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PURIFICATION OF MgF_2 AND GROWTH OF SINGLE CRYSTALS

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Abstract

A modified Bridgman-Stockbarger method was used to grow single crystals of MgF_2 weighing about 200 gms. The purity of the charge material was critical. Purification was achieved by first drying technical grade MgF_2 and then vaporizing in vacuum. Spectral transmission of the single crystals was measured: in comparison with CaF_2, MgF_2 was slightly less transparent in the infrared region and had about the same transparency in the ultraviolet region. Modulus-of-rupture values were also obtained in several orientations. No plastic flow was observed.

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I. Introduction

During the course of an investigation of the mechanical properties of alloys in the LiF-MgF_2 system, it became necessary to obtain pure single crystals of MgF_2. A modified Bridgman-Stockbarger method was adopted for simultaneous purification and single-crystal growth. This paper describes the techniques of purification and some of the properties of the single crystals obtained. Single-crystal MgF_2 has also been prepared by Duncanson and Stevenson, and they have reported measurements of many of the optical and physical properties of this material.[1]

II. Equipment

Purification and single-crystal growth were carried out in vacuum using a molybdenum-wound resistance furnace. A diagram of the furnace is shown in Fig. 1. The furnace core is 2-1/2-in. ID and 30 in. long, and the resistance winding is on the center 10 in. of the core. The resulting natural temperature gradients existing from the hot zone towards the cooler ends were utilized.

It was found that when alumina thermocouple tubing was in contact with the inside or outside of the furnace core, there was electrical leakage above 800°C from the winding to the thermocouple. This leakage caused the thermocouple to float at up to 60 volts A. C. above ground, and caused electronic potentiometers to indicate erroneous temperatures up to 40°C. The electrical leakage and the temperature error were eliminated by insulating the thermocouple tubing from the furnace winding with boron nitride as shown in Fig. 2.

The graphite crucible used to hold the MgF_2 was 2-in. O. D. and 4-1/2-in. high with a 1/8-in. wall. It had a cone at the bottom with an angle of about 130 deg.

III. Purification and Single-Crystal Growth

The MgF_2 starting material was a purified commercial grade which was found, during the course of this work, to be actually a technical grade material with the approximate composition: MgF_2 - 80% H_2O - 17% MgO - 2% and other metals - 1%. It was purified in several steps.

The water was removed by first drying in air at 400°C and then heating in vacuum at 50°C per hour to the melting temperature of 1255°C.[1] A plot of the water loss vs drying temperature at equilibrium in air is shown in Fig. 3. The material could not be dried completely in ambient air at 600°C, because above 500°C the reaction

$$MgF_2 + H_2O \rightleftharpoons MgO + 2HF$$

became noticeable. Also, slow heating in vacuum was necessary to prevent the charge from blowing out of the crucible. Melted and zone-cooled ingots of this material were white and opaque with no apparent impurity segregation, indicating that purification beyond that of drying was necessary.

A first-stage purification was accomplished by evaporating MgF_2 from molten dried material. The graphite crucible was held in the upper part of the hot zone of the furnace where a temperature gradient existed. The bottom of the crucible was then at a temperature above the melting point, and the crucible lid was about 200° C below the melting point. Purified MgF_2 grew as clear needle-like crystals on the crucible lid with a deposition rate of 0.14 to 0.2 $g/hr\text{-}cm^{-2}$.

This deposition rate was about a factor of 10 less than the value calculated by using the Langmuir equation, from the vapor pressure of MgF_2 determined by Hammer and Pask.[2] There are several possible reasons for this discrepancy, such as depletion of the molten MgF_2 during the run, or the temperature of the crucible lid being too high. However, the point to be noted is that the yield from this method of purification probably could be substantially increased. The purification obtained by one evaporation is shown in Table I. X-ray diffraction analyses indicated that MgO, CaF_2, and $MgCl_2$ were concentrated in the residue, while only MgF_2 was present in the condensate.

