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SINGLE CRYSTAL GROWTH OF ZIRCONIA UTILIZING A SKULL MELTING TEC--ETC(U)
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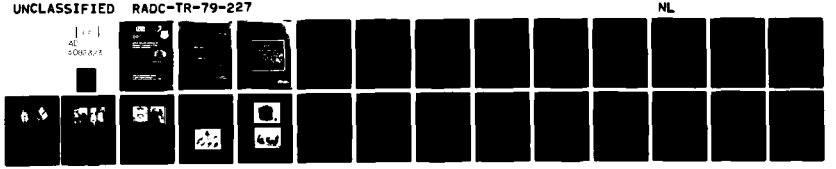

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Investigation into the growth of single crystal materials are often hindered, or in some cases not initiated, because of the lack of suitable crucible materials and/or crystal growth systems. This is especially true for refractory oxides where the effect of an oxidizing atmosphere with growth temperatures in excess of 2000° C present very serious technological problems. The selection of a crucible material which is non-reactive with the charge material under these conditions is extremely limited, or not possible.

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Because of the pressing demand for increasingly sophisticated materials for Air Force scientific and technological applications, new techniques must be developed, improved, and exploited at the earliest possible time.

One relatively new process involved direct high-frequency induction heating of an oxide within a water-cooled support structure. The melt is contained by a sintered shell or "skull" of identical composition so that the problems of reaction and contamination, traditionally the most severe conditions, have been virtually eliminated.

This report reviews the problems associated with the high temperature growth of non-metallic single crystals, particularly refractory oxides. Various approaches to circumvent the problems of melt contamination and containment are discussed. The cold wall R. F. heated skull technique is discussed in detail. This technique is applied to the growth of yttria stabilized zirconia to meet specific requirements, and to establish the viability of this technique. The resulting crystals are characterized by a number of optical, chemical, and physical techniques.

Contents

1. INTRODUCTION 7
2. BACKGROUND 8
3. EXPERIMENTAL TECHNIQUE 11
4. EXPERIMENTATION 14
5. ANALYTICAL RESULTS 16
6. DENSITY 18
7. HARDNESS 18
8. THERMAL CONDUCTIVITY 19
9. INDEX OF REFRACTION 20
10. OPTICAL MEASUREMENTS 21
11. CONCLUSIONS 21
12. FUTURE PLANS 23
REFERENCES 24

Illustrations

1. Cutaway View of Skull Crucible 11
2. Section View of Skull Crucible 11
3. Stabilized Zirconia Powder Being Added to Skull Container 12
4. Adding High Purity Zirconium Pellets 12
5. Skull Crucible in Operation 13
6. Breaking Hole in Melt Crust to Add Powder 13

7. Large, Clear Zirconia Single Crystals 14
8. Section of Charge Showing Zirconia Crystals 15
9. Oxygen-Deficient Zirconia Crystals 15
10. Percent Transmission vs Wavelength 22
11. Percent Transmission vs Wavelength 22

Tables

1. Lattice Parameter vs Yttria Content 17

Preface

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Single Crystal Growth of Zirconia Utilizing a Skull Melting Technique

1. INTRODUCTION

Investigations into the growth of single crystal materials are often hindered, or in some cases not initiated, because of the lack of suitable crucible materials and/or crystal growth systems. This is especially true for refractory oxides where the effect of an oxidizing atmosphere with growth temperatures in excess of 2000°C present very serious technological problems. The selection of a crucible material which is nonreactive with the charge material under these conditions, is extremely limited or not possible. Because of the pressing demand for increasingly sophisticated materials for Air Force scientific and technological applications, new techniques are being developed, improved, and exploited.

One relatively new process involves direct high-frequency induction heating of an oxide within a water-cooled support structure. The melt is contained by a sintered shell or "skull" of identical composition so that the problems of reaction and contamination, traditionally the most severe problems in containment of molten oxides under oxidizing conditions, have been virtually eliminated.

This report reviews the problems associated with the high temperature growth of nonmetallic single crystals, particularly refractory oxides. Various approaches to circumvent the problems of melt containment and contamination are discussed. The cold wall R. F heated skull technique is discussed in detail. This technique is applied to the growth of yttria stabilized zirconia to meet a specific requirement

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and to establish the viability of this technique. The resulting crystals are characterized by a number of optical, chemical, and physical techniques.

