Analysis of Electroceramics by Laser Ablation ICP-MS

Application

Semicondutor

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Abstract

TDK is one of the leading electronic component manufacturers supporting the advance of cell phones, personal computers, and car electronics. As the electroceramic chip parts used in these devices become smaller, thinner, and lighter, new analytical methodology is needed to meet the demand for faster, more sensitive methods of quantitative analysis of solid materials. In addition, environmental regulations are expected to become increasingly stringent, which will impact on the need for reliable methods for the trace analysis of solids. To meet these challenges, researchers at TDK have developed a method based on laser ablation inductively coupled plasma mass spectrometry which offers simultaneous quantitative analysis of major and minor elements with high sensitivity, spatial resolution of 10 µm, robustness, and rapid analysis. The results are based on a new normalization method which can compensate for the sample introduction rate differences between samples or between different sites. The technique is applicable to the simultaneous analysis of major, minor, and trace elements in electroceramics as well as other sample types in other industry sectors.

Introduction

All ceramics, including electroceramics, can be defined as polycrystalline nonmetallic materials. By using precisely controlled compositions and additives, their unique electrical (dielectric, piezoelectric), optical, and magnetic properties can be optimized for use in many key technologies such as communications, electronics, and automation. For example, dielectric materials are used in chip capacitors, whereas magnetic materials are used in transformer coils using ferrite, chip beads, and other components.

Currently, there is a drive to make electroceramics lighter and more compact, and to achieve thinner packages, higher compositeness, and lower levels of power consumption [1]. For instance, ceramic capacitors are one form of electroceramics that are in high demand. They were initially comprised of a single layer, but with developments in multilayering and chip technology, larger capacity and more compact capacitors are now widely used. The ability to make multilayer ceramic chip capacitors smaller, lighter, and thinner has contributed greatly to the propagation of mobile devices such as cellular telephones. As these materials continue to become smaller and thinner, there is an increased need to conduct composition analysis at lower limits of detection (LOD).

Furthermore, the need for fast, high-sensitivity analysis is not restricted to the production and processing industry. Electroceramics are used

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primarily in electrical and electronic devices, and in recent years, environment-related regulations pertaining to electrical and electronic devices have grown increasingly stringent worldwide. Two new environmental regulations that will take effect in the European Union (EU) in 2006 are the directive on Waste Electrical and Electronic Equipment (WEEE) and Restriction on the Use of Certain Hazardous Substances (RoHS). The WEEE directive is associated with the disposal of waste electrical and electronic equipment; while RoHS, restricts the use of certain hazardous substances present in electrical and electronic equipment. The proposal for the RoHS directive will prohibit the use of mercury, cadmium, lead, hexavalent chromium, and other toxic substances from electrical and electronic equipment. Also, in Japan there are pressures on the electronics industry to eliminate lead and to restrict the use of other toxic substances.

In this application note, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to analyze electroceramics. A method was developed that enables rapid, convenient, and highly sensitive compositional analysis. Further details were described in a previous report [2].

Inorganic Analysis of Electroceramics

The techniques generally used for the inorganic analysis of electroceramics are X-ray fluorescence (XRF), inductively coupled plasma atomic emission spectroscopy (ICP-AES), or inductively coupled plasma mass spectrometry (ICP-MS). Inorganic analysis of micro portions is generally performed using an electron probe micro-analyzer (EPMA) or an energy dispersive X-ray analyzer attached to a scanning electron microscope.

The XRF enables convenient analysis of major elements and minor components. XRF measurement targets include bulk, particle, and thin film samples. The technique is extremely effective in characterizing unknown samples; however, conducting high-sensitivity analysis requires a larger measurement diameter and is relatively slow. When measurements are required at lower LODs than is possible via XRF analysis, the sample is usually dissolved using acid, or fused with alkali and then dissolved and analyzed using ICP-AES or ICP-MS. Drawbacks associated with these methods include: the additional time required for sample dissolution, the risk of sample contamination during sample preparation, and the fact that “local” analysis of solids is not possible. In many cases, microfield analysis, EPMA, which has an element mapping function, is used. However, EPMA requires some sample preparation, and because the sample chamber is contained within a vacuum, time is required before measurements can be performed. In addition, analysis cannot be performed at a sufficiently high level of sensitivity, with typical detection limits (DL) at ppm levels.