The second-stage purification was attained by normal freezing or zoning during the growth of a single crystal. The condensate obtained by evaporation was melted, with the crucible held near the lower end of the furnace hot zone. The crucible was then lowered into the cooler zone at 1/2 in. per hour. Impurities that lowered the freezing point were thus concentrated in the center of the ingot. Several single crystals weighing about 200 g each were obtained. In every case, the crystals were cracked into several pieces. This cracking occurred both when the crystals were quenced and when they were slowly cooled at 50°C per hour after growth. Cracking probably occurred during growth because of the steep temperature gradient employed. However, the crystals were large enough for subsequent use, and no further attempts were made to grow larger crystals. The additional purification resulting from one pass of normal freezing is shown in Table I.

IV. Some Properties of Single Crystals

The MgF_2 crystals were clear and colorless. They showed fair cleavage on the a planes and no cleavage on the c planes. The material was easily cut on a diamond saw with a smooth water-cooled abrasive blade. Cut single crystals showed no apparent effect from 1-hour immersions in boiling water, boiling 1/2 N HNO_3, boiling concentrated phosphoric acid, or boiling 50% phosphoric acid.

Figure 4 shows the ultraviolet and infrared transmission of a cut, polished MgF_2 single crystal window. The reported transmission curves for BaF_2 and CaF_2 are also shown.[3,4]

Single crystals of MgF_2 were cut in the various orientations shown in Fig. 5. The specimens were first annealed in vacuum for 4 hours at 900°C and then broken in four-point loading in an Instron testing machine using a crosshead speed of 0.002 in./min. The total test span was 0.75 in., and the central span was 0.25 in. The resulting values for the modulus of rupture are indicated in Fig. 5. No plastic flow was apparent; the recorded load-deflection line was straight up to the fracture stress. The reported modulus of rupture values for oriented single crystals of BaF_2 and CaF_2 are 3370 to 4700 psi and 5440 to 7180 psi, respectively,[5] in contrast to the range of 7250 to 15,130 psi obtained for MgF_2.

V. Acknowledgments

The author wishes to thank Professor Joseph A. Pask for his interest and encouragement, and Mr. Eugene Kregg for his help in the construction and operation of the vacuum furnace.

VI. Footnotes and References

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At the time of this work, the author was a Graduate research engineer, Department of Mineral Technology, University of California, Berkeley, California. He is presently research fellow, Houldsworth School of Applied Science, University of Leeds, Leeds, England.

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2. Reuben R. Hammer and Joseph A. Pask, "Vapor Pressure of Magnesium Fluoride," submitted for publication in J. Am. Ceram. Soc.
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4. M. A. Vasilyeva, "Growing Lithium and Sodium Fluoride Single Crystals of High Transparency in the Ultraviolet and Infrared," ibid., pp. 191-96.
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Table I. Spectroscopic analyses of MgF_2

	Si	Fe	Al	Cu	Na	Ti	Ca	Cr	Ba
Original	0.1	0.03	0.5	Tr	0.2	0.01	0.3	0.005	ND*
Evaporated	0.01	0.01	ND	ND	ND	ND	0.08	0.005	0.0001
Zoned	0.02	0.002	ND <.005	ND <.0002	ND <.06	ND <.005	0.001	ND <.0002	ND

*ND means not detected with upper limit as shown.

Figure Legends

Fig. 1. Schematic diagram of the vacuum furnace used for purification of materials and single-crystal growth.

Fig. 2. Detail of the boron nitride mounting for the temperature-control thermocouple.

Fig. 3. Loss of water from technical-grade MgF_2.

Fig. 4. Spectral transmission of some single-crystal alkaline-earth fluorides.

Fig. 5. Modulus of rupture in four-point loading of MgF_2 single crystals in orientations as shown.

