Effect of CuO addition on the high-field and high-pressure behavior of microwave-prepared lead vanadate glasses

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High-field and high-pressure behavior of microwave-prepared $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ ($x = 0$ to 20) glasses were investigated for the first time. It was found that the addition of CuO significantly alters the nonlinear I - V characteristics of these glasses; while the glasses with $x = 10$ exhibit a current-controlled negative resistance behavior associated with a memory type transition, glasses with $x = 15$ show a threshold-type behavior. Remarkable differences were also noticed in the high-pressure electrical resistivity behavior between the low- and high-CuO-containing glasses. Corroborative thermal, electrical, microscopic, and spectroscopic measurements were carried out to understand the structure-property relations. A structural model was proposed, which is based on the chemical nature of the constituents present in the glasses. The model accounts well for the various observed properties of these glasses.

I. INTRODUCTION

Transition metal oxide containing glasses¹⁻⁵ are of interest due to their possible technological applications in electrical and optical switching devices.⁶⁻⁸ Transition metal (TM) ions can exist in multiple valence states which give rise to semiconducting behavior of the glasses.^{9,10} Electrons hop from one valence site to another as between V^{4+} and V^{5+} centers in vanadium-containing glasses^{11,12} and contribute to the conduction process. Oxide glasses containing TM ions^{13,14} also exhibit interesting nonlinear electrical properties like electrical switching (high-field behavior) which is a transition from the low-conducting state to a high-conducting state denoted as OFF and ON states respectively, under the action of an electrical field.^{15,16} The switching behavior could be either memory (irreversible) or threshold (reversible) type¹⁷ and may involve a stable current-controlled negative resistance region (CCNR).¹⁸ The mechanism of switching could be thermal in which conducting channel formation occurs as in vanadium phosphate glasses¹⁹ or both electrical and thermal.

Switching has also been considered to be due to semiconductor-metal transition of VO_2 crystals supposedly present²⁰ in vanadate glasses.

Pressure brings about both permanent and reversible changes in the electrical properties of glassy materials. Pressure is an effective thermodynamic variable to alter the properties of noncrystalline materials.²¹⁻²³ It is possible that the mechanism of transport and transition can be understood more clearly from the pressure dependencies of conductivity.²⁴ Motivated by this background, we have investigated for the first time both the high-field and high-pressure behavior of the electrical properties of microwave prepared $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ ($x = 0$ to 20) glasses. Remarkable changes were noticed both in the high-field and high-pressure behaviors of these glasses around 10 mol% CuO. Thermal, microscopic, and spectroscopic measurements have been carried out, and the structural basis of the observed changes has been discussed.

II. EXPERIMENTAL

The transition metal oxide containing glasses of the system $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ ($x = 0$ to 20) have been prepared using a microwave melting method.²⁵ Appropriate amounts of starting materials (analytical reagent grade powders of CuO, PbO, and V_2O_5) were thoroughly mixed (batch weight = 5 g) and kept in a silica crucible on fire brick inside a domestic microwave

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oven (Batliboi, Eddy, India) operating at 2.45 GHz and at a tunable power level up to a maximum of 980 W. Within 5–7 min of microwave exposure a good homogeneous melt was obtained (which is only a fraction of the time required in conventional glass preparation methods), which was immediately quenched between polished stainless steel plates. The silica crucible was found to remain clean and unaffected during the short duration of melting. Energy dispersive x-ray analysis (EDAX) also confirms the absence of Si in the glass. Glass disks obtained in this manner are black in color. It was found from independent experiments²⁵ that V_2O_5 and CuO are both good microwave susceptors whereas PbO is not. The samples were confirmed to be amorphous by x-ray diffraction (XRD; Philips, Netherlands, Model PW 1050/70) and glassy using differential scanning calorimetry. Microscopic examination with cross polarization also revealed the absence of any crystallization.

Densities and in turn molar volumes of the glass samples were determined using the Archimedeian principle with xylene as a densitometric fluid. A Sartorius balance (accuracy = 10^{-4} g) was used for the weight measurements. The glass transition temperature (T_g), crystallization temperature (T_c), and heat capacity (C_p) measurements have been carried out using a Perkin-Elmer differential scanning calorimeter (DSC-2). Amounts of 50-mg samples were used, and a heating zone of 10 deg/min was employed in DSC experiments. Single-crystal sapphire was used as a standard for determining the sample heat capacities (C_p). Glass heat capacities were recorded from room temperature to slightly above T_g ($T_g + 25$ K) so that the change in heat capacity (ΔC_p) at the glass transition temperature could be calculated. Heat capacity evaluation on PbO by the same method gave satisfactory ($\pm 2\%$) heat capacity values compared to literature values between 300 and 500 K.