Thus, conventional methods of analysis have fallen short of the mark with regard to speed, convenience, sensitivity, dynamic range, and microfield analysis. In contrast, LA-ICP-MS enables local analysis of solid samples while maintaining the high sensitivity of ICP-MS. ICP-MS also offers a wide linear dynamic range. For example, the working analytical range of the Agilent 7500 ICP-MS extends to nine orders with very high sensitivity. In addition, the detection circuit used in the 7500 Series ICP-MS means acquisition speed is not compromised when analyzing higher concentration elements and ensures that transient signals from a laser ablation pulse can be measured over such a wide dynamic range. This is a key advantage in the determination of trace and major elements in inclusions, where the analyte signal is very short-lived, and analyte concentrations vary widely.

This report summarizes investigations into the possibility of applying a new LA-ICP-MS method to compositional and impurities analysis of electroceramics.

Analysis Using Laser Ablation ICP-MS

Evaluation of LA-ICP-MS

LA-ICP-MS is widely used to determine inorganic elements in solid samples. A laser is used to irradiate the solid sample and to generate microparticles. The particles are carried on a steady gas stream to the ICP-MS, where the sample is ionized and measured. Thus, solid samples can be analyzed directly without preprocessing, and element analysis can be performed at a high level of sensitivity. LA-ICP-MS is often used as a means of qualitative analysis, although it is also used in quantitative analysis. Typical applications include the determination of trace elements in iron [3] and the characterization of geological samples [4, 5, 6]. At the same time, however, the elements involved in these analyses are trace components, and few studies have been conducted on assays that included everything from principal to trace components.

Advantages of the technique include:

- Measurement speed: There is no need to draw the sample chamber into a vacuum, so sample measurements can be carried out rapidly.
- High sensitivity and wide dynamic range: Gases and micro-particles generated by laser ablation are introduced directly into the ICP-MS for measurement, enabling high-sensitivity analysis. Moreover, the ICP-MS has a wide dynamic range, enabling a broad spectrum of analysis ranging from principal component elements to impurity elements.
- Local analysis is possible: The laser beam is narrow and a charged coupled device (CCD) camera can be attached, enabling local analysis of specific subsections of the sample.
- Changing the analysis field: The area being analyzed can be modified by changing the diameter of the laser beam.
- Analyzing a wide range of samples: Almost any sample can be fused and ablated using the fourth higher harmonic (266 nm) or fifth higher harmonic (213 nm) of an Nd:YAG laser, or using an excimer laser (193 nm).
- Measuring samples of various shapes: Bulk, particle, thin film and other types of samples can be measured. However, a smoother sample field, that has no bumps or projections, achieves more stable results.

Some disadvantages include:

- Problems with stability: The efficiency with which samples can be introduced varies for each sample, so analysis values are sometimes not stable.
- Quantitative analysis is difficult: Quantitative analysis of solutions by ICP-MS is carried out using a method of calibration that uses external standards or standard addition. However, in the case of LA-ICP-MS, internal standards are difficult to add to solid materials. The internal standardization can be used if there are principal component elements for which the concentrations are already known, but then the method cannot be applied in all types of analysis.

Semiquantitative Analysis

Because quantitative analysis using external standards is difficult via LA-ICP-MS, generally the concentration conversion coefficient is calculated separately for each element being measured, and semiquantitative analysis is performed. In this case, either National Institute of Science and Technology (NIST) 611, 612, 613, or 614 glass, which contains multi-elements, or a manufactured standard that is similar to the material being tested, is used for calculating the concentration conversion coefficient (k). If NIST glass is used, the concentration conversion coefficients of the various elements contained in the NIST glass are calculated ahead of time. Then the actual test sample is analyzed and the semiquantitative values for the actual test sample are determined from the data obtained using the concentration conversion coefficients. However, when NIST glass is used, the sample introduction efficiency is different for the material being measured, in many cases. This increases the error in the semiquantitative values. When a standard sample that is similar to the material being tested is used as the standard sample, there are also problems such as the sample introduction efficiency being different depending on the location being analyzed.

