CRYSTAL GROWTH AND CHARACTERIZATION OF BAMGF4(U)
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CRYSTAL GROWTH AND CHARACTERIZATION OF BaMgF₄

FINAL REPORT FOR:
13 MARCH 1983 - 31 MARCH 1984
CONTRACT N00014-83-C-0061

PREPARED FOR:
OFFICE OF NAVAL RESEARCH
DEPARTMENT OF NAVY
800 N. QUINCY STREET
ARLINGTON, VA 22217

PREPARED BY:
Defense and Information Systems Division
Sandia National Labs
SANDERS

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BaMgF<sub>4</sub> is an interesting crystal for optical applications. This compound crystallizes in the orthorhombic crystal structure exhibiting 2mm symmetry. BaMgF<sub>4</sub> exhibits high transmission between 200nm and 8 microns as well as high optical damage resistance. Single crystals of BaMgF<sub>4</sub> were grown by Czochralski technique using growth rates of 1.0mm/hr to 5.0mm/hr. Clear crystals up to 2.0cm diameter by 8mm in length were grown. Clearage in the (100) direction was noted. Samples were oriented and fabricated along crystallographic direction -over-
1.0 INTRODUCTION

1.1 BACKGROUND

A variety of new optical materials are under development in various laboratories for advanced electro-optic system applications. A new class of laser materials under investigation, are generally characterized by broadband energy transition, consisting of divalent rare earth ion and transition metal ion activators. The energy transitions for divalent rare earth ions are between d-f levels, and are generally broad due to the d level continuum. Transition metal ions, although characterized by electronic forbidden transitions, between d-levels, exhibit energy level broadening which is strongly influenced by host lattice. Both transition metal and divalent rare earth ions are affected by crystal field interactions and as a result strongly depend upon the chemistry of the host compound and the optical quality of the host crystal. The application of tunable lasers has resulted in specific constraints upon optical components.

While tunable solid state laser research has produced a number of solid state lasers with a limited tuning range, this approach is limited by fundamental considerations—the product of the laser stimulated emission cross section (effectively a measure of gain attainable in the laser medium), the fluorescent lifetime, and the frequency bandwidth of the laser transition is approximately constant. Broadband lasers typically exhibit short fluorescent lifetimes and/or low gain.

Short lifetimes impose difficulties in optical pumping of the laser media. Operation of lasers exhibiting short pulse duration is limited by the ability of the flash lamp to withstand the high peak power. The alternative of laser pumping may not be a practical solution for system development.

Low gain transitions impose severe operating conditions for the optics, because the optical field intensities needed to extract energy from low gain media often approach the optical damage threshold of key optics including the laser media. The constraint imposed upon optical materials for a low gain laser can be visualized by examining the threshold condition for an oscillator:

\[ R_1 R_2 \exp((g - 1) L) = 1 \]
where $R_1$ and $R_2$ are the laser mirrors, $g$ - material gain, $l$ - resonator loss, and $L$ - resonator length. For a laser crystal with low gain, any loss due to the optics significantly impacts the operating efficiency. Furthermore, assuming low loss optics, the low optical gain requires a high value of mirror reflectivity to reach threshold resulting in appreciable optical field intensities circulating within the resonator.

Fluoride materials exhibit fundamental properties which are suited to the development of low loss, high damage resistant optical components. These include: (a) low growth temperature - nil crucible solubility and low residual strain, (b) low linear and non-linear indices of refraction, (c) negligible self-focusing, and (d) excellent u.v. transparency. BaMgF$_4$ is examined during this program as an electro-optic material to fulfill some of the requirements for advance lasers.

BaMgF$_4$ is a new electro-optic material exhibiting favorable optical properties including uv and IR transmission as well as high optical damage resistance. The host lattice potentially exhibits a site for both transition metal ions at the Mg$^{2+}$ position and for divalent rare earth ions at Ba$^{2+}$ position. Finally the orthorhombic structure of BaMgF$_4$ lacks a center of symmetry, suggesting potential application as a pockel cell.