2. BACKGROUND

The history of modern crystal growth has been closely associated with procedures and techniques to overcome or circumvent limitations imposed by available crucible materials. When the transistor was invented in 1948 it stimulated many efforts to purify germanium and to grow large relatively perfect single crystals. The zone-refining process developed by Pfann[1] eliminated much of the purity problem in germanium because principal impurities had favorable segregation coefficients. There was no chemical reaction, and extremely limited solubility of germanium at its melting point (940°C) with the graphite boats. Similarly, the Czochralski[2] process enabled the growth of relatively large and perfect crystals from the zone-refined material. Again, the availability of highly purified graphite crucibles simplified the use of this growth technique.

When silicon became important (originally to meet Air Force temperature specifications beyond the capability of germanium) difficulties ensued because silicon reacted with graphite at the silicon melting point (1412°C). The use of quartz crucibles provided very limited success because of oxygen and boron contamination from the crucibles available at that time. The wetting of quartz by molten silicon discouraged the use of the horizontal-zone technique.

Success in the development of ultrapure quartz-ware eliminated much of the impurity contamination with the exception of oxygen. These difficulties accelerated research into new techniques for purifying silicon in chemical intermediate forms such as $SiCl_4$, and into new physical processes for growing crystals without crucibles to help eliminate many crystal growth problems.

The flame-fusion apparatus was invented by A. Verneuil[3] over 75 years ago and has been used for growth of sapphire, ruby, spinel, rutile, and other refractory crystals. The process consists of feeding finely powdered material into a high-temperature oxyhydrogen torch directed downward at a pedestal or seed crystal. The powder particles are melted in the flame produced by the torch, and fall upon the seed which is placed in the lower part of the flame so that only its surface is molten. As the melt is enlarged by powder dropping on the seed, the pedestal which supports the seed is withdrawn slowly so that the position of the liquid-

1. Pfann, W. G. (1958) Zone Melting, John Wiley and Sons, New York.
2. Czochralski, J. (1917) Z. Phys. Chem. 92, 219; (1925), Z. Among Chem.
3. Verneuil A., (1902) Comp. Rende. 135:791-794.

crystal interface is maintained at a constant level. This method allows refractory crystals to be grown at temperatures for which crucibles are either nonexistent or unsatisfactory. This technique is used to grow single crystal materials whose melting temperatures do not exceed 2400° C.

A device has been invented[4] for diverting the flow of a carrier gas (oxygen) from the normal flow pattern of a conventional Verneuil apparatus, which was a batch process and closed system. Replenishment of the feed container can be accomplished, thus allowing growth of unusually long crystals of varying compositions.[5]

For the more refractory crystals with higher melting points, the crucible problem becomes more severe. Platinum has been used for oxides at temperatures up to 1800° C. Iridium crucibles have been used for Al_2O_3 (mp 2050° C) but are very expensive, and crystals can contain iridium contaminants if crucible interior surfaces are not carefully prepared.

The continuing requirement for single crystals with melting points considerably above 2000° C led to the development of a number of specialized techniques. Lamb and Porter[6] demonstrated that through the technique of forming a "cold surface," a crucible can be maintained non-reactive for containing molten silicon. While this technique was not expanded to other materials, it clearly indicated that if the walls of the crucible are cooled so that the surfaces in contact with the charge are at some temperature below the melting point of the charge material, the molten charge does not wet or attack the walls of the container and there is no adhesion upon solidification. A water-cooled boat and crucible was developed at Standard Telecommunications Laboratory[7] by Sterling and Warren and later perfected at Oxford University[8] by Professor Hukin. In this technique, induction heating and properly designed cold hearths are used to grow relatively contamination-free crystals of refractory metals even at temperatures above 3000° C. For high-temperature oxides and non-metals a number of modifications of high frequency, water-cooled "skull" crucibles are being used.

Fay, Brandle, and Corbitt[9] of Union Carbide Corp., Linde Division, developed the general concept of skull melting under a U. S. Navy-ARPA contract,

4. Adamski, J. A., (1969) Rev. of Scientific Inst. Vol. 40, 12:1634-1635.
5. Adamski, J. A., Powell, R. C., and Sampson, J. L., (1968) J. Cryst. Growth, 3, 4:246-249.
6. Lamb, D. M., and Porter, J. L., (1961) Proc. Ultrapurification Semiconductor, Mat Brooks & Kennedy, Ed.
7. Sterling, H. F., and Warren, R. W., (1963) Metallurgical 67, 301.
8. Hukin, D. A., (1971) Claredon Lab, Univ. of Oxford Rep. 24/71.
9. Fay, H., Brandle, C. D., and Corbitt, B. J., (1965) Office of Naval Research Contract NONR - 4131 (00), Report SRCR-65-9.

