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SPECTRAL PROPERTIES OF Cr$^{3+}$ DOPED TETRA- AND PENTA- PHOSPHATE CRYSTALS

M. MALINOWSKI(1), R. WOLSKI and W. WOLINSKI

Institute of Electron Technology P.W., Koszykowa 75,
PL-00-662 Warsaw, Poland

Spectroscopic properties of Cr$^{3+}$ doped KYP$_4$O$_{12}$ and YP$_5$O$_{14}$ crystals are presented for the first time. Both systems exhibit simultaneous broad-band $^4T_2 \rightarrow ^4A_2$ and the weak narrow-band $^2E \rightarrow A_2$ emissions. Ligand field parameter $10D_q$ in KYP$_4$O$_{12}$: 5% Cr$^{3+}$ has been evaluated to be about 15500 cm$^{-1}$. Time resolved spectra, lifetimes and $^4T_2$ effective emission cross sections have been studied in chromium doped Y- tetraphosphates.

INTRODUCTION.

In attempts to realize the efficient tunable, solid state laser system various ions in different matrices have been the subject of recent investigations. Especially, trivalent transition metal ions in oxide crystals were studied intensively. These studies resulted, for example in succesful laser action of Cr$^{3+}$ in several Ga- garnet structured compounds [1] or Alexandrites [2] as well as Ti$^{3+}$ in Al$_2$O$_3$ [3]. In order to obtain strong, wide band $^4T_2 \rightarrow ^4A_2$ emission of chromium the crystal field at the Cr$^{3+}$ site has to be weak. This is commonly realized when Cr$^{3+}$ substitutes for ions having much larger ionic radius; Ga, La or Lu.

In this work we present the preliminary results of the spectroscopic studies of Cr$^{3+}$ doped ittrium tetra- and penta- phosphate crystals. These systems when activated by trivalent rare-earth (RE) ions showed its value as the succesful laser hosts [4]. Because of our earlier studies of crystal growth and spectroscopic properties of RE-potassium tetrametaphosphates [5] we have synthesized for the first time KYP$_4$O$_{12}$: Cr$^{3+}$ crystals. YP$_5$O$_{14}$: Cr$^{3+}$ crystals have been also obtained in our laboratory and in the other Polish institute in the same time [6].

EXPERIMENTAL.

The samples were prepared from the solution of K$_2$CO$_3$ and chromium and ittrium oxides in 85% ortophosphoric acid at the temperature range of 350 - 400 C. The resulting crystals had dimensions of several mm

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(1) Present address : Laboratoire de Physico-Chimie des Matériaux Luminescents, CNRS UA-442 CNRS, 43 Blvd du 11 novembre 1918, Université Lyon I, F-69622 Villeurbanne Cedex, France

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and were pale pink-violet coloured. The Cr\(^{3+}\) concentrations were determined to be \(2 \times 10^2\) cm\(^{-3}\) which correspond to about 5\% doping level. Room temperature absorption spectra of the investigated samples are presented in Fig.1. The emission spectra and fluorescence lifetimes were measured under frequency doubled, pulsed Nd:YAG laser excitation at 532 nm. The fluorescence spectra taken at different temperatures are presented in Fig.2. In Fig.3 we show the 4.4 K time resolved fluorescence spectra of KYP\(_4\)O\(_{12}\): 5\% Cr\(^{3+}\) crystals. Fluorescence decay of Cr\(^{3+}\) ions in tetraphosphates is presented in Fig.4.

**DISCUSSION AND CONCLUSIONS**

The absorption spectra presented in Fig.1 show several anomalies in the 600-700 nm range which cause that the ligand field strength evaluation from the maximum of the \(^4\)A\(_{2}\)\(^\rightarrow\)\(^4\)T\(_2\) absorption is not precise. It could be found that the 10-Dq value is about 15500 cm\(^{-1}\). This is in agreement with the values found in Cr\(^{3+}\) doped phosphate glasses 14500...
The details of the absorption spectrum could be interpreted in terms of Fano antiresonances [8] however, further more precise studies must be undertaken to establish its real nature. The fluorescence spectra presented in Figs 2 and 3 demonstrate the broad-band emission in the range from 720 to 880 nm. The sharp decrease of the signal intensity at 900 nm results from the limit of sensibility of the used AsGa photomultiplier. In the region of 695 nm several sharp emission lines could be observed, they are attribute to the $^2E \rightarrow ^4A_2$ transition (R lines) and its pair or vibronic satellites. These structure is much more intense in the case of pentaphosphates. Time resolved fluorescence spectra presented in Fig.3 show that the relative intensity of the 695 nm emission increases for longer times. The decay curves for the KYP$_4$O$_{12}$: 5% Cr$^{3+}$ crystals presented in Fig.4 show that the $^2E \rightarrow ^4A_2$ emission is strongly nonexponential. It is possible to distinguish fast 20 $\mu$s and long about 3.9 ms decay. $^4T_2 \rightarrow ^4A_2$ emission measured at 780 and 850 nm deviates slightly from exponential behaviour. Lifetimes obtained from the exponential part of the decay are 30 and 36 $\mu$s respectively. The observed nonexponential behaviour may result from the existence of different Cr$^{3+}$ sites each having different transition rates or from the Cr-Cr interaction in this relatively strongly concentrated system. From the Tanabe-Sugano diagram resulted that simultaneous occurrence of $^4T_2 \rightarrow ^4A_2$ and $^2E \rightarrow ^4A_2$ emissions is taking place for Cr$^{3+}$ ions located in sites of intermediate ligand field strength. This confirms our analysis of 300 K absorption spectrum of KYP$_4$O$_{12}$: 5% Cr$^{3+}$. Finally, on the base of absorption measurements the effective emission cross section for the $^4T_2 \rightarrow ^4A_2$ transition was evaluated to be $\sigma_0 = 1.2 \times 10^{-20}$ cm$^{-4}$.

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