This report describes research on the crystal growth and spectroscopic properties of 4d and 5d transition metal ions in halide and oxide host materials. Problems encountered with getting the doping material in the halide crystals are discussed. The spectra of Rh$^{3+}$ in oxide hosts are compared to the well known Cr$^{3+}$ spectra.
SPECTROSCOPIC INVESTIGATIONS OF MATERIALS
FOR TUNABLE INFRARED LASERS

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Principal Investigator:
Richard C. Powell
Department of Physics
Oklahoma State University

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This report summarizes the work performed on this contract during the first twelve months and describes the work planned for the second year. The research centers on the investigation of 4-d and 5-d transition metal ions in fluoride and oxide host crystals as possible tunable infrared lasers. The research effort is divided into three parts: acquisition of materials and equipment; crystal growth; and spectral analysis.

I. ACQUISITION OF MATERIALS AND EQUIPMENT

During this initial reporting period a significant amount of time was spent in acquiring the required materials, supplies, and equipment for this research. The equipment included a digital balance, furnace parts and crucibles for the crystal growth laboratory and infrared detection equipment for the spectroscopy laboratory. The major supplies needed were the chemicals for the starting materials for crystal growth. We obtained both oxides and chlorides of Ru, Rh, Re, Os, Ir, and Pt. Because of the unusual nature of these materials it took several months to receive the order and this created a significant delay in our work schedule.

II. CRYSTAL GROWTH

Single crystals of doped halides were grown by the Bridgeman technique. Each run required eight days and in each case the result was a single crystal of excellent optical quality having dimensions of about 6 cm in length and 2 cm in diameter. The samples grown during this time period are:

\[
\begin{align*}
2 \text{K}^\text{MgF}_3:\text{RhCl}_3(1\%) & & \text{CsBr:RhCl}_3(1\%) & & 2 \text{RbMgF}_3:\text{Rh}_2\text{O}_3(0.5\%) \\
\text{K}^\text{MgF}_3:\text{RuCl}_3(1\%) & & \text{KCl:IrCl}_3(1\%)
\end{align*}
\]

Single crystals of Bi$_4$Ge$_3$O$_{12}$:Rh(1%) and Bi$_4$Ge$_3$O$_{12}$:Cr (1%) were grown by the Czochralski technique. These samples had good optical quality except for nonuniform distribution of dopants.
As anticipated, the substitution of active ions in the halide crystal hosts is the major problem in this research project. The chloride dopants decompose at such low temperatures that they do not go into the host melt even for materials with low melting temperatures such as KCl. We are constructing double enclosed crucibles in the shop to inhibit the decomposition of the chloride dopants. Two crystals were obtained commercially for this project – LiNbO$_3$:Rh(1%) and LiNbO$_3$:Cr(1%). During the next reporting period samples of MgF$_2$:Ti(1%) and MgF$_2$:Cu(1%) will be obtained commercially.

III. SPECTROSCOPIC ANALYSIS

For each of the crystals grown during this time period, absorption spectra were run in the ultraviolet, visible, and infrared spectral regions. No spectral details associated with dopant transitions could be observed in any of the halide crystals.

The spectra in oxide host crystals were analyzed to determine their possible usefulness as tunable lasers. The Rh$^{3+}$(d$^6$) ion in oxide hosts is in the very strong crystal field limit. In LiNbO$_3$ crystals the emission occurs as a broad $^1T_1$ band between 520 and 640 nm. Preliminary calculations indicate that the peak stimulated emission cross section should be of the order of $7 \times 10^{-18}$ cm$^2$ and the threshold parameter should be $3 \times 10^{24}$ cm$^{-2}$ sec$^{-1}$. These parameters and the tuning range compare favorable with known tunable laser ions such as Cr$^{3+}$, Co$^{2+}$, and V$^{2+}$. The weaker crystal field environment in the germanate host shifts the spectra into the infrared region as desired. The absorption band peaks near 1 mm and we are now in the process of analyzing the infrared emission. The absorption spectrum of Cr$^{3+}$ in Bi$_4$Ge$_3$O$_{12}$ is a broad band peaking near 7000 Å and again we are in the process of measuring the emission.

During the next reporting period we will complete the detailed spectral analysis of the samples discussed above plus other fluoride samples grown during this period.
IV. OTHER INFORMATION

a. No technical papers or reports were published during this reporting period.

b. Two student research assistants worked on this project: Greg Quarles and Robert Schweitzer. In addition, Professor J.J. Martin assisted with the crystal growth, and Visiting Research Professor J. Cabrera assisted with both the crystal growth and the spectroscopy measurements.

c. No students earned degrees on this contract.

d. During this reporting period the principal investigator also worked on two other projects:

Use of Laser Spectroscopy Techniques for Investigating Energy Transfer Among Ions in Crystals.

National Science Foundation
$29,000 15 March 1982 - 14 March 1983.

and

Spectroscopic Investigation of Materials for Frequency Agile Laser Systems

Army Research Office
$69,830 15 January 1982 - 14 January 1983