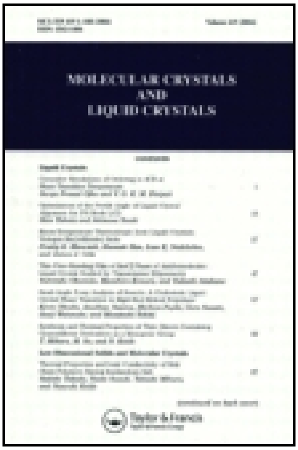

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Non Linear Optics in Zirconium Phosphate Layered Phases

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Non Linear Optics in Zirconium Phosphate Layered Phases

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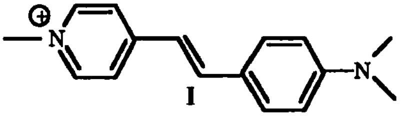
The stilbazolium chromophore 4-[4-(dimethylamino)-α-styryl]-1-methylpyridinium (DAMS) ion can be exchanged with the α and γ forms of zirconium phosphate to give single phase materials of interlayer distance 16.5 and 16.4 Å respectively. The latter has a second harmonic generation efficiency, measured at 1.9 μm, equal to that of urea, whilst the former is inactive. Both compounds have been characterised by fluorescence emission and visible spectroscopies.

Keywords: non linear optical properties; zirconium phophate; dyes intercalation

INTRODUCTION

Host-guest chemistry has already provided a number of new compounds having non-linear optical (NLO) properties [1]. In previous publications, some of us have recently reported that materials exhibiting second harmonic generation (SHG) properties could be prepared *via* the intercalation of stilbazolium chromophores into layered MPS_3 [2,3]. No contribution to this effect was expected from the centrosymmetric host, and a model involving the formation of dye J-aggregates in the interlamellar space was suggested to rationalise the observed results. In order to assess the influence of the nature of the host matrix on the observation or not of SHG properties, we recently extended our study to the inclusion of the same 4-[4-(dimethylamino)-α-styryl]-1-methylpyridinium (DAMS, I) chromophore in other hosts, such as bentonite [4], and present here the results obtained on DAMS-exchanged α and γ-zirconium phosphate (ZrP).


I

EXPERIMENTAL SECTION

α and γ-zirconium phosphates were prepared using published methods [5,6]. The synthesis of $DAMS^+I^-$ has been reported previously [7]. In initial experiments, ethanolic or aqueous solutions of DAMS iodide were contacted with pristine host zirconium phosphates for a period of up to 1 week (0.1 g zirconium phosphate suspended in 100 ml of ethanol or water containing 0.3 g $DAMS^+I^-$). For α-ZrP, a route was also developed making use of a trimethyldodecylammonium (TMDDA) exchanged phase, prepared *via* pre-expansion with propylamine vapour. α-ZrP(TMDDA)$_{0.67}$ (0.1 g) was then suspended in a water - ethanol (4 : 1) mixture containing 0.3 g $DAMS^+I^-$, and gently heated for 1 week. Products of all reactions were recovered by centrifugation, thoroughly washed with water and water - ethanol (4 : 1) and dried in air.

Powder X-ray diffraction patterns were recorded using Cu Kα radiation, thermograms on a Stanton STA 781 balance, emission spectra with a SPEX fluorimeter, using front face excitation at λ_{exc} = 500 nm, visible spectra with a Cary spectrophotometer, and FTIR spectra with a BOMEM 180 spectrometer. Non-linear optical measurements were performed on samples sieved for particles under 100 μm, using the Kurtz-Perry powder technique[8], using a picosecond Nd:YAG pulsed laser operating at 1.9 μm.

RESULTS

Direct ion exchange between the protons of γ-ZrP occurs, avoiding the need for a pre-expansion step. In the case of α-ZrP, no direct insertion of $DAMS^+$ could be achieved, although ready ion-exchange occurs with a surfactant type ion such as trimethyldodecylammonium. The diffraction patterns of the dye-intercalated phases indicate interlayer distances of 16.5 Å and 16.4 Å for the α-ZrP and γ-ZrP hosts respectively. Although close in absolute value, the gallery height is different in each case since the thickness of the zirconium phosphate layers is different in the α- and γ-ZrP structures (*ca.* 6.4 and 9.2 Å respectively).