during the 1963-1965 period. Skull melting is described as the containment of a liquid "melt" in a solid skull of the same composition, or a composition in equilibrium with the melt. The term was applied to describe a process wherein the liquid is used as its own susceptor for coupling of electromagnetic radiation from a radio-frequency oscillator. Several vertical, experimental, water-cooled containers were tried, and stable melting of $BaTiO_3$, $BaSrO_3$, $SrTiO_3$, and Al_2O_3 was achieved. Some success was achieved in pulling crystals from these melts by the Czochralski technique. The research efforts were not continued at Union Carbide, and this technique was not exploited in this country at the time. Some excellent work, however, was done at the Lebedev Physical Institute[10] of the USSR Academy of Sciences in Moscow, and the skull technique was perfected and utilized for the growth of single crystals of many refractory materials. Initial work in this country on a refined skull melter and improved skull-melting technique was accomplished by Wenckus[11] of A. D. Little Co., under an Air Force Contract.

A cut-away view of the basic skull-melting apparatus is shown in Figure 1. Cooling of the structure is obtained by flowing water through the outside concentric copper tubes with a water outlet through the inner tubes. Care must be taken to provide sufficient water turbulence in the incoming bottom water chambers to eliminate any possibility of a stagnant water condition in any of the vertical, concentric copper tubes. In order to eliminate large R. F. circulating currents in the crucible structure itself, the crucible is constructed in two sections as shown in Figure 2. This eliminates power absorption by the crucible, and allows most of the R. F. energy to be absorbed directly by the charge material.

The two major types of cold crucibles are often confused. The Sterling-Warren-Hukin type relies mainly on surface tension and levitation effects to keep molten metals from direct contact with the cold walls of the crucible. The skull type relies mainly on a layer of unmelted material of the same composition as the melt to shield the metal from the cold crucible walls.

The float zone melting technique requires no crucible and has been used to produce high purity crystals of semiconductors, and many high-temperature alloys. In this technique, a molten zone normally heated by R. F. energy is established between two vertical cylindrical rods, and is supported by the surface tension of the liquid. The mechanical stability of such a configuration is a function of the radius of the rods, the length of the molten zone, and the surface tension of the liquid, gravity, and the shape of the liquid-solid interface. This technique has produced extremely pure crystals of silicon, mostly limited to 3 in. in diameter, and of many high-temperature metals such as tungsten, molybdenum, and tantalum.

10. Aleksandrov, V. I., et al., (1973) vestnik AKAD NAUK SSSR 12, 29.

11. Wenckus, J. F., et al., (1974) AFCRL-TR-74-0314 Contract F19628-74-C-0097.

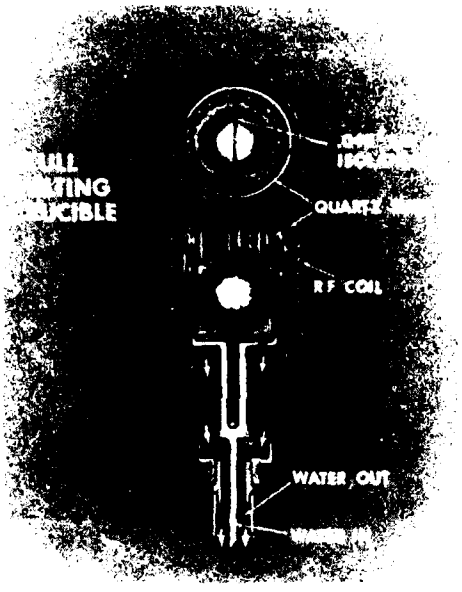

Figure 1. Cutaway View of Skull Crucible

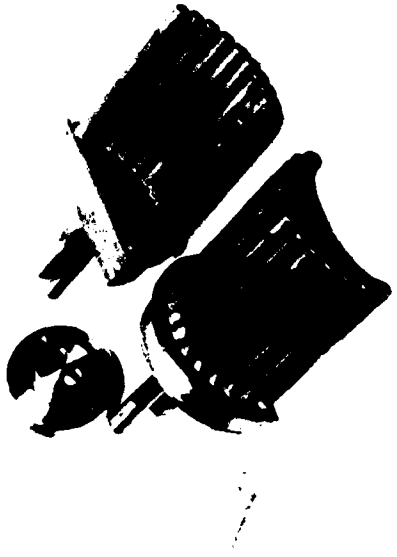

Figure 2. Section View of Skull Crucible

It has met with little success with non-metals with melting temperatures above 2000°C. One exception is Al_2O_3 which has been grown by this method using optical and electron-beam heating.

