

THE DETERMINATION OF MAJOR AND SOME MINOR CONSTITUENTS IN LEAD ZIRCONATE-TITANATE COMPOSITIONS BY X-RAY FLUORESCENCE AND ATOMIC ABSORPTION SPECTROMETRY

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Compositions of lead zirconate-titanate (PZT) are of great interest for manufacturing piezo-electric ceramics. During manufacture selective volatilization of elements can occur in high-temperature treatments. Therefore, the chemical composition of these materials should be determined after these treatments. Further, the amounts of unreacted oxides must be known for production control. Analytical procedures for this purpose have been described by Goode *et al.*¹ and by Robinson and Joyce².

However, relatively accurate determinations of minor additions of elements ("dopes") are also required. Here, emission spectroscopy, as described by Mirti and Shivak³, lacks the accuracy desired and few other analytical methods have been proposed in the literature to solve this problem.

Moreover, these analytical procedures may run into difficulties, if certain minor constituents are present, and the sophisticated instruments described may not be easily available. X-Ray fluorescence spectrometry carried out with suitable standards and homogeneous samples is very precise, accurate and highly selective. In addition, the application of a borax fusion technique for sample preparation⁴ enables sufficient exclusion of matrix effects on determinations of elements. Along these lines, together with analysis by means of atomic absorption, it was possible to achieve satisfactory analysis of PZT composition. This paper describes the development of the X-ray fluorescence spectrometric methods for the determination of lead, zirconium and titanium as major constituents, the determination of minor constituents (K, La, Sm, Yb) and the determination of some of the unreacted oxides (ZrO_2 and TiO_2). Atomic absorption spectrometric methods have also been developed for cases (PbO, Mg) where X-ray fluorescence seemed less appropriate. The methods described are applicable, with obvious modifications, to many types of materials.

Total lead, zirconium and titanium

The above major constituents were determined by X-ray fluorescence spectrometry, consideration being given to the following points*.

For precise results, standards and samples should be matched closely. Where

* In this section "intensity" means the number of counts per fixed time measured with the X-ray fluorescence spectrometer on the line of the element.

a large variation in sample composition is expected, this is most easily done by a sample pretreatment, *e.g.* dilution in molten borax and addition of a heavy absorber. Here the general method previously described⁴ was used; standards are easily prepared from assayed compounds of the elements of interest.

Although a high dilution combined with a large amount of heavy absorber is applied, changes in concentration of a major element (*e.g.* lead) can still influence to some extent the intensity of any other element (*e.g.* zirconium), even when the latter does not change in concentration. The occurrence and degree of mutual influence was tested as follows: standards were prepared containing zirconium and titanium and varying amounts of lead by mixing the appropriate amounts of oxides; next these were analysed as described under the heading procedures.

From the intensities measured it appeared that: (a) the calibration line of zirconium is linear; (b) the variation in lead content has an influence, although small, on the zirconium intensity; and (c) this influence is proportional to the lead content (Fig. 1).

For titanium a similar, but smaller, effect from the lead content was measured. However, there was no perceptible influence from zirconium on titanium or *vice versa*, nor had zirconium or titanium any perceptible influence on the lead intensity.

