



Effect of laser irradiation on the structure and valence states of copper in Cu-phosphate glass by XPS studies

G.D. Khattak, A. Mekki, M.A. Gondal *

Physics Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

The effect of laser irradiation using three different wavelengths (IR, visible and UV) generated from Nd:YAG laser on the local glass structure as well as on the valence state of the copper ions in copper phosphate glass containing CuO with the nominal composition $0.30(\text{CuO})-(0.70)(\text{P}_2\text{O}_5)$, has been investigated by X-ray photoelectron spectroscopy (XPS). The presence of asymmetry and satellite peaks in the Cu 2p spectrum for the unirradiated sample is an indication of the presence of two different valence states, Cu^{2+} and Cu^+ . Hence, the Cu $2p_{3/2}$ spectrum was fitted to two Gaussian-Lorentzian peaks and the corresponding ratio, $\text{Cu}^{2+}/\text{Cu}^{\text{total}}$, determined from these relative areas clearly shows that copper ions exist predominately (>86%) in the Cu^{2+} state for the unirradiated glass sample under investigation. For the irradiated samples the symmetry and the absence of satellite peaks in the Cu 2p spectra indicate the existence of the copper ions mostly in Cu^+ state. The O 1s spectra show slight asymmetry for the irradiated as well as unirradiated glass samples which result from two contributions, one from the presence of oxygen atoms in the P–O–P environment (bridging oxygen BO) and the other from oxygen in an P–O–Cu and P=O environment (non-bridging oxygen NBO). The ratio of NBO to total oxygen was found to increase with laser power.

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1. Introduction

Oxide glasses containing transition metal (TM) ions [1–5] are of continuing interest because of their applications in memory switching, electrical threshold, and optical switching devices [6–8]. The general condition for semiconducting behavior in these glasses is that the TM ion should be capable of existing in more than one valence state so that conduction can take place by the electron transfer from ions in a lower valence state to those in a higher valence state [1–5,9,10]. The unpaired electron induces a polarization of the TM ion around it and forms a polaron.

It is well known that laser irradiation could modify the surface chemistry of transition metal oxide glasses. There are many interesting applications of surface modification using high intensity laser beams such as hardening of materials, bonding of different materials or alloys, thin films for corrosion inhibition, etc. There are two conditions generated in laser-matter interaction experiments that make many of the applications possible, and

motivate the researcher to apply this technique. The first is that intense lasers can locally heat up matter above 1000 °C and this induces different photochemical reactions at the surface only. The second is that at high laser intensities, the optical properties of materials behave in altogether new ways.

The effect of the laser irradiation is up to the depth of few microns and less than 1 mm. The time of the laser irradiation is of the order of few nanoseconds. Hence, this is a surface effect and we applied XPS, which is a surface investigation technique, to study the effect laser irradiation on the samples.

Recently thermal oxidation or reduction of copper at or above the glass transition temperature (T_g) has been reported [14–16]. In this work, polyvalent metals such as Fe, Mn, Cu, Ce, Ti, V, and Cr, were oxidized in air and reduced in H_2/N_2 at their respective glass transition temperature for some period. During the heat treatment, a crystalline oxide surface layer is created on the glasses under the oxidizing condition, and the metallic ions are oxidized from lower to higher valence state, and diffuse outward or inward depending on the type of the polyvalent ions for the same conditions of heat treatment.

Most of these experiments have been carried out at high temperatures above 600 °C which require special setups including high vacuum systems and control environment such as hydrogen or N_2 . Since laser irradiation at moderate influence could raise rapidly (in nanoseconds) the temperature of the glass surface to

* Corresponding author at: Physics Department, King Fahd University of Petroleum & Minerals, Mail Box 372, Dhahran 31261, Saudi Arabia. Tel.: +966 38602351.

E-mail address: magondal@kfupm.edu.sa (M.A. Gondal).

