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**SURFACE MODIFICATION OF SODIUM ALUMINOSILICATE GLASSES USING MICROWAVE ENERGY**

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**ABSTRACT**

Microwave energy has been used in ion exchange reactions for four sodium-aluminosilicate compositions. The exchangeable cation in the glass ( $\text{Na}^+$ ) was replaced at the surface by a larger atomic radii cation ( $\text{K}^+$ ). Secondary ion mass spectroscopy (SIMS), electron microprobe analysis (EMP) and x-ray mapping were used to evaluate the effect of microwave heating on the extent and rate of ion exchange in comparison to conventional heating.

**INTRODUCTION**

Glasses have been known to man for thousands of years, and their applications have gone from rudimentary purposes to top-of-the-line technology. Today's world has broadened the use of oxide glasses in diverse and far-ranging fields such as telecommunication, electronics and aerospace. The intrinsic brittle behavior of oxide glasses and their catastrophic failure have been major drawbacks to their use in applications which require mechanical strength and durability.

In general, brittle materials fail to exceed more than a fraction of their theoretical strength. This characteristic behavior has triggered extensive research aimed at developing higher strength bodies. The desired strength can be achieved by various methods that can be split into two broad categories; bulk and surface techniques. The surface techniques aim at developing a compressive stress distribution on the glass surface. The resulting strength becomes the original strength of the glass plus the strength added by surface compression. These surface modification techniques can be summarized as the following: thermal strengthening, chemical strengthening, surface crystallization, thin coating, cladding, etching and related techniques[1].

Strengths greater than those obtained by thermal toughening can be reached by chemical strengthening. However, any significant strengthening is unlikely to be achieved within times compatible with the modern production rates[2], due to the slow reactions involved in the ion exchange process. For this reason, chemical strengthening techniques are applied where safety predominates over economics.

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Within our microwave processing center at the University of Florida, we have been investigating techniques that could enhance ion exchange reactions. Processes by which deeper penetration of a selected ionic species into a glass matrix can be achieved when compared to the conventional techniques.

The present study was undertaken to evaluate the effect of microwave radiation on the ion exchange reactions of  $K^+$  for  $Na^+$  in four different compositions of sodium aluminosilicate glass. For the four chosen glass compositions, we are reporting the penetration depth and the relative concentration of the alkali ions achieved after processing. A comparison is made of the penetration depths accomplished by microwave processing and those achieved by conventional processing for each of the sodium aluminosilicate compositions.

The sodium aluminosilicate system was found to be the system of choice for surface modification using microwave energy. Indeed, this system exhibits major structural changes accompanied with significant dielectric properties differences when the ratio of alumina to alkali ion is taken as a variable.

## THEORETICAL BASIS

### Ion Exchange Process

Ion exchange reactions in oxide glasses are limited substantially to alkali ions[3]. Ion exchange is a process by which at least two ionic species exchange with each other, as shown by



Where the subscripts represent glass and molten salt solution, respectively. The driving force for the reactions is a concentration gradient which is the natural phenomenon of mixing. A constructive approach to this phenomenon is to partially replace an ionic species pre-existing within a given glass matrix by another with a larger radius. The exchanged glass layer tries to expand. It cannot, due to restraint from the underlying bulk glass. The surface is thus put under compression.

The process mentioned above is diffusion controlled. The concentration of the selected species and its penetration depth are of primary importance and are related directly to the rate of exchange. The objective was to evaluate the effect of microwave heating on the extent and rate of ion exchange in comparison to conventional heating.

### Microwave Processing

It is reported in the literature that an array of ceramic products have been heat treated in the presence of microwave radiation. Characterization of these materials revealed major microstructural differences when compared to those conventionally processed. It is our belief that the addition of activations other than those of a thermal nature, namely electrical and magnetic, account for the observed property differences.

Microwave heating is intrinsically different from conventional heating. It is a volumetric heating in which the sample itself generates heat due to the ability of the electric and magnetic fields to polarize molecules and the inability of the molecules to keep up with the rapid reversal of the fields [4]. The resulting dielectric losses account for the volumetric heating. Microwave radiation falls within a range of frequencies at which the orientation polarization is the predominant polarization mechanism. There are losses from the other polarization mechanisms due to the extended tails of the loss curves which are different for each given system.

In glasses, the ionic dipole motions can be split into two categories: (1) deformation

polarization in which permanent dipoles oscillate under an applied electric field and (2) defect associated dipoles which oscillate between several equilibrium positions. The temperature of glass plays an important role because, at high enough temperatures, the conductivity of the glass is such that a discharge of the induced dipoles occurs.