Given these challenges with the semiquantitative analysis of electroceramics, we developed a method in which the semiquantitative values are standardized in order to suppress fluctuation of the sample introduction efficiency. Moreover, in order to reduce the error of the semiquantitative values, a solid reference sample was used that was similar to the material being measured. To carry out standardization, however, it was necessary to measure all of the elements and determine the semiquantitative values. In other words, it was necessary to calculate the concentration conversion coefficients (k) for all of the elements. Because the solid reference sample contained only some of the components of the electroceramic, it was not possible to calculate the concentration conversion coefficients (k) for all of the elements. In this case, a concentration conversion coefficient (k-aqua) was calculated by measuring the SPEX multi-element standard solution (XSTC-1, 7, 8, 13). This value was then corrected to take account of the element being present in the solid rather than in solution, to give a k-aqua* value. The k-aqua* values were used as the concentration conversion coefficient (k) for the calculations.

The procedure for semiquantitative analysis of the electroceramic test sample is described below:

1. Using pneumatic nebulization, aqueous standards containing SPEX XSTC-1,7,8,13 were measured over the entire mass range (m/z 2 to 260 amu).
2. Semiquantitative factors (SF) were calculated for the elements in the aqueous standard.
3. Using LA-ICP-MS a solid standard was measured across the entire mass range (m/z = 2–260).

4. For those elements where the concentration is known, semiquantitative factors (SF) were calculated in the solid standard.
5. For those elements that occur in both the aqueous and solid standard and for which SF values were calculated, the coefficient (k) was generated.
6. The k coefficient can be used to convert SF values obtained using the aqueous standard into those useful for solid standards (SF obtained by pneumatic nebulization ICP-MS) × (coefficient (k)). This way, SF values of elements that are not in the solid standard could be generated.
7. The concentration conversion values for all elements were converted to the equivalent oxide.
8. Using the sum of the oxide conversion values of the detected elements, standardization was performed, and the standardized semiquantitative values were determined. For an example of semiquant factor calculations see Table 2.

Oxide conversion was carried out at this time because electroceramics are primarily oxides.

Table 2. Semiquant (SQ) Factor Calculation

Case 1			
	SQ Factor of LA	**SQ Factor of nebulizer**	
Fe	100	200	
Co	?	1000	
Ni	2000	4000	
Coefficient (k) of Fe is 100/200			= 0.5
Coefficient (k) of Ni is 2000/4000			= 0.5
Coefficient (k) of Fe and Ni is same			
Co SQ factor is 1000 × 0.5			= 500
Case 2			
	SQ Factor of LA	**SQ Factor of nebulizer**	
Fe	100	200	
Co	?	1000	
Ni	3000	4000	
Cu	?	2000	
Zn	4000	4000	
Coefficient (k) of Fe is 100/200			= 0.5
Coefficient (k) of Ni is 3000/4000			= 0.75
Coefficient (k) of Zn is 4000/4000			= 1.0
Co SQ factor is 1000 × ((0.5 + 0.75)/2)			= 625
Cu SQ factor is 2000 × ((0.75 + 1.0)/2)			= 1750

Using the above method results in the following advantages:

- Elements not contained in the solid reference sample can be measured.
- Standardization processing makes it possible to correct the sample introduction efficiency between samples, or for each of the measurements, thus minimizing disparities and offset from the true values.

Using this method of analysis, we investigated the possibilities of semiquantitative analysis of an area measuring several mm^2 on a ferrite bulk sample. In addition, we attempted analysis of a spot on a barium titanium oxide ($BaTiO_3$) disk, to determine whether we could apply this method of analysis to local analysis of an area measuring several tens of µm^2.

Semiquantitative Analysis of Ferrite Bulk Samples

Ferrite is a typical magnetic material for electroceramics, and is used for a wide range of components, from bulk-shaped parts such as transformer coils and deflecting yoke coils to chip-shaped parts such as chip beads. Two types of ferrite samples with different compositions were used. The samples were manufactured in-house and measured 2.0 cm in length, 1.0 cm in width, and 0.5 cm in height. For a solid reference sample, we used a nickel-copper-zinc (NiCuZn) ferrite sample, and calculated the concentration conversion coefficient. Table 1 shows the measurement conditions used in the test. A 100-µm beam diameter at 2 mJ output energy and repetition rate of 10 Hz was used. The measurement was carried out over the entire mass range (m/z = 2 ~ 260), and the integration time for the various masses was set at 0.05 s, with measurements being performed three times. To compare the analysis values, the same sample was analyzed using XRF. The results measured using the LA-ICP-MS for the two types of ferrite samples are shown in Figures 1 and 2 respectively.