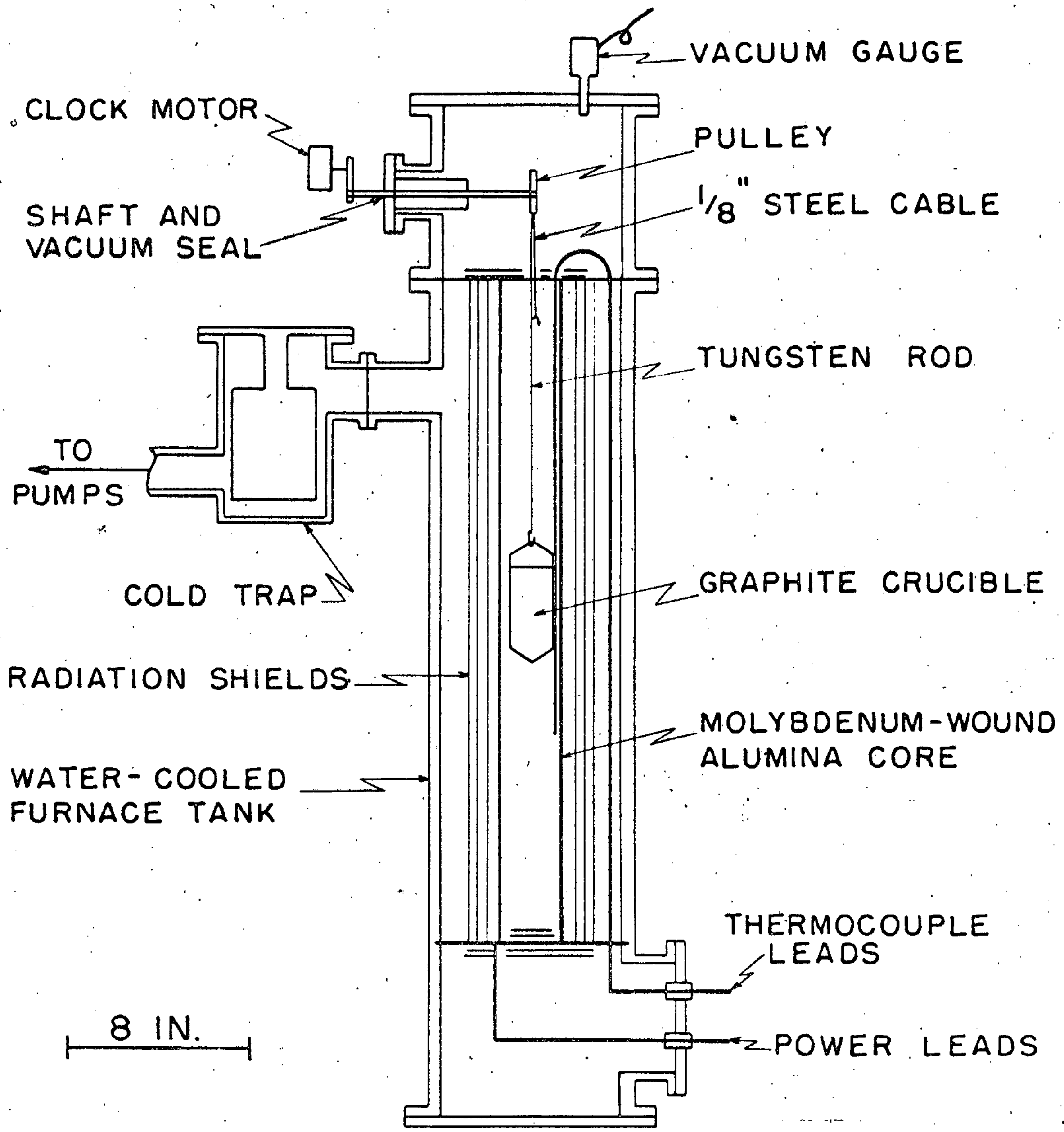

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FIG. 3

DIAGRAM OF VACUUM FURNACE USED FOR PURIFICATION OF MATERIALS AND SINGLE CRYSTAL GROWTH.