T. B. Reed of MIT Lincoln Laboratory grew refractory materials from a cold hearth tri-arc furnace by the Czochralski technique.[12] While crystals are small, this unique triple-arc arrangement provided uniform melting of the charge materials.

3. EXPERIMENTAL TECHNIQUE

The small skull melter apparatus, 2.75" ID x 4" high, shown in Figure 3, is loaded with a stabilized zirconia charge. The charge is hand-packed during the loading process to obtain as compact a charge as possible. At a predetermined height, small pieces of 99.99% zirconium metal are added (Figure 4). While the size of the zirconium metal is not critical, care must be taken to use relatively

12. Reed, T. B., Pollard, E. R., (1968) J. Cryst. Growth, 2:243.

Figure 3. Stabilized Zirconia Powder Being Added to Skull Container

Figure 4. Adding High Purity Zirconium Pellets

small pieces to prevent small explosions of the metal due to the rapid heating process when the R.F. energy is applied. Severe scattering of the metal and hot charge-powdered material can result. The filling process is then completed by adding additional powder during the heating process. Because of the desire to obtain as large a charge as possible, the small crucible was filled to the top. A dome shape helps reduce radiation losses. An overall view of the system in operation is shown in Figure 5. The crucible must be isolated electrically from the cooling water supply and the crucible-lowering mechanism. This electrical isolation is required to prevent any problem with arcing. The energy is supplied by a Lepel dual-frequency 50 kW R.F. generator operating at 3.5 MHz. The generator has a frequency capability of 450 kHz and 3.5-8.0 MHz. The power initially couples into zirconium, which, in turn, heats the zirconia charge, lowering its electrical impedance so that the R.F. couples to the charge directly, at relatively low R.F. power levels. As the charge reaches a molten state, additional powder is added slowly, through a hole broken in the sintered dome (Figure 6). Power is increased gradually during this period. The total charge is about 2 kg.

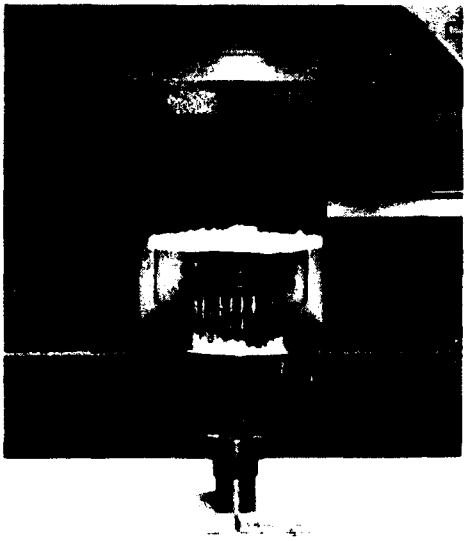

Figure 5. Skull Crucible in Operation

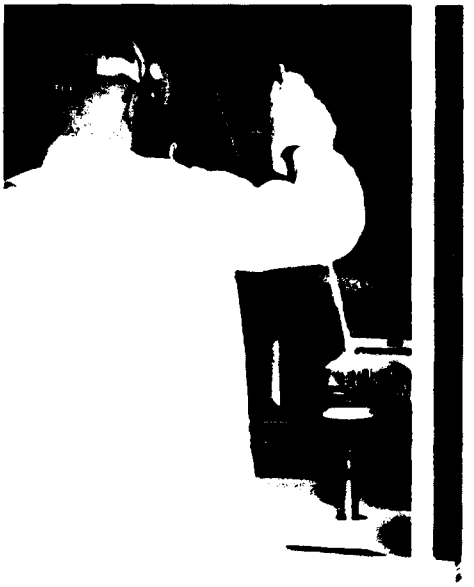

Figure 6. Breaking Hole in Melt Crust to Add Powder

A yttria plate with a hole in the center is placed over the crucible, and supported by the R.F. coil. This helps prevent shorting the coil in the event of a bubble overflow, especially when the crucible has full capacity charge. A spherical reflector is placed over the crucible to help reduce the vertical temperature gradient, attenuate the visible radiation, and help maintain an opening in the surface of the melt for adding powder, or for Czochralski pulling.

The crucible is raised gradually through the coil until the lower turn is about 1 in. from the bottom of the crucible. The temperature of the melt reaches approximately 2850°C at a power level of 23 kVA. After a soak period of one hour for temperature stabilization, the crucible is lowered through the coil at a rate of 1 cm per hour for a total distance of 4-5 cm. When the withdrawal period has been completed, the power is decreased by an automatic clock-controller at a non-linear rate, at approximately 2 kVA per hour.