## EXPERIMENTAL

The selected compositions in the sodium aluminosilicate system are shown in Table 1. The glasses that were studied had a constant concentration of alkali ions (15mol% of Na<sub>2</sub>O). The molar ratio of alumina to sodium oxide, defined as  $\Gamma$ , was taken as a variable and was equal to 0.2, 0.5, 1.0 and 1.1.

The glasses were melted in alumina crucibles at 1500°C for 24 hours and annealed at 600°C for 5 hours. The alumina crucibles were cut to provide workable samples. Care was taken to disregard the glass areas that were in contact with the crucible walls. The faces that were to be ion exchanged were polished to a 1 $\mu$ m finish. The samples were coated with a potassium containing medium<sup>1</sup>.

Electron microprobe analysis was used to evaluate the penetration depths involved in the ion exchange reactions. The change of x-ray intensity of the alkali species was found, by several investigators, to be related to time and to be proportional to the electron beam current, specimen temperature and bulk composition of the glass [5].

In the present study, we avoided the use of a stationary electron beam and conducted the analysis using a scanning beam sweeping a 100 $\mu$ m by 1.5 $\mu$ m area. The samples edges to be analyzed were polished to a 1 $\mu$ m finish.

The ion exchange reactions were performed in a multimode microwave oven<sup>2</sup> (2.45 GHz) using hybrid heating [6,7]. The samples were placed in an insulating material lined with a microwave susceptor which, in turn, heated the sample. The reactions temperatures were controlled with an error of  $\pm 6^\circ\text{C}$  using an Inconel-shielded K-type thermocouple.

Table 1. Compositions of the Glasses Investigated.

Components	$\Gamma=0.2$	$\Gamma=0.5$	$\Gamma=1.0$	$\Gamma=1.1$
Na <sub>2</sub> O	15.0	15.0	15.0	15.0
Al <sub>2</sub> O <sub>3</sub>	3.0	7.5	15.0	16.5
SiO <sub>2</sub>	82.0	77.5	70.0	68.5

## RESULTS AND DISCUSSION

The results for the interdiffusion of Na<sup>+</sup>↔K<sup>+</sup> at 400°C for 30 min are shown in Figure 1. The

<sup>1</sup> Ceramcoat, G-C International Corp., Scottsdale, AZ 85260

<sup>2</sup> Radarline Model QMP-2101B-6, Raytheon Co., Waltham, MA.

general trend is an increasing potassium penetration in the different glass compositions as  $\Gamma$  increases from 0.2 and 0.5 to 1.0. As  $\Gamma$  goes above 1.0, interdiffusion appears to decrease.

If we define  $P_m^i$  and  $P_c^i$  as the respective penetration depths of microwaved and conventionally prepared samples, and  $\Delta P_{m,c}^i$  as the difference between these penetrations for the (i) compositions. We found that  $P_m^i$ ,  $P_c^i$  and  $\Delta P_{m,c}^i$  all reach a maximum in the  $\Gamma=1.0$  composition.

Initially, as  $Al_2O_3$  is introduced into a binary alkali-silicate glass, only  $AlO_6^-$  is formed [8]. As  $\Gamma$  increases, there is more formation of  $AlO_6^-$  along with  $AlO_4^-$ . The ratio  $AlO_6^-/AlO_4^-$  decreases with further increase of  $\Gamma$ . The  $AlO_6^-$  concentration goes through a maximum, the point

