

Optical and electronic properties of (Fe+Sb):PVA for real time holography

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The electron transfer processes induced by the ultraviolet exposure of the Fe and Sb doped polyvinyl alcohol (PVA) thin films were studied in comparison with those appeared in the correspondent mono (Fe or Sb) doped ones. Samples with different thickness and subjected to different exposures were analysed by optical absorption as well as by ⁵⁷Fe and ¹²¹Sb Mossbauer spectroscopy. The influence of each element from the pair on the electronic mechanism activated by the ultraviolet exposure was investigated. Accordingly, the (Fe+Sb) doped PVA presents improved electronic characteristics, in respect to the specific behaviour of single metal doped polymer recording media for real time holography.

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1. Introduction

Polymer materials present an increasing interest for the optical data processing technologies. They may be used as convenient data storage materials as well as in the fabrication of the passive and active light guides. One decade ago, the ion doped polymers were proposed as a new class of organic materials for real time holographic recording [1-5]. Among them, the ferric chloride doped polyvinyl alcohol Fe:PVA was carefully analysed in respect to their holographic properties [4,5]. Subsequent studies performed via Mössbauer spectroscopy have emphasised the electronic processes responsible for the observed optical behaviour [6-8]. Such polymeric materials have the advantage that under the light exposure, permanent local electron delocalization processes take place, with the direct influence on either the optical absorption or the refractive index. Consequently, the interference patterns specific to the holographic process are recorded into the material through the spatial variation of the refractive index or of the transmittance. The hologram is directly recorded and does not involve a subsequent processing of the material. The Fe:PVA was proved to be sensitive to the ultraviolet (UV) exposure, showing a very high diffraction efficiency. Both the refractive and the absorption coefficient of Fe:PVA thin films are influenced by the UV exposure. The refractive index decreases at low exposure energy, whereas the absorption coefficient in the visible range begins to increase only at higher exposures. The variation of the refractive index was related to the relative content of new Fe²⁺ species induced under exposure[8]. The trend of optical absorption coefficient in the visible range seems to be better correlated with the isomer shift variation in the

Mössbauer spectra and therefore it was interpreted in terms of an electron redistribution process around the metal ion, which does not change its valence [7]. More recent data on films of polymers doped with different mixed valence ions have shown that the UV exposure induce significant valence changes of the metal ion mainly for polymers containing residual water while the electron transfer phenomena depend strongly on the doping metal [9]. In order to tailor materials with improved properties within the doped polymer class, the first step is to understand and control the electronic mechanisms involved in the optical behaviour. Different pairs of doping metal ions might be used in order to control better the acceptor/donor processes between the doping metal and the polymer matrix and also to increase the material optical sensitivity. The present work reports on the electronic transfer induced by the UV exposure of films of PVA doped with a pair of mixed valence metal ions, namely Fe and Sb. The phenomena are studied with respect to the behaviour of the single metal ion doped polymers, e.g. Fe:PVA and Sb:PVA respectively. The electron delocalisation processes and local configurations obtained by Mossbauer spectroscopy are corroborated with data provided by optical absorption.

2. Experimental

A solution of 10% wt. PVA in distilled water has been prepared. Two elements, Fe and Sb as well as their combination were used as doping metals. The inorganic salts (FeCl₃ and SbCl₃) had the following wt. concentration relative to PVA: $m_{\text{MeCl}_3}/m_{\text{PVA}}=5\%$ ($m_{\text{FeCl}_3}=m_{\text{SbCl}_3}$ for the case of pair doping). The analysed samples and their characteristics are presented in Table 1.

Table 1. The analysed samples and their corresponding label.

No	Sample	polymer content in distilled water	Metal ion content relative to PVA
1	Fe:PVA	10%	5% m _{PVA}
2	Sb:PVA	10%	5% m _{PVA}
3	(Fe+Sb):PVA	10%	(2.5%+2.5%) m _{PVA}

Thick polymer films up to several tenths of microns were prepared on glass supports by gravity deposition from solution, for Mössbauer measurements. Much thinner films (a few μm) were obtained by spin coating over similar supports, for optical absorption measurements. The thinner films were completely dried after a few hours after deposition and the thicker ones after a few days. The films were exposed to UV light ($\lambda < 400 \text{ nm}$, $P = 25 \text{ mW/cm}^2$) in subsequent steps, up to 1000 s. The absorption spectra were recorded using a standard SHIMADZU UV-VIS Spectrometer. ^{57}Fe and ^{121}Sb Mossbauer spectra were obtained with a conventional set-up with a symmetrical waveform at room temperature (RT) for ^{57}Fe and at 4.2 K for ^{121}Sb . ^{57}Co in Rh matrix and $\text{Ca}^{121\text{m}}\text{SnO}_3$ were used as Mössbauer sources. The isomer shifts are reported relative to metallic iron and CaSnO_3 , respectively

3. Results and discussion

The absorption spectra of differently exposed Fe:PVA, Sb:PVA and (Fe+Sb):PVA thin films are presented in Fig. 1, 2 and 3 respectively. Two absorption bands at about 300 and 380 nm are observed for samples of Fe:PVA, in agreement with our previous results obtained on similar compounds. The intensity of the second band (at 380 nm) decreases faster with the exposure time and the band disappears after 600 seconds exposure.

