the ellipsoid is known as the "hot zone".

This is where the seed and feed rods are passed through and where melting and joining of the material occurs. Once this occurs, the crystal starts growing from the melt as can be seen in Figure 2.

Fig. 1. This is a Dual Halogen Optical Floating Zone unit which is similar to the XeOFZ. The difference is in the type of lamp and number of lamps. The XeOFZ has one Xenon lamp (rather than two halogen lamps), but the principal is the same.

Figure 2. Joined Er_2O_3 feed and seed rods. The rods rotate opposite each other to provide convective heat transfer as they are passed through the hot zone. The melted material then solidifies as it exits the hot zone.

EXPERIMENTAL PROCEDURE

The erbia feed stock used for this experiment was supplied by Advanced Materials Resources (AMR). The as-received powder was cold isostatically pressed (CIP) into rods of approximately 70% theoretical density. The idea behind using rods with such a low density was that the large amount of porosity would reduce the material's susceptibility to thermal shock in the large gradients

inherent in OFZ growth. The low density feed and seed rods also provided a more stable melt zone than in previous runs, where higher density material was used.

Besides using low density rods, other factors, such as growth rate and atmosphere have to be taken into account. When slow growth rates are used, the erbia rapidly forms "flakes" around the hot-zone which blocks the radiation directed toward it. This causes the temperature within the melt to decrease, which in turn causes instabilities in the growth. If the growth rate is increased, the flakes have less time to form, resulting in an inherently more stable run. However, there are problems associated with a fast growth rate, including various effects of residual stresses due to steep thermal gradients inherent in the system and bubble or void formation. A slow growth rate tends to counter these effects.

Various atmospheres were used, included air, inert (Ar), reducing (Ar with 6% H₂), and strongly oxidizing (O₂). The main reason for changing the atmosphere was to determine if it would affect the flake formation.

After the crystals were grown, the material was sectioned and oriented using Laue back-reflected x-ray diffraction. The sections were then prepared for hardness measurements which were performed with a Nikon QM2 hot hardness indenter using Vickers tips. At the low end of the temperature range (room temperature to 600 °C) a diamond tip was used, but it was noted in previous work that erbia carborizes at elevated temperatures, so a sapphire tip was used at the higher temperature range (800 °C to 1200 °C). Measurements were taken every 200 °C.

Figure 3. Er₂O₃ crystal grown in compressed air atmosphere, 10 mm/hr growth rate showing the "flaking" characteristic associated with Er₂O₃ melt synthesis. The arrows indicate the solid/melt interface at which the flakes form.

RESULTS AND DISCUSSION

Previous attempts at synthesizing erbia single crystals from the melt failed due to the formation of flakes near the melt zone which can be seen in Figure 3. The flake effect was counteracted by increasing the growth rate to the detriment of the sample morphology. Microscopic analysis of the crystal showed increased porosity, large grains (rather than a single crystal), and a large amount of residual stress.

The growth atmosphere was varied as indicated above in an attempt to moderate the flake formation. The use of

"house" air, Ar and pure O₂ did not reduce the flake problem. The best atmosphere was a reducing atmosphere. When erbia was grown in a compressed air atmosphere with an overpressure of 83 kPa and at a fast growth rate, it grew with reduced flake formation (Figure 4), but exhibited a skin. This skin and some of the flakes were x-rayed and proved to be erbia. It was believed that due to the fact that the boiling point of Er (2800 °C) is close to the melting point of erbia that there is a high Er vapor pressure over the melt during crystal growth. Once the Er is out of the hot-zone, the Er vapor would re-oxidize and deposit in the

Figure 4. Er₂O₃ crystal grown in compressed air, 83 kPa overpressure, 40 mm/hr growth rate. The arrow indicates the solidification interface and the beginning of the "skin." Also shown is the "skin" as it "ribbons" down the left side of the solidified melt.

"skin" did not form.

Samples were taken from erbia grown in compressed air with an overpressure of 83 kPa and erbia grown in reducing (Ar/6% H₂) atmosphere with an overpressure of 117 kPa. These samples were prepared for hardness measurements and were indented in a Nikon QM2 hot hardness tester.

