PHYSICAL REVIEW B VOLUME 51, NUMBER 2 1 JANUARY 1995-II

Structure and properties of nonconventional glasses in the binary bismuth cuprate system

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(Received 29 March 1994; revised manuscript received 22 September 1994)

The glass structure and physical properties are reported for the nonconventional binary bismuth cuprate glasses of compositions $(CuO)_x(Bi_2O_3)_{100-x}$, for $x = 27-70$ mol %, prepared by the roller-quenching technique. It has been observed that stable glasses with nearly the same topology can be obtained in this system for a larger composition range compared to the multicomponent bismuth cuprate glasses. The network structure is built up of $[BiO_3]$ pyramidal units. The strength and connectivity of the glassy network increase at nearly equimolar glass composition. The nearly equimolar glass composition crystallizes to tetragonal Bi_2CuO_4 crystal. The appearance of hyperfine structure in the ESR line shapes for the glass compositions with high CuO content is not clear at this moment.

I. INTRODUCTION

Multicomponent nonconventional glasses based on Bi_2O_3 are of great interest because they form amorphous materials without any conventional network formers like P_2O_5, SiO_2, etc., and they can be used to produce glass ceramic superconductors (high T_c) with controllable microstructure.[1-6] However, few studies have been reported on the Bi_2O_3-based glasses.[7-9] The glass structure and crystallization kinetics are not understood yet. Although Bi_2O_3 does not form glass by itself, it has been pointed out[8] that bismuth ions are highly polarizable and the coordination number of the Bi^{3+} ion may decrease and the cations may exist in the glass network in $[BiO_3]$ pyramids in the presence of conventional glass-forming cations such as P^{5+}, Si^{4+}, B^{3+}, etc. Based on x-ray and infrared studies, it has been shown that Bi^{3+} ions participate in the network structure above 45 mol % Bi_2O_3 in B_2O_3-Bi_2O_3 conventional glass.[7] Nonconventional glasses using Bi_2O_3 as the basis of the glass network of multicomponent systems have been investigated by Dumbaugh.[8,9] It was observed that the addition of Th, Cd, Ba, Zn, and Fe oxides results in a large glass-formation domain and addition of gallium oxide to PbO-Bi_2O_3 and CdO-Bi_2O_3 dramatically improves glass stability. However, the glass-formation domain, structure, etc. of binary glasses using Bi_2O_3 as a unique network former have not been reported yet to our knowledge. In this paper, we report the glass formation, structure, and properties of binary CuO-Bi_2O_3 glass in which Bi_2O_3 acts as a glass network former.

II. EXPERIMENTAL PROCEDURE

Bismuth cuprate glassy samples of compositions $(CuO)_x(Bi_2O_3)_{100-x}$, where $x = 27-70$ mol %, were prepared using reagent-grade Bi_2O_3 and CuO. These chemicals were first mixed in a mortar and then melted in alumina crucibles in the temperature range 1000–1200 °C depending on their molar ratio. Glassy samples were achieved by quenching the melts using a twin-roller technique.[10] X-ray-diffraction patterns of the samples as prepared and heat treated at different temperatures for different duration of time were recorded in a Philips x-ray diffractometer (model PW 1050/51). The scanning electron micrographs of the polished surfaces of the samples were taken in a Hitachi scanning electron microscope (model S-415A). A ~150-Å-thick gold coating was deposited on the polished surface of the sample by vacuum evaporation for conducting-layer function. The atomic absorption was carried out in a Varian atomic absorption spectrometer (model AA 1475) to determine the final glass compositions as well as to estimate the total copper ion concentrations. The density of the samples was measured at room temperature by Archimedes' principle using acetone as the immersion liquid. Differential thermal analysis (DTA) was performed in air atmosphere for all samples using a Shimadzu thermal analyzer (model DT-40). Infrared (ir) spectra of the prepared samples as well as the starting chemicals in KBr matrices were recorded at room temperature in a Perkin-Elmer spectrophotometer (model 783) in the wave-number range 200–4000 cm^{-1}. The concentration of Cu^{2+} ions was determined from magnetic-susceptibility measurements in an EG&G Parc vibrating-sample magnetometer (model 155) at room temperature. The electron-spin resonance (ESR) spectra of the samples were recorded in a JEOL *X*-band ESR spectrometer (model JES-RE1X) at room temperature.