1000 °C which is above Transition glass temperature (T_g) so laser post-treatment of glasses for reduction of Cu has the advantages of friendly environment, reduction in processing time, economy costs, as it does not require costly and sophisticated vacuum systems. The laser treatment using pulsed laser depends on fast (at nanosecond scale) thermal process. The free electrons absorb the laser light, transferring this energy into the atomic lattice. Depending upon the incident laser energy, melting and some vaporization of the target material could occur during this process. Because of the difference in latent heat of vaporization for different chemical materials (or elements present in glass material), a thermal mechanism may induce strong fractionation. Moreover, if the incident laser photon energy is higher than the bonding energy between neighboring atoms in the glass matrix, the electromagnetic laser radiation can directly break the atomic lattice, inducing ion and atom ejection without traditional heating effects. This happens mostly at very high intense laser beams to create breakdown (plasma) on the surface of glass by focusing the laser beams at a small focal point. In this experiment we did not use any focusing lens to reach the plasma state at the glass surface rather laser radiations were employed only for thermal treatment for the reduction of Cu states. The above-mentioned facts and advantages are key factors for our motivation to use laser radiations instead of conventional heating setups for reduction of Cu states.

In this paper, we investigated the effect of laser irradiation using different wavelengths on the local glass structure as well as on the valence state of the copper ions of copper phosphate glass containing CuO, with the nominal composition 0.30(CuO)–(0.70)(P₂O₅), by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) has proven to be a powerful technique for investigating not only the electronic structure in solids, but also the bonding and hence the local structure [11–13]. More recently, this technique has been shown to be a useful quantitative probe of the short-range structure in the oxide glasses as well. In particular, the O 1s spectrum is typically resolved into separate contributions from bridging and non-bridging oxygen resulting from different structural units of oxygen atoms in the oxide glasses. The XPS technique has also been successfully used to quantitatively investigate the valence state of TM ions in the glass structure.

The structural and electronic (as well as optical, magnetic and mechanical) properties of these glasses depend on the relative proportion of different valence states of the TM ions. In order to account for the effect of these valence states on the structure and properties of these glasses, it is important to control and measure the ratios of the ion concentration in the different valence states of these TM ions.

2. Experimental details

2.1. Glass preparation

The glass with nominal composition 0.30(CuO)–(0.70)(P₂O₅) was prepared by melting dry mixtures of reagent grade CuO and P₂O₅ in alumina crucibles. P₂O₅ was preheated at 150 °C before mixing it with copper oxide in proper ratio. Approximately 20 g of chemicals were thoroughly mixed to obtain a homogenized mixture. The crucible containing the batch mixture was then placed in an electrically heated melting furnace and maintained at 1340 °C for about 1-to-2 h under atmospheric conditions during which the melt was occasionally stirred with an alumina rod. The homogenized melt was then cast onto a stainless steel plate mold to form glass buttons for laser irradiation and glass rods of approximately 5-mm diameter for XPS measurements. X-ray powder diffraction analysis indicated that the glass formed was completely amorphous.

2.2. X-ray photoelectron spectroscopy (XPS) measurements

Core level photoelectron spectra were collected on a VG scientific ESCALAB MKII spectrometer equipped with a dual aluminum–magnesium anode X-ray gun and a 150-mm concentric hemispherical analyzer using Al K α ($h\nu = 1486.6$ eV) radiation from an anode operated at 130 W. Photoelectron spectra of Cu 2p, and O 1s core levels were recorded using a computer-controlled data collection system with the electron analyzer set at a pass-energy of 20 eV for the high resolution scans. The energy scale of the spectrometer was calibrated using the core level of Cu 2p_{3/2} (=932.67 eV), Cu 3p_{3/2} (=74.9 eV), and Au 4f_{7/2} (=83.98 eV) photoelectron lines. For self-consistency, the C 1s transition at 284.6 eV was used as a reference for all charge shift corrections as this peak arises from hydrocarbon contamination and its binding energy is generally accepted as remaining constant, irrespective of the chemical state of the sample. For XPS measurements, a glass rod was cleaved in the preparation chamber at a base pressure of 2×10^{-9} mbar before being transferred to the analysis chamber where the pressure was maintained at $<2 \times 10^{-10}$ mbar.

