Photoinduced changes in photorefractive PVA films doped with Cr^{3+} and VO^{2+}: EPR and PAS investigations

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Abstract. In order to understand the mechanism of optical image storage in photorefractive polyvinyl alcohol (PVA) films, photo-EPR and photoacoustic spectral investigations were carried out on PVA films doped with Cr^{3+} and VO^{2+}. The EPR spectrum of Cr^{3+} has shown reduction in intensity on *in situ* illumination with copper vapor laser (CVL). The decay and recovery of Cr^{3+} signal, with and without CVL illumination respectively, was monitored at different temperatures in 10–300 K region. These were found to obey a double exponential, with one time constant independent of temperature, and the other showing significant temperature dependence. From $\tau(T)$, activation energy for the charge carrier transport in one of the processes was estimated to be 0.016 eV. The PA spectra showed shift towards lower wavelength side on consecutive runs. On the other hand, VO^{2+} doped PVA film has not shown any significant changes in intensity on laser illumination. These observations suggest (i) interaction of PVA matrix with excited Cr^{3+} and (ii) predominant non-radiative relaxation in VO^{2+} : PVA system with no change in the oxidation state.

Keywords. Electron paramagnetic resonance; photoacoustic spectroscopy and polyvinyl alcohol.

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1. Introduction

Polymer-based materials are reported to exhibit photoconductivity and associated non-linear optical properties [1]. Polyvinyl alcohol (PVA) films impregnated with transition metals are also reported to be promising materials for optical image storage through photoinduced electron transfer and cross linkage phenomenon [2]. However, no photoconductivity was reported in PVA. Electron paramagnetic resonance (EPR) is a well-established spectroscopic technique for monitoring the changes in valence on photoexcitation. This is particularly useful for the transition metals: V^{4+}, V^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+} and Cu^{2+}. These paramagnetic ions give EPR at room temperature. The changes in their valences can be monitored by following the photoinduced reduction in the EPR signals of these species. This technique is invaluable in not only monitoring the valence change but also to monitor the changes in chemical bonding. In addition to EPR, electron absorption spectra also gives information on some of these aspects. In thin films, it is not always possible to get electronic absorption by conventional spectrophotometry. Photoacoustic spectroscopy

(PAS) can be effectively used for this purpose in case of organic films. In PAS, the signal is essentially due to non-radiative part of the de-excitation of photoexcited chromophore. The positions of the bands coincide with absorption but their relative intensities need not necessarily reflect those observable in 'pure absorption' spectrum. The PAS spectrum can be used to determine the crystal field and Racah parameters wherever possible.

A few reports are available on transition metals doped PVA films regarding optical absorption studies and photoreduction phenomenon. Budkevich *et al* [3] have reported the conversion of Fe(III) to Fe(II) with the removal of one chlorine radical (Cl•) which later reacts with alcohol and forms HCl. The conversion of Cr(VI) to Cr(III) was also reported [4]. We present in PVA films, photo-electron paramagnetic resonance (EPR) and photoacoustic spectroscopy (PAS) evidence to suggest that the concentration of Cr^{3+} goes down on photoexcitation whereas the VO^{2+} complex is insensitive to photoexcitation.

2. Experimental

Polyvinyl alcohol is prepared by the alcoholysis of polyvinyl acetate. Vanadium and chromium (5% by weight) doped polyvinyl alcohol films were grown by slow evaporation method at room temperature [4]. Initially PVA was dissolved in quartz double distilled water and then slightly heated under I.R. lamp for a few minutes. Subsequently vanadium chloride/chromium chloride was mixed with PVA solution which was used for preparing thin films by spreading drops on the plain surface of glass. The films were peeled off from the glass after 48 h. Films were washed with alcohol and completely dried before carrying out the experiment. The EPR spectra were obtained at room temperature and 15 K on a Bruker ESP-300 X-band spectrometer. A closed cycle helium refrigerator was used for 15 K experiment. The samples were loaded in a rectangular optical transmission cavity (# ER 4104-OR) with a provision for optical illumination through a window. The optical illumination was done using copper vapor laser (CVL). The PA spectra were obtained on a home built photoacoustic spectrometer in 350–800 nm range using 250 W tungsten–halogen (T–H) lamp as a source [5].