Electrical switching characteristics of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses have been studied using a dedicated PC-based system.²⁶ Glass samples polished to different thicknesses were mounted in a cell between a flat plate bottom electrode and point contact top electrode (cathode) made of brass. A programmable, constant direct current (0–50 mA) was passed through the sample, and

the voltage developed across is measured. A resistive heater placed in thermal contact with the bottom electrode heated the sample. The sample temperatures are controlled to better than ± 1 K.

Scanning electron microscopic (SEM) investigations of the switched glass samples have been carried out using a Cambridge Instruments Stereoscan 360 SEM. The composition of the switched region could not be determined using EDAX, but it was confirmed that no contamination (or metal diffusion) from the electrodes took place into the switched zone.

The effect of pressure on the resistivity of CuO–PbO– V_2O_5 glasses was studied up to 9 GPa using a 12-mm tungsten carbide opposed anvil system²³ (Bridgman setup). Pyrophyllite was used as the gasket material, and steatite, as the quasi-hydrostatic pressure-transmitting medium. In situ calibration with Bi has been adopted for accurate measurement of pressures. No increase in the sample temperature was noted under pressure. Pressurization of the samples was carried out slowly to enable the glasses to reach equilibrium conditions. Experiments were repeated several times to ensure reproducibility. A range of 0–10 GPa was used in the present studies.

The direct current (dc) electrical resistivities of the glasses have been measured as a function of CuO content using regularly shaped thin discs of glass coated with Ag electrodes on the parallel surfaces. Contacts were found to be ohmic. Resistivities were measured at different temperatures to confirm the semiconducting nature of the glasses. From the Arrhenius type semilogarithmic plots ($\log \rho$ versus $1000/T$) obtained, the activation barriers for dc conductivity have been calculated.

Electron paramagnetic resonance (EPR) spectra of the powdered glass samples, taken in quartz tubes, were recorded at room temperature on an x-band EPR spectrometer (Varian model), Cambridge Instruments, U.S., Stereoscan 360 SEM. The microwave frequency was kept at 9.2 GHz, and the magnetic field was scanned from 1300 to 5300 G. Polycrystalline DPPH was used as a standard field marker. Infrared (IR: BIO-RAD, Japan, FTIR spectrometer) spectra of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses have been recorded in the range of 400–4000 cm^{-1} using thin pellets made of sample powders with KBr.

TABLE I. Densities, molar volumes, and other properties of CuO–PbO– V_2O_5 glasses.^a

Glass no.	Composition (mol%)	Density u (g/cm^3)	Molar Volume V_m (cm^3)	ΔC_p ($\text{J K}^{-1} \text{mol}^{-1}$)	C_p at ($T_g - 20$) K ($\text{J K}^{-1} \text{mol}^{-1}$)	EPR g value
1	45PbO:55 V_2O_5	4.78	42.44	13	82.8	1.97
2	5CuO:40PbO:55 V_2O_5	4.71	41.42	13.5	83.3	2.06
3	10CuO:35PbO:55 V_2O_5	4.58	40.98	13	87.2	2.07
4	15CuO:30PbO:55 V_2O_5	4.46	40.40	14.5	98.3	2.04
5	20CuO:25PbO:55 V_2O_5	4.34	39.89	15	97.1	2.03

^aDulong–Petit heat capacity values for all the above glasses = $118.5 \text{ J K}^{-1} \text{mol}^{-1}$.

III. RESULTS AND DISCUSSION

A. Densities, molar volumes, and thermal properties

Table I lists the density, molar volume, and thermal properties (like T_g , C_p , etc.) of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses as a function of CuO content. The density of the microwave-prepared binary glass $45\text{PbO}:55\text{V}_2\text{O}_5$ is about 4.78 g/cm^3 and lies in between the density values reported for $50\text{PbO}:50\text{V}_2\text{O}_5$ (5.01 g/cm^3) and $40\text{PbO}:60\text{V}_2\text{O}_5$ (4.60 g/cm^3) glasses.²⁷ The density (ρ) and molar volume (V_m) of lead vanadate glasses show a marginal decrease with the incorporation of CuO. The 6% decrease in molar volume (from $x = 0$ to 20) suggests that the glasses become slightly more compact with the incorporation of CuO. The decrease in density ($\approx 9\%$) could be due to the replacement of heavier (bigger) PbO by the lighter (smaller) CuO in the glassy network.

