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**CRADA Final Report
for
CRADA Number ORNL-92-0091**

**THE GROWTH OF LARGE SINGLE
CRYSTALS OF MgO**

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**Michael Urbanik
Commercial Crystal Laboratories, Inc.
Naples, Florida**

**Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
Lockheed Martin Energy Research
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for the
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CRADA ORNL92-0091

Final Report

PI: L. A. Boatner, Oak Ridge National Laboratory, Solid State Division
PARTICIPANT : Commercial Crystal Laboratories, Naples, Florida

HIGHLIGHTS OF MAJOR ACCOMPLISHMENTS

Commercialization:

A domestic commercial source of an increasingly important high-technology material, single-crystal MgO, was developed where none existed before. As a result of the CRADA activities, Commercial Crystal Laboratories (CCL) of Naples, Florida can now compete effectively in the international market for MgO crystals, and the U.S. is no longer totally dependent on foreign sources of this material.

Scientific & Technical Progress:

New methods for the growth of MgO single crystals with significantly increased size were developed during the CRADA. The availability of these larger MgO crystals is expected to lead to the further development of new commercial applications for MgO and to electronic devices based on MgO crystals that were, heretofore, not possible.

Licenses:

During the ORNL/CCL MgO crystal-growth CRADA, interest developed on the part of CCL in other ORNL-developed crystal-growth technologies. This interest subsequently led to the licensing of two ORNL patents covering the growth of potassium tantalate-based single-crystal substrates, and CCL is presently marketing these new materials as well.

Awards:

The collaborative effort between ORNL and CCL in the growth of MgO crystals and in the commercialization of new tantalate-based single-crystal substrates for film growth was recognized in the form of an R&D 100 Award presented jointly to ORNL and Commercial Crystal Labs. in 1996. Additionally, the cumulative interaction between ORNL and CCL encompassing the MgO CRADA and the tantalate substrate growth resulted in the receipt of a 1997 Federal Laboratory Consortium Award for Excellence in Technology Transfer by ORNL research staff members L. A. Boatner and Ron Feenstra.

THE GROWTH OF LARGE SINGLE CRYSTALS OF MgO

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Final Report

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PARTICIPANT : Commercial Crystal Laboratories, Naples, Florida

ABSTRACT

The progressive identification of new high-technology applications and requirements for MgO single crystals in the commercial realm, as well as in DOE and other government-agency project areas, has resulted in an increased demand and international market for this material. Specifically, the demand for MgO crystals in large sizes and quantities is presently increasing due to existing and developing applications that include: (a) MgO substrates for the formation of electro-optic thin films and devices, (b) epitaxial substrates for high-temperature thin-film superconducting devices, (c) MgO optical components – including high-temperature windows, lenses, and prisms, and (d) specialty MgO crucibles and evaporation sources for thin-film production. In the course of CRADA ORNL92-0091, carried out with Commercial Crystal Laboratories of Naples, Florida as the commercial participant, we have made major progress in increasing the size of single crystals of MgO produced by means of the submerged-arc-fusion technique -thereby increasing the commercial utility of this material. Prior to the accomplishments realized in the course of this CRADA, the only commercially available single crystals of MgO were produced in Japan, Israel, and Russia. The results achieved in the course of CRADA ORNL92-0091 have now led to the establishment of a domestic commercial source of MgO single-crystal substrates and components, and the U.S. is no longer totally dependent on foreign sources of this increasingly important material.

CRADA OBJECTIVES:

Commercial Objectives

Although a commercial market for single crystals of magnesium oxide was already established prior to the initiation of the ORNL-Commercial Crystal Lab. CRADA in 1992, the market demand was met entirely by foreign producers and suppliers. Additionally, at that time it was clear that the market for MgO crystals would continue to increase at a relatively rapid rate corresponding to the development of new device applications for high-temperature superconducting thin films, thin-film ferroelectrics, and thin-film electro-optic devices (all devices that are grown on MgO single-crystal substrates) and for high-temperature optical systems using MgO components. Accordingly, the major commercial goal of the CRADA was to exploit the achievement of the technical goals of the project, as described in the following section, in order to establish a competitive domestic commercial source of MgO single crystals. In addition to the market demand for MgO as noted above, it appeared that there was also a potential latent market for large MgO crystals in sizes that were not commercially available at that point in time. For example, by developing new growth techniques for the production of the large crystal sizes required for applications in the optical components field, it was felt that it would be possible to generate entirely new applications for this material and, at the same time, gain a competitive advantage over the foreign sources of MgO crystals.