III. RESULTS AND DISCUSSION

A. X-ray-diffraction and electron microscopic studies on glass formation

X-ray-diffraction patterns of three sample compositions are shown in Fig. 1. The diffractograms show only broad diffuse scattering at low angles characteristic of long-range structural disorder. In this way, glass formation in the binary CuO-Bi_2O_3 system was confirmed for the range 27–70 mol % Bi_2O_3. It may be mentioned that this range of glass formation in the binary system is much

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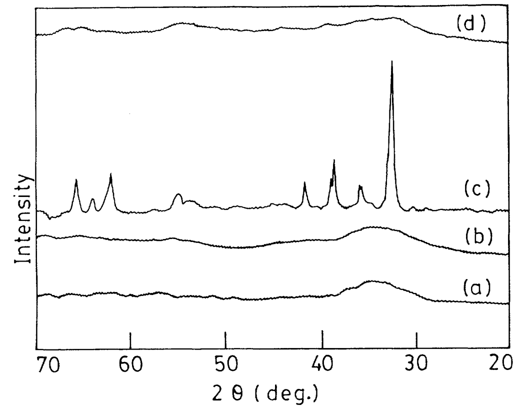

FIG. 1. X-ray diffractograms of several samples: (a) 27.15 mol % CuO, (b) 45.70 mol % CuO, (c) 45.70 mol % CuO heat treated at 500 °C for 20 h, and (d) 67.60 mol % CuO.

wider than that of the multicomponent Bi_2O_3-SrO-CaO-CuO system.[11] The diffractogram of the 45.70 % CuO–54.30 % Bi_2O_3 glass composition heat treated at 500 °C for 20 h [curve (c) in Fig. 1] shows crystalline peaks corresponding to the tetragonal structure of the crystalline Bi_2CuO_4 with *P*4/*ncc* space group, as reported earlier.[12]

Figure 2 shows the scanning electron micrographs of several compositions as prepared as well as heat treated at 500 and 750 °C for 20 h. It is clear that the micrographs [Figs. 2(a) and 2(b)] of the as-prepared samples exhibit a surface without any presence of microstructure, confirming the amorphous nature of the samples. However, the micrographs [Figs. 2(c) and 2(d)] of the heat-treated 45.70% CuO–54.30% Bi_2O_3 sample show crystalline structure. The micrographs also indicate that the volume fraction of the crystalline phases increases with the increase of heat-treatment temperature.

