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Er^{3+} INDUCED INFRARED ACTIVE MODES IN TRANS-POLYACETYLENE, $(\text{CH})_x$

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ABSTRACT

We have investigated the infrared active modes in undoped and Er^{3+} doped trans- $(\text{CH})_x$. The characteristic infrared absorption bands are always observed at 875 cm^{-1} , 1000 cm^{-1} , 1125 cm^{-1} , 1275 cm^{-1} and 1375 cm^{-1} for Er^{3+} doped trans- $(\text{CH})_x$. Our experiments have shown, for the first time, that the intensity of these absorption bands is obviously increased by the implantation of Er^{3+} ions. The intensity of the absorption band at 1375 cm^{-1} which is associated with the number of charged centers increases with the dopant concentration. It is a charged soliton mode. The increase of other bands (for example at about 875 cm^{-1} , etc) is also caused by Er^{3+} , but their increases are lower than that of band at 1375 cm^{-1} . The absorption band at 875 cm^{-1} is attributed to the localized phonon mode around a soliton, and hence, we think it is doping induced infrared active mode.

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INTRODUCTION

Polyacetylene (PA), $(\text{CH})_x$, is the simplest linear conjugated polymer. The electrical conductivity of films of $(\text{CH})_x$ can be varied over 12 orders of magnitude by doping the cis or trans isomer with acceptor or donor ions, but the nature of the donor and acceptor impurities in this semiconducting polymer, especially rare earth ion impurities, has not been studied using optical absorption in detail. Various electron acceptor or donor ions can be used to yield n-type or p-type material. In order to understand much problem, in recent few years, the studies of the localized vibrational modes of PA have been made extensively [1-3]. However the experimental study of the infrared active modes of lightly Er^{3+} doped PA system has not been published till now. Because Er^{3+} doped PA will have some novel

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optical properties for technique application, so we will discuss the characteristics of the infrared active localized modes in rare earth ion Er^{3+} implanted $\text{trans}-(\text{OH})_x$ in this paper.

EXPERIMENTAL

Thin ($10 \sim 100 \mu\text{m}$) films of PA were synthesized using techniques similar to those developed by Shen and collaborators [4] in the presence of a rare earth catalyst with polymerization carried out at -78°C . $\text{Trans}-(\text{CH})_x$ ($>98\%$) was obtained by the heat treatment of cis isomer at 190°C for about 2 hours. The X-ray diffraction studies show that thin films of any cis and trans-composition are polycrystalline. Typical PA films were $80 \mu\text{m}$ (0.08mm) in thickness. Doping technique was the ion implantation and has been described in an earlier publication [5]. With $\text{trans}-(\text{CH})_x$ films at 300K , an implantation fluences of $5 \times (10^{13} - 10^{14})$ erbium ions cm^{-2} at an ion flux of $0.2 \mu\text{A cm}^{-2}$ and a beam energy of 80 Kev were used. The suitable doping level (surface density of implanted erbium ion) used in these experiments was $5 \times 10^{13} \text{ Er}^{3+}/\text{cm}^2$. The infrared absorption spectra in the region of $400 \sim 2000 \text{ cm}^{-1}$ were recorded using a 599 Perkin-Elmer Spectrophotometer.

RESULTS AND DISCUSSION

We have investigated the infrared active modes in undoped and Er^{3+} doped trans-PA . Figure 1 shows the characteristic infrared absorption bands which are always observed at 875 cm^{-1} , 1000 cm^{-1} , 1125 cm^{-1} , 1275 cm^{-1} , 1375 cm^{-1} for Er^{3+} doped $\text{trans}-(\text{CH})_x$ and at 1015 cm^{-1} for undoped $\text{trans}-(\text{CH})_x$. Our experiments have shown, for the first time, that the intensity of these absorption bands is obviously induced by the implantation of Er^{3+} ions. These absorption maxima are caused by Er^{3+} . The increase of the band at about 875 cm^{-1} or 1000 cm^{-1} is lower than that of the band at about 1125 cm^{-1} , 1275 cm^{-1} or 1375 cm^{-1} (see Table 1). The intensity of the absorption band at 1375 cm^{-1} , which is a charged soliton mode and associated with the number of charged centres, increases with the dopant concentration. The 1275 cm^{-1} band is also a charged soliton mode. These two infrared active modes, at 1375 cm^{-1} and 1275 cm^{-1} , are intrinsic feature of soliton, while 875 cm^{-1} is considered as a pinning Goldstone mode [6], it is the effect of Er^{3+} and increased by Er^{3+} . The two characteristic absorptions around 1000 cm^{-1} and 1125 cm^{-1} shown in Fig. 1 appear also to be increase features of Er^{3+} doped $\text{trans}-(\text{CH})_x$.

