

COORDINATION COMPOUNDS OF CALCEIN BLUE FOR NEW LASER MATERIAL

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Coordination compounds of calcein blue with Al, Ca, Sr, and Ba were found to lase. Al-calcein blue efficiently lases at around 419 nm and the others lase at around 450 nm.

Hundred kinds of fluorescent organic dyes have been found to give laser emissions.^{1,2)} Significant advantages of dye lasers are that coherent light can be obtained at almost any wavelength from 330 to 1200 nm and that the lasing wavelength of a single dye laser is continuously tunable over a few hundred angstroms.

Few organic coordination compounds have been reported to show laser action by use of its own broad fluorescence emission. Mg and Al phthalocyanines are laser materials of this kind³⁾; however, they are insoluble in water. Although europium benzoacetate and some similar compounds were found to give laser action⁴⁾, the laser emission is sharp and intrinsic to the metal atom. Organic coordination compounds of calcein blue (see Fig.1) with Al, Ca, Sr, and Ba have recently been found to give laser emission, correlated with their broad fluorescence emissions, and the results are communicated in the present letter.

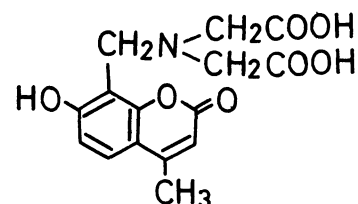


Fig.1 Calcein blue
(4-methylumbelliferone-methyleneiminodiacetic acid)

The pumping source is a pulsed N₂ laser, which is similar to that described by Basting et al.^{2,5)} Its maximum output power is 700 kW and the pulse length is 2.5 nsec. The calcein blue was commercially obtained from Dojindo Co. Calcein blue and equimolar of the metal ion were dissolved in buffer solutions. The output light of N₂ laser was focussed into the solution of the lasing material in a 1 cm square fluorescence cell.

Lasing characteristics of the material studied are shown in Fig.2 and Table 1. While calcein blue lases at around 446 nm at pH 5, the coordination compound with aluminum has the fluorescence maximum at the shorter wavelength and lases at around 418 nm. The fluorescence maxima of those with Ca, Sr, and Ba shift a few nanometers to the longer wavelength at pH 12 and

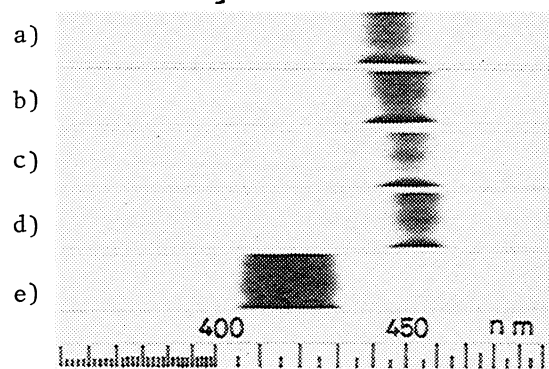


Fig.2 Lasing wavelength; a)calcein blue(pH 5), b)Ca-calcein blue(pH 12), c)Sr-calcein blue(pH 12), d)Ba-calcein blue(pH 12), e)Al-calcein blue(pH 5)

they lase at around 450 nm. The lasing wavelength, the fluorescence wavelength, and the quantum efficiency of the solutions of calcein blue with Ca, Sr, and Ba at low pH value are identical to those of calcein blue, and it seems the optical properties of calcein blue are not perturbed by the metal ions at the low pH value.

Since these compounds lase either at different wavelength region(Al) or at different pH region(Ba, Sr, Ca) compared with calcein blue itself, it was concluded that the coordination compounds show laser action, which is correlated with their own broad fluorescent emission.

The shortest wavelength of laser emission of coumarins which are very efficient laser materials is reported to be about 440 nm.²⁾ Some scintillators such as POPOP show laser emission in the 350-450 nm region²⁾; however, their insolubility in water restricts their practical application. Laser materials which lase at shorter wavelength and are soluble in water have been desired. It is found in the present study that the coordination compounds, which are soluble in water, give laser emission at shorter wavelength and their lasing properties can be varied by the replacement of metal atom or by the alteration of the pH of the solution. Many other different coordination compounds may be useful for such laser materials.

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Table 1 Characteristics of lasers of coordination compounds

material	pH	lasing wavelength (nm)	threshold (relative to 4-MU)	fluorescence wavelength (nm)	quantum efficiency (relative to 4-MU)
calcein blue	5	446	11	445	99
calcein blue	12	---	no lasing	454	52
Al calcein blue	5	418	11	412	103
Al calcein blue	12	---	no lasing	453	54
Ba calcein blue	5	446	11	445	98
Ba calcein blue	12	454	13	453	92
Sr calcein blue	5	446	11	445	98
Sr calcein blue	12	452	13	451	98
Ca calcein blue	5	446	11	445	98
Ca calcein blue	12	450	12	449	100
4-MU ^{a)}	10	453	10	452	100
POPOP ^{b)} in dioxane	--	423	4	422	92

solvent; water except for POPOP(insoluble in water). concentration; 10^{-3} mol/l.

a)4-methylumbelliferone

b)1,4-bis-[2-(5-phenyloxazoly)]-benzene

(Received September 5, 1974)