PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

TOF-SIMS Analysis of the Glass Phase in Alumina-Zirconia-Silica (AZS) Materials

Introduction

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) offers important capabilities for the analysis of small regions in glass and ceramic materials. The combination of submicron spatial resolution, parts-per-million sensitivity, and the ability to analyze electrically insulating materials makes TOF-SIMS capable of performing surface analysis measurements which are difficult or impossible with other analytical techniques.

Alumina-Zirconia-Silica, commonly referred to as AZS, is a refractory glass-ceramic material. A major industrial application of AZS is for lining the walls of glass production furnaces. Many of the physical properties of AZS are determined by the composition of the glass phase. However, characterization of this glass phase presents a difficult analytical challenge. The glass (silica) phase is small, with domain sizes from submicron up to 30 µm. During analysis, several of the alkali components in the glass (e.g. Na, K) are mobile under continuous charged particle beam bombardment. Therefore, good charge neutralization is necessary to obtain accurate quantitative results. In addition, low atomic weight elements are present at low concentrations and are of primary interest. This makes it difficult to use X-ray detection methods such as SEM-EDS and makes TOF-SIMS the analysis method of choice.

Experimental

The AZS materials were prepared as polished cross-sections. Glass standard reference materials (SRM 93a, 1411 and 1412) were purchased from the National Institute of Standards and Technology (NIST). All TOF-SIMS data was acquired using a 25 keV Ga^+ liquid metal ion gun pulsed at 5 kHz. Charge neutralization was accomplished by interleaving a pulsed 20 eV electron gun. Depth profiles were acquired using two sets of ion beam conditions. Sputtering was accomplished by rastering a 2 nA 25 keV Ga^+ DC beam over a 500 µm x 500 µm area for 30 sec/cycle. Analysis was performed by rastering a pulsed Ga^+ beam over a 200 µm x 200 µm area in the center of the sputtered area.

Results and Discussion

A secondary electron image acquired with the Ga^+ beam is shown in Figure 1. This image illustrates the size and distribution of the three phases in an AZS material. The main goal of this analysis was to quantify the boron level in the glass phase of materials from the three different manufacturers.

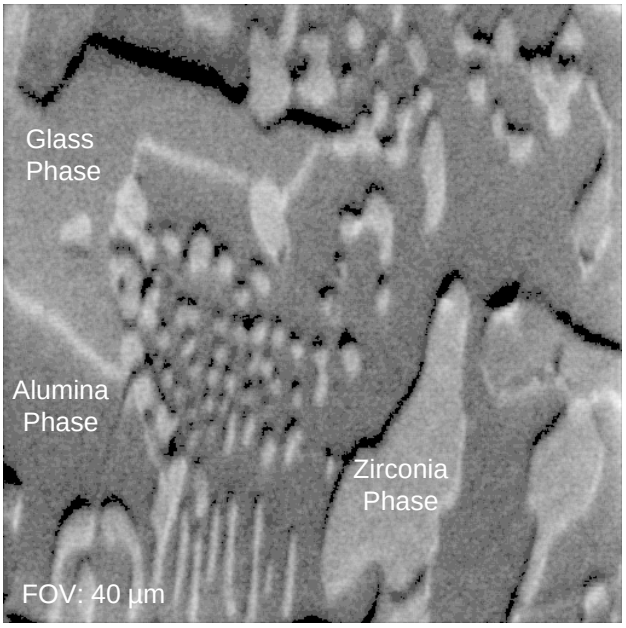

Figure 1. Ion beam induced secondary electron image.

Figure 2 contains TOF-SIMS images of Al^+, Zr^+, Si^+, and Na^+. Aluminum is present in both the alumina and glass phases. Zirconium is present in two phases, pure zirconia and a coprecipitated alumina-zirconia phase. Silicon and sodium are present only in the glass phase. These images clearly demonstrate that TOF-SIMS has sufficient spatial resolution to limit the analysis to only the glass phase, thereby allowing quantitative analysis for AZS materials with different physical properties. Prior to making the TOF-SIMS measurements, the polished surfaces were depth profiled until the elements reached a steady state peak intensity.