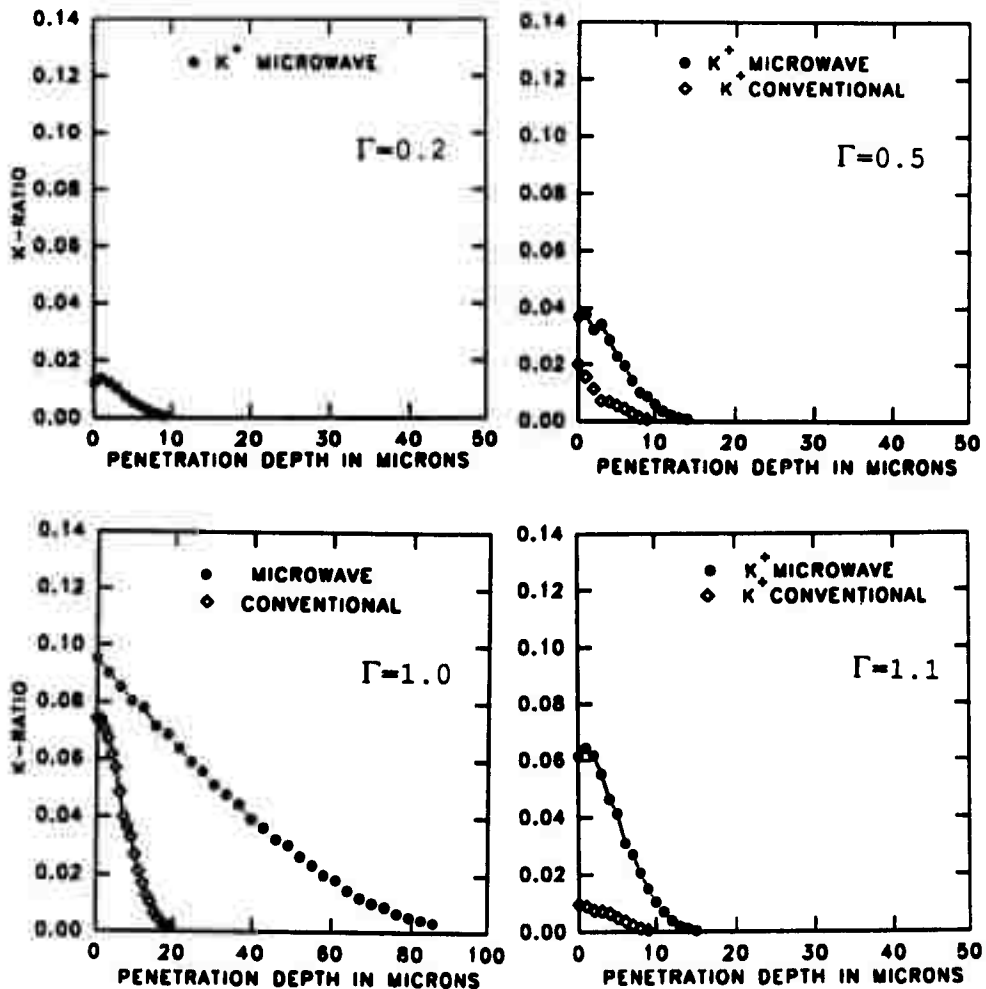


Figure 1. Penetration depths(in  $\mu m$ ) of potassium into the glass compositions. K-ratios are relative to tugtupite for sodium and biolite for potassium.

where the activation energy for alkali diffusion is at a maximum. With further increasing values of  $\Gamma$ , mainly  $\text{AlO}_4^-$  groups will be formed [9], and both the electrical and steric interactions of the alkali ion with the glass network decrease. This is reflected by a rise in the alkali ion diffusion coefficients. Increasing the amount of alumina in the alkali silicate glass reduces the number of oxygens which are only bound to one network former, either  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$ . The number of non-bridging oxygen ions decreases to a minimum for  $\Gamma=1.0$  in which all the alkali ions are positioned to the negative charge of the  $\text{AlO}_4^-$  groups [10]. The activation energy for diffusion reaches a minimum for  $\Gamma=1.0$ . For compositions having  $\Gamma>1.0$ , the alumina can no longer be present only as  $\text{AlO}_4^-$  tetrahedra because of the absence of compensating positive charges. Thus,  $\text{AlO}_4^-$  triclusters groups will form. The increasing packing density makes it more difficult for the alkali ion to move out of or through the triclusters. This translates into a small diffusion coefficient [10]. This trend of interdiffusion is retorted by the conventional curves in Figure 1.

The dielectric properties of sodium aluminosilicate glasses at microwave frequencies exhibit changes when the compositional factor,  $\Gamma$ , is taken as a variable [11]. It was found that the temperature-dependent losses were due to the broad tail of the migration loss mechanisms. The temperature-independent losses are due to the deformation losses and are not associated with the concentration of the non-bridging oxygens. Those losses were attributed to resonance with vibrational modes involving large atomic grouping.

The dielectric losses followed the structural model and were found to increase with increasing values of  $\Gamma$  up to  $\Gamma=1.0$  at which the dielectric losses exhibit maximum values. When compared to conventionally heat treated samples,  $P_m^1$  can be correlated to the loss tangent of each of the glass compositions [11].

Two characterization techniques were used to verify the findings of the electron microprobe analysis. Figures 2 and 3 correspond to x-ray mapping and SIMS depth profiling of the  $\Gamma=1.0$  composition for microwaved and conventionally processed samples. As shown, there were higher surface concentrations and deeper penetration of the  $\text{K}^+$  into the  $\Gamma=1.0$  glass composition that were heat treated in the presence of microwave radiation.