4. EXPERIMENTATION

Initial experiments were conducted to determine the optimum percentage of yttria to be added to the zirconia, to stabilize the zirconia fully in the cubic form. There are three well-defined polymorphs of pure zirconia, namely the monoclinic, tetragonal, and cubic structures. The monoclinic phase is stable to approximately 1100°C, and then transforms over a 100°C temperature range to the tetragonal phase. At about 2370°C it adopts the cubic fluorite structure (bcc). It is, however, possible to stabilize cubic zirconia so that it remains cubic on cooling to ambient temperatures by adding select impurities like Y_2O_3, or CaO. Visible changes in the crystals are readily apparent as the yttria content is reduced below 15 weight percent. First is the evidence of cloudiness at the grain boundary surfaces which become more opaque as the quantity of yttria is decreased. Horizontal cracking increases dramatically at 10 weight percent. At 20 weight percent (Figure 7), large single crystals of very clear pure material with a [100] growth direction can be grown even in a small crucible. Figure 8 shows the interior of a crystallized charge, split in half along grain boundaries. Large, clear, single crystals can be seen easily. Figure 9 shows the interior sections where the core crystals are very light amber. These crystals are oxygen deficient due to excess

Figure 7. Large, Clear Zirconia Single Crystals

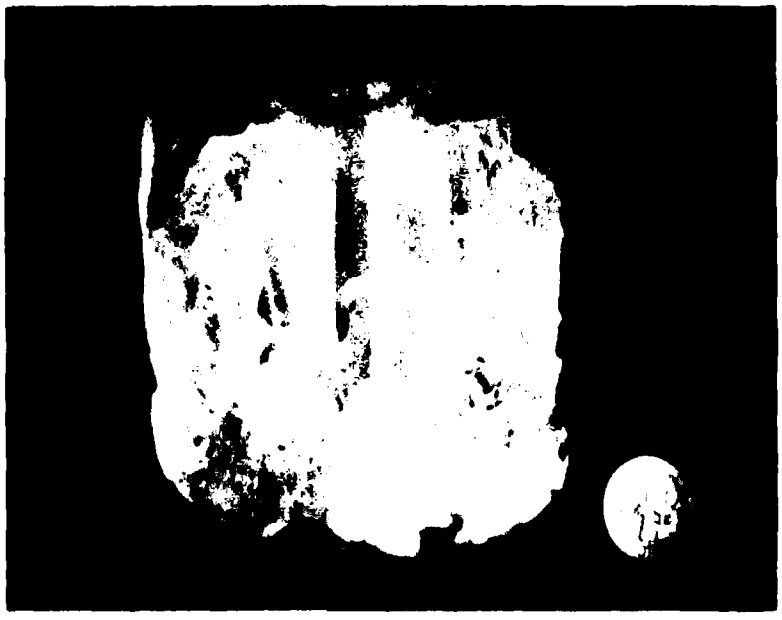

Figure 8. Section of Charge Showing Zirconia Crystals

Figure 9. Oxygen-Deficient Zirconia Crystals

zirconia metal and insufficient oxygen during the early part of the growth process. Some of these amber crystals were annealed thermally at 1450°C in an oxygen atmosphere for 24 hours. After annealing, the crystals were perfectly clear and colorless.

The zirconia powder used in these experiments was obtained from N. L. Industries, Inc. Samples of the powder with 25 weight percent Y_2O_3 added, were analyzed using emission spectroscopy, and the following results were obtained for the powder and resulting crystals:

Element	PPM Powder	PPM Crystals	Element	PPM Powder	PPM Crystals
Boron	1.0	0.5	Titanium	500	500
Sodium	N.D.	N.D.	Chromium	0.05	0.05
Magnesium	50	2	Manganese	0.5	0.1
Aluminum	500	200	Iron	10	4
Silicon	150	10	Nickel	100	75
Hafnium	N.D.	N.D.	Copper	0.6	0.5

N.D. - NOT DETECTED

The yttrium oxide powder used to stabilize the zirconia had a purity of 99.99% or better, and was purchased from Rhodia, Inc.