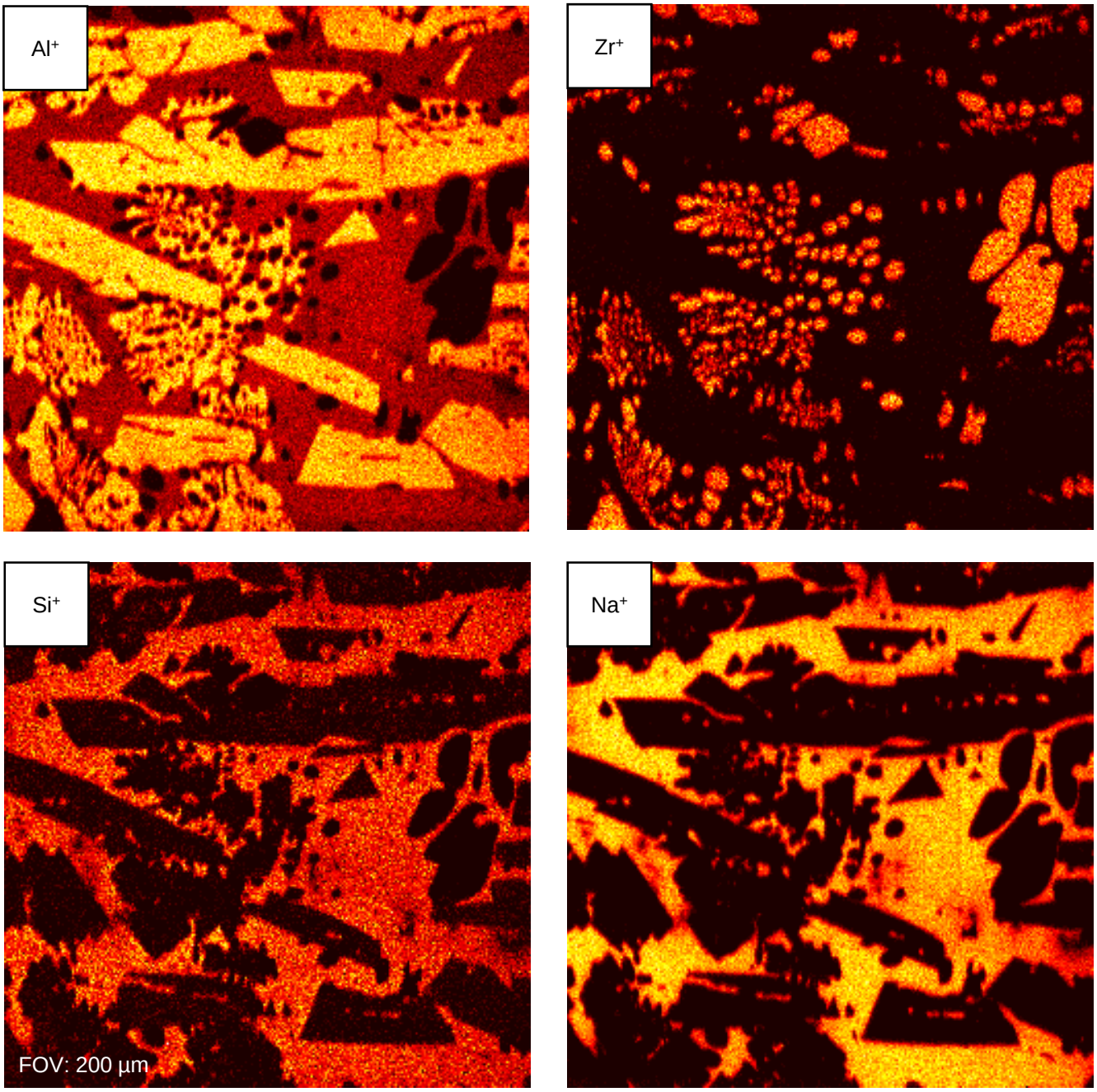

Figure 2. TOF-SIMS images of Al^+, Zr^+, Si^+, and Na^+.

