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ELECTRICAL AND INFRARED PROPERTIES OF GLASSES IN THE SYSTEM Bi_2O_3-TeO_2

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ABSTRACT

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The region of glass formation in the binary system TeO_2-Bi_2O_3 has been defined. The electrical properties (resistance and capacitance) of these glasses, at room temperature and at liquid nitrogen temperatures, and the infrared transmission spectra have been determined.

Author

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SUMMARY

Glasses characterized by electronic conduction may find important use in space applications since high conductivity can be obtained in the glass without the presence of polarization. Glasses containing alkali ions may have the desired order of magnitude of conductivity, but the current carriers have polarization characteristics. The elimination of polarization in glasses having low temperature coefficients of resistivity may find application in surface junction detectors.

Also an advantage could be gained concurrently from the optical properties of semiconducting glasses. If these glasses are opaque to visible light but transmit infrared, they may be useful as infrared detection devices or in infrared signaling.

The region of glass formation in the binary system TeO_2-Bi_2O_3 has been defined. The electrical properties of these glasses have been determined at room temperature and at liquid nitrogen temperatures. The infrared transmission spectra have been determined.

INTRODUCTION

Inorganic glasses have generally been considered to be characterized by ionic conductivity. In recent years, however, glass compositions have been developed which have semiconducting properties. The majority of these are vanadate and phosphate glasses. Munakata reported glasses with specific resistances of 10^3 to 10^4 ohm-cm, the conduction arising from valence electron exchange between V^{4+} and V^{5+} (Ref. 1). Stanworth, Rawson, and Denton found that vanadium phosphate glasses have low resistivities (Ref. 2). Hamblen, Weidel, and Blair studied semiconducting glasses consisting of up to 85% (wt.) of V_2O_5 and the metophosphates of barium, lead, lithium, sodium, cadmium, and potassium (Ref. 3).

Other systems have led to a similar conclusion that inorganic glasses can be characterized by electronic conduction. McMillan indicated that $MnO \cdot Al_2O_3 \cdot SiO_2$ glasses are highly conducting (Ref. 4).

Tellurium-based glasses have semiconducting properties. Stanworth et al. found that the system V_2O_5-TeO_2 has glasses which have resistivities in the semiconducting range (Ref. 5). A glass consisting of 60% V_2O_5 and 40% TeO_2 has a resistivity that varies between 10^5 to 10^6 ohm-cm from room temperature to 150°C (300°F). This is less than one order of magnitude of resistivity. Chase and Phillips have studied the phase equilibria of this system, the boundaries of glass formation, and their semiconducting properties (Ref. 6). A glass consisting of 15% BaO, 31.4% TeO_2, and 53.6% V_2O_5 had a resistivity of $10^{6.8}$ at room temperature (Ref. 5).

Tellurate glasses have other interesting electrical properties. A composition consisting of 80% TeO_2, 14% PbO, and 6% BaO has been reported to have a dielectric constant of 25, which is large for an inorganic glass (Ref. 7).

Glasses characterized by electronic conduction may find important use in space applications since high conductivity can be obtained in the glass without the presence of polarization. Glasses containing alkali ions may have the desired order of magnitude of conductivity, but the current carriers have polarization characteristics. The elimination of polarization in glasses having low temperature coefficients of resistivity may find application in surface junction detectors (Ref. 3).

Advantage could also be gained concurrently from the optical properties of semiconducting glasses. If these glasses are opaque to visible light but transmit infrared, they may be useful as infrared detection devices or in infrared signaling (Ref. 4).

There is no work reported in the literature for combinations of either Bi_2O_3 and TeO_2 or of elemental Bi and Te in the glassy state. Glasses of these compositions may have electrical and optical properties which would find application in space as semi-conducting and optical devices; much effort has been devoted to the compound Bi_2Te_3 as a semiconducting device. In view of this, the boundaries of glass formation in the binary system Bi_2O_3-TeO_2 have been established. The electrical properties of the resultant glasses have been studied at cryogenic and room temperatures, and their infrared transmission spectra have been determined. Attempts to make glasses containing Bi and Te in the approximate composition of stoichiometric Bi_2Te_3 are also reported.

Acknowledgment

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EXPERIMENTAL PROCEDURE

Exploratory batches (100 grams) of chemically pure TeO_2 and Bi_2O_3 were mixed thoroughly in a Fisher-Kendall mixer. These mixes were then melted in porcelain crucibles in an electric furnace at 900°C (1652°F). The resultant melts were cast in preheated graphite molds and annealed at 250°C (482°F). After annealing, the melts were examined petrographically, by X-ray diffraction, and by electron diffraction to determine the degree of glass formation. A Perkin-Elmer Model 521 Spectrophotometer was used to determine the infrared transmission spectra of specimens that were one millimeter thick.