3. Results and discussion

3.1 EPR investigations

The EPR spectrum obtained on Cr doped PVA film at room temperature consists of a single, rather broad, line with $g = 1.973 \pm 0.001$ [6]. Cr^{5+}, CrO^{3+} and Cr^{3+} are expected to give single EPR line. Here experimentally obtained g value 1.9734 ± 0.001 did not match with reported values of either Cr^{5+} or CrO_3^+ species [7, 8]. Furthermore optical absorption bands obtained on Cr doped PVA also did not indicate presence of Cr^{5+}. Therefore the possibility of formation of Cr^{5+} is ruled out [9]. Cr^{3+} should show three fine structure transitions $(-3/2 \rightarrow -1/2, -1/2 \rightarrow 1/2$ and $1/2 \rightarrow 3/2)$. But in the present case only the central transition with line width of 245 G was observed. The outer transitions $(\pm3/2 \leftrightarrow \pm1/2)$ are more sensitive to crystal field. In a glassy matrix-like PVA, they are likely to get much broadened beyond recognition. The reduction in EPR signal
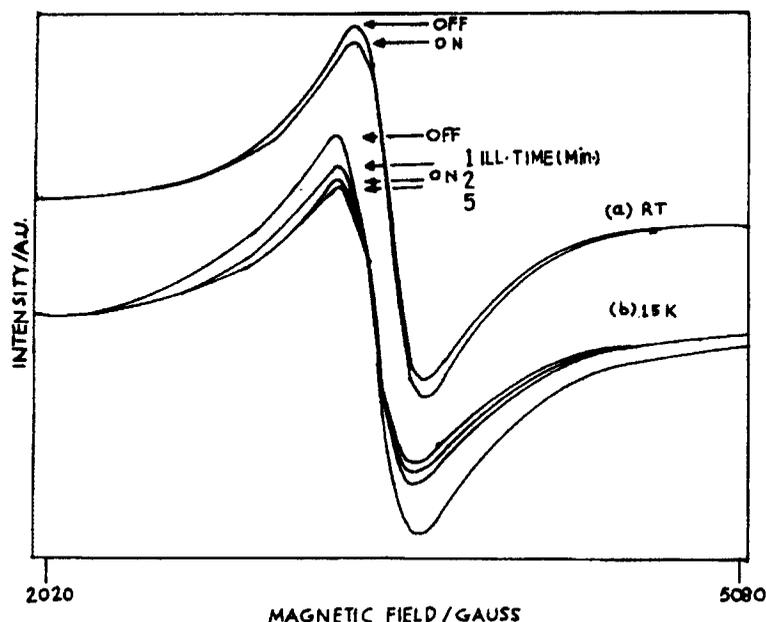
Figure 1. (a) EPR spectra of Cr^{3+} doped PVA film at room temperature with and without CVL illumination. (b) EPR spectra Cr^{3+} doped PVA at 15 K with and without CVL illumination. The EPR spectra were also obtained at the intervals of 1, 2 and 5 min during CVL illumination at 15 K.

was observed on *in situ* CVL-illumination of the sample. These spectra are shown in figure 1(a). These measurements were done at different temperatures down to 15 K. The EPR spectra were obtained at the intervals of 1, 2 and 5 min during CVL illumination. The EPR intensity decreased with increasing CVL illumination time. The maximum reduction of signal was observed in 5 min. However, no significant change was observed in the line widths. These spectra are shown in the figure 1(b).