Based upon the successful crystal growth of BaMgF$_4$ initially demonstrated on this contract, BaMgF$_4$ was further investigated as a laser host. On an Air Force Program contract number F33615-82-C-1823 BaMgF$_4$ doped with divalent samarium and Europium was grown and spectroscopy characterized. Both Sm:BaMgF$_4$ and Eu$^{2+}$:BaMgF$_4$ exhibited broad emission in the visible spectrum.

This report describes the work on BaMgF$_4$ carried out by Sanders Associates between 14 March 1983 to 30 March 1984. The principle emphasis was given to the crystal growth development, measurement of the electro-optic coefficients and assessment of BaMgF$_4$ as a laser host crystal.
1.2 PROGRAM GOALS AND OBJECTIVES

The performance goals of this program were to develop the crystal growth for BaMgF$_4$ and assess the electro-optic applications. To achieve this goal specific materials problems were addressed, including czochralski crystal growth, crystallography, and electro-optic property measurements. Specifically, the technical objectives of this program were:

a) Develop the crystal growth process for BaMgF$_4$. Proper growth conditions are key in fabricating optical materials exhibiting low strain and defect concentrations. Optical requirements suggest that single crystal boules 1.2 to 1.5 cm in diameter by 5.0 to 6.0 cm in length are required for practical applications.

b) Orient and fabricate BaMgF$_4$ crystals for electro-optic characterization.

c) Measure the electro-optic coefficients of BaMgF$_4$.

d) Assess applicability of BaMgF$_4$ as a laser host crystal.

1.3 PROGRAM RESULTS

a) A crystal growth process employing the czochralski technique was developed. Single crystals up to 2.0 cm in diameter by 7.0 cm in length were grown.

b) Laue back reflection x-ray techniques coupled with optical microscopy were used to orient crystals with respect to the crystallographic axis and optical axis.

c) The electro-optic coefficients for BaMgF$_4$ were measured experimental as compared to KDP. No non-zero coefficients were detected, within the sensitivity of the experiment.

d) Analysis of the BaMgF$_4$ structure indicates appropriate lattice sites for both divalent rare earth ions and divalent transition metal ions. The combination of substitutional sites and low growth temperature results in the potential as a laser host crystal.
2.0 TECHNICAL DISCUSSION

2.1 PROPERTIES OF BaMgF$_4$

The group of ionic fluoride crystals based on the formula BaMF$_4$ where M = Mg, Zn, Fe, Co and Ni was extensively studied in the early to mid 1970's. This family of crystals was characterized with high damage resistance (high damage resistance appears to be a characteristic of fluoride materials partly due to the low growth temperature, ionic bonding, uv transparency and low index of refraction) and useful dielectric properties. The ferro-electric properties coupled with excellent optical properties led to the research of these materials for non-linear optical devices (Ref. 1, 2, 3, 4). BaMgF$_4$ in particular, appears to be a practical material for laser applications. (Figure 1 lists known properties of BaMgF$_4$).

STRUCTURE

BaMgF$_4$ crystallizes in the orthorhombic structure with point group symmetry 2mm (Ref. 1). No phase transitions were observed cooling to room temperature. The crystals are formed by sheets of MgF$_6$ octahedra joined at the corners (Ref. 2). The sheets run parallel to the (010) plane bonded together by Ba$^{2+}$ ions. The relative weak nature of this bond results in a dominant cleavage plane parallel to the (010) plane. Cracking parallel to (010) was observed during cool down after crystal growth or if the crystal was stressed.

OPTICAL PROPERTIES

BaMgF$_4$, similar to other fluorides, exhibits low values for the indices of refraction (Ref. 3). BaMgF$_4$ is a biaxial crystal, with three independent index values.

Clear undoped crystals exhibit wide transmission range, with the uv edge reported at 170nm and the IR edge out to eight microns.