A non-linear, least-squares algorithm was employed to determine the best fit to each of the O 1s and Cu 2p_{3/2} spectra with two Gaussian–Lorentzian curves in order to represent bridging and non-bridging oxygen and two possible copper oxidation states (Cu²⁺ and Cu⁺), respectively. The fraction of non-bridging oxygen and Cu²⁺ were determined from the respective area ratios from these fits. Based on the reproducibility of similar quantitative spectral decompositions of spectra taken from other surfaces on the same glass samples, uncertainties of ± 5 and $\pm 10\%$, respectively, were estimated for these area ratios. A period of approximately 2 h was required to collect the data set for each sample and there was no evidence of any X-ray induced reduction of the copper in the glass samples during this period.

2.3. Laser irradiation

For irradiation of glass samples at three different laser wavelengths, Nd:YAG laser (Quanta-Ray, Model GCR-250) was employed. Since Nd:YAG laser emits fundamental wavelength at 1064 nm so for the generation of second and third harmonic at 532 and 355 nm, frequency doubling and tripling, crystal (KDP) was used. The pulse width of the laser was about 8 ns and rep rate was 10 Hz. In order to compare, the effect of different wavelengths (1064, 532, and 335 nm) of laser radiations on glass samples, the laser intensity, laser irradiation time and laser beam diameter were kept constant. The laser energy was measured with a calibrated energy meter (ophir model 300). In this experiment, we placed a 5 mm diameter aperture inside the path of laser beam in order to get a uniform beam shape. The pulse energy applied in this experiment was 100 mJ at different wavelengths and the laser fluence (peak power/area) estimated was 1.27×10^{11} W/m². In order to expose the sample homogeneously with laser beam and to avoid the development of any crust on the surface of glass samples due to repeated exposure of laser on the same spot, the samples were mounted on a rotary table.

3. Results

3.1. Copper spectra

The Cu 2p spin–orbit doublet spectra for the unirradiated and irradiated glass samples are shown in Fig. 1. One first notes that the intensities of these Cu 2p peaks for the irradiated samples are very low compared to that of the unirradiated sample. In addition, the Cu 2p peaks show significant asymmetry for the unirradiated sample. Thus, it is realistic to assume the presence of two separate