An obviously expected result of CVL illumination of the sample is increase in its temperature. It was confirmed that the observed changes were not due to thermal effects. This was done by using an EPR signal from sapphire rod, exhibiting very sharp temperature dependence both in its intensity and line position. Using this signal, change in temperature on optical illumination was estimated to be 2 K. For this temperature rise, such large changes in EPR of Cr^{3+} were not expected. To ensure that the observed changes in intensity are not artifacts of changes in Q-value of the cavity the signal intensity was normalized against a DPPH signal. In a prior experiment it was ascertained that DPPH signal does not change with optical illumination. When the DPPH speck was covered with a 'white paint', its signal intensity did not change with prolonged (1 hour) exposure to light.

The decay and recovery of Cr^{3+} signal with laser illumination ON and OFF respectively, was monitored by following the time dependence intensity of EPR with field fixed at the peak position of EPR signal. This was done at different temperatures. A typical decay and recovery curves at room temperature and 15 K are shown in figures 2(a) and 2(b). The decay was found to give satisfactory fit with double exponential decay. The experimental and theoretical fit is shown in figure 3 for a typical case of 30 K. One of the decay constants
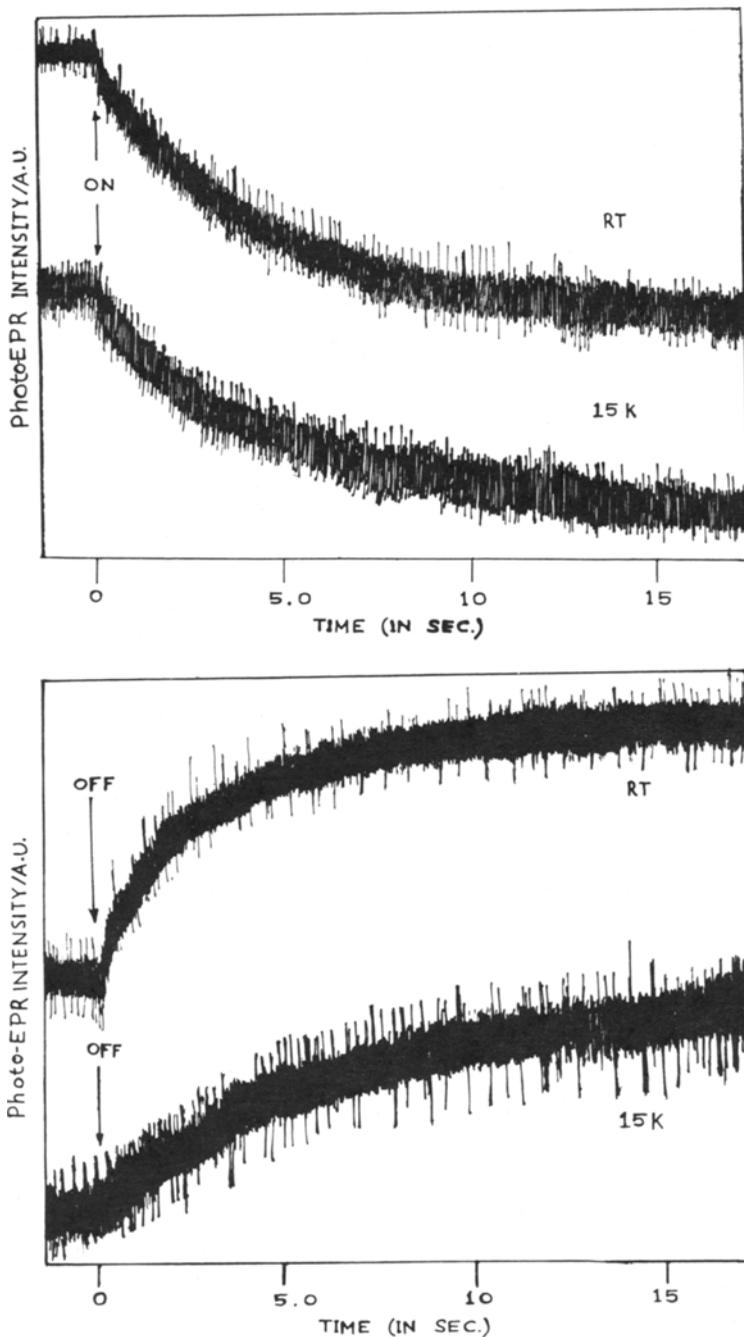
Figure 2. (a) The decay of Cr^{3+} signal with CVL illumination ON with fixed magnetic field $H = 3317$ G. (b) The recovery of Cr^{3+} signal with CVL illumination OFF with fixed magnetic field $H = 3317$ G.
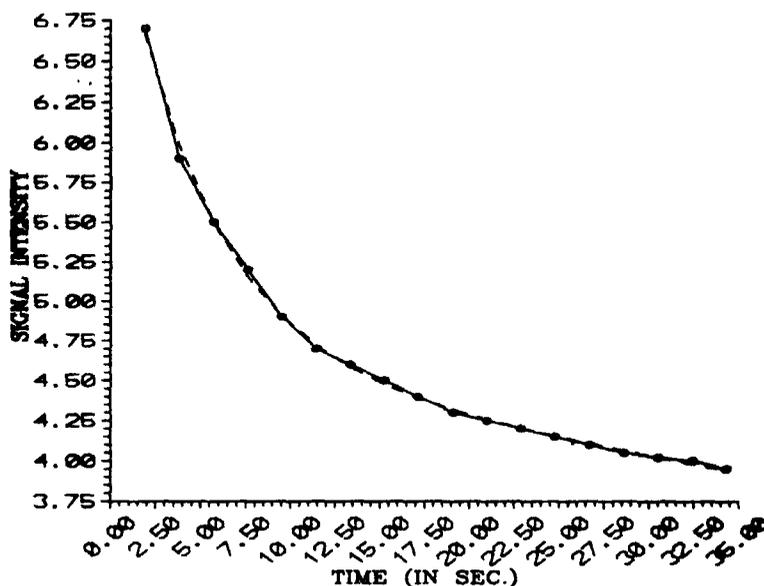
Figure 3. The experimental points and theoretical fit to a double exponential for the decay of EPR signal on CVL illumination. Typical results at 30 K are shown.