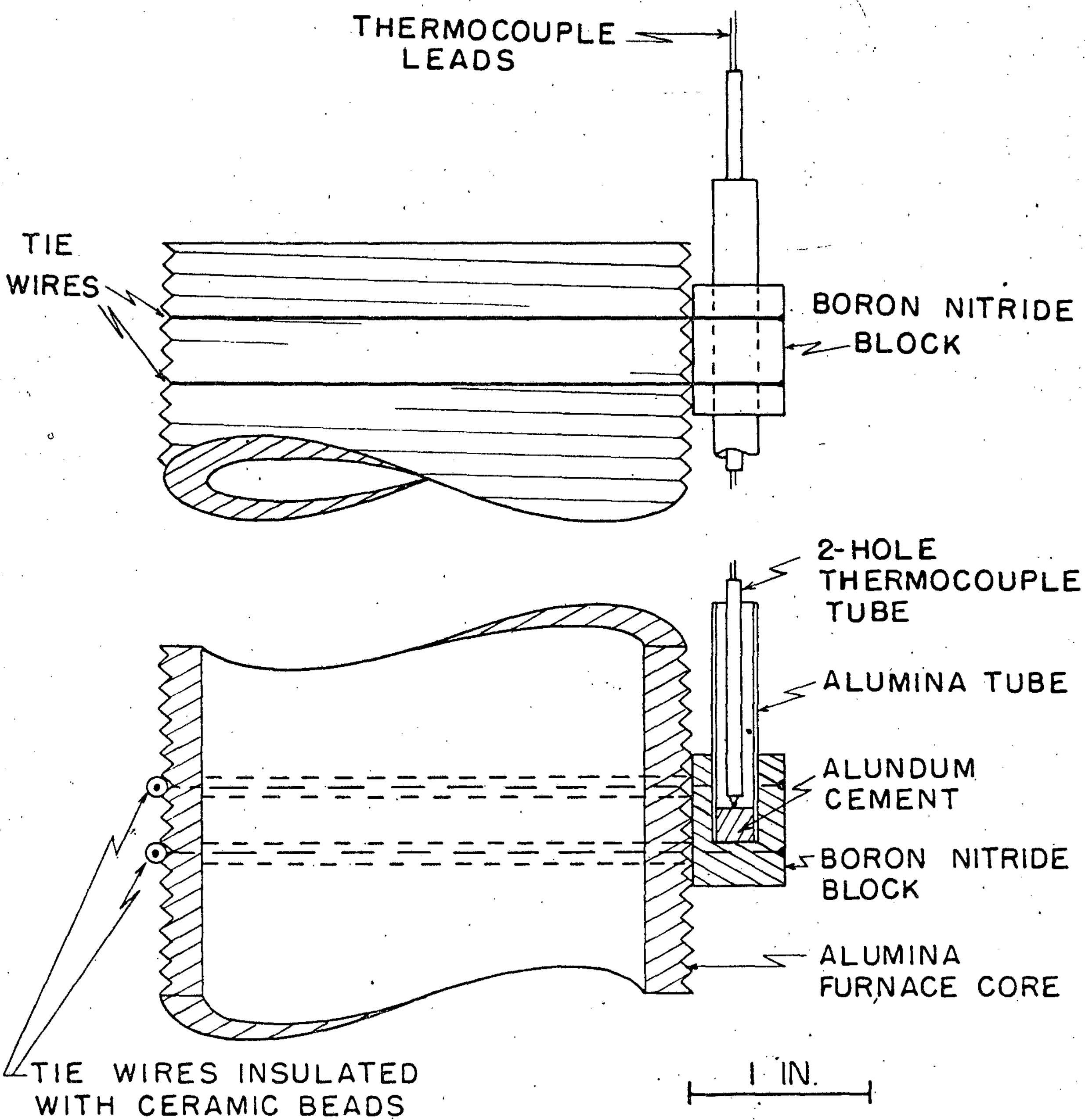

FIG. 4

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