The non-linear coefficients were reported relative to d$_{11}$ (SiO$_2$) using a Q-switched Nd:YAG laser operating at 1.06 microns (Ref. 3). SHG tensor is a third rank tensor. However, the number of non-zero coefficients is reduced to five, due to symmetry constraints. The linear electro-optic tensor also follows similar rules and is reduced to five non-zero coefficients.
FIGURE 1
PROPERTIES OF BaMgF$_4$

Structure
Orthorhombic

Symmetry
2mm

Index of Refraction
\( \lambda = 1.06 \mu \)
\( n_1 = 1.467 \quad n_2 = 1.439 \quad n_3 = 1.458 \)

Transmission
uv. \( .18 \mu \)
I.R. \( 8.0 \mu \)

Non-Linear Coefficients
[SHG relative to \( d_{11} (SiO_2) \)]
\( d_{33} = .05 \quad d_{31} = .07 \quad d_{15} = .07 \quad d_{32} = .13 \quad d_{24} = .07 \)

Dielectric Constants
@ 10mHz
\( \varepsilon_1 = 8.40 \quad \varepsilon_2 = 14.75 \quad \varepsilon_3 = 8.24 \)

Thermal Expansion
Coefficients
\( (10^{-5}/^\circ C) \)
\( \alpha_1 = 11.5 \quad \alpha_2 = 21 \quad \alpha_3 = 20 \)

Elastic Constants \( (20^\circ C) \)
\( C_{ij} \)
\( (10^{11} \text{ dyn cm}^{-2}) \)
\begin{align*}
11 & 22 & 33 & 44 & 55 & 66 & 12 & 13 & 23 \\
10.4 & 8.1 & 13.0 & 3.2 & 5.5 & 2.5 & 2.9 & 6.4 & 3.6
\end{align*}

Piezoelectric Constants
@ 20°C
\( d_{ijk} \)
\( (10^{-8} \text{ esudyn}^{-1}) \)
\( 24.2 \quad 7.5 \quad -12.5 \quad -15.9 \quad -3.7 \)

\( e_{ijk} \)
\( (10^{-5} \text{ esucm}^{-2}) \)
\( 1.83 \quad .84 \quad .19 \quad -.79 \quad -.42 \)
DIELECTRIC AND MECHANICAL PROPERTIES

The structural characteristics, i.e. polar bonding and 2mm symmetry of BaMgF$_4$ along with isostructural compounds were investigated for dielectric and piezoelectric applications. The Curie-Weiss temperature for BaMgF$_4$ was reported as $990^\circ \pm 5, 135^\circ$ above the melting point. The dielectric constants are reported in the three property directions.

BaMgF$_4$ is reported to exhibit high coupling piezoelectric coefficients, potentially yielding a higher efficiency than quartz for ultrasonic devices. The third order tensor coefficients are also presented for both isothermal and adiabatic conditions (Ref. 5).

The elastic constants determined by the Schaeffer-Bergmann method (Ref. 5) for BaMgF$_4$ are also listed in Figure 1. A significantly high anisotropy of the elastic constants for BaMgF$_4$ is reported. This characteristic will affect the mechanical properties of this crystal.

2.2 CRYSTAL GROWTH

OVERVIEW

BaMgF$_4$ crystallizes congruently at 920°C. A series of growth experiments were run applying the czochraski technique for growth. The purpose of the experiments were two-fold: first, to optimize a growth process for BaMgF$_4$; second, to supply the necessary samples for the electro-optic characterization. Details of the growth technique applied to BaMgF$_4$ are described in the following sections.

CRYSTAL FURNACE

The furnace uses vacuum technology for basic construction and seal design. This provides a system that can effectively prevent any interchange between the internal and external atmospheres for an extended period. When an inert atmosphere such as helium or argon is employed, very high purity gasses can be used without changing during the course of a run.
The interior of the furnace is constructed with few areas that cannot be easily cleaned by reaching through the door opening. The entire growth chamber has watercooled walls to remove the radiated and conducted heat and reduce the outgassing that would occur if the temperature of the walls were to increase. The upper chamber is uncooled because of the minor amount of heat that can reach that area. The upper and lower chamber are separated by a gate valve to permit the seed rod to pass through when the valve is open, yet separating the chambers when closed. The seed rod and the crucible-positioning rod each pass through a double-pumped seal to prevent inboard leakage that would contaminate the high purity atmosphere contained within the furnace.