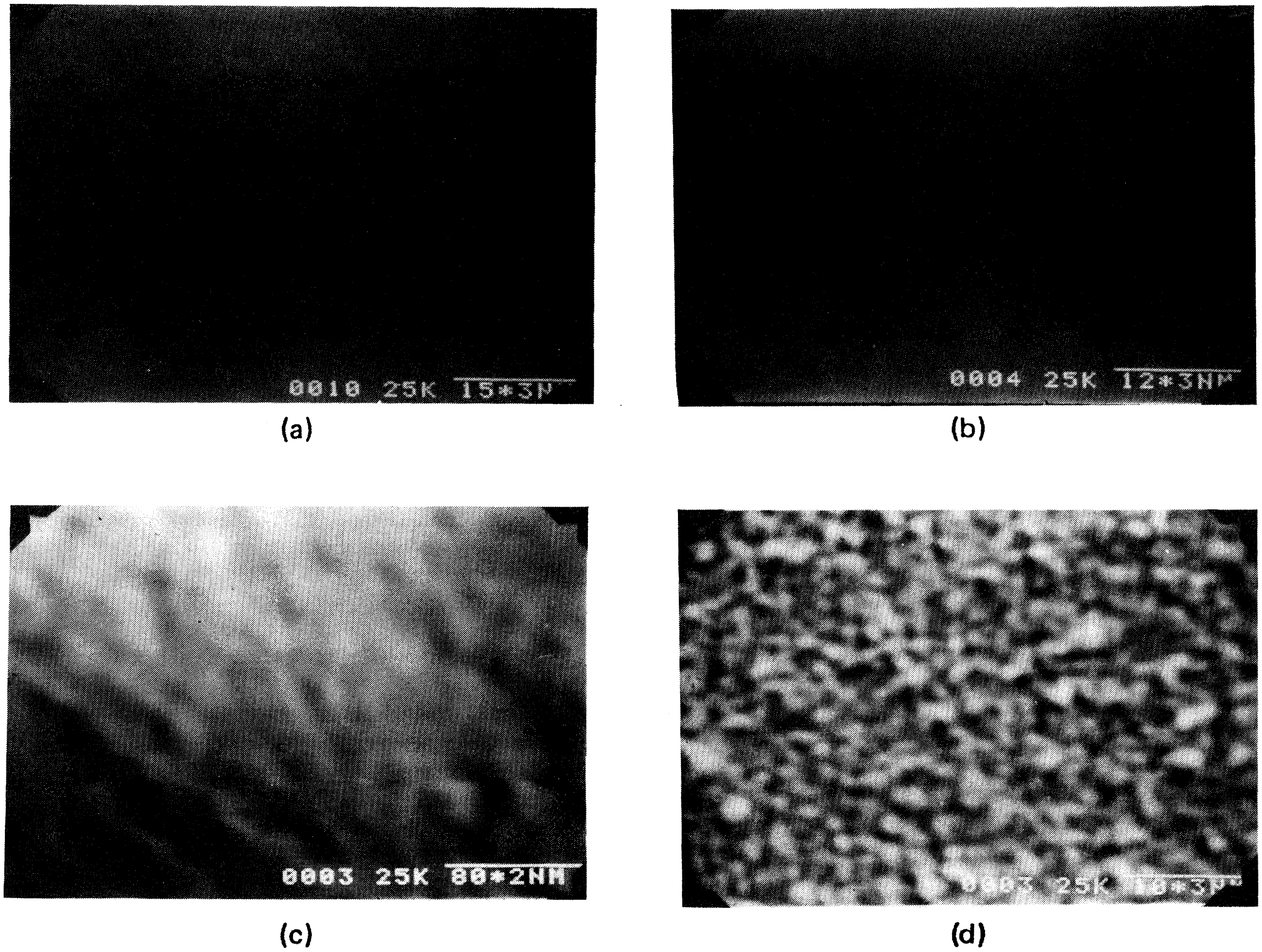

FIG. 2. Scanning electron micrographs of several samples: (a) 45.70 mol % CuO (× 2000), (b) 67.60 mol % CuO (× 2500), (c) 45.70 mol % CuO heat treated at 500 °C for 20 h (× 3800), and (d) 45.70 mol % CuO heat treated at 750 °C for 20 h (× 3000).

TABLE I. Different physical parameters estimated from atomic absorption, density, magnetic measurement, and DTA for the bismuth cuprate glasses.

Analyzed glass composition Bi$_2$O$_3$ (mol %)	CuO (mol %)	Density (g cm^{-3})	N (10^{21} cm^{-3})	[Cu$^+$] (10^{21} cm^{-3})	C [Cu$^+$]/N	T_g (°C)	T_c (°C)
72.85	27.15	8.29	3.70	2.72	0.74	280	340, 370 410, 460
64.65	35.35	8.20	5.30	3.39	0.64	290	310, 370, 410, 420
54.30	45.70	7.99	7.60	4.87	0.64	350	420, 540, 580
44.38	55.62	7.75	10.35	6.79	0.66	350	410
32.40	67.60	7.54	14.98	10.94	0.73	340	430, 555

B. Analyzed compositions, density, and molar volume

Table I shows the analyzed glass compositions which are somewhat different from the batch compositions due to evaporation losses during melting. From the studies of atomic absorption and the magnetic susceptibility, it is concluded that copper ions exist in two oxidation states in all glass compositions. The concentrations of the reduced copper ions [Cu$^+$] were determined by subtracting the concentration of Cu^{2+} ions from the total copper ion concentration N. The concentrations of the reduced and total copper ions and their ratio C are shown in Table I, from which it may be noted that both the total and reduced copper ion concentrations increase in consistence with the CuO content in the glass compositions. However, the values of C are approximately constant for all glass compositions. Assuming the copper ions to be uniformly distributed in the glassy matrix, the average copper site separation R (Table II) was estimated from the total copper ion concentrations. The values of R increase with decrease of CuO content in the glass compositions.