There was excellent agreement between the principal composition and the reference values

Table 1. Laser Ablation and ICP-MS Conditions

Laser ablation		**ICP-MS**	
New Wave Research LUV266X		Agilent 7500s	
Wavelength:	266 nm	RF power:	1200 W
Pulse frequency:	10 Hz	Carrier gas:	1.15 L/min
Laser energy:	2 mJ for Ferrite	Plasma gas:	16.0 L/min
Ablation pattern:	Raster, 100-µm spot diameter for Ferrite,	Number of masses:	*m/z* = 2 to 260
Scan speed:	50 µm/s for Ferrite	Integration time:	0.05 s
Laser warm-up:	10 s		

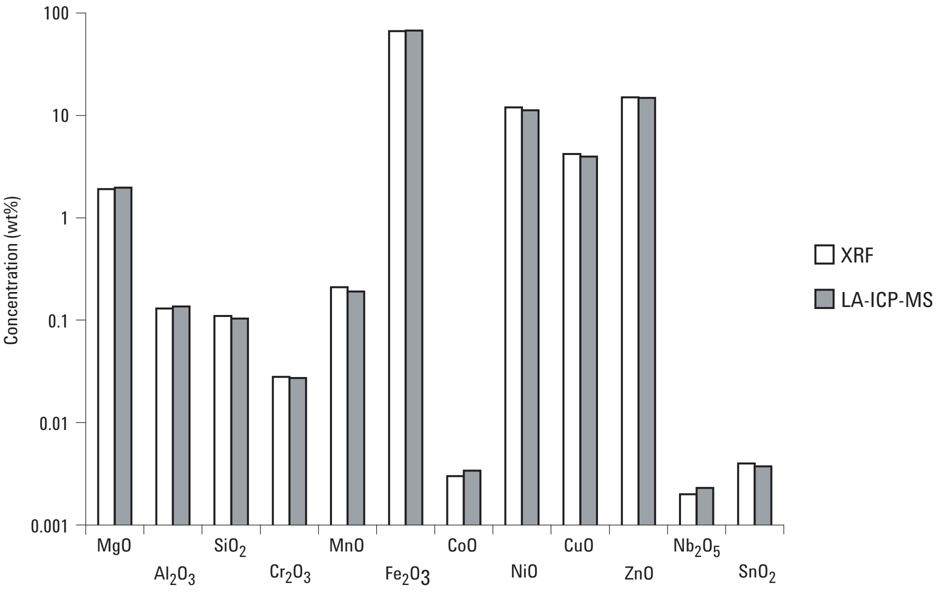

Figure 1. **Comparison of results of semiquantitative analysis using LA-ICP-MS and XRF analysis conducted on ferrite sample A.**

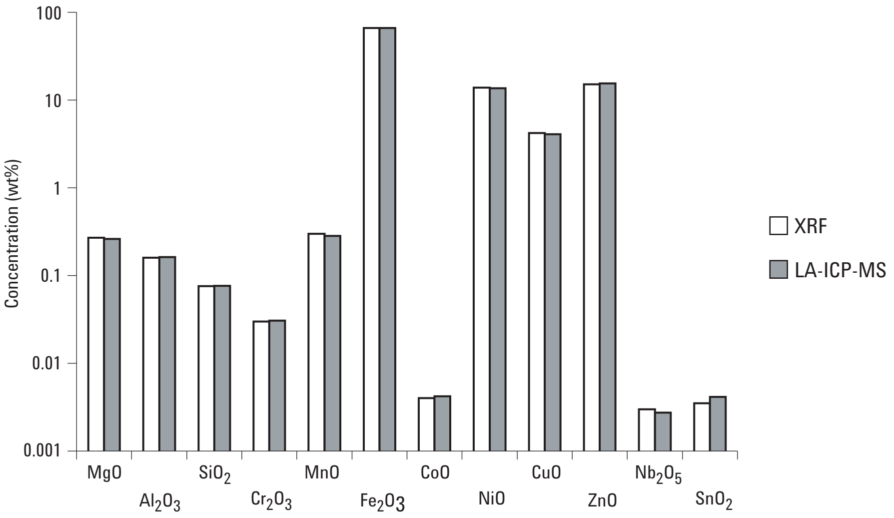

Figure 2. **Comparison of results of semiquantitative analysis using LA-ICP-MS and XRF analysis conducted on ferrite sample B.**

obtained via XRF, with variations of only several percent. Even for the trace components, the difference from the reference value was within 10%. The disparity among the three measurements was approximately 5% to 10% for the bulk elements, and approximately 20% for the trace elements. Using this analysis method, it was possible to suppress the fluctuation in the sample introduction efficiency that is peculiar to LA-ICP-MS. Table 3 shows the analysis values for all of the elements detected with the LA-ICP-MS measurement of ferrite sample A.