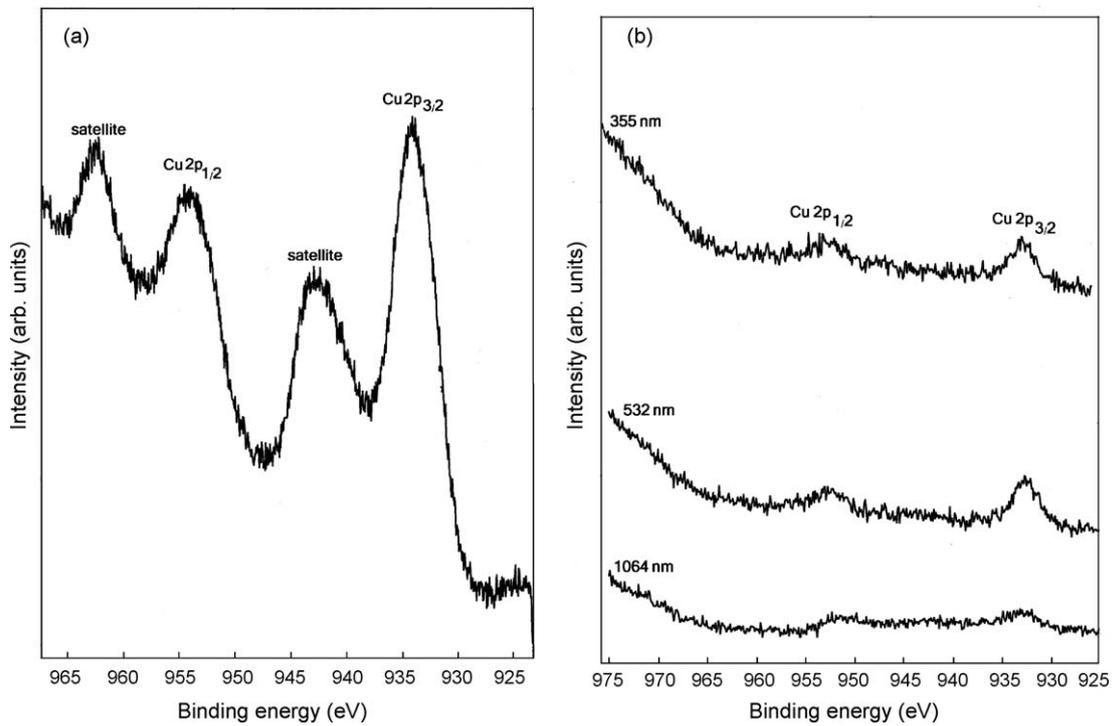


Fig. 1. Core level Cu 2p spectra for (a) the unirradiated and (b) irradiated glass.

peaks, one associated with divalent (Cu^{2+}) and the other with monovalent (Cu^+) copper ions as these are the only two oxidation states in which Cu can exist in various glasses [17]. Thus the Cu $2p_{3/2}$ spectrum for the unirradiated glass sample was subsequently fitted to two Gaussian–Lorentzian peaks. The Cu 2p peaks for the irradiated samples look more symmetric and were fitted to only one peak. Lastly, satellite peaks are observed at about 10 eV on the higher binding energy side of both Cu 2p peaks for unirradiated

sample but these satellite peaks are missing from the Cu 2p spectra for the irradiated samples.

3.2. Oxygen spectra

Fig. 2 depicts the O 1s core level spectra for all samples investigated in this study. Upon closer inspection of the O 1s spectra, a slight asymmetry in the O 1s peak is apparent, which