One analysis option would be to limit the ion beam rastered area to only the glass phase. However, a preferable method is to acquire a "raw data stream" from an area such as shown in Figure 2, then use software to reconstruct spectra from user selected areas. This avoids the charging problems which can result from limiting the ion beam to a very small rastered area. In addition, by carefully outlining the region of interest on selected ion images, one can more carefully avoid sampling surrounding phases which would alter the quantitative measurement. This concept is illustrated in Figure 3 where an area was outlined on the total ion image and a spectrum was selectively extracted from the glass phase. Quantification can then be performed using peak intensities from the selected area spectrum, normalizing the peak intensities by the number of pixels in the user defined areas.

In order to generate relative sensitivity factors (RSF's) for quantifying the glass composition, three NIST Glass Standard Reference Materials (SRM) were analyzed. These glass SRM's had the composition shown in Table 1. Of interest was whether the RSF for boron would be dependent on the glass composition. The boron RSF was calculated using the equation;

$$RSF = \frac{I_B / [B]}{I_{Si} / [Si]}$$

I_X = peak area for element X

[X] = known concentration of element X

Even though the glass composition varied amongst the three SRM's, the RSF was calculated to be 0.7 for all three standards. This provides some confidence that the measured B/Si ratio could be quantified using a single RSF independent of the glass composition (matrix effects).

