Influence of dye concentration on optical properties of rhodamine 6G doped KAP crystals

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Crystals of potassium acid phthalate (KAP) doped with rhodamine 6G (Rh 6G) were grown by slow evaporation method from aqueous solutions. Crystals of good optical quality suitable for optical applications were obtained. Different concentrations of rhodamine 6G (10^{-5} M, $2x10^{-5}$ M, $5x10^{-5}$ M and 10^{-4} M in the growth solutions) were used in order to tune the optical properties of the crystals. Depending of the dye concentration, the absorption spectra of the dye-doped crystals show several bands in the range between 360 nm and 526 nm. The photoluminescence of the KAP crystals induced by the dye-doping reveals two emission bands peaking at 540 nm and 560 nm.

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1. Introduction

Potassium hydrogen phthalate or potassium acid phthalate (KAP) is a material soluble in water that crystallizes in normal conditions in a pseudo-hexagonal shape having an orthorhombic symmetry. Studies regarding the potassium acid phthalate micro and nanostructures growth were performed [1]. The KAP crystal is used in devices due to its electro-optical properties [2]. Also, these crystals play an important role in the field of non linear optics [3] and show interesting piezoelectric, pyroelectric and elastic properties that are useful in many applications [4, 5]. The relation between growth conditions and the morphology of pure [6, 7] and doped [8, 9] KAP crystals was extensively studied by numerous authors.

Recent papers showed extremely interesting optical properties of dye doped single crystals such as KAP [10]. An important accent was put on the luminescence and up conversion due to second harmonic generator properties of the KAP crystals doped with different dyes [11-13].

Studies regarding solid-state lasing materials are mainly aimed on dye-doped polymers, clays or liquid crystals. An easily growing non-linear optical (NLO) single-crystalline material that combines the qualities of liquid dye-lasers such as high efficiency and broadband tuneability with the flexibility and the convenience in operation offered by a single crystal it is a very interesting alternative. Such an alternative may be represented by the dye doped single crystals of KAP.

This paper presents studies regarding the influence of dye concentration on the optical properties of rhodamine 6G (Rh 6G) doped potassium acid phthalate crystals. The results obtained using optical transmission and photoluminescence measurements are reported.

2. Experimental

KAP crystals were grown by the evaporation technique from aqueous solutions prepared using deionized water (Millipore Ultra-Q, 18.2 MΩcm resistivity at 25°C) and A.C.S. grade (meets the specifications of the American Chemical Society) potassium hydrogen phthalate ($C_8H_5O_4K$) supplied by Aldrich. Rhodamine 6G Basic Red 1 of 99 % purity (Aldrich) was used without further purification as dopant. After reaching over 1 cm in size, the crystals were harvested from the solution.

The solubility of KAP was calculated using the equation [14]:

$$c(T) = 9.283 - 0.059T + 0.0058T^2 \quad (1)$$

where c(T) is the solubility of KAP (g/ml of water) and T is temperature in °C.

For the optical measurements we used three Rh 6G concentrations, 10^{-5} M, $5x10^{-5}$ M and 10^{-4} M respectively.

Pure and dye-doped KAP crystals have an orthorhombic symmetry with the space group $Pca2_1$ and show a perfect cleavage along (010) plane. Platelets of 1.5 mm thickness were cleaved in order to perform the optical measurements.

The grown crystals have been characterized by the room-temperature transmission and absorption spectra recorded using a Cary 5000 UV–vis–NIR spectrophotometer. The emission spectra of doped crystals were detected using a Perkin Elmer LS55 spectrometer (200-800 nm) and an Edinburgh Instruments FL920 spectrometer (200-900 nm) with a 450 W Xe lamp.

3. Results and discussions

The as-grown Rh 6G doped KAP crystals are presented in Fig. 1. Rh 6G doped KAP crystals present the same pseudo-hexagonal shape as the pure KAP crystals. Rh 6G doping of the KAP crystals in a concentration of 10^{-5} M results in a fairly uniform pink coloration of the samples (Fig. 1 (a)). Usually, high concentration of dye in the growth solution results in the dye segregation. In this case, islands of high dye concentration can be observed (Fig. 1 (b)).