The glass transition temperatures of the CuO–PbO– V_2O_5 glasses are given in Fig. 1 as a function of composition. There is a slight increase in T_g with increase of CuO content, suggesting a mild increase in the lattice rigidity. The DSC traces of the copper lead vanadate glasses are depicted in Fig. 2. All the glasses exhibit a single glass transition and multiple crystallizations (or phase transition). The DSC thermogram obtained for the binary lead vanadate glass compare well with the literature report²⁸ on this glass. In the equimolar $50\text{PbO}:50\text{V}_2\text{O}_5$ glass²⁸ it was found that the first exothermic peak corresponds to the transition of the homogeneous glassy phase to metastable crystalline PbV_2O_6 phase and the second exothermic peak corresponds to the phase transition of the metastable lead metavanadate to a stable

FIG. 1. Variation of the glass transition temperatures of CuO–PbO– V_2O_5 glasses with composition. The line is drawn as a guide to the eye.

FIG. 2. DSC thermograms of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses.

polymorphic crystalline phase of PbV_2O_6 . While the glasses with 0 and 5 mol% CuO (memory type compositions; see later) exhibit two exothermic transitions, the high CuO containing glass compositions (15 and 20 mol% CuO) show more than two exotherms. The nature and origin of the exotherms, particularly in terms of crystallizations and subsequent phase transitions, have not yet been fully established. However the indication is that CuO leads to formation of complex structural units in lead vanadate glasses and the devitrification is also expected to be complex. Also since there was no indication of multiple glass transition, the glasses are most likely not phase separated. No further tests were, however, performed to confirm the absence of phase separation.

The heat capacity values (C_p) are listed in Table I for the CuO–PbO– V_2O_5 glasses. The experimental heat capacities are generally lower than the Dulong–Petit heat capacities ($118.5\text{ J K}^{-1}\text{ mol}^{-1}$) suggesting that the vibrational modes are not fully excited at these temperatures ($<T_g - 20\text{ K}$). However the difference between the Dulong–Petit and experimental heat capacities systematically decreases with increase of CuO content. This indicates that the incorporation of CuO decreases the concentration of short covalent bonds in the glass. The magnitude of ΔC_p values increase slightly suggesting an increase in ionic bonding as CuO increases in the glasses.

B. High-field behavior

The I - V characteristics of the $\text{CuO-PbO-V}_2\text{O}_5$ glasses as a function of CuO content are given in Figs. 3 and 4. All the glasses exhibit a distinct transition from linear ohmic behavior to current-controlled negative resistance (CCNR) behavior at a particular threshold voltage (V_t). The I - V characteristics exhibit, in general, four distinct regions in CuO-poor glasses (see Fig. 3). They are designated as A, a linear ohmic region, B, a negative resistance region, C, a second almost flat negative resistance region, and D, a highly conducting region corresponding to the ON state. The threshold voltage for the transition varies as a function of composition, thickness, and temperature of the sample. Due to limitations in the experimental setup, voltages could be measured only up to 350 V. Therefore samples which exhibited higher threshold voltages at room temperature were preheated to a reasonable temperature less than their T_g . For example, glasses with $x = 0$ to 15 were heated to temperature less than their T_g . For example, glasses with $x = 0$ to 15 were heated to temperatures between 320 and 520 K in order

FIG. 3. I - V characteristics of memory type $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses.

FIG. 4. Switching characteristics of threshold type $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses.

to lower the V_t to less than 350 V. Glasses with composition $x \leq 10$ exhibit a CCNR behavior which can be described as “memory” type (irreversible). That is, once switched from the linear ohmic region (OFF state, denoted as A) to a high-conducting ON state (denoted as D), the material gets permanently latched on to that state (D). Any subsequent I - V cycles exhibit only the high-conducting D region (see inset in Fig. 3). This memory behavior of $x \leq 10$ composition was observed in all thicknesses and at all temperatures below T_g . Similar memory behavior has been observed earlier in $\text{BaO-V}_2\text{O}_5$,²⁹ $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$,⁶ and calcium iron phosphate³⁰ glasses. In all these glasses only the above type of memory switching was observed, albeit with reduction of V_t values at higher concentrations of transition metal ions.

