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LETTER TO THE EDITOR

A Novel Method of Preparation of Inorganic Glasses by Microwave Irradiation[1]

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Microwave heating is shown to provide an extremely facile and automatically temperature-controlled route to the synthesis of glasses. Glass-forming compositions of several traditional and novel glasses were melted in a kitchen microwave oven, typically within 5 min and quenched into glasses. This is only a fraction of the time required in normal glass preparation methods. The rapidity of melting minimizes undesirable features such as loss of components of the glass, variation of oxidation states of metal ions, and oxygen loss leading to reduced products in the glass such as metal particles. This novel procedure of preparation is applicable when at least one of the components of the glass-forming mixture absorbs microwaves. © 1994 Academic Press, Inc.

Some new applications of microwave heating in the preparation of materials have been reported recently (1–4). The real advantages of the method appear to be rapidity of heating and selectivity in energy transfer from the microwave field. We would expect that the preparation of glasses by quenching the melts should be assisted enormously by this possibility, and in this letter we report the first such application of microwaves in the preparation of inorganic glasses.

The present method of preparation of glasses involves melting of the appropriate amounts of the ingredients (having a batch weight of 5–10 g) in an ordinary microwave oven (Batliboy Eddy) operating at 2.45 GHz up to a power level of 980 W. The homogeneous melts obtained after a few minutes of exposure to microwaves were quenched between polished, fused quartz slabs or stainless steel plates. In Table 1, we present the various glass compositions prepared by this simple method. While the first few glass-forming compositions in Table 1 (Nos. 1–13) have been reported in the literature, the others are reported here for the first time. Some of the important details such as the time required for the preparation and the method of quenching are also listed in this table. All the glass samples so prepared were found to be X-ray amorphous. The glass transition temperature, T_g, which is a characteristic feature of glasses, was determined by differential scanning calorimetry. The T_g values are listed in Table 1; T_g values for some of the glasses reported in the literature are given in parentheses. The T_g's of the known glasses prepared by conventional and microwave methods are comparable.

The preparation of sodium-oxide- and barium-oxide-containing glasses involved the use of carbonates (Na_2CO_3, $BaCO_3$), which readily decompose in the mixture, although the pure carbonates themselves do not absorb microwaves. The completion of the decomposition of carbonates was confirmed by the absence of infrared absorption in the region 1500–1800 cm^{-1} in the final glass. It is likely that the microwave absorber (V_2O_5) in the mixture efficiently transfers heat to the carbonates and assists the decomposition.

It is noteworthy that the entire melting operation of the various compositions listed in Table 1 took under 10 min. The melts, once formed, stay without any change or any further escalation of temperature, except in the cases of fast ion conducting glass compositions (FICs) where longer exposures to microwaves (at the maximum power level of 980 W) produced sparking on the surface of the melts. The melt temperature generally levels off as indicated in Fig. 1 in the case of two compositions. The leveling-off temperatures are evidently different for various mixtures. This is a unique advantage, since the temperatures of the melts are self-regulated.

When the glasses were ground and exposed to microwaves, there was no microwave absorption except in AgI-rich FIC glasses. Microwave absorption thus appears to be an intrinsic property of some of the starting materials.

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TABLE 1
List of Glasses Formed Using Microwave Heating

No.	Glass system	T_g (K)	Preparation conditions			Ref.
			Time (min)	Crucible used	Type of quenching	
1	xPbO:(100-x)V_2O_5 [x = 40–50]	520–522	5	S	SSPQ	(7, 8)
2	$50GeO_2$:$50V_2O_5$	491	6	S	SSPQ	(7)
3	$33BaO$:$67V_2O_5$	551	5	S	SSPQ	(7)
4	$30Na_2O$:$30B_2O_3$:$40V_2O_5$	470(468)	6	S	SSPQ	(9)
5	$50AgI$:$25Ag_2O$:$25MoO_3$	348(340)	5	S	QPQ	(10)
6	$50AgI$:$25Ag_2O$:$25WO_3$	419(427)	6	S	QPQ	(10)
7	$50AgI$:$25Ag_2O$:$25CrO_3$	298(294)	3	S	QPQ	(10)
8	$50AgI$:$33Ag_2O$:$17GeO_2$	392(402)	5	S	QPQ	(11)
9	$60AgI$:$20Ag_2O$:$10MoO_3$:$10WO_3$	345	3	S	QPQ	(12)
10	$40AgI$:$30Ag_2O$:$15WO_3$:$15B_2O_3$	460	5	S	QPQ	(13)
11	$60AgI$:$20Ag_2O$:$10MoO_3$:$10V_2O_5$	351	2	S	QPQ	(14)
12	$30CuI$:$35Cu_2O$:$35MoO_3$					
	In air	390	3	S	SSPQ	
	In NH_3 atm.	393(404)	10	S	SSPQ	(15)
13	xB_2O_3:(45-x)PbO:$55V_2O_5$ [x = 0–20]	520–515	7	S	SSPQ	(16)
14	$xSiO_2$:(45-x)PbO:$55V_2O_5$ [x = 0–15]	520–531	5	PZ	SSPQ	
15	xZnO:(45-x)PbO:$55V_2O_5$ [x = 0–40]	520–541	5	S	SSPQ	
16	$xMoO_3$:(45-x)PbO:$55V_2O_5$ [x = 0–35]	520–515	5	S	SSPQ	
17	xCuO:(45-x)PbO:$55V_2O_5$ [x = 0–20]	520–536	5	S	SSPQ	
18	xWO_3:(45-x)PbO:$55V_2O_5$ [x = 0–15]	520–531	5	S	SSPQ	
19	xBi_2O_3:(45-x)PbO:$55V_2O_5$ [x = 0–10]	520–537	4	S	SSPQ	