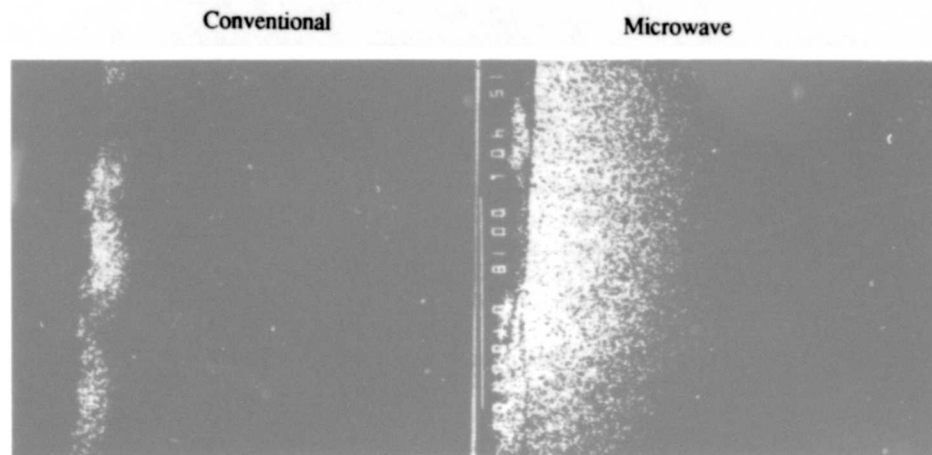


Figure 2. X-Ray mapping of potassium in the  $\Gamma=1.0$  composition

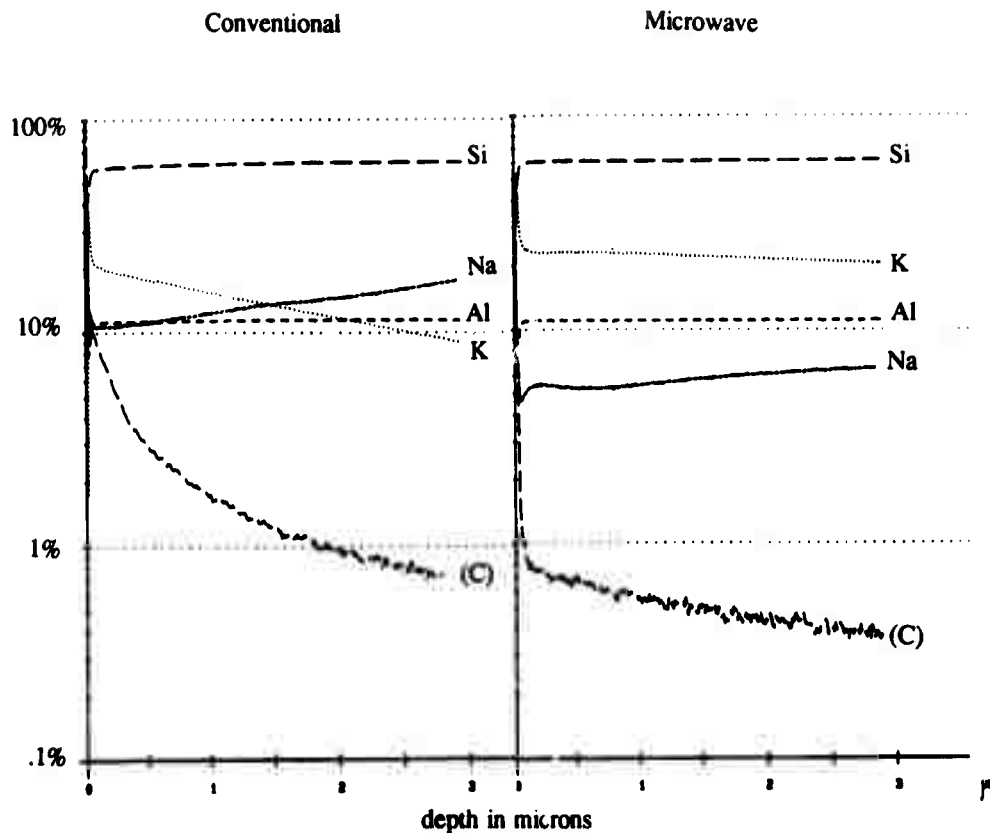


Figure 3. SIMS depth profiling on  $\Gamma=1.0$  composition

## CONCLUSIONS

It is premature to give definite reasons for the high interdiffusion in the case of microwave heating. We believe that the vibrational frequency of an ion within a potential well is increased due to the electric field of the microwave radiation. The rapid reversal of the electric field might be increasing the local temperature of the ion, thus making the ionic jump out of the well easier. More work needs to be done in order to understand fully how microwave radiation affects interdiffusion.

The ion exchange process using microwave energy provides a means by which deeper penetration and higher surface concentrations can be achieved, as compared to conventionally ion exchanged glass. The sodium aluminosilicate compositions having  $\Gamma=1.0$  exhibited the deepest penetration of  $K^+$ , as compared to the compositions  $\Gamma=0.2, 0.5$  and  $1.1$ . A correlation can be drawn between the dielectric losses of the different compositions and their corresponding  $K^+$  depths of penetration.

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