Table 3. A Comparison of the Principal Components and Trace Element Concentrations (wt %) of Ferrite Sample A with the Concentrations Obtained from XRF (The % RSD for the LA-ICP-MS Indicates the RSD for the Three Measurements)

Elements	XRF	LA-ICP-MS	
	Reference value	Mean	%RSD
MgO	0.27	0.26	11.0
Al_2O_3	0.16	0.16	9.7
SiO_2	0.076	0.076	10.1
Cr_2O_3	0.030	0.031	4.1
MnO	0.30	0.28	0.8
Fe_2O_3	66.0	66.0	0.5
CoO	*	0.004	3.1
NiO	13.8	13.6	2.8
CuO	4.2	4.1	0.8
ZnO	15.1	15.5	2.3
Y_2O_3	*	0.00004	18.9
ZrO_2	*	0.001	20.8
Nb_2O_5	*	0.003	6.5
MoO_3	*	0.004	8.6
In_2O_3	*	0.00004	8.1
SnO_2	*	0.004	14.7
Sb_2O_3	*	0.0002	17.0
BaO	*	0.001	15.6
WO_3	*	0.0004	4.1
Bi_2O_3	*	0.0001	11.7

* Not detectable

Trace components, such as V_2O_5, Y_2O_3, ZrO_2, MoO_3, Sb_2O_3, BaO, WO_3, and Bi_2O_3, which could not be detected with XRF, could be measured using the LA-ICP-MS. Heavy elements could also be measured and have sub-ppm DLs. Although not included in our samples, the technique offers good DLs for cadmium, lead, mercury and other elements which will be targeted by the RoHS directive, so the proposed method will be effective in the analysis of toxic metals.

The time required for analysis was 40 seconds per measurement, and the total time for the three repititions, including the time spent changing the samples, was approximately 5 minutes. Moreover, no sample preparation was carried out when the measurements were taken. In our opinion, this semiquantitative LA-ICP-MS method satisfies the requirements for electroceramics analysis in terms of speed, convenience, and high sensitivity.

Semiquantitative Analysis of Spots on a $BaTiO_3$ disk

Next, we investigated whether the technique could be applied to feature (local) analysis of a dielectric material. A 1-cm diameter $BaTiO_3$ disk, manufactured in-house, was used. $BaTiO_3$ is a major component of chip capacitors. Depending on the elements added to $BaTiO_3$, the baking conditions, and other parameters, black spots sometimes appear on the surface during manufacture. The LA-ICP-MS quantitative technique described above was used to characterize both these spots and normal areas on the $BaTiO_3$ disk. The following laser conditions were used in this measurement: beam diameter of 10 µm at 10 Hz and 0.02 mJ. In addition, for comparison purposes, we analyzed the entire disk using XRF. The results are shown in Figure 3.