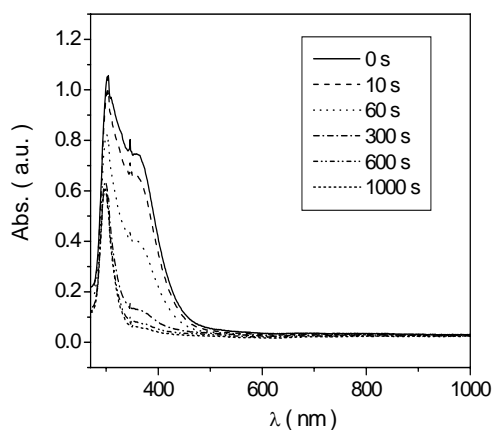


Fig. 1. Optical absorption spectra of thin films of Fe:PVA, after different exposure time.

The evolution of the absorption coefficient in the UV range is strictly dependent on the relative fraction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ species in the exposed samples [6,7]. The absorption spectra of Sb:PVA, are quite different, presenting a peak at about 300 nm, with a large tail, spread out over the whole visible range. No significant changes of the absorption coefficient vs. exposure time were evidenced. On the contrary, the absorption spectra of the polymer film doped with Fe-Sb pairs show a strong variation of the absorption coefficient in the UV range, similar to the Fe:PVA case. A high energy absorption band suggesting two sub-components at about 300 nm and 380 nm is evidenced in the unexposed sample. The 380 nm component decreases in intensity very fast and the absorption spectra obtained after exposure times longer than 600 s present similarities with the absorption spectra of Sb:PVA samples.

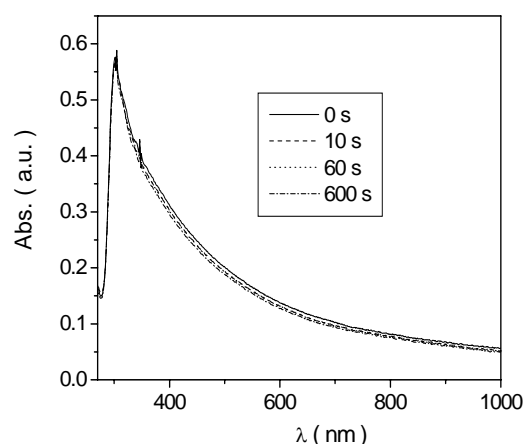


Fig. 2. Optical absorption spectra of thin films of Sb:PVA, after different exposure time.

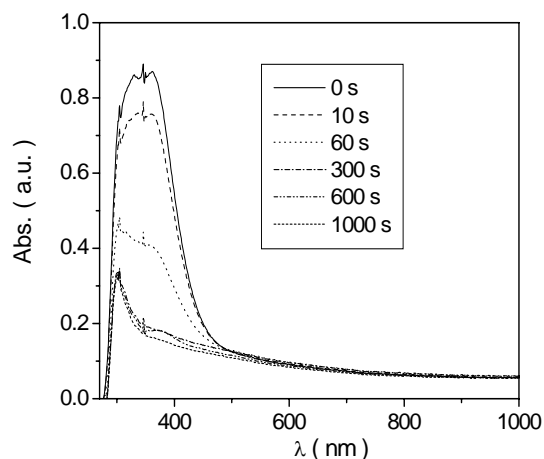


Fig. 3. Optical absorption spectra of thin films of (Fe+Sb):PVA, after different exposure time.

In order to detail the electronic processes related to the above mentioned optical behaviour, it was proceeded to a microscopic analysis based on Mössbauer spectroscopy. The Mössbauer spectra (MS) of samples of Fe:PVA and Sb:PVA exposed for different times are presented in Figs. 4 and 5 respectively. The involved metal ion species and their configurations can be estimated through the hyperfine parameters of the corresponding subspectra, namely the isomer shift (IS) and the quadrupole splitting (QS).