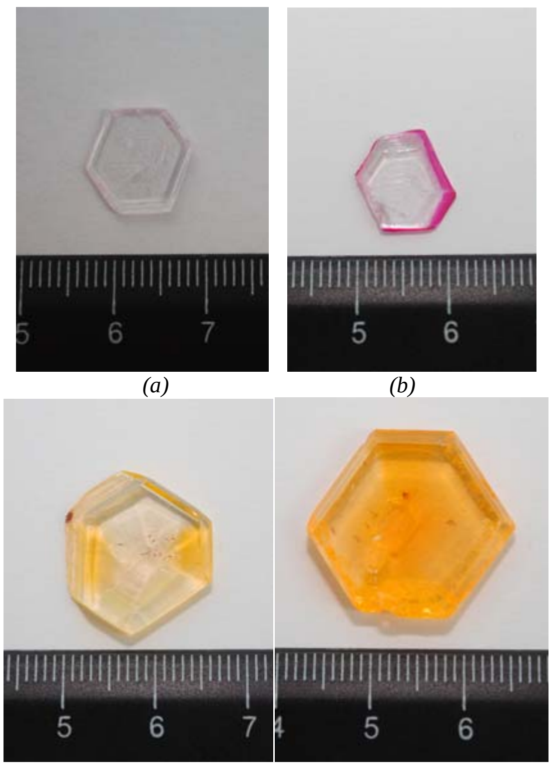

Fig. 1. Rh 6G doped KAP crystals with different dye concentrations in the aqueous solutions: a). 10^{-5} M, b). $2x10^{-5}$ M, c). $5x10^{-5}$ M and d). 10^{-4} M.

We have been able to grow more intensely coloured crystal by using undersaturated aqueous solutions and increasing the dye concentration by water evaporation. In this way we obtained Rh 6G doped KAP crystals with 5×10^{-5} M and 10^{-4} M dye concentration in solution, presented in Fig. 1 (b) and (c).

The dye-doped crystals with good transparency window were characterized by optical measurements. The transmission and absorption spectra were obtained using unpolarized incident light perpendicular to the [010] growth face of the crystals. The UV-vis-NIR spectrum is very important for any kind of non-linear optic material because wide transparency window are needed in further applications. The optical transmission spectra of Rh 6G doped KAP crystals were measured between 200 and 1500 nm (Fig. 2 (a)). It can be observed that rhodamine 6G do not change the UV cut-off or the transparency of the crystals.

Absorption spectra were recorded in the UV-vis region. The rhodamine-induced absorption bands with maxima between 360 nm and 526 nm are presented in Fig. 2 (b). The dye concentration has an obvious influence on the number and intensity of absorption bands in the spectrum. Using deconvolution of the absorption spectra, as illustrated in the inset, we were able to determine the wavelength of the absorption bands maxima. The crystal with the lowest dye concentration (10^{-5} M) presents only 3 bands induced by the dye, peaking at 400 nm, 480 nm and 526 nm, respectively. Those bands have a very low intensity as suggested by the distilled colour of the crystal. In the crystal doped with $5x10^{-5}$ M of Rh 6G the number of the absorption bands is increasing, being possible to distinct the overlapping absorption bands peaking at approximately 382 nm, 420 nm, 445 nm, 470 nm and 506 nm. For the crystal with the highest dye concentration (10^{-4} M) the number of bands is increasing and they have a higher intensity. Thus, there can be distinct several bands, with maxima around 372 nm, 385 nm, 400 nm, 420 nm, 445 nm, 470 nm and 506 nm, overlapping in the absorption spectrum.

