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PHOTOCONDUCTIVITY AND PHOTOTROPY

IN

NON-CRYSTALLINE SOLIDS

GPO PRICE \$
CFSTI PRICE(S) \$
Hard copy (HC) <u>9.00</u> Microfiche (MS)
ff 653 July 65

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30	N66 37580	
Y FORM 6	(ACCESSION NUMBER)	
FAGILIT	(NASA CR OR TMX OR AD NUMBER)	(CODE) 26 (CATEGORY)

1. Introduction

The reversible phenomena of photoconductivity and phototropy (or photochromism) have been known for a long time. Most of the studies reported have been on crystalline solids and until recently relatively little is known concerning these two interesting electronic properties for non-crystalline solids. Although both organic and inorganic materials can exhibit photoconductivity and phototropy, this survey paper will be restricted to inorganic systems. Most published work on non-crystalline solids, in particular those on photoconductivity, have been concentrated on the understanding of the mechanisms only rather than a correlation of the phenomena with the structures of the materials involved. In this review, attempts will be made to indicate the equal importance of the understanding of material structures. Before we proceed to review the observed properties, . therefore, it is pertinent to clarify the meaning of "non-crystalline" solids.

II. Non-Crystalline Solids

Non-crystalline solids can be prepared by a large number 1 of grossly different methods. The two most important methods, particular for the present review, are (a) by cooling the melt until it is rigid in the absence of crystallization, and (b) by condensation of the vapor on a solid substrate at some temperature at which the condensate is rigid. In either case, absence of crystallinity is usually assumed if diffuse x-ray

or electron diffraction patterns similar to that given by a liquid are obtained. It is generally accepted by workers in the field of glass science and technology that the noncrystalline solid obtained by method (a) termed a glass or a vitreous solid . This glassy solid is a metastable phase whose frozen-in structure corresponds to the structure of a liquid or a supercooled liquid at some higher temperatures. A non-crystalline solid obtained by vapor deposition is generally referred to as an amorphous solid. The structure of an amorphous solid is dependent on many factors some of which are interrelated. For example, the structures of the vapor species, the substrate temperature, the rate of deposition and the duration of deposition. If a substance can be rendered into a non-crystalline state by both methods (a) and (b), for instance selenium, it is unlikely that the structures of the two non-crystalline solids will be the This will be further clarified when selenium is same. discussed below. Although there appears to be some evidence that non-crystalline oxides obtained by different methods are structurally similar, this is to be regarded as anomalous at present . In any study of the properties of non-crystalline solids, therefore, the preparation history must be considered as an important factor.

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III. Photoconductivity

(a) <u>Semiconducting Non-Crystalline Solids</u>

Electronic conduction in semiconductors is not confined to crystalline solids. Ioffe and Regel have presented extensive data which has shown conclusively that semiconduction is primarily governed by short-range order and not long-range order. Thus the mechanism of semiconduction in a molten semiconductor may be similar to that in the corresponding crystal providing the short-range order in the two phases are similar. It is of course frequently difficult to define exactly the meaning of short-range order. Semiconducting behavior has been reported long ago for amorphous films of elementary solids such as antimony, germanium, silicon and tellurium. More recently, semiconducting behavior has been found in many oxide glasses as well as non-oxide glasses based on mixtures of elements such as S, Se, Te, P, As, Tl, Si and Ge. Photoconductivity has only been reported for the latter materials. In general, these semiconducting glasses have relatively low electrical conductivity $(10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ or})$ less) and the mobility of the carriers is small (1 cm² v^{-1} sec^{-1} or less). There is at present little quantitative understanding concerning such low-mobility solids. Both n-type and p-type conduction have been reported. It is interesting to note that for some of these glasses, whereas

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thermoelectric power measurements indicate that the major carriers are positive holes, Hall measurements suggest that electrons are the primary carriers. It was suggested that this anomaly could be the result of inhomogeneities in the 7 glass . Recently, however, it was reported that this anomaly persisted when glasses of the systems As₂Se₃ and As₂Te₃ were 8 heated to temperatures corresponding to the liquid state. It is unlikely therefore that inhomogeneities are the dominant factor.