However in the present system, the glass samples containing more than 10 mol% CuO behave differently and exhibit a reversible threshold CCNR behavior (Fig. 4); i.e., the material does not get latched on to the high-conducting state permanently. The glasses ($x = 15, 20$) show an initial ohmic response (region A) and at V_t change course to a stable negative resistance state (region B), which is also characterized by high-rise conductivity. Upon decrease of current values the I - V trajectory C follows closely region B with slight hysteresis to ultimately revert to region A which is the OFF state. The

samples can be switched from the OFF state to the ON state (through A, B, and C stages) for a large number of cycles with only a little change in their threshold voltages ($\approx 2\%$ decrease of V_t was observed from the first switching cycle to the 10th cycle, which may be due to some type of “forming” effect), though in the present experiments we have examined a maximum of 20 cycles. This remarkable change in the nonlinear electrical behavior of CuO–PbO– V_2O_5 glasses as a function of CuO content suggests that the switching mechanisms operative in the two regimes, $x = 0, 5$, and 10, or the low CuO glasses showing memory type, and $x = 15$ and 20, or high CuO glasses exhibiting threshold type, may be different and critically dependent on the glass compositions.

The temperature dependence of the ON state resistance of 10CuO:35PbO:55 V_2O_5 glass is shown in Fig. 5. The observed increase in the ON state resistance with increasing temperature clearly indicates the metallic nature of the switched state in the memory type glasses. At any given temperature and thickness the V_t decreases with CuO content. The threshold voltage increases with increasing sample thickness [Fig. 6(a)] for both the memory type ($x = 10$) and threshold type ($x = 20$) glass compositions suggesting that switching is a bulk effect. Similar dependence of V_t on sample thickness has been reported in semiconducting chalcogenide glasses earlier.³¹ For fixed composition and thickness, V_t is reproducible within ± 2 V.

Figure 6(b) gives the dependence of V_t on sample temperature for the representative memory ($x = 10$) and threshold ($x = 20$) glasses. In both cases the threshold voltage decreases in a linear fashion with increasing temperature, which corroborates well with the behavior observed in other transition metal oxide containing glasses. Temperatures corresponding to $V_t = 0$ for the two glasses shown in Fig. 6(b), however, bear no relation to the glass transition temperatures of the glasses reported in the previous section. It is interesting to note that there is a decrease in resistance of these semiconducting

FIG. 5. Variation of ON state resistance of 10CuO:35PbO:55 V_2O_5 glass as a function of temperature. The line is drawn to guide the eyes.

(a)

(b)

FIG. 6. (a) Dependence of threshold voltage (V_t) with sample thickness and (b) temperature dependence of V_t .

glasses with increasing temperature and a corresponding decrease of V_t . In binary vanadate glasses, models based on thermal effects have been proposed to explain the memory switching behavior.^{32,33} The irreversible switching phenomenon has been attributed to the formation of a conducting filament in the switched region, which is understandably facilitated at higher temperatures.¹⁹ But the models which assume the presence of VO_2 type structure in vanadate glasses and attribute the switching behavior to the semiconductor–metal transition of VO_2 require that V_t should approach zero at 340 K, which corresponds to the transition temperature of bulk VO_2 . However, the presence of submicroscopic crystalline VO_2 whose transition temperature could be higher than 340 K when embedded in a glassy matrix has not been fully examined in this work. The finite threshold voltages observed at this temperature in the present glass samples invalidate this viewpoint. In the present glass system even if the irreversible memory behavior observed in low-CuO glasses ($x \leq 10$) is considered as a thermal effect,^{32,33} which is due to transition of VO_2 to its conducting phase (in the zone of switching), the reversible threshold switching observed in high-CuO (15% and 20%) glasses may need both thermal and electronic effects of this type discussed later in this work. We may note the similarity in behavior of the present glasses with those in semiconducting Al–As–Te chalcogenide glasses in which a transition from memory to threshold type switching behavior occurs as a function of composition.³⁴

That there is a significant difference in the behaviors of memory and threshold switching effects is corroborated by the scanning electron microscopic investigations. Figures 7(a) and 7(c) show the SEM micrographs of the memory type glasses ($x = 0$ and 10, respectively) after switching. Figures 7(b) and 7(d) are the magnified view of the switched zone alone in these glasses which indicates that a significant permanent change has occurred upon switching. There is also evidence of local melting due to joule heating. Thus there is an irreversible microstructural change associated with the memory type behavior of low-CuO glasses. Figures 8(a) and 8(b) present the SEM micrographs of the virgin and switched regions of the threshold switching 20CuO glass (after six cycles). It is evident that there is no evidence of the formation of different microstructure in the switched region. The ability to switch again and repeatedly obviously requires the absence of any structural changes. However detailed corroborative experimental and theoretical investigations are necessary to get more insight into the exact mechanism of switching in these glasses. EDAX analysis did not reveal any change in composition in the switched region.