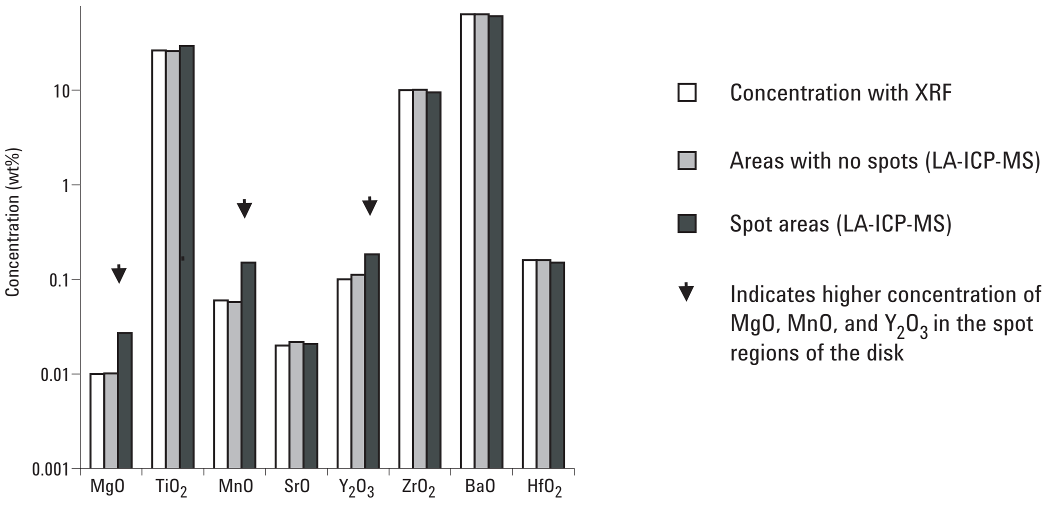

Figure 3. A comparison of results obtained using the LA-ICP-MS for semiquantitative analysis of areas of the $BaTiO_3$ disk with no spots and areas with spots, compared with the results obtained using XRF analysis.

The calculated semiquantitative values for the normal areas of the $BaTiO_3$ disk using LA-ICP-MS were approximately equal to the results for the disk as a whole, as obtained using XRF. Analysis of the black spots (an area of several micrometers) on the $BaTiO_3$ disk indicated significant disparities in the amounts of MgO, MnO and Y_2O_3. Figure 3 illustrates the analysis of the spots compared to the normal areas of the $BaTiO_3$ disk. It is thought that the spots on the $BaTiO_3$ disk were caused by aggregation of MgO, MnO, and Y_2O_3. Figures 4 and 5 show a CCD image of the $BaTiO_3$ disk before and after LA-ICP-MS analysis, and, as the photographs illustrate, there was very little damage to the sample with the laser diameter set at 10 µm.

As described above, our analyses indicate that the LA-ICP-MS method of semiquantitative analysis is effective as a means of local analysis of areas measuring several tens of micrometers in diameter.

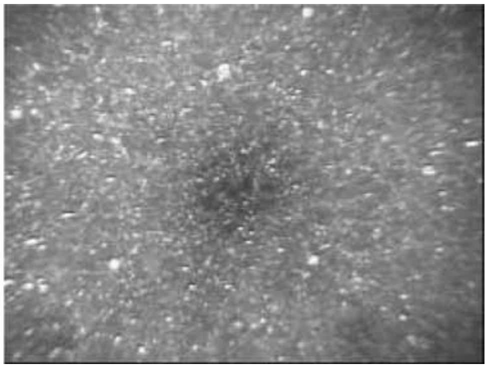

Figure 4. CCD image of the $BaTiO_3$ disk prior to laser irradiation.

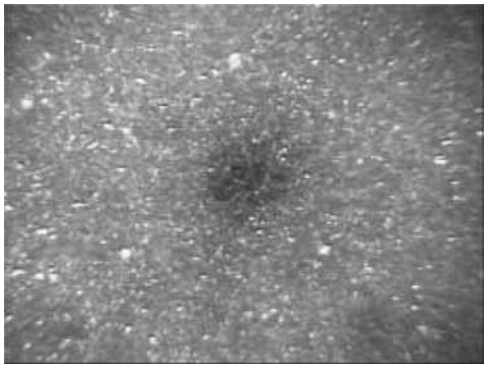

Figure 5. CCD image of the $BaTiO_3$ disk after laser irradiation showing minimal damage (laser diameter was 10 µm).

Conclusions

Not only are electroceramics becoming smaller and more heavily layered, but the boards themselves are becoming more hybridized as capacitors and magnetic elements begin to share space on the same board. To keep apace with these developments, methodology for the trace analysis of impurities will continue to evolve. In addition, environmental regulations are expected to become increasingly stringent, which will impact on the need for reliable methods for the trace analysis of solids. Therefore, the demand for newer, faster, and more convenient methods of semiquantitative analysis, such as the LA-ICP-MS technique discussed in this application note, will continue to grow.

Using concentration conversion coefficients obtained from an aqueous standard and solid reference samples and by measuring all of the elements, we found that LA-ICP-MS provides an effective technique for rapid semiquantitative analysis. The technique can be applied to measurements across a wide dynamic range from bulk to trace components of materials. Furthermore, this method is not limited to electroceramics and can be applied to various other materials and substances.

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