At the time of the initiation of the CRADA, there were three commercial competitors in the field of the growth of single crystals of MgO. These were: Dead Sea Periclase in Israel, a Japanese company, Tateho Chemical, Co., and emerging sources in the former Soviet Union. Dead Sea Periclase and Tateho, in fact, entered into a joint venture in which Tateho invested approximately 23 million U.S. dollars in the existing MgO production facilities operated in Israel by Dead Sea Periclase. While not all of this investment was directed toward MgO single-crystal products for high technology applications, the combination of these two companies represented formidable competition. Accordingly, the Commercial goals of the CRADA were to attack the high-technology, high-purity substrate and optical component market by developing new crystal-growth methods that would be

capable of producing high-purity, high-quality crystals which were significantly larger than those available from other sources. Fortunately, the large-scale operation mounted by Israel through the Japanese investment was directed toward "lower-technology" applications of fused MgO rather than more-sophisticated substrate and optical-component applications in which crystal purity and quality are critical. It was these critical and demanding applications that represented the focus of the CRADA between ORNL and Commercial Crystal Laboratories.

Technical Objectives:

The overall technical goal of this project was to develop new and innovative crystal-growth methods for the formation of high-quality MgO single crystals that would be larger than those commercially available from foreign sources. This goal was to be accomplished by building on and extending the existing capabilities of the submerged-arc-fusion technique, which had been used for many years at ORNL for the growth of research specimens that were employed in Basic-Energy-Sciences-supported activities. Specifically, the research addressed a number of technical issues including: (a) controlling the nucleation of MgO single-crystal grains, (b) determining the parameters that affect grain growth and development during solidification of the melt pool formed by arc heating, and (c) developing and analyzing techniques for the controlled addition of feed material to the melt pool in order to enhance the growth of large crystals.

In addressing the technical goals of the CRADA, studies of various technical parameters which affect the crystal growth process were carried out. These parameters included: (1) the three-phase-arc power levels, (2) graphite-electrode configurations, (3) the control of the spatial variation of the density of the growth feed charge, and (4) the effects of doping and impurity levels on crystal development.

The scientific and technical aspects of growing large, high-quality single crystals of MgO are a necessary but not sufficient condition for the development of a commercially viable high-technology product. Therefore, the technical goals of the research effort also encompassed various aspects related to the fabrication of the as-grown single crystals into marketable products. In particular, this latter aspect of the cooperative research effort was addressed in detail by the industrial partner, Commercial Crystal Laboratories.

CRADA Objectives-Results

The specific primary technical objective of the CRADA between ORNL and Commercial Crystal Labs. was the development of new crystal-growth techniques for the reproducible growth of large (up to 3" diameter) single crystals of optical-quality MgO. In the course of carrying out the CRADA activities, new insights were obtained into the growth processes responsible for the formation of MgO single crystals by means of the submerged-arc-fusion technique. These new fundamental insights subsequently led to the formulation of a new concept for the nucleation and growth of this material. Through the application of this new concept, significant improvements were subsequently made that resulted in the reproducible growth of MgO crystals from which substrates greater than 2" in diameter can be cut – with the occasional growth of MgO single crystals up to 3" in diameter. These accomplishments have placed this research and development effort at the forefront of MgO crystal-growth technology worldwide. Additionally, these developments provide the enabling technology for the use of this material in a wide variety of new, and heretofore impossible, applications.

From the commercial point of view, the original dual goals of, first, avoiding total reliance on foreign manufacturers and suppliers of MgO single-crystal substrates for thin-film growth and the manufacture of electronic devices and, second, of meeting new and increasing demands for large bulk MgO single crystals for optical and other applications have been met. Commercial Crystal Laboratories is now marketing MgO substrates and bulk single crystals both domestically and in the international marketplace. CCL has worked closely with a number of U.S. high-technology industries, such as IBM, in a variety of product-development and research and development activities, and they are also presently one of the major suppliers of MgO substrates to U.S. universities and government laboratories. Additionally, in the course of the CRADA work, Commercial Crystal Labs., Inc. developed new methods for the preparation of epitaxial-quality polished surfaces on MgO single crystals, and at this point in time, they are capable of meeting the most demanding requirements in the thin-film substrate field. According to a recent report from Allied Business Intelligence, the single-crystal and crystal-oscillator business is expected to grow to a level of \$3 billion by 2001, and it is vital that the U.S. maintain a proportionate share of this economically significant and

technologically critical market. The development of a domestic commercial source for a material such as single-crystal MgO is small, but significant, step in this regard.

