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BRIEF COMMUNICATION

Reversible Color Changes and Structural Implications of Microwave Melting Ion-Conducting Glasses

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Ionically conducting glasses in the AgI–Ag_2O–B_2O_3–SiO_2 system (e.g., 2AgI–Ag_2O–2($0.95B_2O_3 \cdot 0.05SiO_2$)) were prepared by melting in a domestic multi-mode microwave oven operating at 900 W and 2.45 GHz. Microwave heating resulted in rapid melting times ($\sim$ 2.5 min), while homogeneity in the quenched glasses was equivalent to or better than glasses obtained by conventional melting at 730°C. Microwave-melted glasses were reddish while the same composition melted in a conventional furnace was yellower. Remelting switched the yellower color to red upon microwave melting and the red color to yellower by furnace melting possibly due to the structural changes and/or differences in Ag^+ mobility suggested by solid state NMR data. © 1997 Academic Press

Inorganic glasses exhibiting very high ionic conductivities, or fast ion conducting glasses (FIC glasses), are being studied for use as solid electrolytes (1) and chemical sensors (2) because of their ease of fabrication and isotropic conductivity. Of these glasses, silver iodoborate glasses are known to exhibit both the highest ionic conductivities and the highest glass transition temperatures (3, 4). The room temperature mobility of silver ions can approach that of Na^+ in a 5% saline solution (5). In the system AgI–Ag_2O–B_2O_3, the composition 2AgI–Ag_2O–$2B_2O_3$ exhibits the highest T_g of about 300°C with a conductivity of about 10^{-3} (Ω cm^{-1}) at room temperature (3, 4). It has been suggested that mixing glass formers (e.g., SiO_2 to B_2O_3) may enhance ionic conductivities (6, 7). Glasses made with the eutectic ratio of SiO_2 to B_2O_3 may exhibit enhanced melting and improved homogeneity and durability. This work describes methods for producing ion-onducting glasses in the system AgI–Ag_2O–($0.95B_2O_3 \cdot 0.05SiO_2$) by melting in a microwave oven. We do not expect the minor addition of SiO_2 to have any significant effect on the T_g or conductivity reported above. The advantages of processing these glasses by microwave heating include rapid and uniform heating on a macroscopic scale and selective heating on the meso- and microscopic scale (8).

Preparation of raw materials was a key factor in creating homogeneous glasses. AgI, B_2O_3, Ag_2O, and SiO_2, obtained from Johnson Matthey, were ground together in the appropriate ratios with a mortar and pestle with acetone, dried, and passed through a 200 mesh screen oxidizer. To minimize silver reduction during heating (9), ammonium nitrate from Fisher Scientific Co. was then added such that it constituted 20 wt% of the total batch and then was ground with the powder with a mortar and pestle with acetone. The resulting mixture was dried overnight in a vacuum desiccator, passed through a 200 mesh screen, and pressed into pellets with a hand press for microwave melting. Powders to be conventionally melted were not pelletized. All batch sizes were 10 g, the minimum required to couple with microwave power and melt. Pellets melted more readily than powder in the microwave oven. Pelletization was not necessary for conventional melting. No more than 20 wt% of the batch could be composed of ammonium nitrate, as its boiling caused the pellets to crumble, decreasing the efficiency of the specimen's microwave power absorption. Less ammonium nitrate resulted in silver reduction.

Conventionally melted glasses were melted in a box furnace in air at 730°C. The powder was poured as a single charge into preheated alumina crucibles and allowed to melt for 20 min. Pellets for microwave melting were deposited in an alumina crucible at ambient temperature and placed in a fiber refractory-lined 900 W, 2.45 GHz domestic microwave oven (Sharp Electronics Corp.) and allowed to melt for 2 to 2.5 min at 100% duty cycle. All glasses were formed by quenching the melt between two copper plates at room temperature.

To determine which of our glasses' components coupled with microwaves, pellets of the individual components were pressed and each was placed into an alumina crucible inside the microwave oven. After heating for 4 min at 100% duty

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cycle, only the AgI pellet warmed and started to melt. This result indicates that, in our raw powder batches, only AgI crystals initially absorbed the microwave energy, which then heated the other components.