For the electrical measurements, samples were electroded with a silver preparation that was baked on the surface at 75°C (167°F). Electrical properties were measured at room temperature and at liquid nitrogen temperature. Capacitance was measured on a type 716C General Radio Capacitance Bridge at one kilocycle using the substitution method. Resistance was measured on a Keithley Model 610R Electrometer.

The temperature of crystallization was determined from differential thermal analysis (DTA) and from time-temperature studies by using draw trial samples.

Specimens of Bi_2Te_3 were melted and quenched in graphite molds. The resultant melts were examined for glass formation.

RESULTS AND DISCUSSION

Molten glasses were cast consisting of 25, 40, 60, 75, 90, 95, and 100% TeO_2 by weight (Table I). The specimens containing up to 60% TeO_2 crystallized; the 75 and 90% TeO_2 compositions formed glasses. X-ray and electron diffraction techniques revealed no crystallinity in these compositions. The 95% TeO_2 specimens were partially devitrified. The X-ray diffractograms exhibited the broad amorphous band characteristic of glass, but the two major reflections of paratellurite were distinguishable in the background. The 100% TeO_2 melts were completely devitrified. The paratellurite phase was the TeO_2 phase that cooled to room temperature.

The colors of the quenched melts are listed in Table I. The crystallized specimens containing up to 60% TeO_2 were yellow, and those that formed glass or partially devitrified were green. The glasses were opaque to visible light. The crystallized TeO_2 melts were white.

The infrared transmission spectra were determined for the 90% TeO_2 composition in the vitreous and crystalline states. Infrared transmission in the glass was good (FIG 1). The cutoff wavelength was at 7.5 microns. Absorption bands were detected at 3.3 and 5 microns. The cutoff wavelength of 7.5 microns shows a definite improvement over the limit of 4 to 4.5 microns of present infrared transmitting glasses. Since the crystallization temperature of the glasses was determined to be 550°C (1020°F), the 90% TeO_2 glass specimens were devitrified at this temperature in a seven-hour soaking period. They became white in color and were opaque to infrared.

The electrical property measurements are listed in Table II. The room temperature resistivities are of the order of 10^{10} ohm-cm, which is intermediate between the resistivities of good semiconductors (10^9 ohm-cm) and insulators. At 400°K (127°C or 261°F), the resistivity of the 90% TeO_2 glass is an order higher than at room temperature. This low temperature dependence of resistivity is in keeping with the observations reported by other investigators of semiconducting glasses. The resistivities at liquid nitrogen temperatures are an order lower than at room temperature. At room temperature, the dielectric constants were high, being in the vicinity of 26; at 77.4°K (-195.8°C), they are lower in value (Table II).

Bi_2Te_3 was melted at 900°C (1652°F) and quenched in air to observe the glassforming ability of elemental Te in combination with Bi. Each cast consisted of two coexisting phases: a devitrified mass and a transparent glassy surface layer, which was about 1/16-inch thick. The crystallized mass consisted of Bi_2Te_3 plus an unidentified phase. Indications are that Bi_2Te_3 may be quenched to the glassy state if a rapid cooling rate could be obtained.

TABLE I

EXPLORATORY COMPOSITIONS

Composition TeO_2 (wt. %)	Composition Bi_2O_3 (wt. %)	State	Color
25	75	Devitrified	Yellow
40	60	Devitrified	Yellow
60	40	Devitrified	Yellow
75	25	Glass	Green
90	10	Glass	Green
95	5	Partially Devitrified	Green
100	0	Devitrified	White