From a practical point of view, glasses are more flexible as an electronic material since chemical compositions are not limited by stoichiometry and also there are no grain boundaries as for polycrystalline solids. Further, unlike semiconducting crystals, the electrical conductivity of the glass is apparently insensitive to the presence of impurities. In Table I, the effect of zone-refining on the variation of electrical properties for the crystalline and glassy phases of the same material is shown.

(b) Photoconductivity of Non-Crystalline Selenium

Photoconductivity was first observed for non-crystalline 10 selenium by Weimer in 1950. The sample was prepared by condensing the vapor on a substrate. The spectral response of the non-crystalline sample as compared to that of the hexagonal crystal is shown in Fig. 1. Although the photo-

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currents are normally very small, because of the high dark resistivity (greater than 10¹⁴ ohm cm at 20°C), they are many times the dark current. From a scientific point of view, after Weimer's discovery, non-crystalline selenium immediately became a challenge with many unexplained properties; among them were: 1) Difference in photon energy for absorption and photoconductivity; 2) Origin of the carriers which are predominantly positive holes; 3) Mobility of the carriers.

From an industrial point of view, the high resistivity of non-crystalline selenium was desirable for the Xerographic 12 printing process . In the past 15 years it has therefore been widely studied. An excellent summary of published work has been made by Pell Almost without exception, research has . been concentrated on the mechanism of photoconduction and or attempts to explain electrical and optical properties by band theory. Important experimental data were obtained from drift mobility measurements, particularly by Spear , and from studies of space-charge limited currents . The electronic states in non-crystalline selenium at room temperature as indicated by optical, photoconductivity, and charge-transport measurements have been summarized recently by Hartke and and reproduced in Figure 2. Regensburger

(c) Structure of Non-Crystalline Selenium

Selenium exists in three known crystalline modifications : 1) A common hexagonal form which is known as grey or metallic

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selenium. The structure of this is made up of parallel infinite spiral chains. (2) \propto -monoclinic; and (3) β -monoclinic. These latter two modifications are made up of puckered Se₈ rings. The hexagonal form is the high temperature stable form and is insoluble in carbon disulphide whereas the monoclinic forms will dissolve in CS2. Molten selenium probably consists of a mixture of Se₈ rings, Se₆ rings, larger rings and chains of varying lengths The distribution of these various units is dependent on temperature and controversy exists between different workers regarding the polymeric units as well as their distribution. The melting temperature of selenium is 217 °C. A glass obtained by quenching the melt from different temperatures will therefore have different structures. It is also to be noted that if a Seg ring were to open there will be two unpaired electrons at the two ends of the resultant chain. Thus the number of unpaired electrons in a glass, say, will depend on the equilibrium distribution of the chain lengths for that particular sample. Unambiguous information on the detailed structures of glasses is not available from X-ray diffraction experiments. This is exemplified by the controversy which exists, for example, 19 who suggested Seg rings and larger rings of between Krebs about 1000 Se atoms to be the basic units of glassy selenium 21 and Richter who postulated Se₆ rings. The glass is

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metastable with respect to the crystalline phases and will devitrify through nucleation and subsequent crystal growth. The temperature at which devitrification will occur and the particular crystalline phase which forms are both sensitive to impurities, atmosphere and mechanical stresses. The glass transition temperature for selenium is approximately 30°C which means that above which, viscous flow will be perceptible.

The vapor species of selenium are temperature dependent. At low temperatures, molecular weight measurements and electron diffraction indicate that the vapor species are likely to be Se₆ rings. When the vapor is condensed on a substrate at 20°C, say, it is unlikely that the amorphous film which is formed will have a structure similar to that of a glass formed by quenching the melt to 20°C. Many workers who studied the photoconductivity of non-crystalline selenium considered their vapor-formed films to be glassy or vitreous. Lanyon , for example, considered his vapor-formed films as a "supercooled liquid". Amorphous selenium films have been deposited at various temperatures as high as 90 °C. At this temperature, the viscosity of selenium is 1×10^6 poise. It is a supercooled liquid since the glass transition temperature is only 30°C. On the other hand, many films were deposited on substrates at 20°C. This will of course make the meaningful correlation of film properties even more difficult. As for