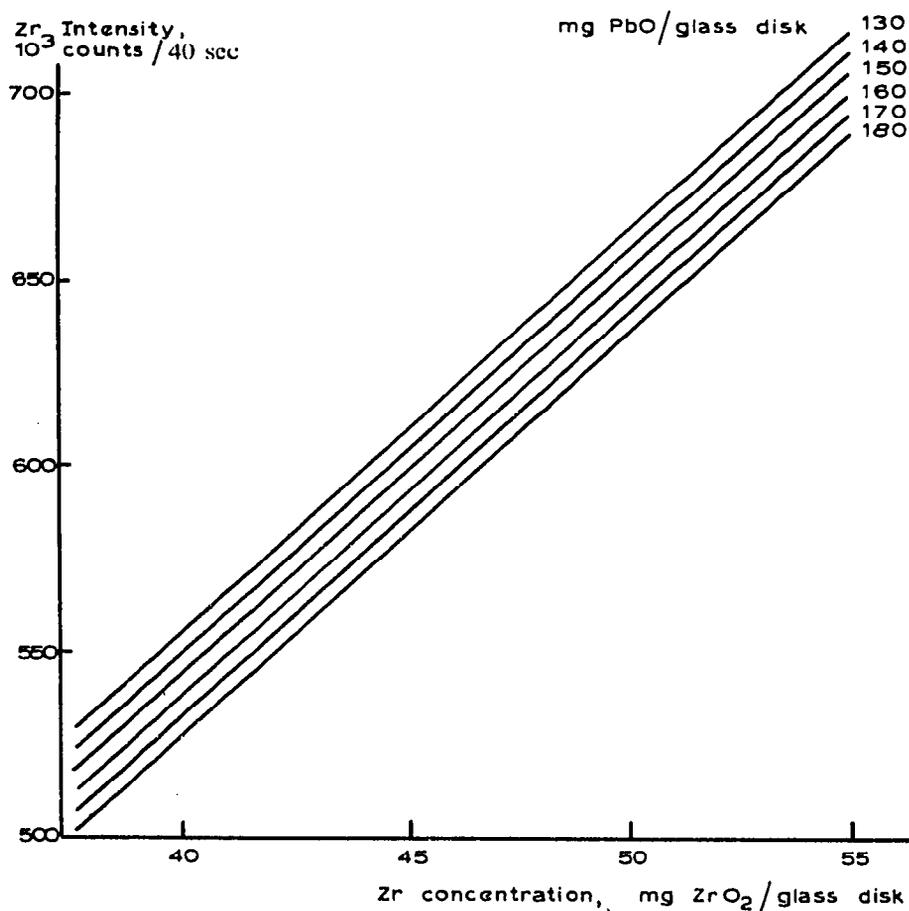


Fig. 1. Zirconium intensity as a function of lead and zirconium concentration.

In the present procedure, the following formulae were applied to calculate the lead, zirconium and titanium concentrations c (element) from the intensities I (element) measured:

$$c(\text{Pb}) = k_1 \cdot I(\text{Pb}) + k_2$$

$$c(\text{Zr}) = k_3 \cdot I(\text{Zr}) + k_4 \cdot I(\text{Pb}) + k_5$$

$$c(\text{Ti}) = k_6 \cdot I(\text{Ti}) + k_7 \cdot I(\text{Pb}) + k_8$$

where k_1, k_2, \dots, k_8 are constants determined from the standards used to obtain Fig. 1 and similar experiments concerning the mutual influence of other pairs of elements. Once the above linear relationships have been established, only three well chosen standards are needed to calculate the constants k_1, k_2, \dots, k_8 .

The X-ray fluorescence spectrometer used had a sample changer with 4 positions. To obtain high accuracy it was necessary to consider possible differences between these 4 positions. In the instrument available, adjustment to a difference between positions smaller than 0.1% proved impossible; for most work this is quite acceptable. Measurement in the same position of the sample changer was advisable for the highest accuracy; at the same time sample holders were selected to be as equal as possible.

Occasionally a "burst", probably caused by external electronical interference, gave rise to a high number of counts. In order to detect such interferences, samples and standards were always counted at least twice.

For routine use it was not necessary to establish a calibration line every day. Once a calibration line had been obtained, only one of the standards was measured for each series of samples, in order to correct the sample intensity for daily variations of the spectrometer.

Dope elements

The X-ray fluorescence spectrometer available was unable to determine magnesium; therefore an atomic-absorption spectrophotometric method was developed. Because of the large influence of the major elements on the magnesium absorption, a standard addition method was applied to account for large variations in sample composition.

The other elements were determined by X-ray fluorescence spectrometry, with an internal standard to compensate for the effect of matrix (*i.e.* sample composition) variations. The internal standard element was chosen so that the mass-absorption coefficients of the sample for the wavelength of the element to be determined and for the wavelength of the internal standard were as equal as possible. These wavelengths should not differ much. The amount of the internal standard element was selected so that the count rates of internal standard and dope elements in the concentration region of interest were approximately equal. The choice of the internal standard may be limited for practical reasons, *e.g.* when barium was used as internal standard for lanthanum, it appeared impossible to keep the glass discs intact, whereas cerium proved satisfactory.