The compositional dependence of the density and oxygen molar volume V_O^* (i.e., the molar volume occupied by 1 g-at. of oxygen in the glassy matrix) is shown in Fig. 3. Both these quantities change monotonically with the glass composition, suggesting that the geometry and topology of the glassy network structure do not change significantly with composition. However, for the glass composition with 67.6 mol % CuO, the decrease of oxygen molar volume shows some deviation from the observed trends for other glass compositions. This indicates that there might be some structural changes for this composition. It has been observed (Table II) that the molar volume of all glass compositions is always higher than that for the ideal packing, calculated assuming that the molar volume of the glasses is simply a sum of the molar volumes of the crystalline Bi$_2$O$_3$ (52.36 cm^3) and CuO (12.43 cm^3). This is due to the fact that the glass structure consists of [BiO$_3$] pyramidal units, as revealed by the ir spectra (see Sec. III D), which may cause the glass structure to loosen, since α-Bi$_2$O$_3$ made up of [BiO$_6$] units is denser than the glass compositions made up of [BiO$_3$] units.

C. Thermal analysis

The DTA curves of the samples, shown in Fig. 4, exhibit glass transition temperatures (T_g) followed by one or more crystallization temperatures (T_c) depending on composition and similar melting temperatures of different cyrstalline phases. It is also observed that the curves for the glasses below nearly equimolar composition are more complex. The T_g's and T_c's (Table I) were calculated within an accuracy of ±5 °C. The inset of Fig. 4 shows that T_g increases sharply at nearly equimolar composition. However, the T_g's are almost independent of composition above and below this composition. Thus, the strength and connectivity of the glass network[13] increase at nearly equimolar composition. A difference of 60–90 °C between T_g and T_c is observed, except for the glass composition with ~35 mol % CuO, indicating stability of these glasses.

TABLE II. Different physical parameters derived from Table I for the bismuth cuprate glasses.

Sample composition (mol % CuO)	Oxygen molar volume (V_O^*) (cm^3 g-at.$^{-1}$)	Molar volume (cm^3 mol^{-1})	Molar volume for ideal packing (cm^3 mol^{-1})	R (Å)
27.15	17.72	43.54	41.52	6.47
35.35	17.51	40.16	38.24	5.73
45.70	17.37	36.23	34.11	5.09
55.62	17.15	32.37	30.15	4.59
67.60	16.48	27.16	25.37	4.06

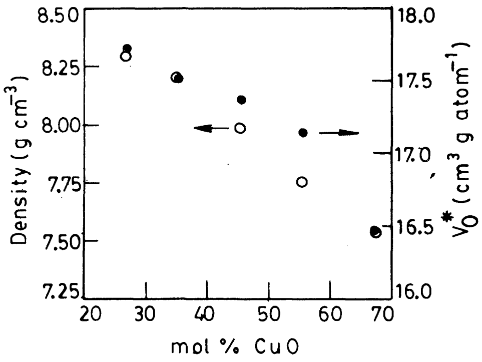

FIG. 3. Density (○) and oxygen molar volume (●) as a function of CuO content in the bismuth cuprate glass compositions.