The Mössbauer spectrum of the unexposed Fe:PVA sample shows 3 different iron positions. The two central doublets ($IS_1=0.25(1)$ mm/s, $QS_1=0.28(1)$ mm/s and $IS_2=0.35(1)$ mm/s, $QS_2=0.65(1)$ mm/s) belongs to two Fe^{3+} sites with different distortions. The less intense external doublet (only 12(1)% relative area) has to be assigned by its hyperfine parameters ($IS_3=1.25(1)$ mm/s and $QS_3=2.87(2)$ mm/s) to an Fe^{2+} site. The relative content of the Fe^{2+} species increases rapidly with the exposure time (from 6% in the unexposed sample up to about 28% after 800 s exposure), mainly on the account of the Fe^{3+} species with higher distortions. The decreasing absorption coefficient in the UV range is related to the $Fe^{3+} \rightarrow Fe^{2+}$ transformation induced by the UV exposure. The optical absorption peak at 380 nm, which decrease faster with the exposure time, has to correspond to the more distorted Fe^{3+} positions and the one at about 300 nm, to the less distorted Fe^{3+} co-ordination.

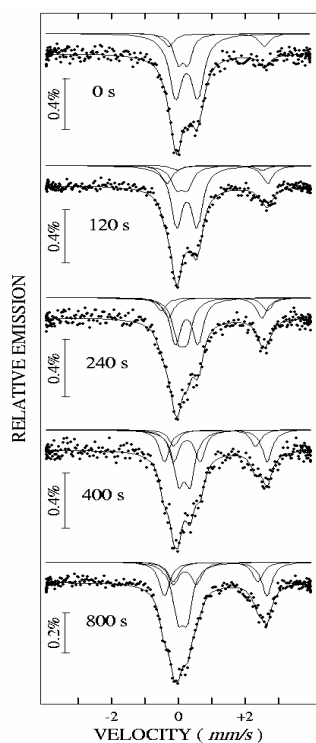


Fig. 4. ^{57}Fe MS of sample Fe:PVA collected at RT after different exposures.

The MS of the Sb:PVA films (Fig. 5) consist in a very broad absorption peak suggesting distributed Sb surroundings. The best fit of the absorption line was

obtained via two different doublets with small quadrupole corrections but quite important negative isomer shifts: $IS_1=-17.3(3)$ mm/s and $IS_2=-16.0(3)$. These values of the isomer shifts stand for the existence of only Sb^{3+} species in the unexposed sample [10]. However, both values are more negatively than the typical isomer shift of $SbCl_3$ [10], proving a modified configuration of the Sb cations in the doped polymers, with a less electronegative character, compared with the $SbCl_3$ case. Only small changes of the relative ratio between the two Sb^{3+} sites are evidenced by the UV exposure, the less negative component decreasing from about 57(1)% in the unexposed sample down to 50(1)% after 3000 s exposure. However, no electron transfer phenomena between the Sb ions and the polymer matrix under UV exposure are to be mentioned, in pretty good agreement with the behaviour observed in the absorption spectra.

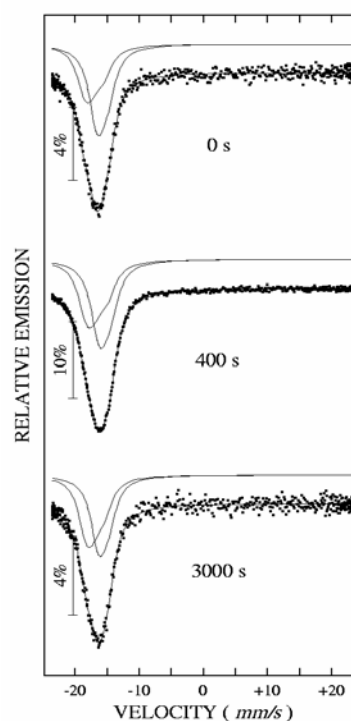


Fig. 5. ^{121}Sb MS of sample Sb:PVA collected at 4.2 K after different exposures.

The electronic processes induced by the UV exposure in the (Fe+Sb):PVA films have been studied by both ^{57}Fe and ^{121}Sb Mössbauer spectroscopy. The ^{57}Fe Mössbauer pattern (Fig. 6) show similar characteristics with the Fe:PVA case, excepting the fact that the narrower central pattern was assigned to only one doublet ($IS_1=0.23(1)$ mm/s, $QS_1=0.28(1)$ mm/s) belonging to an Fe^{3+} specie. Under the UV exposure, the relative amount of the Fe^{2+} species increases from about 11%, in the unexposed sample up to about 80% after 800 s exposure, namely 3 times more compared with the increase found in the Fe:PVA films. The different electronic behaviour has to be correlated with the presence of the Sb ions. The ^{121}Sb Mössbauer spectrum of the unexposed sample (Fig. 7), show this time two different absorption peaks, one centred