Unreacted oxides

The methods described by Robinson and Joyce² were used to separate the unreacted oxides from the reaction product PZT. The lead oxide was dissolved in

TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF ELEMENTS BY X-RAY FLUORESCENCE SPECTROMETRY

<i>Element</i>	<i>Pb</i> (total)	<i>Zr</i> (total)	<i>Zr</i> (unreacted)	<i>Ti</i> (total)	<i>Ti</i> (unreacted)
X-ray tube	W	W	W	Cr	Cr
High tension, kV	50	50	50	40	50
Current, mA	20	20	20	24	20
Radiation path	air	air	air	vacuum	vacuum
Collimator	fine	fine	fine	coarse	coarse
Analyzing crystal	LiF(200)	LiF(200)	LiF(200)	LiF(200)	LiF(200)
Line	$L\alpha_{1,2}$	$K\alpha_{1,2}$	$K\alpha_{1,2}$	$K\alpha_{1,2}$	$K\alpha_{1,2}$
Detector	scint.c	scint.c	scint.c	flow c	flow c
Voltage (V)	850	825	825	1650	1650
Attenuator position	2	2	2	4	4
Pulse height discrimination	no	no	no	no	no
Lower level scale	150	150	150	150	150
Window scale	---	---	---	---	---
Counting time, s.	40	40	100	40	100
Approx. net no. of counts	770,000	650,000	150,000	760,000	70,000
For a conc. in the orig. sample, %	63	15	0.6	7.2	0.1
Internal standard used	---	---	---	---	---
Amount (mg) and compound used, respectively	---	---	---	---	---
Diam. of sample holder bottom hole, mm	28	28	23	28	23

<i>K</i> (dope)	<i>Ca</i> (int.st.)	<i>La</i> (dope)	<i>Ce</i> (int.st.)	<i>Sm</i> (dope)	<i>Cr</i> (int.st.)	<i>Yb</i> (dope)	<i>Ni</i> (int.st.)
Cr	Cr	W	W	W	W	W	W
50	50	50	50	50	50	50	50
20	20	20	20	20	20	20	20
vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum	vacuum
coarse	coarse	coarse	coarse	fine	fine	fine	fine
PE	PE	LiF(200)	LiF(200)	LiF(200)	LiF(200)	LiF(220)	LiF(220)
$K\alpha_{1,2}$	$K\alpha_{1,2}$	$L\alpha_{1,2}$	$L\beta_1$	$L\alpha_{1,2}$	$K\alpha_{1,2}$	$L\alpha_{1,2}$	$K\alpha_{1,2}$
flow c	flow c	flow c	flow c	flow c	flow c	scint.c	scint.c
1600	1600	1650	1650	1650	1650	900	900
3	3	4	4	4	4	2	2
no	no	yes	yes	no	no	no	no
150	150	350	350	150	150	150	150
---	---	200	200	---	---	---	---
40	40	40	40	40	40	40	40
100,000	300,000	80,000	100,000	75,000	150,000	80,000	330,000
0.3	---	1.5	---	1.5	---	1.5	---
Ca	---	Ce	---	Cr	---	Ni	---
30	CaCO ₃	50	CeO ₂	80	K ₂ Cr ₂ O ₇	40	NiO
28	28	20	20	20	20	28	28

EDTA (0.02 M), but a back-titration of the excess of EDTA² appeared unattractive. A direct method of determination was applied. Here, X-ray fluorescence spectrometry might have been used, but atomic-absorption spectrometry is much quicker. The 283.3 nm line of lead was chosen, because this line is less prone to interferences and is sufficiently sensitive, that no dilution or concentration of the extracted lead solution was necessary.

The acid-insoluble residue (zirconium oxide and titanium oxide) was taken into a borax melt and determined by X-ray fluorescence spectrometry; sodium chloride was added to prevent cracking of the glass disc.

EXPERIMENTAL

Apparatus

Some of the instrumental conditions applied for the determination of the elements with a Philips PW 1540 XRF spectrometer are shown in Table I; further, use was always made of the sample spinner.

The instrumental conditions applied for the determination of the elements by means of a Jarrell-Ash 82-547 atomic-absorption spectrophotometer are shown in Table II. The instrument was provided with a premix Techtron AB51 laminar burner, and a total consumption Hetco turbulent burner. Westinghouse hollow-cathode lamps were used. A Hamamatsu R213 photomultiplier and a grating blazed for 300 nm were used. Entrance and exit slits of the monochromator were 100 and 150 μm respectively. For the Hetco burner the light was passed 5 times through the flame. For both lead and magnesium determinations, hydrogen and air were the fuel and oxidant gases, respectively.

TABLE II

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF THE ELEMENTS BY ATOMIC ABSORPTION SPECTROMETRY

Element	Pb	Mg
Wavelength, nm	283.3	285.2
Burner	Techtron	Hetco
Hollow cathode lamp, current, mA	6	8
Photomultiplier voltage, V	380	380
Gas pressure, kg cm^{-2}	4	4
Gas flow, l h^{-1}	10	13
Oxidant pressure, kg cm^{-2}	4	4
Oxidant flow l h^{-1}	125	96

Reagents

All reagents used were analytical-reagent grade. Either the assay values of the actual batch reported by the manufacturer were accepted, or the chemicals were analysed by wet-chemical methods⁵⁻⁷.