A graphite resistance heating element surrounds the outer surface of the platinum crucible in its graphite support; the heat zone is insulated by a heat shield made of six layers of molybdenum sheet. The heat shields are relatively poor insulation, but cause minimum contamination of the atmosphere. The heat load that arrives at the interior wall of the furnace chamber is removed by water flowing between the double walls of the lower chamber. Doors provide access to each of the chambers. The furnace with the doors open is shown in Figure 2 with the heat shield pack removed. Four windows are provided in the lower chamber of viewing the growth process.

The furnace chambers can be pumped independently by a common high vacuum pumping system. Typical pressures that are attained after overnight pumping are about $2 \times 10^{-7}$ torr at the ionization gauge.

ATMOSPHERE

The growth of $\text{BaMgF}_4$ crystals must take place under an atmosphere, rather than a vacuum, to reduce the evaporation of the melt. Two types of atmosphere can be considered: active and inert. An active atmosphere, such as HF, maintains a clean melt through its own chemical behavior. Other crystal growers have grown fluorides in HF but there is a penalty because of its chemical activity toward many materials of construction, plus an added safety burden because of the large volume in the furnace chamber when compared to the hydrofluorination reactor.
We have chosen to use extremely pure argon as an inert atmosphere. The gas is available commercially with an impurity content of less than five parts per million (PPM) and can be purified further by reaction with a heated charge of titanium that reacts strongly with almost all contaminants, and has a purity level of 1 PPM. Helium is another potential candidate if it has been purified in the same manner, but it is soluble in the melt, interfering with the growing crystal, and sometimes leading to internal voids in the grown crystal.

RAW MATERIAL PROCESSING

Sanders has investigated a variety of feed processing techniques and has developed procedures to ensure uniform quality starting materials irrespective of contaminants in the feed materials from chemical companies. Purification and synthesis of fluoride materials are being carried out using a variety of modern wet chemical separation techniques, zone refining, and low temperature hydrofluorination. The raw material chosen from BaMgF₄ was supplied by Harshaw Chemical Company. BaF₂ and MgF₂ were obtained in a crystallized high purity form. As such, we choose not to use many of the purification techniques described. However, the components were mixed and BaMgF₄ formed by melting the appropriate composition in the hydrofluorination reactor.

The commercial feed material was mixed and purified in flowing Hydrogen Fluoride (HF), in an enert reactor. A platinum reactor is used to contain the HF, while a platinum crucible holds the material. The effluent from the reactor is trapped in a solution of KOH, and the entire apparatus is contained in a vented hood, illustrated in Figure 3.

RESULTS

The crystal growth experiments were directed to optimize furnace conditions. In all cases, oriented seeds were used. The first series of experiments were conducted with the growth direction parallel to the "c" crystallographic direction. The growth runs are summarized in Figure 4.

The relative seeding and growth temperature was examined in the first run, #634. Melt back temperature reached as high as 970.3 as read by a thermocouple,
Figure 3. Hydrofluorination Furnace
## FIGURE 4

**SUMMARY OF CRYSTAL GROWTH**

<table>
<thead>
<tr>
<th>RUN NUMBER</th>
<th>VARIABLE EXAMINED</th>
<th>RESULTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>634</td>
<td>Seeding and growth temperature range determined.</td>
<td>Boule was clear, elliptical in shape. Fractured in [010] direction</td>
</tr>
<tr>
<td>663</td>
<td>Seed rotation varied from 5 to 15 RPM</td>
<td>No change in boule elliptical shape. Lower portion of boule polycrystalline and cloudy.</td>
</tr>
<tr>
<td>670</td>
<td>Crucible and seed position raised in hot zone.</td>
<td>Boule fractured during cool down.</td>
</tr>
<tr>
<td>670A</td>
<td>Growth rate varied from 1 to 5 mm/hr.</td>
<td>Boule grew clear up to a rate of 2 - 3 mm/hr.</td>
</tr>
</tbody>
</table>
.500 inch below the bottom of the crucible. Growth on the seed was noted at 910°C, and the diameter of .75 inch was reached at 882°C. A pull rate of up to 1 mm/hr was used for this run.