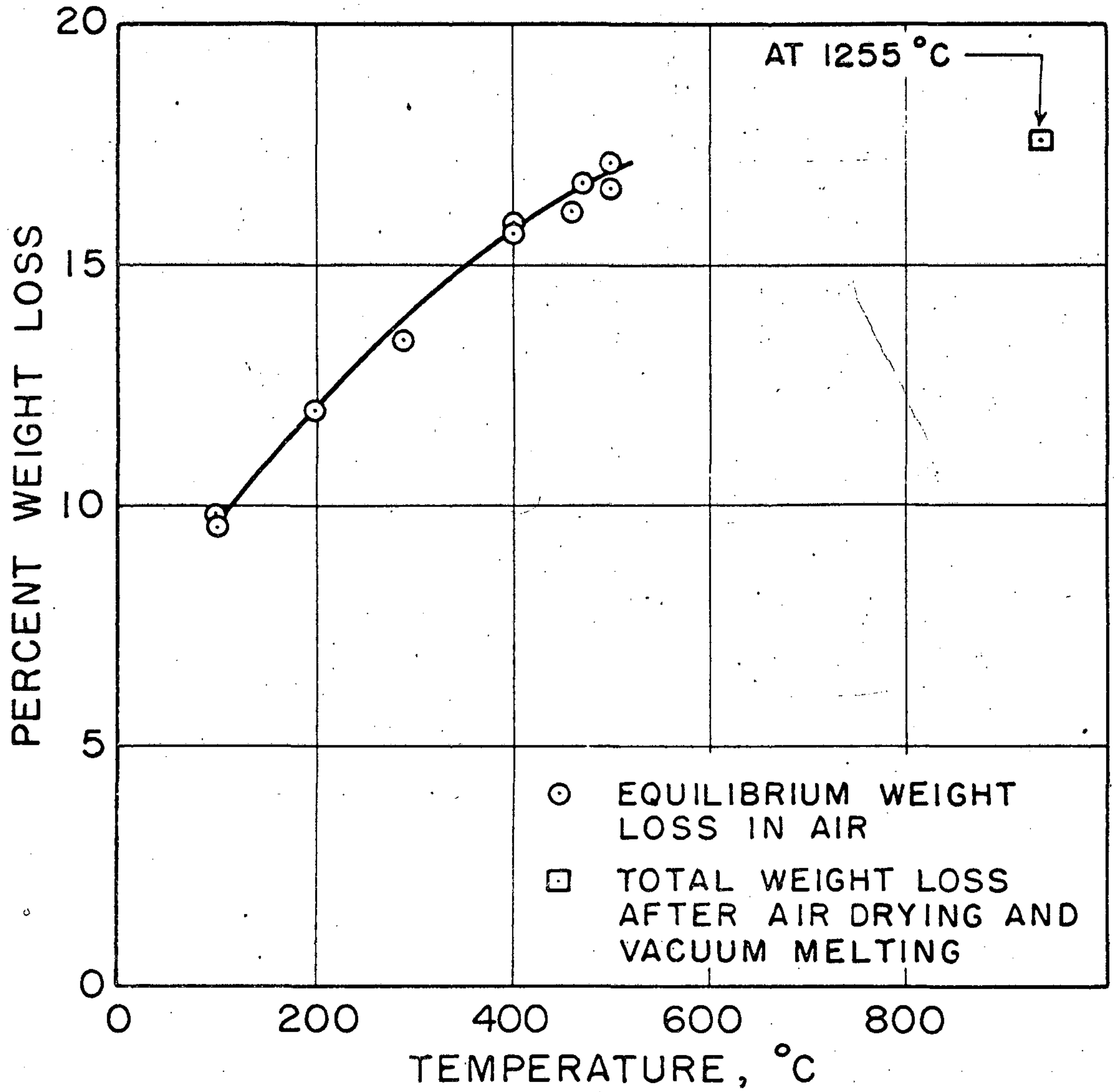
DETAIL OF THE BORON NITRIDE MOUNTING FOR THE TEMPERATURE CONTROL THERMOCOUPLE.



