ELECTRICAL RESISTIVITY AND STRUCTURE OF GLASSES IN THE $xK_2O{\cdot}(1-x)Na_2O{\cdot}4SiO_2$ System

W. E. Martinsen and T. D. McGee

School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, Oklahoma, and Department of Ceramic Engineering, Iowa State University, Ames, Iowa

Glasses in the $xK_2O{\cdot}(1\text{-}x)Na_2O{\cdot}4SiO_2$ system exhibit the mixed alkali effect. That is, as K_2O is replaced by Na_2O, while the total mole per cent of K_2O+Na_2O is kept constant, many physical and electrical properties show disproportionate changes. For example, the D.C. electrical resistivity, ρ, changes as shown in Figure 1.

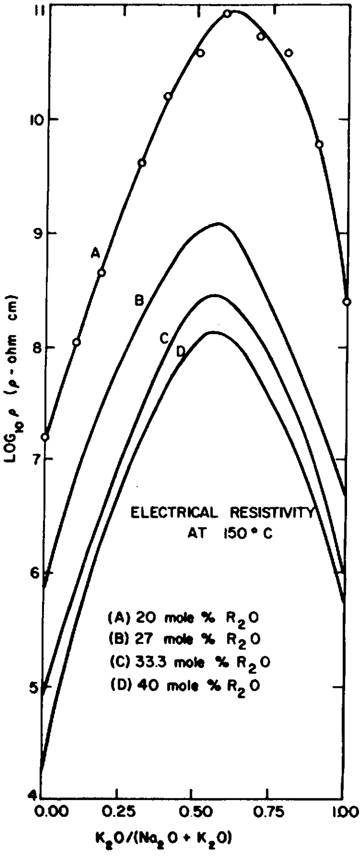

FIGURE 1. Direct current electrical resistivity as a function of composition. ($R_2O = Na_2O + K_2O$). A. From this research. B, C, D, From Mazurin and Borisovskii (1).

Many explanations have been proposed for this phenomenon, but little experimental evidence exists to substantiate these theories. This study was undertaken to see if any correlation existed between the electrical resistivities of these glasses and their microstructures as observed by electron microscopy.

Eleven glasses of varying $K_2O:Na_2O$ ratios, all with mole per cent $K_2O + Na_2O$ equaling 20%, were prepared from reagent grade silicic acid, anhydrous sodium carbonate, and crystallized potassium carbonate by melting at 1600 C in an induction furnace. After cooling, a portion of each glass was ground and polished to form a flat disk with parallel faces. One-quarter-inch diameter silver electrodes were applied to both sides of the disks by vacuum evaporation. Each disk was then placed in a small furnace at 150 C and the D.C. resistivity was measured by the drop in voltage across the specimen by using a Keithley electrometer.

Electron microscope samples were made by replication of etched fracture surfaces. The etching was carried out by a 30 sec immersion in a solution of 1% HF and 1% HCl in distilled water. The etched surface was replicated with collodion, shadowed with chromium, and backed with silicon monoxide in a vacuum evaporator. The stripped replicas were placed on copper grids and the collodion was removed with amyl acetate. All samples showed signs of phase separation as seen in Figure 2. The disconnected phase etched faster and, therefore, was higher in alkali than was the matrix.

Samples of three of the glasses were crushed and leached with boiling water for

Proc. Okla. Acad. Sci. 51: 100-101 (1971)

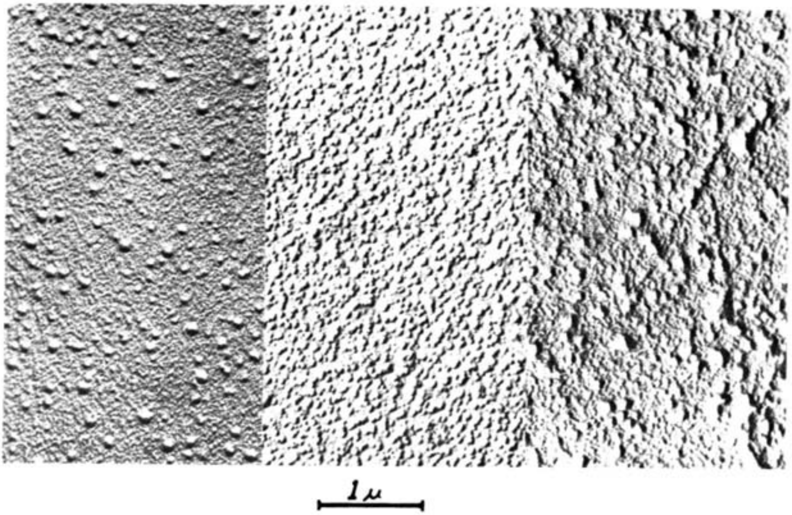

FIGURE 2. Electron micrographs of etched fracture surfaces. From left to right, the $K_2O/(Na_2O + K_2O)$ ratios for these three glasses are: 0.00; 0.50; and 1.00.

TABLE 1. *Na:K ratios (mol basis).*

Leached Portion	Overall Glass
10.33 : 1.00	4.00 : 1.00
3.08 : 1.00	0.67 : 1.00
1.02 : 1.00	0.25 : 1.00

30 min. The solutions were analyzed by flame photometry to determine the Na:K ratio. The results are shown in Table 1. Results indicate that the dispersed, high alkali phase has a higher ratio of Na to K than the overall composition. Thus, the smaller and more mobile sodium ions are more likely to be found in the dispersed phase, thereby leaving the potassium ions as the major current carriers in the matrix. This finding was predicted by Charles (2) and by Warren and Pincus (3), and it could well account for the tremendous increase in resistivity. Not only are fewer current carriers present in the continuous phase, but the majority of those that are present are the species of lower mobility. However, it is not possible at this time to say conclusively that this is the proper explanation of the mixed alkali effect. Other alkali silicate systems and other compositions need to be investigated to see if they exhibit equivalent behavior.

REFERENCES

1. O. V. MAZURIN and E. S. BORISOVSKII, Soviet Phys. Tech. Phys. 2: 243-254 (1957).
2. R. J. CHARLES, J. Am. Ceram. Soc. 48: 432-434 (1965).
3. B. E. WARREN and A. G. PINCUS, J. Am. Ceram. Soc. 23: 301-304 (1940).