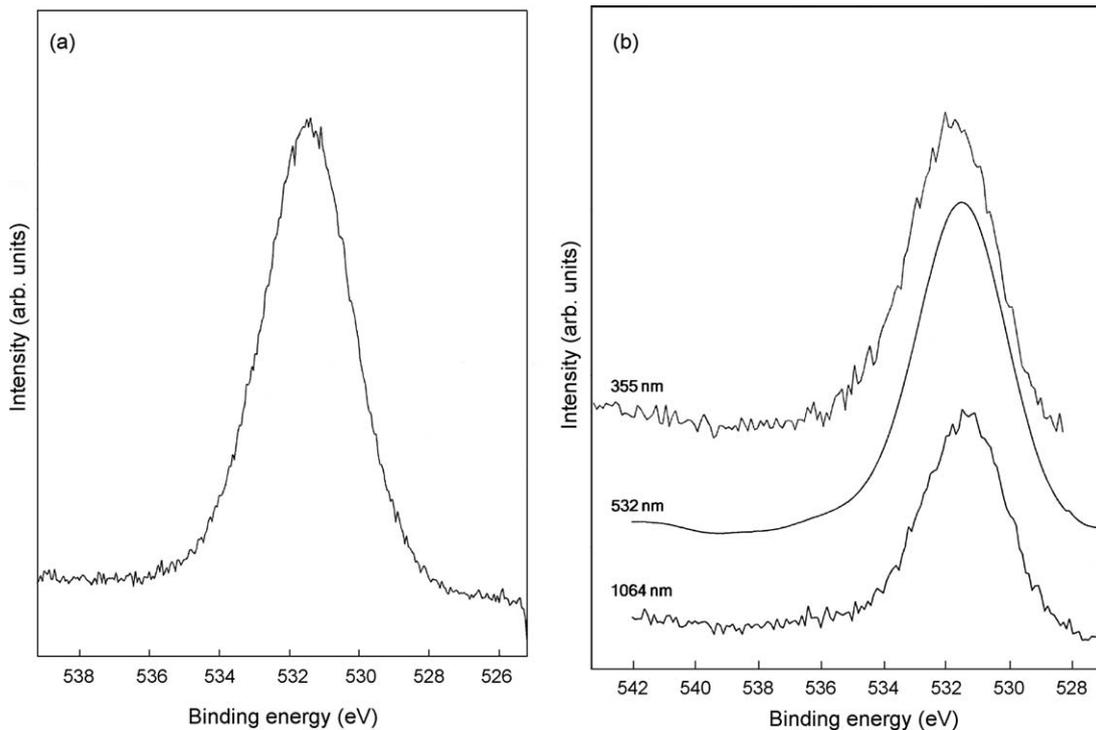


Fig. 2. Core level O 1s spectra for (a) the unirradiated and (b) irradiated glass.

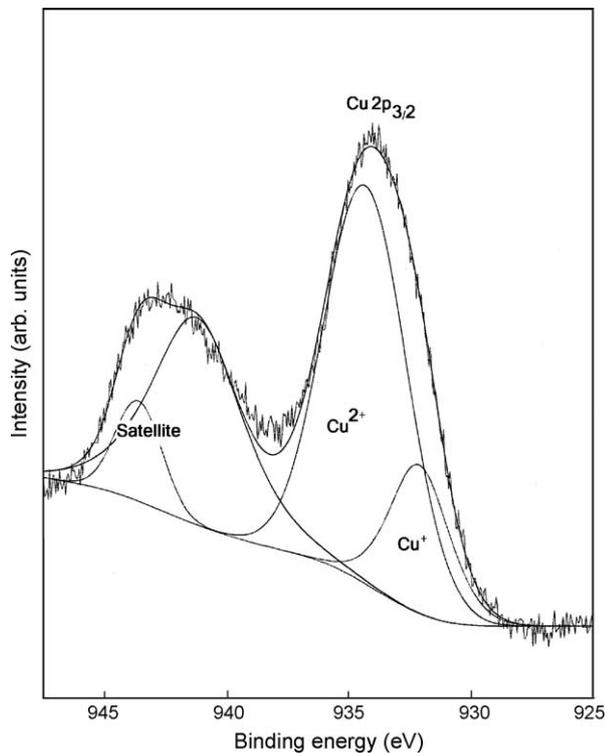


Fig. 3. Cu 2p_{3/2} core level spectra fitted with two contributions, one due to Cu⁺ and the other due to Cu²⁺ for the unirradiated glass.

would be indicative of two different types of oxygen sites in these glasses. Hence, all O 1s spectra were fitted to two (Gaussian–Lorentzian) peaks in order to determine the peak positions and relative abundance of the different oxygen sites.

4. Discussion

As described earlier, the Cu 2p peaks for the unirradiated sample show significant asymmetry with a shoulder on the lower binding energy side of the main peak. Indeed the asymmetry observed in the Cu 2p spectrum is an indication of the presence of two different valence states for the copper ions in the glass. Further, it is well known that copper compounds containing Cu²⁺ have strong satellite peaks while compounds with just Cu⁺ have no satellites [18,19]. Hence the appearance of the satellite peaks at about 10 eV on the higher binding energy side of the main Cu 2p peaks provides definitive evidence for the presence of Cu²⁺ ions in the unirradiated glass sample. Since the only other oxidation state of copper is Cu⁺, the Cu 2p_{3/2} spectrum was fitted to Gaussian–Lorentzian peaks as shown in Fig. 3 (one should note that the satellite peak is fitted to two curves in order to accurately determine the area under the satellite peak and do not represent a

separate contribution from Cu⁺). The corresponding peak positions and FWHM (full width at half maximum) determined from the fitting procedures are listed in Table 1. As previously reported [20] the areas under these peaks plus the area under the satellite peak can be used to determine the ratio of Cu²⁺ ions to total Cu ions present. Defining

A1 = area under Cu⁺ peak which is proportional to the concentration of Cu⁺.