5. ANALYTICAL RESULTS

A series of samples obtained from eight experimental runs were subjected to the following kinds of examination:

a. Back-reflection Laue patterns were taken of the most prominent surface on each type of specimen. In most cases, those surfaces are conchoidal-type partings along the length of the specimen; the length being defined as the direction from the cap of the solidified melt downward through the section. In all cases the Laue photographs showed that the fractured surface was not a major plane, but, in all cases, the surface was very near the (110) pole. The surface was about 15-20° from the (110) pole, and usually along the zone containing the (201) and (310) poles.

b. Portions of the crystalline material from each run were powdered to about a 325-mesh particle size and then run on an x-ray diffraction goniometer. A complete pattern of the material can be indexed as the cubic form of ZrO_2. In order to obtain data relative to any possible changes in the lattice parameter of this material due to the additions of yttria to the zirconia, a series of measurements

were made using the (220) and (311) lines of the pattern. The lines were recorded at a reduced scan speed; 1/4° 2-phase scanning was used for these line positions. From the position of the K-alpha peak, the "d" values were measured and converted to the lattice parameter, a_o, using the appropriate (hkl) values for that line.

No attempt was made to obtain the absolute value of the lattice parameter, but changes in the parameter were noted. It is noted, however, that the lattice parameters measured for these samples, a_o in the range of 5.15-5.17Å, are in the range of the reported values for yttria-stabilized zirconia.

c. Solid sections from each of the specimens were then mounted, polished, and carbon-coated for examination in an electron microprobe. Typical data for each specimen consisted of a chemical composition of the sample. In all cases, the only peaks noted were those for zirconium and yttrium. A second scan was taken to define the yttrium distribution across the sample. These distributions were taken at different positions, relative to the length of the section, but were taken across the width of the sample at that point. These scans did not indicate any significant concentration gradients in any portion of the specimens examined. The data obtained from the electron microprobe scans were then used to obtain semiquantitative data on the composition of the various samples by comparing the intensity of the yttria peaks to the intensity obtained from a powder sample of 80 weight percent ZrO_2 plus 20 weight percent Y_2O_3. The percentages of yttria in the samples were estimated by a direct comparison of the maximum intensities of the yttria line. In order to obtain some type of relative comparison of these various samples, it was noted that the samples could be listed and ranked according to both the lattice parameters and the yttria content of the material. The comparisons are shown in Table 1.

Table 1. Lattice Parameter vs Yttria Content

Sample	Lattice Parameter	Yttria Content of Crystals w/o	Yttria Content Starting Power w/o
A	5.155	7.0	10
B	5.1647	7.8	12
C	5.1647	9.6	15
D	5.1743	11.3	17
E	5.1747	11.7	20
F	5.1743	10.9	20
G	5.1743	11.7	20
H	5.1842	13.9	25

It should be noted that these data are being used for a relative ranking of the material obtained during various runs. The data are very qualitative and do not represent the absolute values for the parameters being noted, but serve to suggest changes or trends in the crystal-growing conditions. The lattice parameters are obtained from the position of the (220) reflection. The calculated parameter is in fair agreement with the data reported for the various types of stabilized zirconia: ZrO_2 (cubic):a_o = 5.26Å ; (ZrCa) O_2:a_o = 5.13Å and (ZrY) O_2:a_o = 5.15Å. The lattice parameters would be expected to increase with the yttria content. These observations suggest that the material in sample A most likely has not been stabilized, and that the cloudiness and cracking in that crystalline charge could be due to phase transformation during the cool-down period. Samples of cubic zirconia stabilized by 15 weight percent yttria in the starting powder were subjected to the following physical parameter measurements. The crystalline charge was transparent and contained large grains due to the nature of the crystal growth process. In some cases the ideal geometry needed for the parameter measurement could not be facricated.

6. DENSITY

The specimens were cut so as to define regular geometries, but the actual volume of the specimens was obtained by immersion in isopropyl alcohol. The data obtained were:

Sample #1 (6.00 g) - 5.898 g/cm^3
Sample #2 (1.96 g) - 5.899 g/cm^3
Sample #3 (2.39 g) - 5.898 g/cm^3.

These values compare favorably with reported values of 5.64 g/cm^3 for pure ZrO_2, 5.65 - 5.71 g/cm^3 $(ZrCa)O_2$ and 5.94 g/cm^3 for $(ZrY)O_2$. The reported values for the yttria-doped material indicate that the grown material contained about 15.8 to 18.3 more percent of Y_2O_3. The data obtained from the samples examined suggest that the material likely contained somewhat less yttria and a portion had been volatilized during the growth process so that the crystallized material contains less than the weight percent added to the starting material.