D. Infrared spectra

Figure 5 shows the infrared spectra at room temperature for all glass compositions along with those for crystalline CuO and Bi_2O_3 for comparison. It is clear that there are four fundamental vibrational bands at $\sim$830, $\sim$620, $\sim$450, and $\sim$350 cm^{-1} present in the ir spectra of all glass compositions. A water band at $\sim$3400 cm^{-1} is also observed in all glass compositions due to the hygroscopic character of the powdered samples. It has been reported earlier[7] that although Bi_2O_3 cannot form glass by itself, in the presence of strong polarizing cations such as Si^{4+}, Bi^{3+} ions can reduce their coordination number (6) from the $[BiO_6]$ octahedral units and form a glass network in the $[BiO_3]$ pyramidal units which belong to the point group C_{3v} with four infrared-active fundamental vibrations: a totally symmetric stretching vibration at 840 cm^{-1}, a doubly degenerate stretching vibration at 540–620 cm^{-1}, a totally symmetric bending vibration at 470 cm^{-1}, and a doubly degenerate bending vibration at 350 cm^{-1}. These vibrations are clearly observed in the ir spectra presented in Fig. 5 for all the glass compositions and crystalline Bi_2O_3. The intensity of these vibrations, however, reduces and broadens significantly for the glass compositions due to their disordered structure. Thus the ir spectra suggest that glass compositions consist of $[BiO_3]$ pyramidal units. The symmetric vibration bands at 830 and 450 cm^{-1} for the glasses have higher wave number compared to the vibration bands of fused Bi_2O_3.[7] This suggests that stronger Bi-O bonds are present in the glass compositions, caused by polarization effects. These observations for the binary bismuth cuprate glasses are in

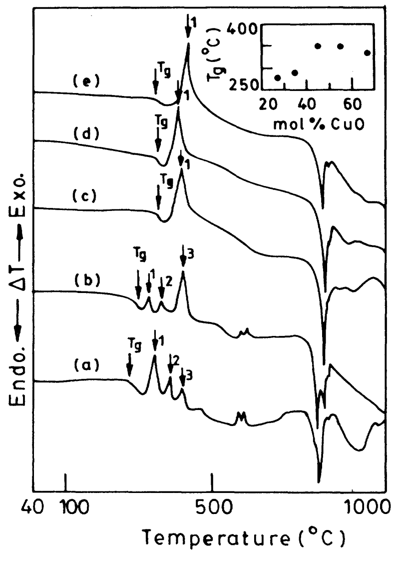

FIG. 4. Differential thermal analysis curves of several samples: (a) 27.15 mol % CuO, (b) 35.35 mol % CuO, (c) 45.70 mol % CuO, (d) 55.62 mol % CuO, and (e) 67.60 mol % CuO. ↓ indicated by T_g is the glass transition temperature and ↓1, ↓2, etc. indicate crystallization temperatures. Inset shows glass transition temperature (T_g) as a function of CuO content.

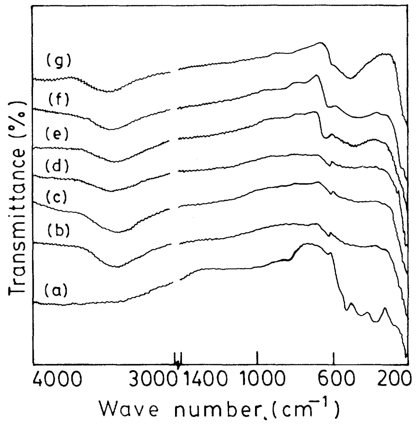

FIG. 5. Room-temperature infrared spectra of several samples: (a) crystalline Bi_2O_3, (b) 27.15 mol % CuO, (c) 35.35 mol % CuO, (d) 45.70 mol % CuO, (e) 55.62 mol % CuO, (f) 67.60 mol % CuO, and (g) crystalline CuO.

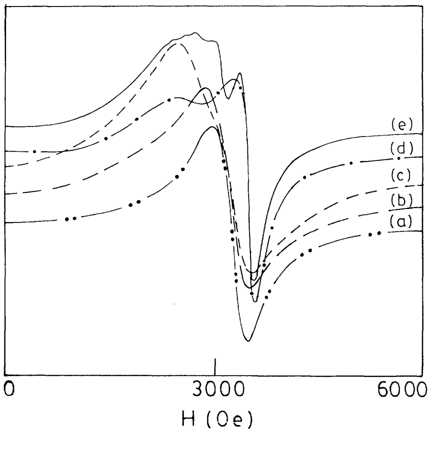

FIG. 6. Room-temperature ESR spectra of bismuth cuprate glasses recorded at a microwave frequency 9.44 GHz. (a) 27.15 mol % CuO (gain = 2.5×10^3), (b) 35.35 mol % CuO (gain = 4.0×10^3), (c) 45.70 mol % CuO (gain = 8.0×10^3), (d) 55.62 mol % CuO (gain = 5.0×10^3), and (e) 67.60 mol % CuO (gain = 6.3×10^3).