C. High-pressure behavior

The electrical resistivity behavior of copper lead vanadate glasses as a function of pressure (up to 9 GPa) for all the glass compositions is given in Fig. 9. Here again significant variations are observed in the behavior of

FIG. 7. Scanning electron micrographs of the memory-switched samples: (a) $x = 0$, both the switched portion and the unswitched surroundings; (b) $x = 0$, magnified view of the switched region alone; (c) $x = 10$, switched and the unswitched portions; (d) $x = 10$, magnified view of the switched region alone.

FIG. 8. SEM pictures of the threshold type switching glass ($x = 20$): (a) micrograph indicating both the switched and the unswitched portions; (b) magnified view of the threshold switched region alone.

low- and high-CuO-containing glasses. The electrical resistivity of low-CuO glasses showed very little pressure response at lower pressures (>3 GPa) and remain essentially flat at higher pressures (above 3 GPa). On the other hand, high-CuO glasses exhibit a large (3 orders of magnitude) change in resistivity under pressure. That is the threshold type glasses show a larger electrical response to pressure than the memory type glasses. However the resistances of the samples (with $x = 15, 20$) even at 9 GPa were found to be higher than typical metallic values, and we suggest that the samples are still semiconducting at this pressure. We have not carried out any post-transition XRD measurements to examine the devitrification of the samples. But the differences in the high-pressure behavior of low-CuO glasses and high-CuO glasses indicate that there could be significant differences in the conduction processes in the two composition

FIG. 9. Effect of pressure on the normalized electrical resistivities of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses.

regimes. The samples generally broke when pressure was released, and efforts of making conductivity measurements on such samples at zero pressure were not successful.

D. Direct-current resistivity with composition

Figure 10 gives the logarithm of electrical resistivities of $\text{CuO-PbO-V}_2\text{O}_5$ glasses as a function of composition. In low-CuO glasses there is little influence of CuO content on the conductivity. But around the composition corresponding to the transition from the memory to threshold type a fairly drastic decrease (a factor of 10) in resistivity is noticed. The resistivity remains essentially constant above this composition. This effect is noticed at different temperatures also. The sudden change in resistivity at a seemingly critical composition is suggestive of a percolation effect. A network connectivity may be established among high-conducting regions present in the glass at this composition. Similar system of glasses of the general formula $x\text{MO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$, where $\text{MO} = \text{ZnO}, \text{MoO}_3, \text{WO}_3, \text{B}_2\text{O}_3$, and SiO_2 , were found to exhibit an increase in the total resistivity with increasing MO content. In the present system therefore the increase in the bulk conductivity with CuO content suggests a major role for CuO in electron transport, which includes switching phenomenon. Differences in the resistivity responses to pressure in low- and high-CuO compositions may also be related to this feature.

The experimentally observed dc activation barriers (ΔE) for the $\text{CuO-PbO-V}_2\text{O}_5$ glasses are given in Fig. 11 as a function of composition. The clear decrease in ΔE with increasing CuO content suggests that the incorporation of CuO significantly alters the electronic band structure of these glasses.

E. EPR studies

The room-temperature electron paramagnetic resonance spectra of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses is given in Fig. 12 as a function of CuO content. The parent

lead vanadate glass exhibits a clear hyperfine signal at $g \approx 1.97$ emanating from the V^{4+} ions present in the glasses. The distinct hyperfine spectrum also suggests that only low concentrations of V^{4+} ions are present in these

FIG. 10. Variation of electrical resistivity of CuO-PbO- V_2O_5 glasses as a function of composition.