The second growth experiment examined seed/crystal rotation rates. Rotation was varied from 5 to 15 RPM. This range is typical for other fluorides. No variation in the growth was observed due to rotation rate, however the boule became progressively cloudy in the lower sections. The precipitation in the boule was either due to raw material impurities or furnace leak. Boule 663 is illustrated in Figure 5.

The thermal shielding was modified for the third experiment. A steeper thermal gradient was achieved and noted by the higher growth temperature. Initial growth was observed about 20°C higher than previous runs. However, the higher gradient result in significant cracking upon breaking contact with the melt, Figure 6. Furnace shielding was returned to the configuration of earlier growth runs.

Growth rate was examined in the fourth experiment. Rates varying from 1 mm/hr to 5 mm/hr were used to pull the crystal from the melt (Figure 7). Each rate was used to grow about 15mm of crystal. Upon completion of the run, the crystal was examined with respect to the growth rate applied. It appeared that between 2 - 3 mm/hr inclusions began to form in the crystal. At 5 mm/hr the entire crystal exhibited a milk-white appearance. Based upon this experiment, a growth rate of 2 mm/hr is appropriate for BaMgF₄ with this furnace configuration.
2.3 CRYSTAL ORIENTATION

The combination of Laue back reflection, x-ray diffraction and optical microscopy techniques were employed to orient BaMgF$_4$ crystals to crystallographic axes and optical axes. The Laue x-ray technique involves exposing the crystal to x-rays exhibiting a broad spectrum of wavelengths. Due to the slight variation of atomic spacing for each set of crystal planes, the condition satisfying Bragg’s equation, $n\lambda = 2dsin\theta$ will occur at different wavelengths. The diffracted rays are recorded on film positioned at the normal to the incident beam. Generally, the film records a geometric pattern of spots. Each spot is a representation of a different set of planes. A specific spot pattern is associated with each crystal lattice axis. The position or spot pattern was compared to existing "maps". Orientation was measured in degrees, and immediately compensated with goniometer. Once properly aligned, the face was ground with a diamond saw.

Once the 100,010 and 001 faces were established on a BaMgF$_4$ crystal, further structural data was generated on a diffractometer. The data and calculated d-spacings are summarized in Figure 8. From this data, the respective lattice constants were calculated, also presented in the table listed in Figure 8. Further orientation to the optic axis was conducted on samples for electro optic characterization.

Typically, the optic axes of a biaxial crystal lie in the a, b plane. $2\nu$, the angle between the optic axes can be estimated from the indices of refraction.

$$\cos V_a = \frac{\alpha}{\beta} \sqrt{\frac{(\gamma + \beta)(\gamma - \beta)}{\gamma + \alpha(\gamma - \alpha)}}$$

where $V_a$ is the angle between the optic axis and the "a" crystallographic axis. For BaMgF$_4$ $V_a$ was calculated as 55.6°, $2\nu = 111.2°$. Therefore, the a direction is the obtuse bisectrix and the b direction is the acute bisectrix, $V_b = 90 - V_a$ or 34.4°.

A BaMgF$_4$ crystal was oriented and cut ~34.0° from the b axis. This angle was in fact experimentally very close to the optic axis as illustrated in Figure 9. Additional samples were oriented for further testing.
FIGURE 8

SUMMARY OF X-RAY DIFRACTOMETER DATA AND LATTICE CONSTANTS

<table>
<thead>
<tr>
<th>CRYSTAL ORIENTATION</th>
<th>REFLECTION PLANE (n)</th>
<th>Θ</th>
<th>λ</th>
<th>d-SPACING</th>
<th>LATTICE CONSTANT</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4, 0, 0</td>
<td>96.48°</td>
<td>1.5405Å</td>
<td>1.0326Å</td>
<td>4.130Å</td>
</tr>
<tr>
<td>010</td>
<td>0, 12, 0</td>
<td>79.12°</td>
<td>1.5405Å</td>
<td>1.209Å</td>
<td>14.51Å</td>
</tr>
<tr>
<td>001</td>
<td>0, 4, 0</td>
<td>63.44°</td>
<td>1.5405Å</td>
<td>1.455Å</td>
<td>5.819Å</td>
</tr>
</tbody>
</table>

