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CaF_2 Laser Crystal Growth
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Director, ARPA:

Considerable progress has been made in the crystal growth of CdF_2 by use of the Bridgeman technique. The pure crystals (no deliberate addition of impurities) presently being grown contain 1-10 ppm of several elements, usually Zn, Ag, Cu, Fe, and Pb. The apparent band edge lies close to 2500 Å which is some 500 Å longer wavelength than that reported for ultra-pure CdF_2. We have grown crystals of CdF_2 containing Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2}, and Nd^{+3}. The crystals are of good quality optically, are probably not one single crystal, but contain large single crystal regions, and are 1/2" x 1" cylindrical boules. The assignment of the oxidation state is based on preliminary analyses of the room temperature and 77°K absorption spectra.

In the case of chromium, the impurity was added both as CrF_2 and CrF_3, otherwise identical crystal growth conditions, and the spectra of the resulting crystals were identical. There are two band systems, centered about 4450 A and 6800 A. The hands show a slight dimunition in intensity on going from 300°K to 2° K and the bandwidth of about 4000 cm^{-1} is almost temperature independent. The indications are that chromium occupies a Cd site as Cr^{+3} and has the full O_h symmetry of the site. In particular the bandwidth and temperature dependence of intensity indicates that the ion is at a centrosymmetric site. The value of Dq is in the range 1000 - 1500 cm^{-1} and the ground state may be partially spin quenched due to a large amount of $^2E(e_g{}^3)$ character. We intend to study this aspect by the use of electron paramagnetic resonance.

The spectra of Mn^{+2} and Ni^{+2} are not yet understood. The spectra are not those expected on the basis of symmetry arguments and Dq values predicted from examination of the spectra of those ions having other geometrical environments with symmetries O_h or T_d. We expected these predictions to give rather precise agreement with observation as was the case with the Co^{+2} ion, but this seems not to be so. The Mn^{+2} spectra shows only a very gradually rising absorption beginning near 1 micron and having the appearance of an absorption edge at about 5000 A. The spectra of Ni^{+2} has two moderately intense bands at 4500 and 5300 A. It is not yet clear if these bands are due to crystal field states of the impurity or if they are of the charge transfer type.

There has also been some success in the attempts to introduce transition element impurities into CaF_2. Crystals were grown by pulling from melts containing 0.1% of MnF_2, CrF_3, and NiF_2. The crystals are green and the absorption spectra are almost identical.

Emission spectra studies have not yet been undertaken. A 2 meter plane grating B and L spectrograph has been received and we are in the process of installing it. The instrument should be in use within a few weeks.

A Fabry-Perot interferometer has been assembled and aligned. The interference pattern of the 6328 A gas laser has been photographed but the theoretical resolving power of 0.005 cm^{-1} has not yet been realized. In preliminary photographs of $CaF_2:Tm^{+2}$ fluorescence at 4^o K, we observe an apparent line width of 0.01 cm^{-1} and a 0.03 cm^{-1} hyperfine splitting. We are also undertaking an experiment to observe the fluorescence through a second $CaF_2:Tm^{+2}$ crystal which acts to absorb some of the incident fluorescence. We will then apply a longitudinal magnetic field and the Zeeman splitting produced acts to reduce the absorption at the center frequency. By varying the field one thus has a method of scanning across the fluorescence line with what amounts to a narrow band filter. We intend to use this method for the line width study.

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