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the glassy selenium, amorphous films will undergo transfor-Weimer , for instance, mentioned that his vapormation. formed amorphous films contained some monoclinic crystals. 25,26 Keck deposited amorphous films at temperatures between 30° and 75°C and reported that at lower temperatures, monoclinic crystals were present but at above 65°C, some hexagonal crystals were formed. Further, crystal growth could occur even at 20°C, the rate being 2700A per day. It is known that the electrical properties of the film are dependent on 12 temperature, duration and rate of deposition Figure 3 is a reproduction of the recent work of Griffiths. The bottom figure shows that the electron diffraction pattern of selenium film deposited on the (100) cleavage face of MgO at 90°C is diffuse. However, the transmission electron-micrograph shows widely separated spherical particles of about 2000A in diameter. Presumably these are non-crystalline droplets. Their separation certainly does not resemble the transmission picture of an ordinary glassy sample.

Further progress in understanding the electrical properties of non-crystalline semiconductors will be difficult if the structures of the materials themselves are neglected.

(d) Photoconductivity of Chalcogenide Glasses

Besides selenium, many chalcogenide glasses have been demonstrated to be photoconductors. Most of the pioneer work

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in this field have been carried out by B. T. Kolomiets of 28 Russia . Examples of some such glasses are shown in Table II. The results showed that the conductivity of a glass increases when the content of the heavier element is increased. In the glass-forming system of As, Se and Te, for example, the activation energy also decreases with increasing As₂Te₃. In Table III, it is seen that the activation energies determined from absorption and photoconductivity are similar although they differ somewhat from that obtained from conductivity.

In Figure 4, it is seen that the conductivity of glasses of the system As, Se and Te varies smoothly from the glassy state to the supercooled liquid state. In Figure 5, the photoconductivity of glassy and liquid $4As_2Se_3 \cdot As_2Te_3$ is seen to be quite similar. Photoconducting amorphous As_2Se_3 films 29 have been made by vapor deposition . The vapor deposition of a polycomponent system can generate an extra degree of complexity since the composition of the condensate may deviate from that of the original material. In Table IV, it is seen that the composition of condensed amorphous films are influenced 30 by evaporation temperature as well as substrate temperature .

IV. Phototropy

(a) Arbitrary Definition

Phototropy or photochromism generally refers to the phenomenon whereby a material changes color when exposed to

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radiation but reverts to its original color in the dark . Both organic and inorganic materials can exhibit phototropy. The phenomenon of solarization, for example, can be included within this broad definition. Results on solarization have 32been summarized by Weyl . In a silicate glass containing small amounts of Mn^{2+} and Fe^{3+} ions, for instance the absorption of a light quantum results in a purple coloration in which can be explained by the reactions:

$$Mn^{2+} + h\nu = Mn^{3+} + \bigcirc$$

 $Fe^{3+} + \bigcirc = Fe^{2+}$

and

Such processes are extremely slow. For practical applications, both the coloration and fading should be controllable. The coloration, in particular should be instantaneous and be sensitive to sunlight. Two types of phototropic inorganic glasses have been developed recently. They have both generated many interesting scientific questions. We will confine this survey to these two types of glasses.

(b) Phototropic Glasses containing Silver Halides

Glasses can be melted with some silver nitrate and sodium halides to give a homogeneous liquid. On controlled cooling and heat treatment, silver halide crystals can be precipitated. 33 Recently, Armistead and Stookey reported that for some glass compositions, if the silver content is between 0.2 to 0.7 percent, and if the silver halide crystals are controlled to 50 to 100A in diameter, a transparent glass is obtained. On

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exposure to sunlight or radiations in the UV, darkening will occur rapidly. This so-called activation and subsequent fading of the glass is exemplified by the results of Fig. 6 34 and Fig. 7 according to Smith . The activity of the glasses, typical compositions of which are shown in Table V, are enhanced by small amounts of copper ions.