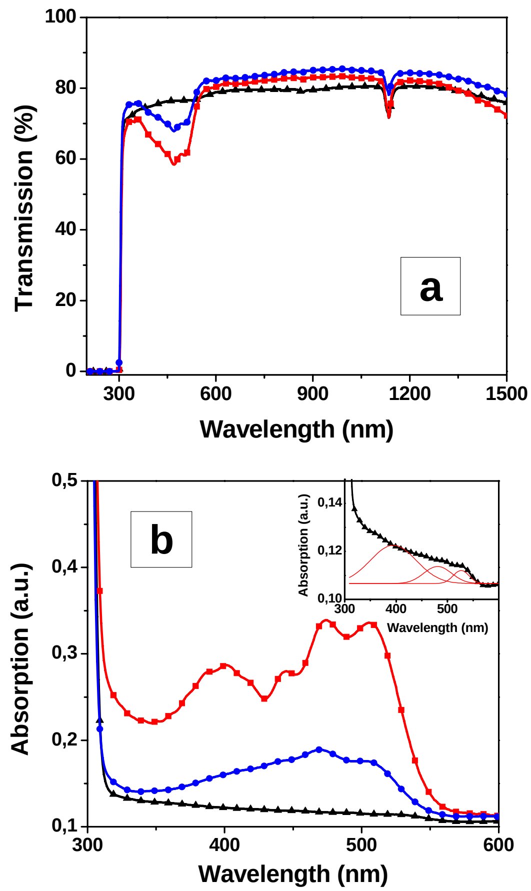

Fig. 2. Transmission (a) and absorption (b) spectra of Rh 6G doped KAP crystals with different dye concentrations: 10^{-5} M (triangles), 5×10^{-5} M (circles) and 10^{-4} M (squares).

This overlapping of the absorption bands is in agreement with the crystals' appearances. While for the lowest dye concentration (10^{-5} M) we distinct only the pink colour induced by the dopant, for the higher dye concentrations we observed pink sectors mixed with orange coloured sectors ($5x10^{-5}$ M) or only orange sectors with different concentration (10^{-4} M). This proves the preferential pattern of dye molecules'incorporation into the KAP host. It was showed for other several dyes that the optical properties of the doped materials depends critically on dye concentration [15] and on the addition pattern of the dye to the host (related to the fact that different crystalographic faces have different affinities of the dyes [11]).

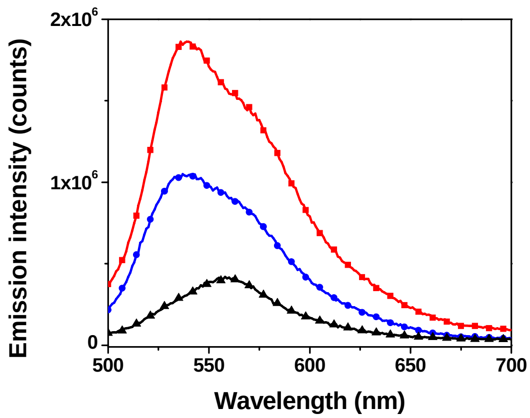

Fig. 3. Emission spectra of Rh 6G doped KAP crystals with different dye concentrations: 10^{-5} M (triangles), 5×10^{-5} M (circles) and 10^{-4} M (squares).

The luminescent properties of the Rh 6G doped KAP crystals were investigated. The emission spectra of doped crystals are presented in Fig. 3. The luminescence studies were carried on within the geometry of the spectrometers using unpolarized light for the excitation. The intensity of the luminescence is high and the photostability is noticeable. Rh 6G doped KAP crystals have wide emission bands excited with 480 nm wavelength. For the lowest dye concentration (10^{-5} M) the emission spectrum presents only one emission band peaking at 560 nm. As expected for the higher dye concentrations, suggested also by the appearance in the absorption spectra of several bands peaking at shorter wavelengths, a band peaking at shorter wavelength (540 nm) appears. This 540 nm band is overlapping the 560 nm band as indicated by the mixture of colors in the crystals. The intensities of the emission bands are increasing with the increasing of Rh 6G concentration in the aqueous solutions used for crystal growth.

4. Conclusions

Crystal growth from aqueous solutions by evaporation technique was employed in order to obtain single crystals of rhodamine 6G doped potassium acid phthalate with different dye concentrations in the growth solutions (10^{-5} M, 2×10^{-5} M, 5×10^{-5} M and 10^{-4} M). The crystals show a preferential pattern of dye molecules' incorporation into the KAP host. Transmission and absorption measurements were performed in order to determine the optical quality of the crystals and the influence of the dye concentration. The rhodamine 6G-doped KAP crystals have a good transparency in the UV-vis-NIR region and the UV cut-off is not changed by the dye doping. The number and the intensity of the absorption bands appearing in the rhodamine 6G-doped crystals' spectra are increasing with the increasing of the dye concentration. Rhodamine 6G-doped KAP crystals exhibit luminescence excited at 480 nm with large emission bands peaking at 540 nm for the lowest dye concentration and at 560 nm for the highest dye concentration.

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