TABLE III. ESR parameters and magnetic-susceptibility data for the bismuth cuprate glasses.

Sample composition (mol % CuO)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})	g_e	ΔH_{pp} (G)	χ (10^{-7} emu)
27.15					2.150±0.028	480	2.48
35.35					2.150±0.028	640	4.88
45.70					2.178±0.028	1040	7.11
55.62	2.495	2.009	235.8	98.5			9.61
67.60	2.458	2.020	153.4	104.5			11.25

sharp contrast to the multicomponent bismuth cuprate glass compositions,[11] in which both the [BiO_6] octahedral and [BiO_3] pyramidal units are present depending on composition. With increasing SrO and CaO content, a conversion of [BiO_6] units into [BiO_3] units was observed, producing nonbridging oxygen atoms.

E. Magnetic susceptibility and ESR spectra

Magnetic susceptibility (Table III) of the prepared glasses measured at room temperature increases with increase of CuO content in the glass composition. The magnetic properties of these glasses arise from the paramagnetic Cu^{2+} ions with $3d^9$ electrons. The concentrations of the Cu^{2+} ions calculated from the susceptibility data are also found to increase with increase of total copper ion concentrations.

ESR spectra at room temperature of several glass compositions are shown in Fig. 6. It is clear that only glass compositions with 55.67 and 67.60 mol % CuO exhibit partially resolved hyperfine structure in the parallel components of the spectra, while other glass compositions show a broad single resonance line. The spectra of the glass compositions exhibiting hyperfine structure can be described by an axially symmetric spin Hamiltonian

$$H=g_{\parallel}\beta H_z S_z+g_{\perp}\beta(H_x S_x+H_y S_y)+A_{\parallel}I_z S_z + A_{\perp}(I_x S_x+I_y S_y)\ ,$$

where $S=\frac{1}{2}$, $I=\frac{3}{2}$, and all other parameters have the usual meaning. The principal g values and the hyperfine constants extracted from the spectra for the two glass compositions are shown in Table III, while for other glass compositions, the effective g values (g_e) and the peak-to-peak width (ΔH_{pp}) are shown. It may be noted that the peak-to-peak width increases with the increase of CuO content in the glass composition. The composition dependence of the ESR line shapes for glasses containing transition-metal ions has been explained previously on the basis of different concentration of the reduced transition-metal ions or phase segregation or different hopping rates of charge carriers in different glass compositions.[14,15] In the present glass compositions, the concentrations of Cu^{2+} ions are nearly constant and no phase separation was obtained in the scanning electron micrographs. It is also observed that the hopping rate of the charge carriers is higher in the glass compositions containing higher CuO content[16] and thus is unlikely to explain the observed hyperfine structure in the high-CuO-content glass compositions. It is thus unclear at this moment why the glass compositions with high CuO content exhibit hyperfine interaction. However, the increase of the peak-to-peak width of the other glass compositions may be explained assuming the existence of clusters of copper ions in the glasses. The interaction between these clusters would give rise to broad ESR peaks.

IV. CONCLUSIONS

Glass formation in the binary bismuth cuprate system is achieved by rapid quenching of the melts for a wider compositional range than for the multicomponent glasses. The topology of the glass structure does not change significantly with composition. The glass structure of all the compositions is built up of [BiO_3] pyramidal units. The composition dependence of the glass transition temperature shows that the strength and connectivity of the glass network change at nearly equimolar glass composition. The nearly equimolar glass composition crystallizes to tetragonal Bi_2CuO_4. The increase of peak-to-peak width of the ESR line shapes is attributed to the interaction between clusters of copper ions. However, the appearance of fine structure in the ESR line shapes of the compositions with higher CuO content is not clear.