After 15–30 sec in the microwave oven the ammonium nitrate component of the pellets began to boil. This indicated that power was being absorbed, probably in a manner associated with size-limiting constraints which would decrease the expected heating rate (10, 11). Subsequently, a plasma was observed in the specimen. We suggest that the plasma resulted from the dielectric breakdown that occurred between adjacent AgI particles in the following manner. Mobility of Ag^+ increases with temperature, thus allowing an induced polarization of AgI crystals. Above a threshold voltage, breakdown can occur, causing localized fusing or melting. Such melting would increase the "characteristic length" which limits power absorption (9), resulting in more efficient microwave heating. In most cases, arcing subsided in about 10 sec and was followed by rapid heating. Power absorption probably followed the relation (10)

$$P_{\text{abs}} = K''VE^2/8\pi, \tag{1}$$

where the power absorbed (P_{abs}) equals the melt's imaginary dielectric constant (K'') times volume (V) times the power of the microwave field ($E^2/8\pi$). Complete melting was assured when the alumina crucible glowed red at points in contact with the specimen.

X-ray diffraction data were collected from the glass powder with a Siemens D-500 diffractometer using Cu$K\alpha$ radiation. The glasses proved to be X-ray amorphous. Fourier transform infrared analysis (FTIR) was performed on a Mattson Galaxy FTIR 3000 by mixing glass powder with mineral oil and measuring the spectra in transmission. Slabs of glass with parallel faces measuring ca. 0.5 mm in thickness were used for ultraviolet–visible spectroscopy (UV–VIS) using a Hitachi U-2000 spectrophotometer in transmission mode. ^{109}Ag NMR data were obtained at 18.65 MHz with a Chemagnetics CMX-400 spectrometer. Spin–lattice relaxation times (T_1) were measured by the saturation-recovery method and, at temperatures below 25°C, the magnetization was detected with a Hahn spin-echo. Within experimental error, all recovery curves were exponential. Spin–spin relaxation rates were determined from the linewidths by a least-squares fit of the frequency spectrum to a Lorentzian curve.

Remarkably, all glasses processed by microwave appear redder than conventionally melted glasses. The UV–VIS absorption spectra show a red shift in absorption edge of the microwave-melted glass of about 10 nm compared with the oven melted glass (Fig. 1). Further tests indicate that the color change is reversible upon remelting of the frit, i.e., redder glasses becomes more yellow after conventional melting, and yellower glasses turn more red after microwave melting. This result indicates that the color differences are not related to compositional differences between the glasses. Differences in the absorption edge are on the order of 90 nm for glasses of different compositions in this glass system and exhibited the similar color reversibility (12). Preliminary experiments using various quench rates and melting temperatures did not produce significant changes in glass color. The color differences may arise from differences between the glasses' structures. Since microwave melting involves significantly different mechanisms than conventional melting, we propose that local motion of the I^- and especially Ag^+ in the melt may have an effect on the structure of the (quenched) glass matrix.

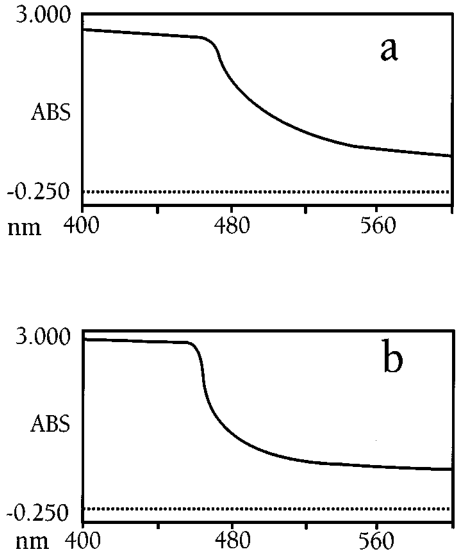

FIG. 1. UV–VIS absorption spectra for (a) oven-melted glass $2AgI–Ag_2O–2(0.95B_2O_3 \cdot 0.05SiO_2)$ and (b) microwave-melted glass $2AgI–Ag_2O–2(0.95B_2O_3 \cdot 0.05SiO_2)$. Note the red shift of ca. 10 nm in absorption upon microwave melting.

FTIR data collected for the diborate glass suggest a different BO_4 environment for microwave-melted glasses. Bands associated with BO_4 units (4) seem to change in relative intensity when compared with conventionally melted glasses (see Fig. 2). ^{11}B MAS-NMR spectra show no significant differences between glasses produced by these processing methods.