NOTE: $d = \frac{n\lambda}{2 \sin \Theta}$
OPTICAL ORIENTATION OF BAMgF$_4$

FIGURE 9
2.4 ELECTRO-OPTIC MEASUREMENT

The phase retardation, or rotation of the plane of polarization introduced by a light modulator of length \( L \), thickness \( t \) and width \( w \) is:

\[
T = \frac{\pi n r V L}{\lambda t}
\]

where \( V \) is the voltage across the thickness, \( \lambda \) is the optical wavelength in a vacuum, \( n \) the index of refraction, and \( r \) is the effective electro-optic coefficient. The Pockels (linear electro-optic) effect refers to the influence of an applied electric field \( (E_k) \) upon the relative optical dielectric impermeability \( (B_{ij}) \). Refractive index \( (n) \) is proportional to the inverse of the square root of the relative optical dielectric impermeability. The relative change in refractive index due to electric field produces a phase retardation to a beam of polarized light passing through the crystal. The Pockels effect is a 3rd order tensor the coefficients \( r_{ijk} \) related to electric field and electric impermeability as:

\[
\Delta B_{ij} = r_{ijk} E_k
\]

For an orthorhombic crystal, 2mm symmetry only five non-zero coefficients will be observed. The five coefficients for \( BaMgF_4 \) are designated as \( r_{13}, r_{23}, r_{33}, r_{42}, r_{51} \) and a relative measurement of the five coefficients was made based upon the detection of the rotation of the plane of polarization of a HeNe laser.

An experiment was set up as illustrated in Figure 10. The intensity of laser energy through the lower channel, detector A, is \( I_0 \), through the upper channel, detector B, is \( I = I_0 \cos^2 \Theta \), where \( \Theta \) is the change of polarization angle of the light through the crystal due to the applied voltage \( V \). However, for small values of \( r \), the change in intensity will be very small, i.e. small \( \Theta \) and \( I_0 \cos^2 \Theta \). Using a differential amplifier increased the sensitivity of the measurement. Comparing the signal from detector B to detector A, results in the following:

\[
\text{Polarization Loss} = A-B = I_0 - I_0 \cos^2 \Theta \text{ or } I = I_0 \sin^2 \Theta
\]

Thus allowing much smaller signal loss to be detected.
EXPERIMENTAL MEASUREMENT OF ELECTRO-OPTIC EFFECT

FIGURE 10
The experiment was calibrated to a commercial pockels cell (KD*P, Inrad 102-020). The laser intensity was detected as a function of voltage applied to the pockels cell. The result is shown in Figure 11. From the graph of $I'$ vs. $V$, the curve can be extrapolated to the point where the intensity $I'$ has reached from second maximum. This point occurred at $V_{1/2} = 1200$ volts. From the specification sheet for the KD*P Pockels cell, the half wave voltage is $V_{1/2} = 1800$ volts. It was determined that the smallest change in $I'$ detected was for a 40 volt change in the applied field. From the relationship $1800/1200$ volts = $x^\circ/40$ volts, the sensitivity of the experiment for the Pockels cell is $6^\circ$ polarization rotation.

A BaMgF$_4$ crystal was cut along an optic axis and replaced the Pockels cell. No change of intensity $I'$ was detected despite the applied voltage $V$ being increased to 5,000 volts. Then the crystal was electrically poled at 800C, the result was still negative. Based on the measurement of the Pockels cell, the minimum value for $V_{1/2}$ is $1.5 \times 10^5$ volts.

2.5 LASER HOST ASSESSMENT

The realization of crystal growth of large, high quality single crystal BaMgF$_4$, stimulated the interest of applying this crystal as a laser host. The principle requirements of a laser host being the ability to grow clear crystals as well as the incorporation of active ions, is met with BaMgF$_4$. BaMgF$_4$ exhibits the potential as a host crystal for two different groups of laser activators - divalent transition metal ions and divalent rare earth ions.