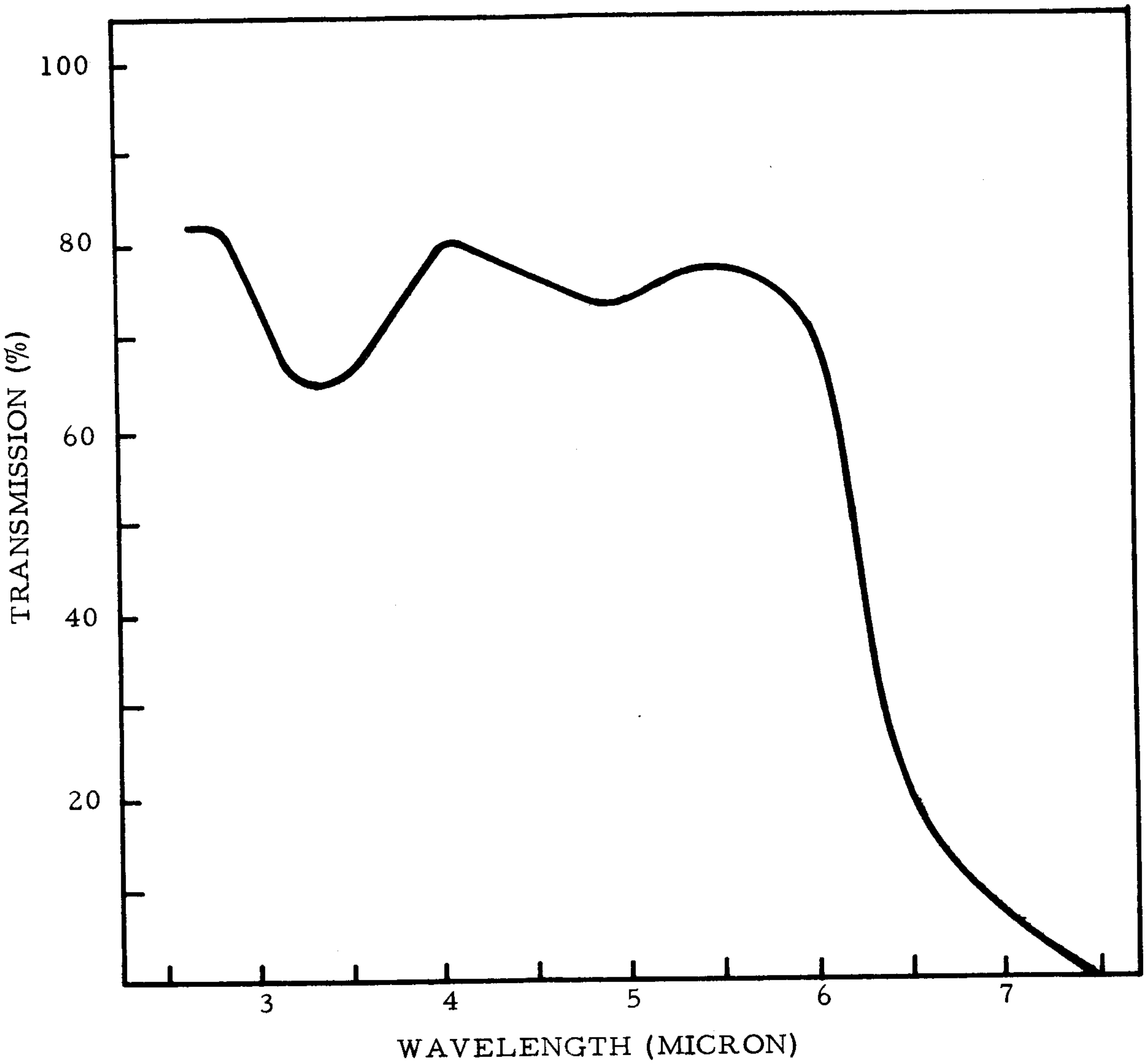

FIGURE 1. INFRARED TRANSMISSION SPECTRUM OF THE 90% TeO_2 - 10% Bi_2O_3 GLASS

TABLE II

ELECTRICAL PROPERTIES OF THE BISMUTH TELLURATE GLASSES

Composition TeO_2	Bi_2O_3 (wt. %)	Temperature (°K)	Resistivity (ohm-cm)	Dielectric Constant
75	25	77.4	3.6×10^{11}	23.9
		300	3.3×10^{10}	25.8
90	10	77.4	2.6×10^{11}	21.7
		300	5.7×10^{10}	26.1
		400	4.7×10^{9}	—

CONCLUSIONS

Tellurium-based glasses have shown promise as semiconductors having good infrared transmission. In this study, the region of glass formation of the binary system TeO_2 -Bi_2O_3 was investigated; the glass-forming area was from 60 - 75% TeO_2 up to 90 - 95% TeO_2. TeO_2 alone would not form a glass. The room temperature resistivities were of the magnitude of 10^{10} ohm-cm, and at liquid nitrogen temperatures, this increased to 10^{11} ohm-cm. The dielectric constants were high. Transmission in the infrared was good, the cutoff wavelength being at 7.5 microns. The glasses were opaque to visible light.

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This document has also been reviewed and approved for technical accuracy.

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