CRADA-Derived Benefits to DOE

In addition to the general national and international commercial and technological implications of the progress achieved in the course of the ORNL/Commercial Crystals Labs. (CCL) CRADA, the results of this effort impact a number of ongoing DOE-supported research and development activities. Magnesium oxide continues to emerge as one of the most important and widely used single crystal substrates for the growth of a diverse range of epitaxial thin films for applications that encompass sensors and control devices for use in energy-related and DOE-defense-related technologies. For example, single-crystal substrates fabricated from MgO are the preferred choice for the growth of epitaxial thin films of both the yttrium-123 and the bismuth-based high-temperature superconductors. MgO substrates are also being increasingly used for the growth of epitaxial thin films of electronic materials – including ferroelectric films and films of electrooptic materials such as barium titanate. As a result of the progress made in the course of the CRADA in increasing the size of MgO single crystals, bulk MgO is now available in a size that is sufficient to permit the use of this material in neutron monochromators and neutron filters for applications in DOE-supported neutron-science programs.

The scientific and technological basis for the ORNL/CCL CRADA for the growth of large single crystals of MgO was developed in the course of long-term DOE basic-research support provided by the Division of Materials Sciences of the Office of Basic Energy Sciences. The submerged-arc-fusion MgO crystal-growth facility employed in pursuing the ORNL/CCL CRADA objectives had originally been designed and constructed during the 1960's for the purpose of growing single crystals of MgO, SrO, and CaO for use in fundamental investigations of radiation damage effects, defect centers, and the electronic properties of impurities in MgO. With the de-emphasizing of these avenues of basic research by the Division of Materials Sciences, the MgO crystal-growth facility at ORNL had become an infrequently used capability. The CRADA took this infrequently used and aging capability and transformed it into an asset both to the U.S commercial sector and to

DOE by developing a production capacity which provides a domestic commercial source of an increasingly important high-technology material.

In addition to the direct scientific and technological benefits to DOE research and development programs and projects arising from the ORNL/CCL CRADA, the interaction between ORNL and CCL led to an increased personal commitment on the part of Mr. Michael Urbanik, the President of CCL, to the DOE energy research laboratories and to DOE programs in general. Mr. Urbanik has become an active and vocal supporter of the U.S.D.O.E. and its R&D efforts as witnessed by the numerous letters of support and commendation that he has written to the Energy Subcommittee Members of the U.S. Congress, to President Clinton and Vice President Gore, to Hazel O'Leary, Secretary of the Department of Energy, and to Martha Krebs, Director of the Office of Basic Energy Research of the U.S.D.O.E. – as well as to the U.S. Senators and Governors from the States of Florida and Tennessee.

Technical Results

In the course of this CRADA, major advances in the development of the application of the submerged arc-fusion technique to the growth of single crystals of MgO have been achieved. These advances have led to significant increases in both the size and quality of single crystals of MgO that can be produced by this method. The specific improvements realized in the application of submerged-arc-fusion technology to MgO crystal growth include: (1) a completely new crystal-growth protocol has been developed in terms of the processing time and electric arc power used in the growth process, (2) a new graphite-arc-electrode configuration has been developed and applied to the control of the dimensions of the molten MgO pool formed during the growth process.

A pioneering application of seeding techniques to the growth of MgO crystals has been developed that is based on the formation of a large "mosaic" seed crystal which is strategically placed in the arc-fusion growth chamber. In this case, during the course of the CRADA-supported research and development effort, new insight was achieved into the growth mechanisms of MgO from the melt. This new information was subsequently applied to the formation of the new type of mosaic seed crystal. The new approach to the creation of large mosaic seeds represents a much more efficient use of smaller MgO single-crystal components that are individually oriented and then assembled to form the final large composite seed required for use in the arc-fusion crystal-growth method. The use of a large-area

mosaic seed fabricated by means of the approach developed during the CRADA effort is not only applicable to the growth of MgO single crystals, but it can also be applied to the growth of large single crystals of strontium and calcium oxides.