was found to be temperature independent whereas the other one had shown reduction with increase of temperature. From the temperature dependence of τ, and using the expression $\tau = \tau_0\, e^{-\Delta E/KT}$, the activation energy for the charge transport has been estimated. It is found to be equal to 0.016 eV.

The +4 oxidation state of the vanadium predominantly exists as the oxovanadium (IV), vanadyl ion, VO^{2+}. V^{4+} has a single $3d(S = 1/2)$ electron and a nuclear spin of 7/2. EPR is ideally suited to identify vanadium through its characteristic eight line spectrum. The EPR spectrum of V doped PVA film comprises of two sets of octets. The lines marked 'a' and 'b' in the spectrum correspond to magnetic field parallel and perpendicular to $V = 0$ direction respectively. This spectrum is characteristic of V^{4+} species in axially symmetric octahedral coordination. This is shown in figure 4. The spin Hamiltonian parameters obtained from the spectrum are $g_{||} = 1.934 \pm 0.001$, $g_{\perp} = 1.984 \pm 0.001$, $A_{||} = 200 \pm 1$ and $A_{\perp} = 80 \pm 1$ G are in good agreement with values expected for VO^{2+} in distorted octahedral coordination [10]. As in the case of chromium doped samples, V doped PVA film was also continuously illuminated with CVL and EPR spectra were recorded. These spectra did not show any significant change after illumination using CVL.