7. HARDNESS

The hardness of the samples was measured by the diamond indenter method. A Knoop type, an elongated parallelepiped type of diamond, as compared to the square-type Vickers indenter, was used for these measurements. Data were

taken with both 100- and 500-g loads, and comparable data on the hardness of similar types of crystalline materials have been obtained. The measurements, all taken at room temperature, are:

ZrO_2 (I) = 1340, 1370 at Knoop Hardness with 500-g load
ZrO_2 (II) = 1361, 1394, 1391 at Knoop Hardness with 500-g load
YAG = 1230, 1248, 1270 at Knoop Hardness with 500-g load
$SrTiO_3$ = 620, 593, 582 at Knoop Hardness with 500-g load

8. THERMAL CONDUCTIVITY

Because of the size and geometry of the specimens available, the thermal comparator method was selected. This type of measurement registers the rate of cooling experienced by the tip of a heated probe when placed in contact with a surface to be measured. The probe is integral with a thermal reservoir held at some temperature T_i, above room ambient. Once the probe, with a known conductivity k_i, contacts the surface of a material at T_2, and having a conductivity k_2, the probe drops to some intermediate temperature T_c. The resulting temperature-differential signals can be related through the expression:

$$(T_i - T_c) = (T_i - T_2)\, k_2/k_i + k_2.$$

The temperature differences are then calibrated against known standards having well-established thermal conductivities, so that working curves can be established to obtain thermal conductivity for unknown materials.

A polished section of the ZrO_2 was measured using this method. The measured thermal conductivity, at room temperature, was:

0.017 - 0.019 W/cm/C°.

As a comparison, standards measured by this same method give values of

Quartz	0.014 W/cm/C°
Glass	0.0115 W/cm/C°
Stainless Steel	0.14 W/cm/C°.

Copper, in the units noted, has a value of 3.88, while diamond is reported about 20 W/cm/C° under these same measurement conditions. This method is very limited in the temperature range, and might be extended to a few degrees over room ambient; however, thermal conductivities over a higher temperature range, up to 600-800°C, will require the special, larger-sized geometries for such measurements.

9. INDEX OF REFRACTION

Since the index of refraction of materials similar to the ZrO_2 are known to be high, and in the range of 2-3, the measurements usually require the use of high index matching fluids, or the fabrication of prisms for the measurement of the angle of minimum deviation. Another method that might give the range of values of the indices without elaborate sample preparation is the use of an ellipsometer. Surface or film constants can be obtained by this method with accuracies of the order of 0.1%.

Ellipsometry is based on the principle that the changes in the ellipsometry of polarized light, after reflection from a surface or from a thin film, can be used to determine the optical constants, both the index of refraction and the extinction coefficients.

A series of ZrO_2 surfaces were prepared, and optical constants obtained by measurements on a Gaertner Ellipsometer Model L 117 which was interfaced to a small microprocessor so that the experimental data could be processed to give the constants noted. As a reference point, the index of refraction was measured for both polished surfaces of YAG and $SrTiO_3$. The data for those known samples are:

$$\text{YAG } N_s = 1.78,\ 1.84$$
$$K_s = 0.03 - 0.04 \quad .$$

These values are to be compared to known values for the bulk coefficients,

$$N = 1.83$$
$$SrTiO_3\ N_s = 2.45$$
$$K_s = 0.10 \quad .$$

Those values are in agreement with the accepted value of 2.41 for the index of refraction of the bulk material. In all cases, the measurements have been made using a He-Ne laser source, or a lambda of 6328Å, so there may be a slight discrepancy with the reported values that normally are noted for the sodium yellow line at lambda of 5250Å. The values obtained for a series of ZrO_2 surfaces, measured under the same conditions are:

$$N_s = 2.11 \quad 1.9875 \quad 1.9883$$
$$K_s = 0.05 \quad -0.1751 \quad -0.1964 \quad .$$

If the angle of incidence of the laser beam is changed to 50° from the previous value of 70°, the values obtained are:

$$N_s = 2.0841 \quad 2.18$$
$$K_s = -0.1693 \quad -0.16 \quad .$$

These data suggest that over the series of samples measured, the index of refraction varied from about 1.98 to 2.18. This is to be compared to the published range of about 2.15 - 2.18.