Apparently, under irradiation, three processes occur simultaneously: darkening or creation of color centers; optical bleaching; and thermal bleaching. The darkening rates, and the optical components of fading rates, are considered to be described by first-order kinetics . The spectral sensitivity is dependent on the particular halide. Thus a glass with AqCl is sensitive in the 3000-4000A region whereas one with a mixture of AqCl and AgBr will be sensitive from 3000-5500A and one with a mixture of AgCl and AgI will be sensitive The darkening rate is apparently not very to about 6500A. sensitive to temperature but the fading rate increases rapidly with increasing temperature. The advantage of this inorganic phototropic system is that even after 300,000 cycles, no fatique was noticed . This is far superior to organic systems.

A tentative model to explain this interesting reversible 33 phenomena has been given by Armistead and Stookey . The primary photolytic reaction can be represented by:

 $Ag^+ + Cl^- + hy = Ag^\circ + Cl^\circ$.

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Thus an electron is freed from the Cl⁻ and is trapped by the Ag⁺. Such silver atoms, or very small aggregates of them, are the color centers. Sensitization by copper ions is attributed to:

 $Ag^+ + Cu^+ + h\gamma = Ag^\circ + Cu^{++}.$

The reaction products are metastable and will return to the original state when the incident radiation is terminated. This suggests that the Cl atoms cannot diffuse away nor will extensive aggregation of the silver atoms occur. The phenomenon is thus reversible as contrast to the normal photographic process which is irreversible. Aggregation of silver and the loss of chloride do occur in the latter process. Further support of this model is available from the similarity of the optical absorptions curves of such glasses to those for crystalline silver halides . The model is admittedly oversimplified and many observations are not yet explainable. For example, the composition of the base glass, and the thermal history are critical factors. Their roles are not yet understood. In addition to silver halides, it has been reported that silver molybdate and silver tungstate crystals can also 36 yield phototropic glasses similar to those described above

(c) Phototropic Glasses Prepared under Highly Reducing

Conditions.

Soda-silica glasses of high purity and melted under

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highly reducing conditions also show phototropic behavior 37when exposed to UV radiations . It appears that the reducing conditions are necessary and that traces of impurities can have large effects on the optical properties. Very careful 38experiments have been reported recently by Swarts and Pressau . For soda-silicate glass, the color center generated is located at 5700A and no deliberately added impurities is necessary although cerium and europium will enhance phototropy. Inhibition of phototropy can also be caused by about 200 ppm of titanium, vanadium or iron. The effects of cerium and europium are shown in Table VI. The parameter K¹ is defined by:

 $K^{1} = 1/d \log (T_{0}/T)$

where d is the thickness of the sample, T is the percent transmission of colored glass at peak of absorption band, and T_o is percent transmission of uncolored glass. Under sustained irradiation, the saturation value of K^1 is designated K_o^1 . Although the rare-earth ions can supply photoelectrons, their exact role is unclear since phototropic coloring is not accompanied by a reversible change in absorption of the reduced rare earth ions.

The change in transmittance of a typical soda-silica glass on UV irradiation is shown in Fig. 8. In Fig. 9, the effects of changing the alkali ions are shown. The position of the peak is apparently unaffected by the concentration of

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the alkali ions. For Na₂0-SiO₂ glasses, for instance, it is constant even when the Na₂O content is varied by as much as 22%. This observation suggests that the color centers in question is dependent on the structure of the glass. It is possible that the reduction reaction during melting generates oxygen-deficient sites which subsequently trap electrons and that the nature of this site is dependent on the nature of the alkali ion.

Typical photoresponse of this type of glass is shown in Figure 10. The formation of the color center is described by first-order kinetics whereas the fading mechanism follows a 38 second-order relation . The coloration was not studied as a function of temperature although the fading rate is very temperature sensitive. For instance, the fading rate at room temperature is about thirty times greater than that at -150°C. Unlike the silver halide phototropic glasses, these "reduced" glasses show fatigue on repeated irradiation. It is known that fatigue is partially due to an acceleration of fading rate. Since no information exists on the effect of fatigue on coloration, the exact causes are unknown.

A number of models to explain this phenomenon has been 39 discussed by Cohen . A trapped electron in an oxygen vacancy near an alkali ion or near a cation donor is considered unlikely. Cohen consideres that the most likely mechanism is one involving

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the photoreduction of a cation trace impurity, most probably the reduction of Ti^{4+} to Ti^{3+} . In view of the large effects of minute traces of impurities and the difficulty in preparing glasses totally void of impurities, the validity of any model must await further research.