at $-15.6(1)$ mm/s and another at $-13.7(1)$ mm/s (both assigned to Sb^{3+} positions), and a third peak centred at about 0 mm/s (assigned to Sb^{5+} positions). After an UV exposure of 400 s, the percentage of Sb^{5+} decreases from about 23% in the unexposed sample down to about 11% . The $\text{Sb}^{5+} \rightarrow \text{Sb}^{3+}$ charge transfer supported by only 12% of the Sb ions may not explain in any case the sharp decrease of the absorption coefficient in the UV range observed in Fig. 3. In this case, one could suggest that the variation of the absorption coefficient has to be correlated mainly with the variation of the charge transfer phenomena at the Fe sites, which is strongly enhanced by the simultaneous presence of the Sb ions. In fact, the ^{121}Sb Mössbauer spectrum of the unexposed (Fe+Sb):PVA sample shows, compared with the one of the unexposed Sb:PVA sample, not only additional Sb^{5+} species but also less negative isomer shifts of the two components belonging to Sb^{3+} . Both aspects prove a stronger delocalisation of the Sb electrons towards the PVA matrix in the (Fe+Sb):PVA sample. These additional electrons are subsequently available to reduce both the Fe^{3+} and Sb^{5+} positions under the UV excitation. Thus, this type of electron delocalization toward the polymer matrix, due to the simultaneous presence of the Sb and Fe metal ions, gives rise under the UV exposure to a relatively increased amount of Fe^{2+} species located in distorted surroundings, as compared to the case of mono-doped Fe:PVA polymer films.

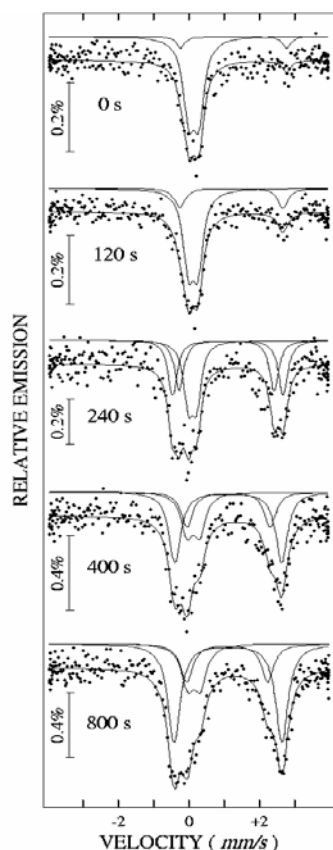


Fig. 6. ^{57}Fe MS of (Fe+Sb):PVA thin films collected at RT after different exposures.

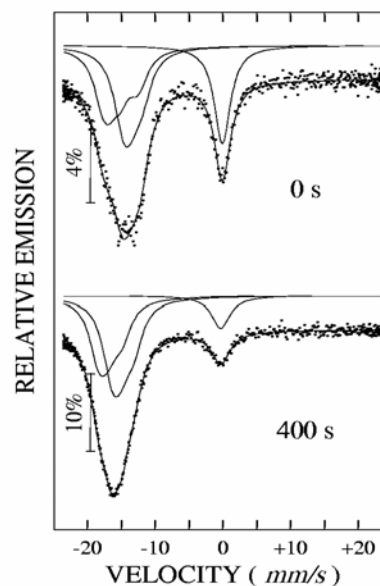


Fig. 7. ^{121}Sb MS of (Fe+Sb):PVA thin films collected at 4.2 K after different exposures.

4. Conclusions

The electronic mechanisms related to the variation of the absorption coefficient in the UV range, were studied in hetero-doped (Fe+Sb):PVA polymers, and compared with those appearing in the corresponding single ion doped polymers, Fe:PVA and Sb:PVA.

The iron is the main active ion responsible for the optical behaviour but the influence of Sb presence was also considered. It is worth mentioning that a much higher value for the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ was found in the (Fe+Sb) hetero-doped polymers after the UV exposure, in respect to the Fe doped polymer. This characteristic was explained by an initial stabilisation of Sb^{5+} and Sb^{3+} species and the higher electronegativity of the Sb^{3+} species in the (Fe+Sb):PVA unexposed sample compared with the Fe:PVA case. It results finally a relative increased electron density in the polymer matrix of (Fe+Sb):PVA films as compared with Fe:PVA films, with the subsequent availability for additional $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ transformation under the UV exposure.

Knowing that the refractive index of the material is very sensitive to the relative fraction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ [8], a much higher diffraction efficiency has to be expected for the (Fe+Sb):PVA films as compared with Fe:PVA samples. Alternatively, the already high diffraction efficiency of the Fe:PVA thin films can be reached under a lower UV exposure, which would mean a higher sensitivity of the material. In optimal conditions, a maximum efficiency of more than 60% was obtained in Fe:PVA under an exposure energy of about 10 J/cm^2 [8]. A same efficiency could be obtained in (Fe+Sb):PVA films, under a 2-3 times lower exposure energy. However, even $3\text{--}4 \text{ J/cm}^2$ are still rather high exposure energies and

further improvements of the material are required for a common use in commercial applications.

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