On a program for the Air Force contract number F33615-82-C-1823 crystal growth of both Sm$^{2+}$ BaMgF$_4$ and Eu$^{2+}$:BaMgF$_4$ was demonstrated. It is postulated that the divalent rare earth sits at the Ba$^{2+}$ site. The key to the successful processing was reducing and maintaining the rare earth ions in the divalent state. Stabilization of both Sm$^{2+}$ and Eu$^{2+}$ was accomplished by employing select atmosphere and crucible materials.
Figure 11. Experimental calibration with KDp cell
I vs. applied voltage
Spectroscopy of $\text{Sm}^{2+}:\text{BaMgF}_4$ and $\text{Eu}^{2+}:\text{BaMgF}_4$ performed on the Air Force contract indicated that in fact, that the divalent states of the rare earth ions were observed. $\text{Sm}^{2+}:\text{BaMgF}_4$ exhibited a mixed characteristic of broad energy transition overlapped with transitions from discrete energy levels. Emission peaks were observed at 676 nm and 713 nm, superimposed on a continuum from 670 to 730 nm. $\text{Eu}^{2+}:\text{BaMgF}_4$ exhibits broad emission between 400 - 500 nm. Further analysis and laser experiments are underway.

Although not demonstrated experimentally, $\text{BaMgF}_4$ also appears a suitable host for divalent transition metal ions.

$\text{BaMgF}_4$ is a member of an isostructural group of compounds consisting of replacement of Mg with Mn, Fe, Co, Ni, or Zn. Properties of the various compounds were found to be all members exhibited ferroelectric characteristics (Ref. 4), and similar optical characteristics (Ref. 6). Furthermore, although various melting points are reported, all compounds appear to melt congruently. It can be inferred that the compounds within this group form stable compounds exhibiting low lattice strain.

**FIGURE 12**

<table>
<thead>
<tr>
<th>$\text{BaMgF}_4$</th>
<th>$T_{mp}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>865 ± 5</td>
</tr>
<tr>
<td>Zn</td>
<td>745 ± 5</td>
</tr>
<tr>
<td>Mn</td>
<td>755 ± 5</td>
</tr>
<tr>
<td>Fe</td>
<td>720 ± 5</td>
</tr>
<tr>
<td>Co</td>
<td>855 ± 5</td>
</tr>
<tr>
<td>Ni</td>
<td>965 ± 5</td>
</tr>
</tbody>
</table>

Based upon the similarity of compounds, $\text{BaMgF}_4$ exhibits potential as a laser host crystal for divalent transition ions including $\text{V}^{2+}$, $\text{Co}^{2+}$ and $\text{Ni}^{2+}$. 

-23-
### IONIC RADIUS OF ELEMENTS SUBSTITUTED IN BAMgF₄

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>IONIC RADIUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba²⁺</td>
<td>1.35 Å</td>
</tr>
<tr>
<td>Sm²⁺</td>
<td>1.15 Å</td>
</tr>
<tr>
<td>Eu²⁺</td>
<td>1.12 Å</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.65 Å</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>0.74 Å</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.72 Å</td>
</tr>
<tr>
<td>V²⁺</td>
<td>0.74 Å</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.69 Å</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.76 Å</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.80 Å</td>
</tr>
</tbody>
</table>

**Figure 13**
3.0 SUMMARY AND CONCLUSION

BaMgF₄ exhibits excellent properties for optical applications, including a wide transmission band as well as a high optical damage resistance. BaMgF₄ is easily grown using the czochraski technique. Large, clear crystals were grown using pull rates between two and four mm/hr.

The application of BaMgF₂ for electro-optical devices is not appropriate, as the pockel's coefficients are very small requiring a high electric field to induce polarization. However, crystal growth of BaMgF₄ has yielded high quality crystals appropriate for optical applications. An alternative application for BaMgF₄ is as a laser host.

Both the Mg²⁺ and the Ba²⁺ ions in BaMgF₄ are host sites for activator ions for laser experiments. Mg²⁺, ionic radius ~.65 is a compatible position for Co²⁺ or Ni²⁺, where as Ba²⁺, ionic radius ~1.35 could be replaced by divalent rare earths, such as Sm²⁺ or Eu²⁺. Further investigation of BaMgF₄ as a laser host material is warranted and is being pursued.
REFERENCES