Acknowledgments

I am grateful to Dr. S. Sakka and Mr. Roger Haskell for their assistance in the preparation of this review and to the National Aeronautics and Space Administration for support under Contract no. NSG-100-60. TABLE I

Type of conduction Д, д Glass 0.9 x 10⁻⁶ 1 × 10⁻⁶ Effect of Impurities on Glass and Crystal Conductivity (n⁻¹cm⁻¹) conduc-tion Type of q 凸 / (cm²/Vs) 15 I Crystal n (cm⁻³) 10¹⁶ I م (0⁻¹ cm⁻¹) 4×10^{-2} 60 before zone after zone refining refining As₂SeTe₂ **As2SeTe2** Material

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TABLE II

Conductivity ranges and photosensitivity limits of some Chalcogenide glasses. (After Kolomiets et al.²⁸).

Systems	Limiting values of conduc- tivity, ohm ⁻¹ cm ⁻¹	Range of Observed spectral peak po- sitions,µ
As ₂ Se ₃ - As ₂ Te ₃	10-13-10-6	0,6 - 1,25
As ₂ Se ₃ - Tl ₂ Se	10 ⁻¹³ -10 ⁻⁷	0,6 - 1,1
$As_2Se_3 - Sb_2Se_3$	10-13-10-12	0,6 - 0,9
Tl ₂ Se • As ₂ Se ₃ - Tl ₂ Se •As ₂ Te ₃	10-7-10-3	1,0 - 1,2
Tl ₂ Se • As ₂ Se ₃ - Tl ₂ Se • Sb ₂ Se ₃	10 ⁻⁸	0,95 - 1,15

TABLE III.Carrier Activation Energies of Glassy Semiconductors

	Activation energy (in eV), determined from						
Composition	adsorption band edge	photocon- ductivity	temperature dependence of conduc- tivity				
As ₂ Se ₃	1.57	1.64	1.96				
4As ₂ Se ₃ •As ₂ Te ₃	1.1	1.3	1.46				
3As ₂ Se ₃ •As ₂ Te ₃	1.05	. 1.20	1.37				
2As ₂ Se ₃ • As ₂ Te ₃	1.01	1.04	1.30				
As ₂ Se ₃ •As ₂ Te ₃	0.94	0.9	1.17				
9As ₂ Se ₃ ·llAs ₂ Te ₃	0.92	0.93	1.17				
^{2As} 2 ^{Se3} ·3As2 ^{Te3}	0.9	0.83	1.04				
As ₂ Se ₃ •2As ₂ Te ₃	0.89	0.83	0.95				
As ₂ Se ₃ ·3As ₂ Te ₃	0.86	0.74	0.94				
As ₂ Se ₃ •4As ₂ Te ₃	0.85	_	0.91				

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Composition of arsenic sulfide non-crystalline films as a function of deposition history. (After Tanaka et al.³⁰). of deposition history. (After Tanaka et al. TABLE IV.

position of glass sheet	ght % As Formula	0 - 65.0 As2S3.0-As2S2.5	0 - 65.0 As2 ^S 3.0 ^{-As2^S2.5}	0 - 61.0 As ₂ s _{3.5} -As ₂ s _{3.0}	0 - 61.0 As2 ^S 4.0 ^{-As2^S3.0}	5 - 54.0 As2 ⁵ .0-As2 ⁵ 4.0	5 - 54.0 As2 ^{S5.0-As2^S4.0}	5 - 48.5 As2 ^S 6.0 ^{-As2^S5.0}	5 - 46.0 As2S6.5-As2S5.5	0 - 40.0 As2 ^S 9.0 ^{-As2^S7.0}	0 - 65.0 As ₂ s _{3.5} -As ₂ s _{2.5}	0 - 57.0 Ås2S4.5-Ås2 ^S 3.5
Com	e C) Weig	61.(61.(57.(54.(48.	48.	43.5	41.5	34.(57.(51.(
control ation	Temperature of condensate deposit e r (°(410 ± 5	410 ± 5	380 ± 5	360 ± 5	340 ± 5	360 ± 5	360 + 5	350 ± 5	330 ± 5	360 ± 5	360 + 5
Temperature of distill	Temperature of batch container (°C)	530 ± 10	530 ± 10	530 ± 10	530 ± 10	530 ± 10	530 ± 10	490 ± 10	490 ± 10	490 ± 10	520 ± 10	520 ± 10
Composition	(mole ratio)	As2S3*	As2S3+S	As2S3+1.5S	As ₂ S ₃ +2S	As2S3+4S	As2 S3+8S	As253+8S	As2S3+8S	As2S3+8S	As+3S	As (anal) +