A2 = sum of areas under Cu²⁺ peak and under satellite peak which is proportional to the concentration of Cu²⁺, then

$$\frac{\text{Cu}^{2+}}{\text{Cu}_{\text{total}}} = \frac{A2}{A1 + A2}$$

The corresponding ratio determined from these relative areas is reported in Table 1. From this ratio, it is apparent that copper ions exist predominately (>86%) in the Cu²⁺ state for the unirradiated glass investigated.

For the irradiated samples the Cu 2p spectra are more symmetric and the satellite peak is also not observed in the spectra. The reason for the absence of the satellite peak may be the low intensity of the main peaks or the reduction of copper ions from Cu²⁺ to Cu⁺ or both. The spectra for the irradiated samples could be fitted to only a single peak as shown in Fig. 4 for 355 nm laser irradiated sample. The peak positions, FWHM, peak areas are presented in Table 1 for these samples. It is evident from Table 1 that both FWHM and the peak positions increase with an increase in laser power (FWHM for the 355, 532, and 1064 nm laser irradiated samples are 3.27, 3.43, and 3.82 eV respectively while the peak positions are 932.43, 932.62, and 933.00 eV, respectively). The peak positions and FWHM for the irradiated samples are closer to those of peak 1 (Cu⁺) for the unirradiated sample and the small increase in the peak positions and their FWHM could be due to the presence of Cu²⁺ ions (the two overlapping peaks for Cu⁺ and Cu²⁺ will make the combined peak broader and with high binding energy). Hence copper ions exist predominantly in the Cu⁺ oxidation state for the irradiated samples.

As mentioned before, Fig. 1 shows that the intensity of Cu 2p spectra for the irradiated samples is very low compared to that of the unirradiated samples. This reduction in intensity could be as a consequence of the evaporation of some copper ions from the surface or the diffusion of copper ions into the bulk or both but no conclusion can be reached based on the available data. The suggestion that it might be due to diffusion of copper from the surface toward the interior of the sample is supported by results in the literature for glasses [21,22]. In these studies, it is reported that thermal reduction of a transition metal can lead to inward diffusion of mobile cations. The mechanism for irradiation reduction could be the same.

In most XPS studies of oxide glasses, the O 1s spectra are more informative with respect to the structure of the glass than the

Table 1

Peak positions, FWHM, peak areas, peak separation, and the ratio Cu²⁺/Cu_{total} resulting from the curve fitting of the Cu 2p_{3/2} peaks for Cu-phosphate glass. The uncertainty in the peak position is ±0.10 eV, in FWHM is ±0.20 eV and in the ratio is ±0.030.

| Sample | Satellite (FWHM) (eV) [peak area] ^a | Cu 2p _{3/2} (1) (FWHM) (eV) [peak area] | Cu 2p _{3/2} (2) (FWHM) (eV) [peak area] | ΔE _{Cu 2p} (eV) | Cu ²⁺ /Cu _{total} % |
|-------------------------|---|---|---|--------------------------|---|
| I Unirradiated | 943.6 (2.2) [2020] 941.2 (4.6) [8553] | 932.1 (3.0) [4023] | 934.3 (4.0) [14,552] | 2.2 | 86 |
| II Irradiated (355 nm) | | 932.4 (3.3) [1060] | | | |
| III Irradiated (532 nm) | | 932.6 (3.4) [1216] | | | |
| IV Irradiated (1064 nm) | | 933.0 (3.8) [154] | | | |

^a Satellite peak was fitted to two peaks in order to precisely find the total area.