Thermogravimetric analysis allow compositions of the two intercalates to be calculated: $\alpha\text{-ZrH}_{1.47}(PO_4)_2(DAMS)_{0.53}\bullet 1.1H_2O$ and $\gamma\text{-ZrPO}_4.H_{1.53}PO_4(DAMS)_{0.47}\bullet 1.2H_2O$, indicating only 25% of the total ion exchange capacity to have been used. At this stage it is useful to consider the possible arrangement of DAMS in the interlayer region. For γ-ZrP, the expansion observed of *ca.* 7 Å is close to that given previously by MPS_3-DAMS and bentonite-DAMS intercalates, and is compatible with an orientation of the DAMS ions standing edge-on to the layers. The increase in interlayer distance (10 Å) is greater in α-ZrP, a result which is best rationalised in terms of DAMS ions having their long axis slightly tilted with respect to the ZrP planes. In fact the ratio of the observed interlayer expansions (*i.e.* 7/10 Å) and the ratio of the surface area available per exchangeable proton (24/35 $Å^2$) are equal, indicating that the volume available per DAMS unit, *i.e.* its packing density, is the same, irrespective of the crystalline form of zirconium phosphate. However, a similar packing density does not imply a similar arrangement of DAMS units in the interlayer region, and this lies at the origin of different NLO properties, as shown below.

Absorption spectra recorded on as-prepared samples in the visible region are shown in Figure 1. Notable differences are seen, with γ-ZrP-$DAMS_{0.47}$ giving a broad band of single maximum at 500 nm, whilst α-ZrP-$DAMS_{0.53}$ shows a structured band of maxima near 500 and 570 nm. The former spectrum is reminiscent of that given by $DAMS^+I^-$ in ethanolic solution, and the latter resembles the visible spectrum of $CdPS_3$-$DAMS^+$. This deformation of the absorption band is usually attributed to the presence of J-aggregates [9], and these aggregates suggested to be responsible for the non-linear optical properties demonstrated by the $CdPS_3$-$DAMS^+$ material [3]. J-aggregate formation is described as clustering into dimers or higher oligomers, and has been reported, for coherence lengths longer than *ca.* 1 μm, to cause non-centrosymmetric packing of interacting chromophores which can lead to the induction of SHG properties [10].

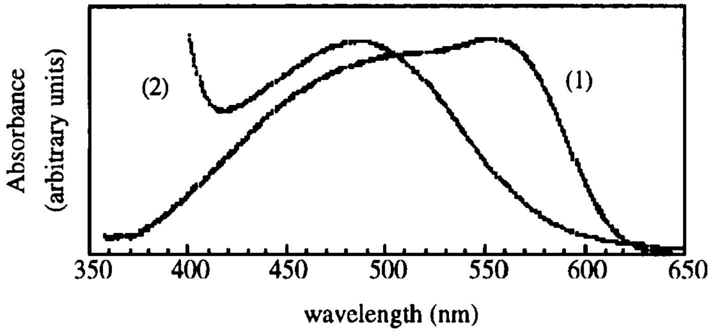


FIGURE 1 Visible spectra of (1) α-ZrP-$DAMS_{0.53}$ and (2) γ-ZrP-$DAMS_{0.47}$

The results of non-linear optical measurements are summarised in Table 1. Only the intercalate prepared using γ-ZrP has an SHG efficiency which arises, as indicated by control measurements made on the host matrices, as a result of intercalation of DAMS.