No light induced changes are observed. The only interesting observation, however, is the blackening of certain regions on long illumination. These are probably regions where vanadium concentration is relatively higher. This suggests that the light absorbed predominantly goes into heating the sample due to non-radiative pathway of relaxation. This proves that VO^{2+} is complexed with PVA through OH groups. The spin Hamiltonian parameters are very close to $[VO(H_2O)_5]^{2+}$ complexes suggesting the involvement of OH of alcohol in the bonding.
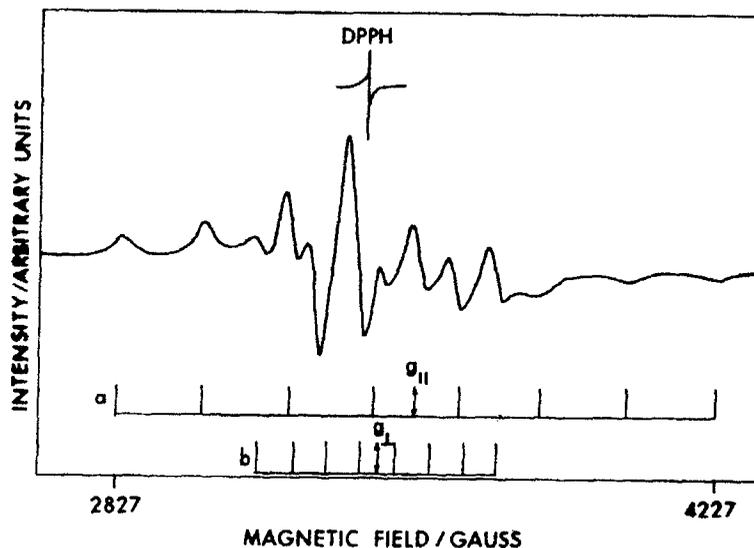
Figure 4. EPR spectrum of VO^{2+} doped PVA film. The octet marked 'a' corresponds to parallel and octet marked 'b' correspond to perpendicular positions of g and A tensors.

3.2 PAS investigations

PA spectra were obtained on Cr doped PVA film in 350–800 nm optical range using T–H lamp as a source. The spectrum has shown the presence of two optical absorption bands at 435 and 595 nm. Both bands are characteristic of Cr^{3+} ions in an octahedral ligand field [11]. Further, consecutive four runs of PA spectrum were recorded on Cr doped PVA film without changing any parameter during the entire experiment. PA spectrum of carbon was also recorded under the same conditions. The carbon spectrum is used for normalizing source intensity variation with wavelengths. The normalized spectra of Cr doped PVA are shown in figure 5. The band at 595 nm was found to be blue shifted after illuminating with light as seen in figure 5. The maximum shift was noticed in 45 min of irradiation. It was confirmed that the blue shifted band of 595 nm wavelength is genuine and not due to instrumental error. PA spectrum of V doped PVA film has shown three bands at 425 and 650 nm with an intense band at 700 nm. This is shown in figure 6. No change was seen on the PA spectrum of V doped PVA on long irradiation with T–H lamp.

Khaled *et al* [11] have described that the optical absorption band that appeared at 595 nm on Cr doped PVA film is due to $^4T_{2g} \leftarrow {}^4A_{2g}$ transition, while the 435 nm band was responsible for the $^4T_{1g} \leftarrow {}^4A_{2g}$ transition. Further they have calculated Racah parameter for unirradiated and gamma-irradiated $CrCl_3$ doped PVA film. Racah parameters on various percentages (10–50%) of $CrCl_3$ doped film are reported. The value of B is given 672 cm^{-1} for unirradiated film whereas it varied from 680 to 730 cm^{-1} for gamma-irradiated film with varying dopant concentration. In the present work, the value of 10 Dq was determined from PA spectrum and the Racah parameter (B) was calculated using plot of transition ratio versus Dq/B graph. The value of B obtained is 731 cm^{-1}. Percentage covalency metal–ligand bond (β) was also calculated using the value of B [12]. All
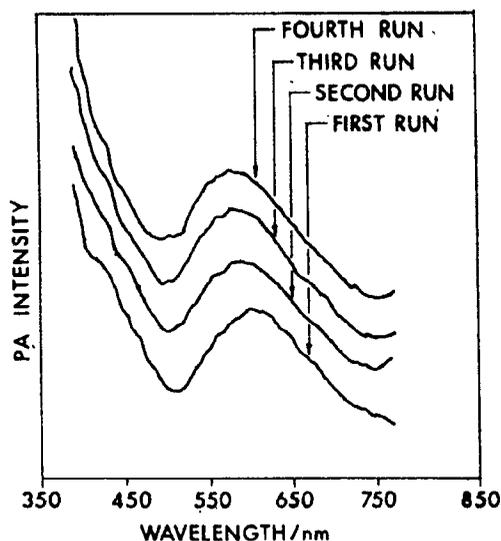
Figure 5. Successive records of PA spectra of Cr^{3+} doped PVA film. Change in the line position with each successive run may be noted. This is attributed to photo-induced changes in chemical bonding (see text). The light was switched off after recording the intensity with 60 min exposure time. The line intensity was restored to its original value, 15 min after the T-H lamp was switched off.