FIG. 11. Composition dependence of dc activation energy (ΔE) of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses.

glasses and the unpaired electron is localized on V^{4+} ion. When CuO is introduced into the glass matrix, only a symmetric single-line EPR signal was observed whose g value (≈ 2.07) lies between the V^{4+} ($g \approx 1.96$) and Cu^{2+} ($g \approx 2.16$) g values. This indicates that in CuO-containing vanadate glasses the unpaired electron is not localized on V^{4+} ions and the g values also suggest the formation of ion pairs of Cu^{2+} and V^{4+} coupled by strong exchange interaction.¹⁴ Indeed mixed clusters formed by different ionic species located at different distances from one another may in general appear in glasses. The exchange may be assisted via the p electron pairs on oxygen, and a decrease of volume (although small) enhances the 180° exchange mode due to decrease in inter ionic distance. The increasing line broadening [ΔH value in Fig. 13(a)] as the CuO concentration increases is in conformity with the suggested interaction. In high-CuO glasses exchange of Cu^{2+} - Cu^{2+} also begins to contribute to the widths. Similar results are observed in CuO-BaO- V_2O_5 glasses.¹⁴ The variation in the intensity of the EPR resonances [Fig. 13(b)] also exhibits similar trends.

F. Infrared spectra

Figure 14 shows the infrared spectra of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses as a function of composition. With best optimization of thickness of films or concen-

FIG. 12. Electron paramagnetic spectra of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses.

FIG. 13. (a) Variation of the width of the ESR signal of CuO–PbO–V₂O₅ glasses as a function of composition and (b) variation of ESR signal intensity with CuO content.

trations in KBr pellets, the spectra do not consist of sharp features. Binary lead vanadate glass exhibits vibrational bands around 840, 743, and 647 cm⁻¹ and a strong shoulder at 936 cm⁻¹ all of which compare well with the reported results.²⁷ These vibrational bands are assigned to two types of stretching vibrations such as $\nu(\text{VO}_3)$ and $\nu(\text{VO}_2)$, suggesting that the glass network consists of VO₄ tetrahedra constituting [V₂O₇]⁴⁻ or (VO₃) in a single chain.^{27,35} The high-frequency band has been assigned to VO₄ tetrahedra and VO₅ trigonal bipyramids.³⁶ We did not observe a water band or an –OH stretching peak, indicating the nonhygroscopic nature of the present

FIG. 14. Infrared spectra of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses.

glass samples though these peaks are sometimes noticed in binary vanadate glasses.²⁸ Also no distinct peaks which could be attributed to CuO-based vibrations were observed.

G. Structural model and the properties of glasses

A fully quantitative explanation of the switching behavior is difficult at this stage. The following structural model is proposed tentatively which provides a new perspective in analyzing the high-field behavior.

There are three oxide constitutions in this glass, all of which exhibit significant covalent bonding. When lead oxide is present in a covalently bonded situation, lead gets bonded to four oxygens with the formation of the $[\text{PbO}_{4/2}]^{2-}$ type of units, which generally assumes square pyramidal or tetrahedral geometry. This has been observed in lead molybdophosphate and lead tungstophosphate glasses.³⁷ When the geometry is square pyramidal, the lone pair on the lead projects away from the plane of four oxygen atoms. When Pb is present in tetrahedral coordination, the lone pair remains in a diffuse 6s orbital. Lead establishes covalent oxide bridges with oxygen-rich polyhedra of other ions in a glass structure. Since PbO consists of only one oxygen and hence is equivalent to $[\text{PbO}_{2/2}]$, it requires to coordinate itself to oxygen atoms from other oxides. In the case of V₂O₅, however, the structure consists of two $[\text{VOO}_{3/2}]$ tetrahedral units. These units remain three connected in the glass structure like $[\text{POO}_{3/2}]$ in phosphate glasses. In analogy to the structure of lead oxide containing phosphate glasses we assume that $[\text{VOO}_{3/2}]$ units provide the necessary oxygen coordination to lead by the conversion of $\text{V}=\text{O}$ to $\text{V}-\text{O}-$ and formulation of $[\text{VO}_{4/2}]^+$ units.

Copper oxide on the other hand can form $-\text{Cu}-\text{O}-\text{Cu}-\text{O}-$ chains, and we assume that these chains permeate the covalent network structure with bends and twists so as to enable the coordination of copper to oxygen to become four. It is possible that oxygen-to-copper dative bonds are formed in the process. In Ca–Sr–Bi–cuprate glasses it was indeed found³⁸ reasonable to assume that the two additional oxygens are connected to Cu through dative bonds. Thus in the present model, all the three metal atoms, namely, Pb, V, and Cu, are four coordinated in the glass structure.