TABLE 1 SHG efficiencies of using 1.9 μm laser radiation. L indicates that the signal was below the limit of detection. All SHG efficiencies are referenced to that of urea.

compound	SHG efficiency
α-$Zr(HPO_4)_2.H_2O$	L
γ-$ZrPO_4(H_2PO_4).2H_2O$	L
α-ZrP-$DAMS_{0.53}$	L
γ-ZrP-$DAMS_{0.47}$	1

The emission spectra given by excitation at 500 nm are shown in Figure 2. The band at around 600 nm corresponds in position to emission from

$DAMS^+$ in aqueous solution, and its presence could be explained by the interaction of interlayer $DAMS^+$ with co-intercalated water.

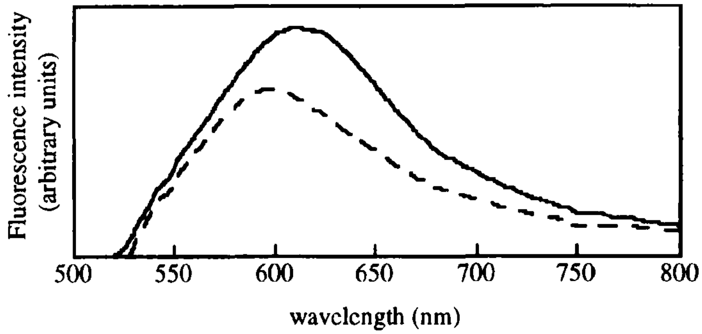


FIGURE 2 Emission spectra of α-ZrP-$DAMS_{0.53}$ (solid line) and γ-ZrP-$DAMS_{0.47}$ (dashed line) recorded at room temperature at λ_{exc} = 500 nm

The emission at 700 nm corresponds to the strongest luminescence from solid $DAMS^+I^-$, or DAMS intercalates of bentonite or MPS_3, and indicates weak interaction between chromophores.

The role played by water in the optical properties of ZrP-DAMS phases was further investigated by studying the absorption spectrum of α-ZrP-$DAMS_{0.53}$ in the visible region after dehydration and rehydration. These spectra are reproduced in Figure 3, where it may be seen that dehydration (120°C, 15 min) profoundly modifies the shape to a single maximum at 500 nm, in place of the structured, two maxima band initially observed.

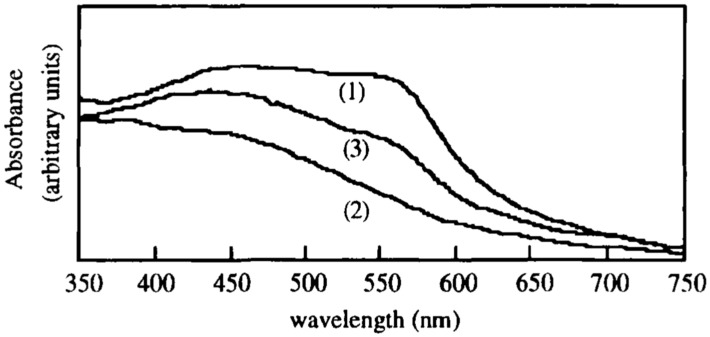


FIGURE 3 Effect of dehydration (1-2))/rehydration (2-3) on the visible spectrum of α-ZrP-$DAMS_{0.53}$

The new band shape is similar to that observed for γ-ZrP-DAMS$_{0.47}$, and is characteristic of isolated (non-aggregated) DAMS^{+}. Rehydration in a humid atmosphere reverts this situation. The existence of J-aggregates in the α-ZrP host would seem to be strongly dependent on the presence of co-intercalated water. No change in the interlayer distance in the dehydrated phase was detected using X-ray diffraction.

As a conclusion, in contrast to the results obtained up until now on other layered phases ion-exchanged with DAMS^{+}, no correlation is found between SHG efficiency and the presence of J aggregates, as deduced from the band shape in the visible spectrum. It is concluded that the γ-ZrP structure induces a non-centrosymmetric arrangement of incoming DAMS^{+}, which lies at the origin of the non-linear optical properties detected. In this respect the different arrangement of DAMS in the interlayer region of α- and γ-ZrP inferred from the different gallery heights in the DAMS intercalates is of greatest importance, and arises from the inherent structural differences (layer charge density, thickness and rigidity of the layers) of the two host matrices.

Acknowledgments

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