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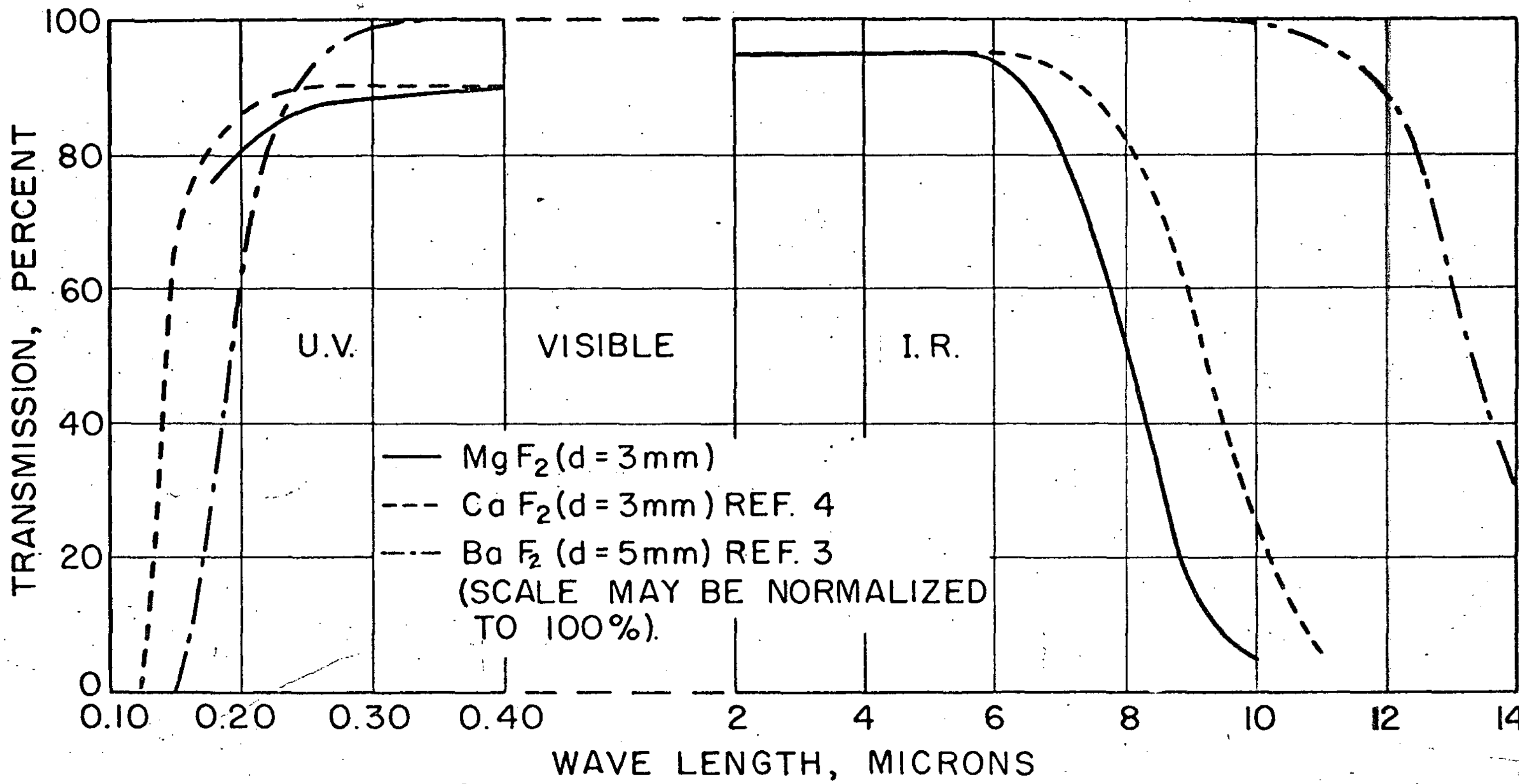
LOSS OF WATER FROM TECHNICAL GRADE MgF_2


100
80
60
40
20
0
TRANSMISSION, PERCENT
0.10
0.20
0.30
0.40
2
4
6
8
10
12
14
WAVE LENGTH, MICRONS
U.V.
VISIBLE
I. R.
Mg F2 (d = 3mm)
Ca F2 (d = 3mm) REF. 4
Ba F2 (d = 5mm) REF. 3
(SCALE MAY BE NORMALIZED
TO 100%).

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