Table 1. Dq, B and β values of Cr^{3+} doped polyvinyl alcohol.

Crystal field parameter	
Dq (in cm^{-1})	1480
B (in cm^{-1})	730
β (in %)	20

parameters are listed in table 1.

The important effects of the optical illumination are: (i) reduction in intensity of EPR on CVL illumination and (ii) blue shifting of the electronic absorption. These are symptomatic of change in electronic state and also the strength of chemical bonding at Cr^{3+} site. This is persistent only during the duration of illumination and the system relaxed back to original state on putting off the CVL.

On photo excitation of Cr^{3+} doped PVA, it can result in electronic excitation and/or electron transfer between dopant and the matrix. When t_{2g} electrons of Cr^{3+} are excited, they go to antibonding e_g orbitals. The energy of CVL-photons is larger than 10 Dq. If the net population in e_g orbitals is significant at any given time, this would result in change in the strength of chemical bonding. This phenomenon being dynamic it gives averaging effect, resulting in small change in the strength of bonding at Cr^{3+} sites. The shift in PAS band position with increased optical illumination does show that there is a net change in the strength of chemical bonding. The relaxation back to normal state, however, appears to take place in much longer time scale than that expected for excited electronic state
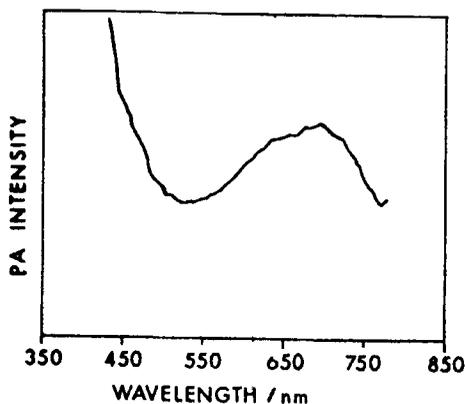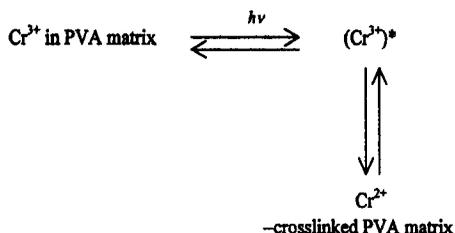
Figure 6. PA spectrum of VO^{2+} doped PVA film.

and it possibly reflects the thermal properties of the sample. The electronically excited Cr^{3+} in the PVA matrix might extract an electron from the PVA matrix reducing Cr^{2+} and subsequently Cr^{2+} getting-crosslinked with PVA. The stepwise reaction is given below:

$$Cr^{3+} \text{ in PVA matrix} \underset{}{\overset{h\nu}{\rightleftharpoons}} (Cr^{3+})^*$$

$$Cr^{2+}$$
$$-\text{crosslinked PVA matrix}$$

The hole trapped on the polymer gets detrapped slowly after the light was switched off recombing at Cr^{2+} site reverting back to Cr^{3+}. The activation energy obtained from $\tau(T)$ may be identified with detrapping of electron deficiency (effective hole) from crosslinked Cr^{2+}. In summary we present EPR and PAS evidence of photoinduced valence changes of Cr^{3+} in PVA matrix with associated changes in strength of chemical bond suggesting that it would be a good dopant for holography. In contrast VO^{2+} ion, strongly complexed with the matrix, does not show any promise for holography/optical image storage.

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