Note. SSPQ, stainless steel plate quenching; QPQ, quartz plate quenching; S, silica crucible; PZ, porous zirconia crucible.

Since AgI is a microwave absorber and it is likely to be structurally and compositionally continuous in the glasses, AgI-rich glass powders also exhibit microwave absorption.

Among the materials examined in this study, we find that V_2O_5, WO_3, CuO, ZnO, silica gel, AgI, and CuI can couple with microwave energy efficiently. These materials can individually be heated up to 1000 K or more by microwave irradiation. However, the maximum temperature reached in microwave irradiation does not appear to exceed about 1250 K [observed in Si and C mixtures as reported elsewhere (3)]. The advantage of microwave heating is that the solid material gets heated throughout the interior, unlike in conventional heating where heat travels from the surface inward. Uniformity of heating (without gradients) is achieved by the fine scale of mixing of the microwave absorber in the initial mixture. The container gets heated only by the dissipated heat, since it is in contact with the hot powder or melt. The entire process is fast, and kinetically slow processes such as oxidation by the ambient air and reduction due to slow loss of oxygen do not seem to take place.

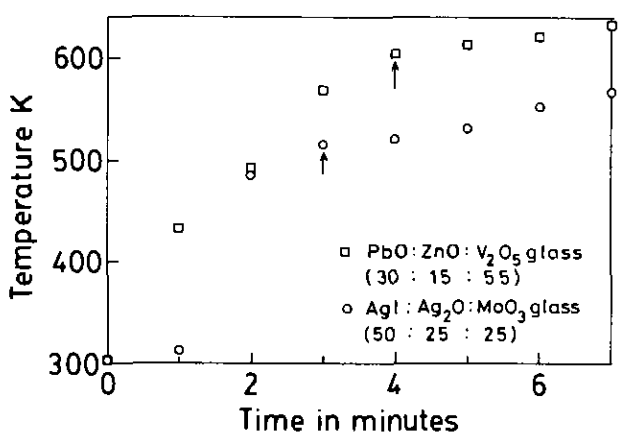

FIG. 1. Dependence of temperature on microwave heating time for two glass compositions. The temperature is measured in between microwave exposures using a Cr–Al thermocouple. The temperature and the time at which the mixtures melted are indicated by arrows.

In CuI-based glasses (No. 12 in Table 1), which are fast ion conductors, copper is reported to be oxidized under normal preparative conditions to the extent of 12–15%. These glasses were therefore prepared by two procedures: (i) microwave melting of the mixtures in an NH_3 atmosphere (produced by simultaneously decomposing a mixture of ammonium metavanadate and V_2O_5 in another crucible kept alongside in the microwave oven) and (ii) microwave melting in air. The Cu^{2+} formed in the glasses were estimated using ESR spectroscopy (by double inte-

gration of the ESR trace of Cu^{2+} in the glasses). The Cu^{2+} content was found to be 0.69 and 0.9%, respectively, in these two preparations, which is far less than the 15% Cu^{2+} formed by oxidation in the conventional preparation of these glasses in open atmosphere (5). The room-temperature conductivity value (0.5×10^{-1} S/cm) of the microwave-prepared glass (in an NH_3 atmosphere) was in good agreement with that of a glass of the same nominal composition prepared in sealed tubes (0.1×10^{-1} S/cm) (6).

Microwave absorption has generally been regarded as being due to high dielectric loss (tan δ) at high frequencies, which is a feature of ionically conducting (lossy) materials. Since rotational excitations also fall in the regime of microwaves, it is possible that some of the glass-forming mixtures avail of this mode of microwave absorption. Since microwave absorption in a material characteristic, the initial solid mixtures and their melts exhibit different microwave absorption features. Thus, when melting occurs, microwave absorption appears to drop abruptly in all the melts examined here. Clearly, a variety of interesting glasses can be prepared conveniently by this simple method if the initial mixture contains at least one microwave susceptor.

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