During the CRADA effort, CCL technical personnel have collaborated with ORNL staff in defining the design criteria for the development of the advanced techniques noted above for the realization of seeded growth of MgO crystals as well as for the continuous feeding of growth charge materials into the molten MgO pool during the arc-heating phase of the process. CCL technical personnel visited ORNL on numerous occasions to work out design details and to carry out actual growth runs in conjunction with ORNL research staff. Additionally, CCL technical personnel have concentrated on the fabrication aspects of the production of commercially viable MgO products, e.g. on the steps subsequent to the arc fusion process that are necessary to prepare epitaxial quality surface polishes on MgO for the commercial-scale production of substrates for film-growth applications. The arc-fusion growth process produces a mass of large unoriented MgO single-crystal grains. During the course of the CRADA, CCL has emphasized research on the conversion of the material in this form to a salable commercial product. This was clearly a critical step in responding to the international competitive situation outlined previously.

Inventions

While no patents have been filed on the development of the mosaic seeding approach to increasing the size of MgO single crystals produced by submerged arc-fusion methods, such actions may be taken in the near future – depending on the decisions taken by the commercial participant in regard to seeking patent protection or continuing to proceed on the basis of proprietary information or trade secrets.

Assessment of Commercialization Possibilities

This CRADA has resulted in the domestic and international commercialization and sale of MgO single crystals for use as substrates for the epitaxial growth of thin films of superconducting devices, ferroelectric materials, and electro-optic films. Additionally, the availability of larger MgO single crystals has stimulated interest in the development of new high-temperature energy producing devices for applications in space on the part of NASA. It is anticipated

that the international market for single crystal of MgO will continue to increase due to the unique properties of this material – including its highly refractory nature (melting point in excess of 2800 °C) and its ability to transmit infrared energy at temperature up to 900 °C. It is believed that this latter quality, coupled with the commercial availability of larger bulk material, will lead to the use of single-crystal MgO in more-traditional optical applications (e.g. as windows, lenses, prisms, etc.) for service at elevated temperatures and in demanding environments.

Plans for Future Collaborations

As a result of the working relationship and interactions that developed in the course of the MgO crystal-growth CRADA with Commercial Crystal Labs., strong interest developed on the part of CCL in other ORNL crystal-growth technology. This interest subsequently led to the licensing by CCL of two ORNL patents dealing with the growth of single crystals of the perovskite materials potassium tantalate and potassium tantalate niobate. Specifically, CCL has now signed a licensing agreement for U.S. Patents No. 5,188,906 and No. 5,110,790, which relate to the growth of single crystals of potassium tantalate and potassium tantalate niobate and their use as substrates for the growth of thin films of high-temperature superconductors and other thin films. These new substrate materials are, in fact, applicable to the growth of thin films of ferroelectrics, electro-optic materials, and metals as well as to various superlattice structures which combine materials of this type in atomically controlled layered structures.

Subsequent to the MgO crystal-growth CRADA between ORNL and CCL, a new small CRADA has also been negotiated and is presently ongoing. This new CRADA deals with the development of new techniques for the growth of single crystals of zinc oxide (ZnO) for substrate applications in film growth as well as in other electronic-device R&D applications. There is a growing market for single crystals of ZnO for use in the manufacture of light-emitting electronic components, and CCL is interested in the development of new and cost-effective approaches to the growth of single crystals of this material.

As a result of the working relationship developed between ORNL and CCL during the subject MgO CRADA, CCL has undertaken a number of very useful activities outside of the scope of the original CRADA. These activities were carried out at no cost to ORNL and were of direct benefit to ongoing research programs at ORNL. For example, CCL personnel worked with ORNL research staff members at the High

Flux Isotope Reactor on the construction of a new neutron monochromator for use in DOE neutron-science activities.

Conclusions:

The following accomplishments can be traced directly to the activities undertaken in the course of the ORNL/CCL MgO crystal-growth CRADA:

1. A domestic commercial source of a valuable and increasingly important high-technology material has been developed where none existed before. This new commercial source is represented by Commercial Crystal Laboratories – a small U.S. business.
2. New methods for the growth of MgO single crystals with a significantly increased size were developed that can now lead to the identification and development of extended applications and commercial markets for single-crystal MgO.
3. As a result of the interaction between ORNL and CCL arising from the CRADA, the two organizations have subsequently collaborated on the commercialization of new single-crystal tantalate substrates developed at ORNL. This activity was recognized in the form of an R&D 100 Award presented jointly to ORNL and Commercial Crystal Labs. in 1996.
4. CCL has licensed two ORNL patents dealing with the growth and application of tantalate substrates, and these materials are also now commercially available.
5. The cumulative interaction between ORNL and CCL in the areas of MgO crystal growth and the subsequent development and commercialization of tantalate substrates resulted in the receipt of a 1997 Federal Laboratory Consortium Award for Excellence in Technology Transfer by ORNL research staff members L. A. Boatner and Ron Feenstra.

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