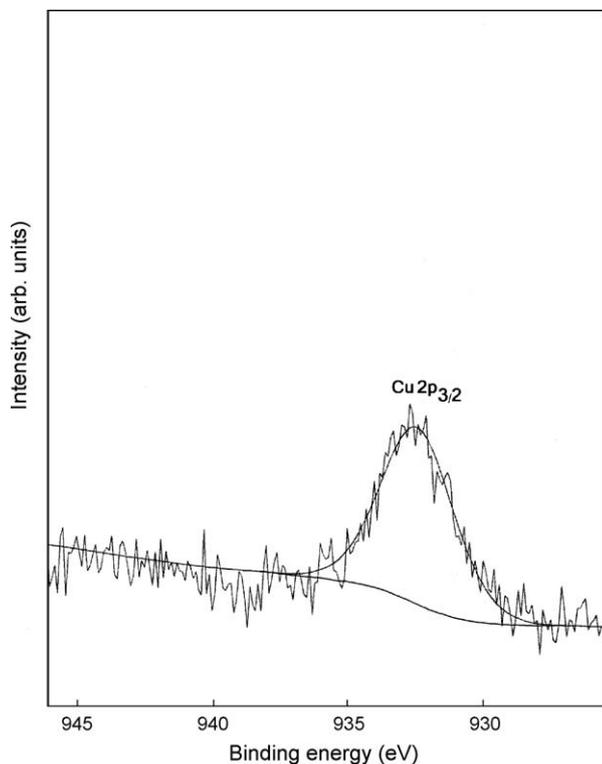


Fig. 4. Cu $2p_{3/2}$ core level spectra fitted with only one contribution due to Cu^+ for the irradiated (355 nm) glass.

cation spectra. Specifically, the binding energy of the O 1s electrons is a measure of the extent to which electrons are localized on the oxygen or in the inter-nuclear region, a direct consequence of the nature of the bonding between the oxygen and different cations. As mentioned earlier, a slight asymmetry in the O 1s core level peak is apparent for all the samples investigated, which indicates two different types of oxygen sites present in these glasses. Correspondingly, the O 1s peaks for these $\text{CuO-P}_2\text{O}_5$ glasses may arise from oxygen atoms existing in some or all of the following structural bonds: P–O–P, P–O–Cu, Cu–O–Cu, and P=O. Oxygen atoms that are more covalently bonded to glass former atoms on both sides are typically called bridging oxygen (e.g., P–O–P), while oxygen atoms that are more ionically bonded, at least on one side, or double bonded to a glass former atom are referred to as non-bridging oxygen atoms (e.g., P–O–Cu, Cu–O–Cu, P=O). Moreover, since the bridging oxygen (BO) is covalently bonded to two glass former atoms while the non-bridging oxygen (NBO) are ionically bonded only from one or both sides, the binding energy of the NBO should be lower than that of the BO. Thus, each O 1s spectrum was deconvoluted into two Gaussian–Lorentzian with the lower binding energy peak corresponding to NBO (P–O–Cu, P=O and Cu–O–Cu) and the higher energy peak to BO (P–O–P) as shown in Fig. 5 for unirradiated sample. In the fitting procedure FWHM's for BO and NBO are kept fixed and the resulting peak positions for the BO and NBO peaks (see Table 2) are within experimental uncertainties the same for all glass samples. One notes that the measured area ratio, [NBO/TO], increases with increasing laser power.