Indents were made at 200 °C intervals from room temperature to 1200 °C. The analysis used for hardness and toughness determination⁹ was by measuring the horizontal and vertical diameters of each indent (6 indents for each temperature) as well as the crack lengths initiated at the indent corners. The Vickers hardness was calculated from:

$$VH = 1.854P/d^2$$

(1)

form of erbia flakes and skin. By using an overpressure of approximately 83 kPa, in air, the skin was still present, but the flakes were greatly reduced. (Figure 4). Further runs in reducing atmosphere (Ar/6% H₂) with overpressures between 83 and 140 kPa produced similar results in that the flakes were greatly reduced (Figure 5), but contrasting in that the

Figure 5. Er₂O₃ crystal grown in reducing atmosphere (Ar/H₂, 6% H₂) illustrating the reduction of flakes. This crystal was grown at a rate of 20 mm/hr with an overpressure of 117 kPa.

where P is the applied load of 1 kg and d is the diameter of the indent. The toughness was calculated from the measured crack lengths using the equation:

$$T = \zeta(E/H)^{1/2}P/c^{3/2} \quad (2)$$

where $\zeta=0.0168$, E is Young's modulus for polycrystalline erbia at the various temperatures¹⁰, H is the average Vickers hardness, P is the load, and c is the average crack length made by the indenter. Figure 6 shows the trend of hardness with respect to temperature. At room temperature the hardness for both crystals is about 6 GPa and goes to about 2 GPa when reaching 1200 °C indicating a decrease of about 75%. Figure 7 shows the approximate trend of the indentations toughness. The indentation toughness for both crystals is between 1 and 3 Mpa√m. The increase in toughness observable in Figure 7 may be due to the different indenters used. The toughness is comparable to reported values for ceramics such as alumina and magnesia¹¹.

CONCLUSIONS

Due to the high melting point of erbia it is best grown from the melt with the use of a XeOFZ unit. Consideration must be made on growth rate, atmosphere and overpressure. So far the best results were obtained with erbia grown in a reducing atmosphere, Ar/6%H₂, at a rate of 20 mm/hr and an overpressure of approximately 117 kPa.

The hardness for both crystals ranges from 6 GPa to 2 GPa indicating a decrease of about 75% upon going from room temperature to 1200 °C. The indentation toughness for both crystals is between 1 and 3 Mpa√m.

ACKNOWLEDGMENTS

Support was provided by UO/UP Los Alamos National Laboratory under a stockpile stewardship educational program, and also by the DOE Office of Basic Energy Sciences (DOE/OBES). The authors would like to thank A. Sandoval, R. Hoover, and J. Garrett.

Figure 6. Hardness with respect to temperature for two erbia crystals. One was grown in compressed air with an overpressure of 83 and the other was grown in reducing atmosphere (Ar/6%H₂) with an overpressure of 117 kPa. The load used for indentation was 300 g. The orientation was $\langle 111 \rangle \pm 5^\circ$.

Figure 7. Indentation toughness with respect to temperature for two erbia crystals. One was grown in compressed air with an overpressure of 83 and the other was grown in reducing atmosphere (Ar/6%H₂) with an overpressure of 117 kPa.

REFERENCES

- ¹ E.R. Andrievskaya, L.M. Lopato, and V.P. Smirnov, "The system $\text{HfO}_2\text{-Y}_2\text{O}_3\text{-Er}_2\text{O}_3$," *J. Am. Ceram. Soc.*, **79** [3], 714-20 (1996).
- ² A. Neuman, M. Platero, R.S. Romero, K.J. McClellan and J.J. Petrovic, "Fabrication and properties of erbium oxide," *Ceramic Engineering and Science Proceedings*, **18** (4), 37 (1997).
- ³ J. Bohm, A. Ludge, and W. Schroder, "Crystal Growth by Floating Zone Melting," *Handbook of Crystal Growth*, 2a, North-Holland, Amsterdam, 213-257 (1994).
- ⁴ P.H. Keck and M.J.E. Golay, *Phys. Rev.*, **89**, 1297 (1953).
- ⁵ P. Kapitza, *Proc. R. Soc., London*, **A-119**, 358 (1928).
- ⁶ W.G. Pfann, *Zone Melting*, Wiley, New York, 2 ed., 1966.
- ⁷ B.J. Costello, "Concentrated Radiant Energy," *Western Elec. Eng.*, **7**, 161 (1962).
- ⁸ T. Akashi, K. Matumi, T. Okada, and T. Mizutani, "Preparation of Ferrite Single Crystals by New Floating Zone Technique," *IEEE transactions on magnetics*, **5** (3), 285 (1969).
- ⁹ B. Lawn, *Cambridge Solid State Science Series, Fracture of Brittle Solids*, Second edition, (edited by E.A. Davis and F. I. M. Ward), Cambridge University Press, New York, NY (1995).
- ¹⁰ W. R. Manning and O. H. Jr., "Elastic Properties of Polycrystalline Yttrium Oxide, Holmium Oxide, and Erbium Oxide: High-Temperature Measurements", *J. Am. Ceram. Soc.*, **52**[9], 492-6 (1969)
- ¹¹ A. Kelly and N. H. Macmillan, *Monographs on the Physics and Chemistry of Materials, Strong Solids*, Third edition, (edited by F. H. Fröhlich, et al.), Clarendon Press, New York, NY (1986).