ACKNOWLEDGMENT

S.H. acknowledges the University Grants Commission (India) for financial support.

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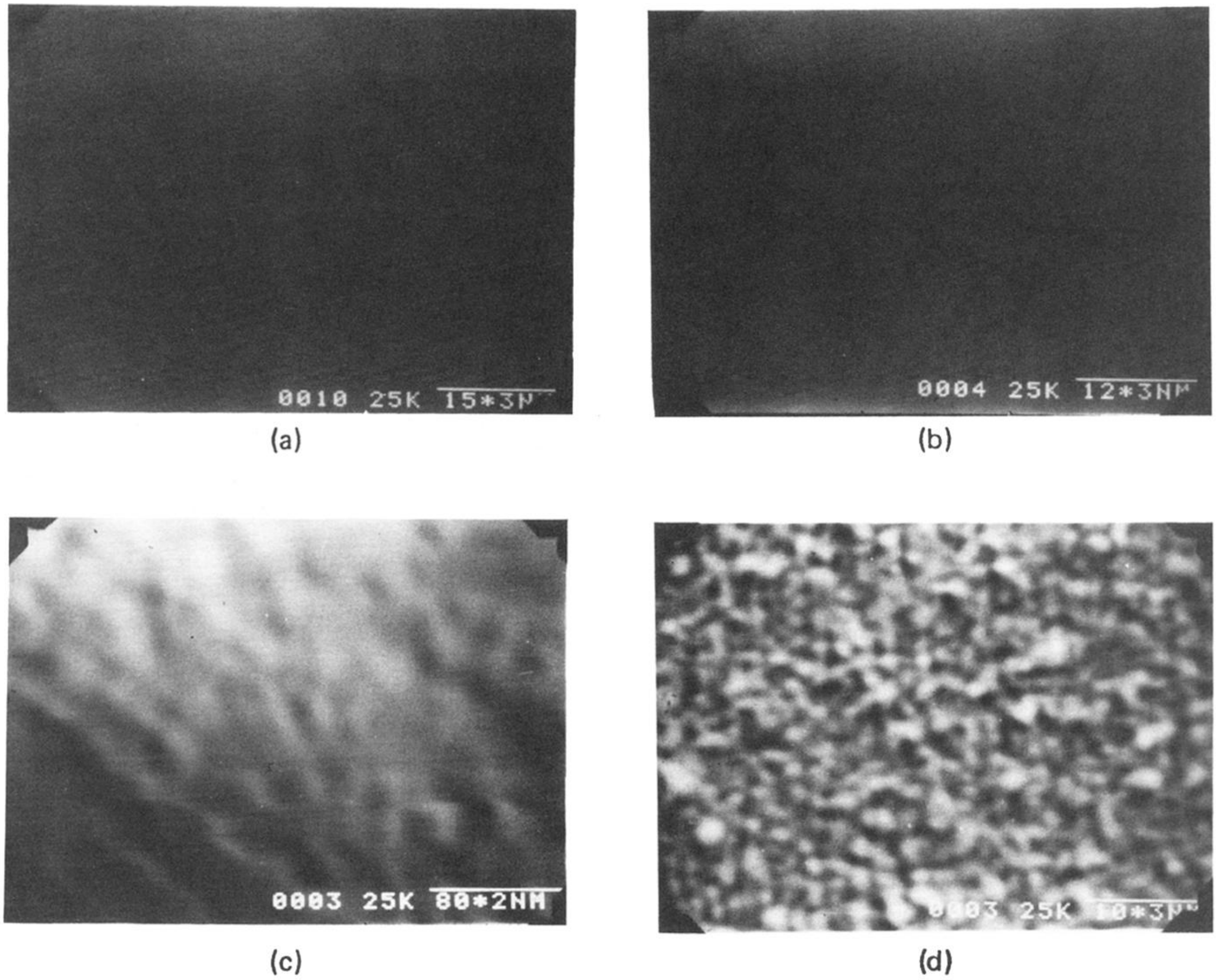

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