We can therefore construct a structural model of $x\text{CuO}:(45-x)\text{PbO}:55\text{V}_2\text{O}_5$ glasses with the above structural prescription, namely, all Pb atoms are present as $[\text{PbO}_{4/2}]^{2-}$ (P') units, all Cu atoms are present as $[\text{CuO}_{2/2}]$ (C) units (but with copper in effectively four coordinated positions), and vanadium atoms, equal to twice the number of Pb atoms in the glass composition, are present as $[\text{VO}_{4/2}]^+$ (V') units. The rest of the vanadium atoms are present as $[\text{VOO}_{3/2}]$ (V) units. The number of such structural units present in the glass are easily calculated and are given in Table II. P' and V' units carry a formal charge while V and C do not. In the glass structure oxygen ions are the largest both in number and size. We can therefore imagine that the glass is a random close-packed assembly of the oxygen ions and the required number of tetrahedral voids in them (which is far less than the number present in the assembly) are stuffed with Cu, Pb, and V ions. The structure is slightly relaxed to optimize the bonding. For example, in $5\text{CuO}:40\text{PbO}:55\text{V}_2\text{O}_5$ glass there are 320 oxygen ions and ≈ 960 tetrahedral voids and only 100 of them are occupied by various cations. It is immediately evident from the structural model that substitution of PbO by CuO should have little effect on the molar volume as indeed is the case (see Table I).

An approximate energy band structure of such a glass can be constructed as shown in Fig. 15, on the basis of the types of bonds present. V–O, Cu–O, and Pb–O bonds contribute to the lowest energy band, which is due to σ bonds. Just above this band are the V=O π -bonds which form a small band which we assume overlaps with the σ band. Immediately above these is the broad and high-

density band due to nonbonding lone pairs³⁹ on all the oxygens and Pb atoms. The top of this band should originate from pure p type lone pairs since admixture with s will render the energies of sp^3 lone pairs lower in comparison. But pure p lone pairs are present on oxygen atoms bonded to the metal atoms through sp -hybridized orbitals. The lone-pair band also constitutes the valence band of these semiconducting glasses. We assume that just above this lone pair band is the π^* -band (with $d\pi-p\pi$ character) due to V=O, which is separated from the former by a gap corresponding to the dc activation energy. Bands still higher are both vacant and formed from antibonding levels and of no direct relevance for the present discussion. This region also consists of empty d levels of vanadium. The schematic is not to scale and illustrative of the plausible disposition of band energy levels.

Referring to Table II, we note that V units increase as the PbO concentration decreases in the glass. This has an effect of broadening the π^* energy band, which decreases the gap and hence the activation barrier for the dc conductivity. This is consistent with Fig. 11. The valence band being itself the lone-pair band is unaffected by composition to a first approximation because of the constancy of the number of oxygen atoms in the structure.

Since the conductivity in these semiconducting glasses occurs via “hopping” which presumably occurs through an activation to a conduction band like state, $\text{V}^{4+}-\text{V}^{5+}$ connectivities are important for examining the magnitude of the conductivities. Vanadium involved in the $\text{V}^{4+} \rightleftharpoons \text{V}^{5+} + e$ equilibrium are only the V centers in Table II, because $[\text{VO}_{4/2}]^+$ units are tied up with $[\text{PbO}_{4/2}]^{2-}$ units rendering them inaccessible for conductivity purposes. It can be seen from Table II that V units increase in the structure as PbO is decreased and a percolation concentration of V (more than 0.27 for random close-packed structure⁴⁰) is reached for composition containing between 10 and 15% CuO. This, as expected, gives rise to a sudden drop in the resistivity as seen in Fig. 10. It is important to note that this is an effect of percolation rather than any step-like change in activation barriers.

Columns under V and C in Table II also suggest that $\text{V}^{4+} + \text{Cu}^{2+} \rightleftharpoons \text{Cu}^+ + \text{V}^{5+}$ could increase very rapidly which is why ΔH in the ESR of Fig. 13(a) increases with CuO concentration. The insensitivity of infrared features is because of the constancy of the nature of the structural units present in the glasses, which again fully supports the model. However spectroscopic work with greater resolution should be able to identify V=O vibrations whose intensity should increase by a factor of 3 in the present composition range.

The conductivity gap is therefore determined largely by the π^* band and the top of the lone-pair band. The effect of pressure on V=O will be minimal in low-CuO glasses because the concentration of V units is very

TABLE II. Different types of structural units present in CuO–PbO– V_2O_5 glasses.