* The yield of glasses obtained from this batch composition was comparatively low.

** The arsenic-sulfur mole ratios are expressed in the form of formulas for each glass sheet.

TABLE V

Composition of Some Typical Photochromic 34 Silver HalideGlasses (After Smith).

Constituent	Glass l	Glass 2	Glass 3	Glass 4	Glass 5	Glass 6	Glass 7
Si02	60.1%	62.8%	59.2%	59.2%	60.1%	52.4%	51.0%
Na ₂ 0	10.0	10.0	10.9	14.9	10.0	1.8	1.7
A1203	9.5	10.0	9.4	9.4	9.5	6.9	6.8
^B 2 ⁰ 3	20.0	15.9	20.0	16.0	20.0	20.0	19.5
Li20	-		-	-	-	2.6	2.5
Pb0	_	-	-	-	_	4.8	4.7
Ba0	_	-	-	-		8.2	8.0
Zr02		-	-	-	-	2.1	4.6
Ag .	0.40	0.38	0.50	0.50	0.40	0.31	0.30
Br	0.17	-		0.60	0.17	0.23	0.11
Cl	0.10	1.7	,0.39	-	0.10	0.66	0.69
F	0.84	2.5	1.45	1.45	0.84	-	-
Cu0	-	0.016	0.016	0.015	0.016	0.016	0.016

Note: C

Compositions in weight percent; halogens are given as weight percent additions to that of the base glass.

TABLE VI.

Equilibrium Phototropic Response of Soda-Silica

Glass to 3660A Radiation. 38 (After Swarts and Pressau).

Additions	K_0^1 (cm ⁻¹)
None	0.025
0.1% Ce	0.28
0.005% Eu	0.70

FIGURE CAPTIONS

- Figure 1. Spectral response of photoconduction and optical absorption in selenium: (a) amorphous, and (b) hexagonal crystal. (After Garlick¹¹).
- Figure 2. Electronic states in vitreous selenium at room temperature as indicated by optical, photoconductivity, and charge-transport measurements. (After Hartke and Regensburger¹⁶).
- Figure 3. Transmission electron micrograph and electron diffraction pattern of selenium films deposited on various substrates. (After Griffiths²⁷).
- Figure 4. Temperature dependence of the conductivity of glasses and supercooled liquids: 1) 4As₂Se₃·As₂Te₃; (2) 3As₂Se₃·As₂Te₃; 3) 2As₂Se₃·As₂Te₃. (After Kolomiets⁹).
- Figure 5. Spectral distribution of the internal photoelectric effect in a glass of the composition $4As_2Se_3 \cdot As_2Te_3$ in the solid (1) and molten (2) states.
- Figure 6. Darkening and fading of typical phototropic glasses containing silver chloride at 23°C. (After Smith³⁴).
- Figure 7. Darkening and fading of typical phototropic glasses containing silver chloride at 46°C. (After Smith ³⁴).
- Figure 8. Spectral change in soda-silica glass irradiated by 2537A UV. (After Swarts and Pressau³⁸).
- Figure 9. The 5700A Color center in alkali-silicate glasses. (After Swarts and Pressau³⁸).
- Figure 10. Phototropic response of glasses containing the 5700A color center. (After Swarts and Pressau³⁸).

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FIGURE 2



FIG. 3. Se on (100) KBr. (a) Electron micrograph \times 8000. (b) Diffraction pattern.



FIG. 4. Se on (100) KCl. (a) Electron micrograph \times 8000. (b) Diffraction pattern.





Figure 4.









(%) NOISSIMENART

FIGURE 8



FIGURE 9