Recently, three infrared active modes around solitons have been found theoretically based on the Su-Schrieffer-Heeger model [3] and they correspond to three infrared

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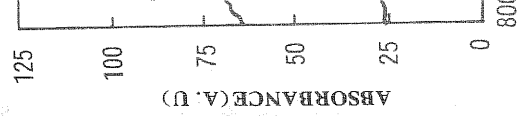


Fig. 1. li
 $\text{trans}-(\text{CH})$

TABLE 1
Change in

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$A_1 = \text{relat}$
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absorption lines at 900 cm^{-1} , 1260 cm^{-1} and 1370 cm^{-1} . 900 cm^{-1} corresponds to the Goldstone mode. The third mode is such close to the staggered mode as the two close standing absorption lines 1260 cm^{-1} and 1370 cm^{-1} . Therefore these three infrared active modes can be used to interpret the observed infrared absorptions. Our measurement data, 875 cm^{-1} , 1275 cm^{-1} , 1375 cm^{-1} , agree well with these calculated infrared active modes.

It will be seen from this that the origin of infrared active mode is phonon mode around a soliton. Especially, under the assistance from the vibrational motion of the dopant

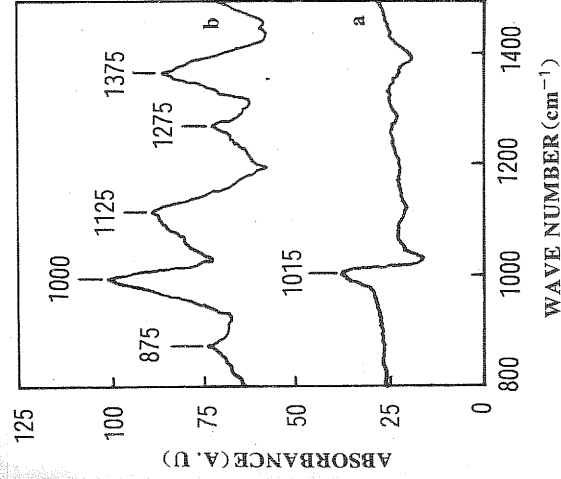


Fig. 1. Infrared spectra for undoped trans-(CH)_x (a) and Er³⁺ (5×10^{13} ion cm⁻²) doped trans-(CH)_x (b).

TABLE 1
Change in relative intensity of absorbance peak

Change	Absorbance peak, cm ⁻¹			
	875	1000	1125	1275
Er ³⁺ doped trans-(CH) _x	74	102	89	73
undoped trans-(CH) _x	27	38	20	23
A ₁ -A ₂ ^a	47	64	69	50
A ₁ -A ₂ /A ₂ (%)	174	168	345	217
				330

^aA₁=relative absorbance intensity of Er³⁺ doped trans-(CH)_x.

A₂=relative absorbance intensity of undoped trans-(CH)_x.

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ed trans-PA. observed at (CH)_x and at st time, that ation of Er³⁺ at about 875 cm⁻¹ or 1375 is a charged ses with the . These two soliton, while of Er³⁺ and d 1125 cm⁻¹ D_x. theoretically iree infrared

(effect of Er^{3+}), due to the acceleration of the rate of intersoliton hopping [5], its intensity depends on the concentration of dopant. In fact, there is a more suitable Er^{3+} -doped concentration ($5 \times 10^{19} Er^{3+}/cm^2$). The effect mechanism of Er^{3+} needs studying further.

CONCLUSIONS

The experimental infrared absorption changes observed upon doping of Er^{3+} are discussed. Implanted doping Er^{3+} can increase intensity of infrared active mode of trans-(CH)_x. The increase of intensity only depend on concentration of dopant and independent on specific dopant. We have also shown that a good agreement between the SSH model calculation and the experimental infrared spectra have been found. The effect of Er^{3+} has been discussed using intersoliton hopping. The infrared active modes of trans-(CH)_x are of the characteristics of soliton. These will help us to understand a novel optical property and a conducting mechanism of trans-(CH)_x.

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ABSTRACT

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