10. OPTICAL MEASUREMENTS

The infrared transmission between 2.78 μm and 7.14 μm of stabilized zirconia specimens was measured on a Digilab FTS-14 double-beam Fourier spectrophotometer in a nitrogen gas atmosphere. The transmission for two samples, 0.508 cm and 1.308 cm thick, measured at room temperature, is shown in Figure 10. The maximum transmission of 81-82% for the 0.508 cm at 4.17 μm measured before onset of lattice absorption is close to that expected from a refractive index of 1.98. The reduced transmission of the thicker (1.308 cm) sample at the shorter wavelength may be due to a slight wedge angle between the surface. The ultraviolet and visible transmission of these samples shown in Figure 11 was measured on a Cary 14 spectrophotometer. Some structure is observed in the vicinity of 0.32 to 0.37 μm in the absorption. The 1.308 cm samples with the wedge angle shows an even more pronounced reduction in transmission in this spectral range.

11. CONCLUSIONS

Large, clear, single crystals of stabilized zirconia have been grown up to 1 in. x 0.75 in. by 2-in. long in a 2 and 7/8-in.-diam., 4-in.-high cold crucible. It was found that the most perfect crystals were grown by stabilizing the zirconia starting powder with 25% yttria. Techniques were perfected eliminating bubbling and overflow during the growth process by adjusting coil configuration, crucible-lowering rates and crucible-filling procedures. It is important that an opening be maintained in the surface, especially during the initial melting and filling cycle, to allow entrapped air and volatiles to vent in order to eliminate bubbling and possible explosions caused by entrapped gases. If power levels are maintained sufficiently high, the surface area will remain molten.

The second phase of this work which will be discussed in a future report includes the results of doping the stabilized zirconia host material with rare earth and transition metal oxides for possible laser applications.

A number of modifications in equipment and technique have allowed demonstration of the potential of the skull method for the growth of refractory oxides in excess of 3000°C.

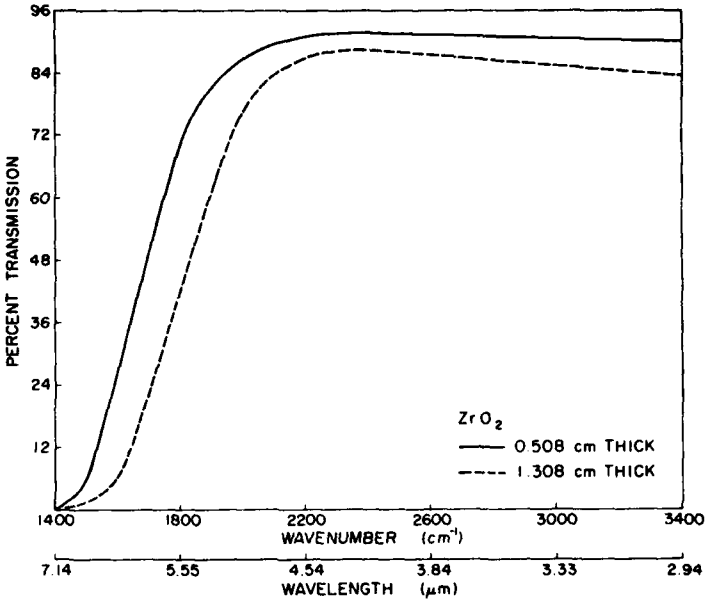

Figure 10. Percent Transmission vs Wavelength

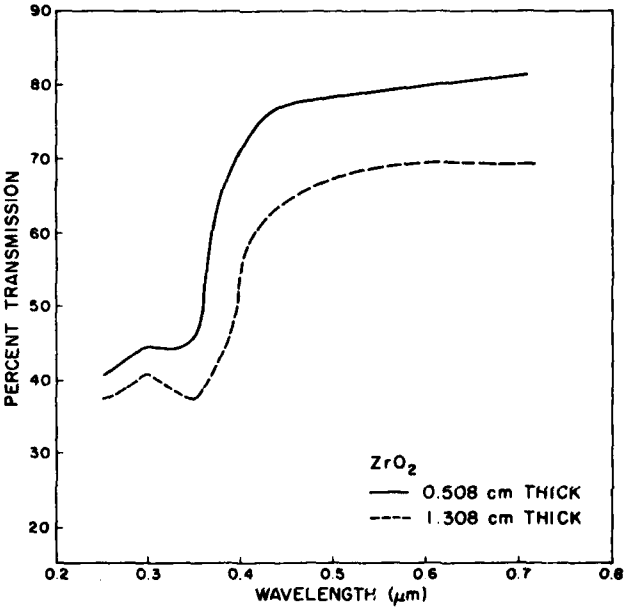

Figure 11. Percent Transmission vs Wavelength

12. FUTURE PLANS

It is planned that the cold crucible be placed inside a high-temperature furnace so that the oxygen content, gas flow, and growth conditions can be controlled carefully.

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