Glass no.	Composition	No. of structural units ^a			
		P'	V'	V	C
1	45PbO:55V ₂ O ₅	45	90	20	0
2	5CuO:40PbO:55V ₂ O ₅	40	80	30	5
3	10CuO:35PbO:55V ₂ O ₅	35	70	40	10
4	15CuO:30PbO:55V ₂ O ₅	30	60	50	15
5	20CuO:25PbO:55V ₂ O ₅	25	50	60	20

^aP' $\equiv [\text{PbO}_{4/2}]^{2-}$; V' $\equiv [\text{VO}_{4/2}]^+$; V $\equiv [\text{VOO}_{3/2}]$; C $\equiv [\text{CuO}_{2/2}]$.

small. Also Cu–O chains may suffer slight “buckling” under pressure so that the top of the valence band (pure p lone pairs) gets a little suppressed because of the hybridization with s orbitals. The effect is expected to be therefore very little, and if there is, it causes a slight increase in the gap. On the contrary when the concentration of V units is very high (comparable to V' in number), V=O units are also subjected to compression due to pressure. The result of this is to cause a spread of the π^* band which dominates over any variation in the shape of the lone-pair band. The result is to decrease the band gap. These effects are well borne out by the pressure variations of the conductivity in Fig. 9.

Most vital to this investigation are the two types of switching observed as a function of composition. Switching itself and the observation of a threshold voltage is a consequence of the high field effect on the charged species present in the structure. When a high electrical field is applied, P' and V' units align and rearrange in the field to annul the electrical force. We further assume that V and V' units are exchangeable in the structure by appropriate switching of the bonds: $V + V' \rightarrow V' + V$. This has the effect of concentrating P' and V' into a region and further to induce polarization of negatively charged P' and positively charged V' toward respective electrodes. Thus, a subtle compositional dehomogenization occurs under the action of the electrical field, first of the formation of (V, C)- and (P', V')-rich regions and second of P'-rich and V'-rich regions. This has the consequence of stretching all the Cu–O–Cu and other oxygen bridges making for a higher density of pure p lone pairs on straining the V=O π bonds. The net effect of this on the band structure in Fig. 15 is to raise the energies of the top of the valence band (p lone pairs) and spread to lower energies of the π^* band. This causes an overlap of the bands bringing about a sudden increase in the conductivity and producing behavior of a “poor” metal. Therefore the switching occurs because of the overlap. When the electrical field is switched off or reversed, compositional and structural dehomogenization which has taken place may not be reversible particularly when CuO concentration is low, which therefore sets in a permanent change which corresponds to the generation of the band structure of a poor metal. In fact if P' and V' regions are sufficiently strongly polarized, it would not be surprising if VO_2 ($\text{VO}_{4/2}$) regions are formed along the conduction path. The model requires that although the primary effect of the electrical field is on P' and V' units, the changes in the features of band structure required for switching to occur are due to V and C units, and therefore, the presence of a larger concentration of CuO brings down the threshold voltages.

At high concentrations of CuO, we have almost equal concentrations of V and V' units which enable restoration of structural features when the fields are reversed,

FIG. 15. Schematic energy band structure for CuO–PbO–V₂O₅ glasses.

because of the availability of the necessary structural entities. This causes a threshold switching which is completely reversible at high CuO concentrations.

Since the switching phenomenon is seen here as a consequence of field-induced rearrangements of the structural units, higher temperatures can be expected to assist such rearrangements. Indeed threshold voltages decrease with increasing temperature [Fig. 6(b)]. The fact that smaller thicknesses exhibit lower threshold voltages—a bulk effect—is built into this model since structural rearrangement is a bulk operation. An important element of the above model is the band structure of the glass. At least the primary features of the band structure can be examined using the powerful technique of photoelectron spectroscopy.

IV. CONCLUSIONS

The nonlinear I – V behavior of microwave-prepared lead vanadate glasses has been found to be significantly altered with the incorporation of CuO. When the glasses with low copper oxide content exhibit memory type (irreversible) nonlinear high-field characteristics, the high-CuO glasses were found to show threshold type (reversible) high-field behavior. Similarly, marked differences have been observed in the high-pressure elec-

trical conductivity behavior of low- and high-CuO glasses. The effect of CuO addition on the local structure and the electronic band structure of CuO-PbO-V₂O₅ glasses has been considered, and a suitable model, which successfully accounts for the variation of the different properties of these glasses, has been proposed.

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