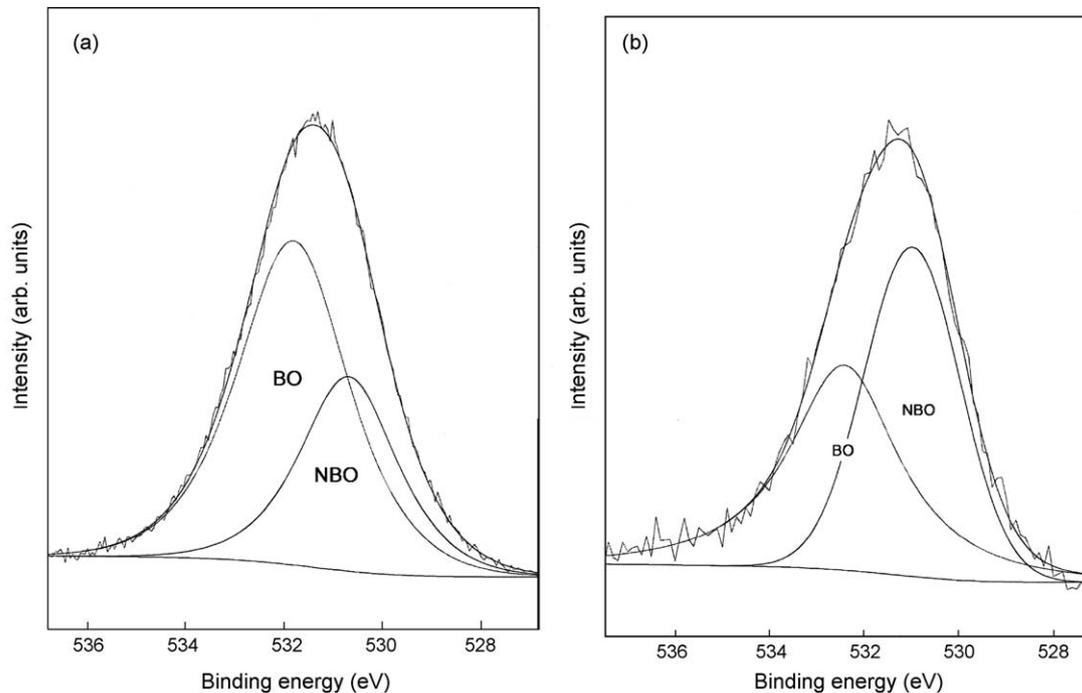


Fig. 5. Core level O 1s spectra for (a) the unirradiated glass and (b) for the irradiated sample (1064 nm) and the resulting NBO and BO peaks (dashed lines) from the least-squares fitting routine of two Gaussian–Lorentzian peaks. The smooth solid line is the resultant sum of the two peaks.

Table 2
Peak positions, FWHM, peak areas, peak separation, and the ratio $\text{NBO}/\text{O}_{\text{total}}$ resulting from the curve fitting of the O 1s peaks for Cu-phosphate glass. The uncertainty in the peak position is ± 0.10 eV, in FWHM is ± 0.20 eV and in the ratio is ± 0.03 .

| Sample | O 1s(1) (FWHM) (eV) [peak area] | O 1s(2) (FWHM) (eV) [peak area] | ΔE O 1s (eV) | $\text{NBO}/\text{O}_{\text{total}}$ (± 0.03) |
|-------------------------|---------------------------------|---------------------------------|----------------------|---|
| I Unirradiated | 530.7 (2.4) [6694] | 531.8 (2.7) [12,850] | 1.1 | 0.34 |
| II Irradiated (355 nm) | 530.7 (2.4) [2502] | 532.3 (2.7) [2987] | 1.6 | 0.46 |
| III Irradiated (532 nm) | 531.4 (2.4) [2540] | 532.7 (2.7) [2441] | 1.5 | 0.51 |
| IV Irradiated (1064 nm) | 531.0 (2.4) [1967] | 532.4 (2.7) [1467] | 1.4 | 0.57 |

5. Conclusion

In the present study XPS was used to investigate the effect of laser irradiation on a Cu-phosphate glass. It was found that more than 86% of copper ions are in the Cu^{2+} state for the unirradiated sample while for the irradiated samples most of Cu ions are in the Cu^+ state. Furthermore the intensities of the Cu 2p core level peak for the irradiated samples had a very low intensity compared to that of the unirradiated sample. This might be due to diffusion of Cu ions from the surface to the interior of the sample. The ratio, $\text{NBO}/\text{O}_{\text{total}}$, as determined from the areas under the various O 1s peaks to total oxygen was found to increase with laser power irradiation.

Acknowledgments

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