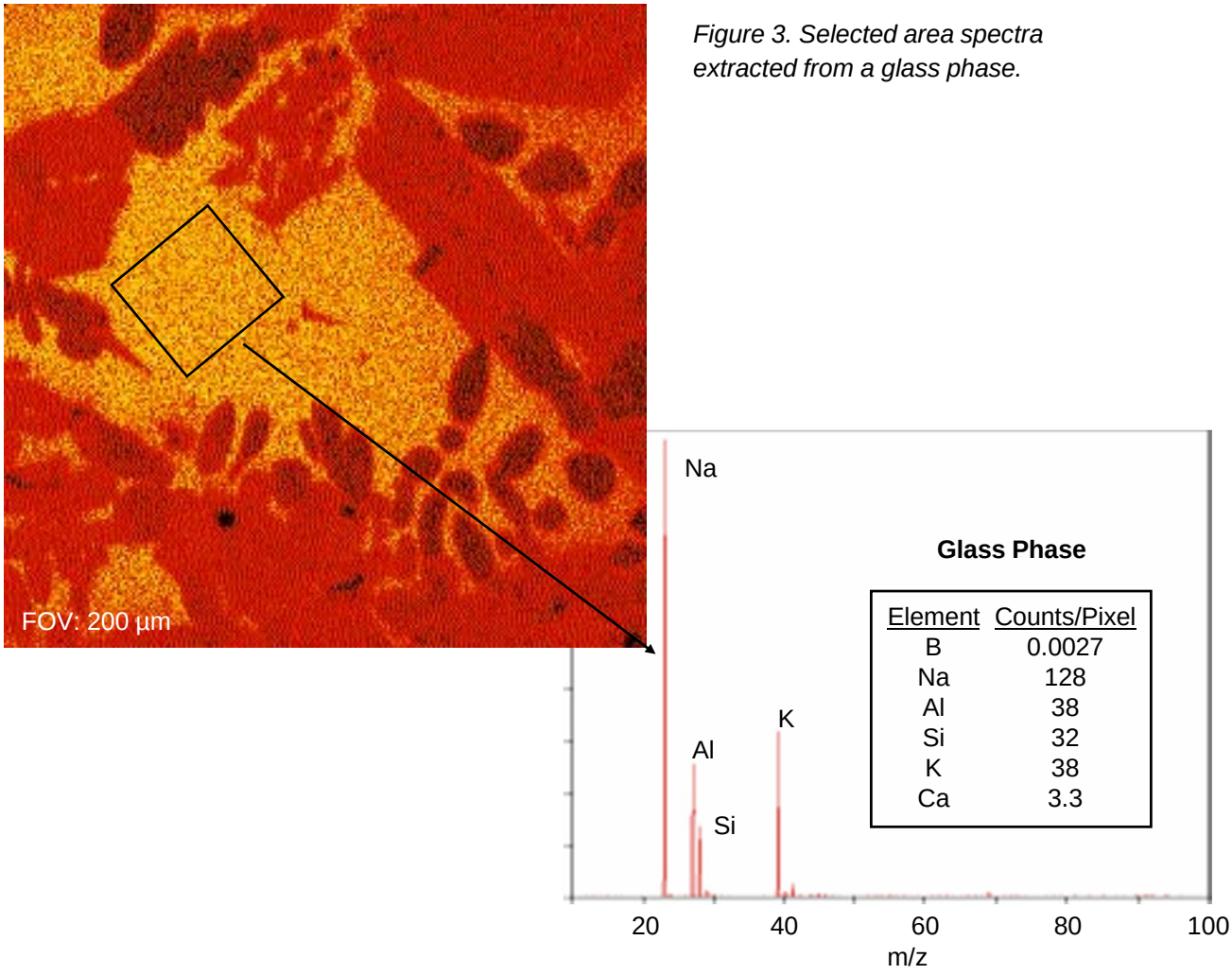

Figure 3. Selected area spectra extracted from a glass phase.

Table 1. Certified Concentration (Atomic %) for NIST SRM's			
Element	SRM 93a	SRM 1411	SRM 1412
O	64.1	59.57	58.04
Si	27.7	21.28	16.36
Na	2.6	7.21	3.51
B	4.4	4.15	1.81
Al	0.6	1.47	2.05
Ca	0.006	1.29	2.81
Mg	0.003	0.28	4.05
K	0.004	1.39	2.04
Li	-----	-----	6.99
Ba	-----	1.08	1.06
Zn	-----	1.57	1.92
Pb	-----	-----	0.69
Cd	-----	-----	1.19

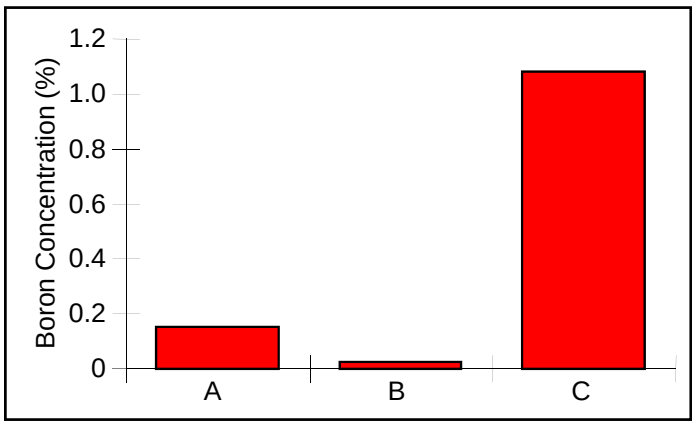

Figure 4. Comparison of the boron concentration measured in three different AZS materials.

Selected areas were defined on the glass phases of AZS materials from three different manufacturers and the counts per pixel for all components of the glass were measured. Applying the RSF of 0.7 to the measured B/Si ratio from the three AZS materials resulted in the boron concentrations shown in Figure 4. Clearly TOF-SIMS has sufficient sensitivity to differentiate between the AZS material with "high" boron content from the other two AZS materials with substantially lower boron content.

Conclusions

This study has shown that TOF-SIMS is an excellent technique for quantifying trace level components in the small glass phases of AZS materials. TOF-SIMS provides the spatial resolution, sensitivity, charge neutralization, and light element detection capabilities that make it an important technique for glass and ceramic microanalysis.

PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

Physical Electronics USA, 18725 Lake Drive East, Chanhassen, MN 55317
Telephone: 952-828-6200, Website: www.phi.com

ULVAC-PHI, 370 Enzo, Chigasaki City, Kanagawa 253-8522, Japan
Telephone 81-467-85-4220, Website: www.ulvac-phi.co.jp