NMR results for ^{109}Ag suggest differences in the Ag^+ ion mobility between the conventionally melted and microwave-processed glasses (Fig. 3). The microwave processing results in spin–lattice relaxation times (T_1) about a factor of two shorter and, above about − 25 °C, a smaller linewidth. Otherwise, glasses produced by both methods show a broad T_1 minimum near 25°C and nonexponential dynamics (evident in the asymmetry of the T_1 curve about the minimum) that are similar to results reported in previous studies (13, 14). For both samples at all temperatures the NMR

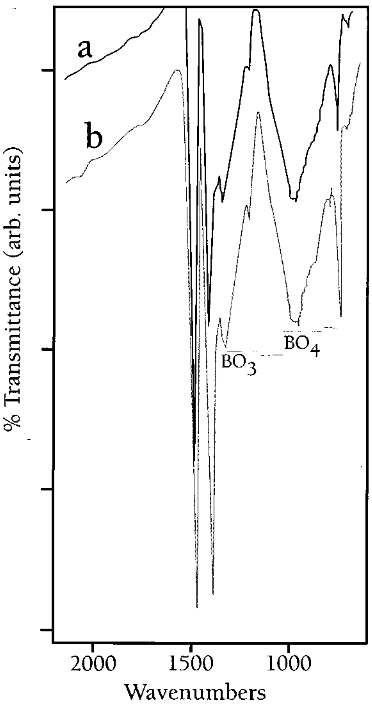

FIG. 2. FTIR spectra of (a) oven-melted glass $2AgI–Ag_2O–2(0.95B_2O_3 \cdot 0.05SiO_2)$ and (b) microwave-melted glass $2AgI–Ag_2O–2(0.95B_2O_3 \cdot 0.05SiO_2)$. Note the minor relative decrease in the absorption bands associated with BO_3 units in the microwave-melted glass.

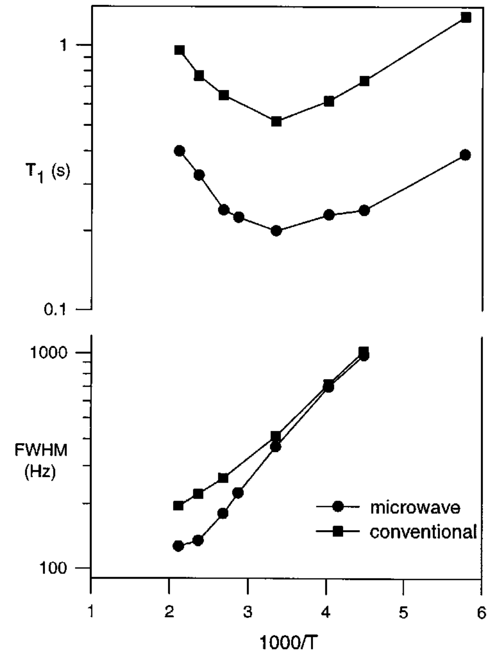

FIG. 3. Temperature dependence of the ^{109}Ag spin–lattice relaxation time (T_1) and the linewidth (full-width at half-maximum) for glasses of composition $2AgI–Ag_2O–2(0.95B_2O_3 \cdot 0.05SiO_2)$ produced by conventional and microwave heating.

spectrum contains a single Lorentzian-shaped peak, except near $-100°C$ where an additional broad peak was observed about 350 ppm upfield from the main peak (FWHM = 200 ppm), containing about 25% of the intensity. The origin of this second component is uncertain; it could correspond to a second population of immobile Ag^+ or part of a powder pattern arising from slowing of molecular reorientation.

In summary, glass of composition $2AgI–Ag_2O–2(0.95B_2O_3 \cdot 0.05SiO_2)$ can be prepared by microwave heating of pressed pellets in a multi-mode, low-power (domestic) microwave oven without the use of susceptors or supplemental heating. Microwave processing presents several advantages over conventional melting, including decreased power consumption, shorter melting times, and probably greater melt uniformity, due to convection induced by the larger thermal gradients across the batch. It is worth noting that lower concentrations of AgI in the batch do not melt well by microwave heating. Glasses with less than 15 mol% AgI or greater than about 40 mol% Ag_2O could not be formed in this manner. Optical absorption, IR, and NMR data show reversible differences related to the heating method that suggest microwave processing results in subtle local structural changes relative to conventionally melted glasses. Furthermore, this work suggests that it may be possible to use AgI as an internal susceptor in other types of glass batches to allow microwave melting where it would not normally occur.

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