The preparation of the flux (45 parts of anhydrous sodium tetraborate, 7 parts of lithium hydroxide, and 16 parts of orthoboric acid) has already been described⁴. Solid dilutions of compounds in flux or borax were used in order to weigh any prescribed small amounts of components accurately.

In order to calculate the amount of each component required, assay values and losses resulting from ignition were taken into account.

Procedures

Major constituents. Accurately weigh 250 ± 1 mg of powdered PZT sample into a Degussa II platinum crucible and add 1200 ± 1 mg of tungsten(VI) oxide and 6500 ± 2 mg of flux*. Mix the powders, melt and pour a glass disc as previously described⁴. Measure the intensity of the major elements of the sample and of a standard glass disc, under the conditions shown in Table I. Correct for daily variation. Calculate the content of the major constituents, applying the formulae described above with constants determined from the intensities of standards prepared from assayed compounds.

Magnesium dope. Accurately weigh about 100 mg of powdered PZT sample and dissolve in 2.5 ml of perchloric acid (70%). Add 2.5 ml of concentrated hydrochloric acid and heat until practically all the hydrochloric acid has evaporated, to dissolve the last traces. Transfer the solution to a volumetric flask and dilute with water to 100 ml for expected concentrations of 0.1–0.3% Mg. If a higher concentration is expected, dilute more.

Prepare in 50-ml volumetric flasks, solutions containing 25 ml of the above sample solution, 25 mg of strontium chloride (as a solution) and increasing amounts of magnesium as chloride (*e.g.* 0, 2.5, 5.0, 7.5 etc. mg Mg). Dilute with water to the mark. Measure the absorbance of these solutions under the conditions shown in Table II. Calculate the magnesium content of the sample by the method of standard additions⁸.

Other dopes. Accurately weigh 2000 ± 5 mg of powdered PZT into a Degussa II platinum crucible. Add an accurately weighed amount of internal standard (see Table I) as a solid dilution (*e.g.* 1:10) in borax. Add powdered borax to give a total weight of 5000 ± 2 mg. Mix the powder, melt and pour a glass disc as previously described⁴. Measure the ratio of intensities of dope element and internal standard, under the conditions shown in Table I. Calculate the dope content from a calibration line, determined from the ratios of intensities in standards, prepared from assayed compounds.

Unreacted lead oxide. Accurately weigh about 250 mg of powdered PZT sample into a dry stoppered flask and add 50.0 ml (or 100.0 ml for high concentrations of unreacted lead) of 0.02 M EDTA solution. Shake the flask for 30 min. Allow the insoluble matter to settle and filter the solution through a dry fine-porosity filter. Discard the first 5 ml. The filtrate should be clear. Determine the absorbance of the filtrate by atomic absorption, under the conditions described in Table II. Calculate the lead content from a calibration line determined from the absorbances of standards prepared from lead nitrate and EDTA.

Unreacted zirconium and titanium oxide. Accurately weigh about 250 mg of powdered PZT sample. Dissolve in 50 ml of hot concentrated hydrochloric acid. Add 50 ml of hot water and filter through a fine-porosity filter. Wash with hot water. Ash the filter in a Degussa II platinum crucible. Add 500 ± 2 mg of a solid mixture of

* If standards and samples are not prepared with the same batch of flux, the amount of flux is: $6500 y/y'$, where y and y' are the residues on ignition of standard batch and new batch of flux respectively.

lead(II) oxide and sodium chloride (6:1 by weight). Add 7500 ± 2 mg of flux, mix the powders, melt and pour a glass disc as previously described⁴. Measure the intensity of zirconium and/or titanium under the conditions shown in Table I. Calculate the zirconium and titanium contents from calibration lines, determined from the intensities of standards prepared from assayed compounds.

DISCUSSION AND RESULTS

The relative standard deviation found⁹ for the determinations of the major elements was about 0.2%. This standard deviation includes sample inhomogeneity, sample changer dissimilarity, etc.

The absolute standard deviation found for determination of the unreacted oxides is reported in Table III. It was not investigated whether 0.02 M EDTA indeed dissolves only free lead oxide. Robinson and Joyce² do not exclude the possibility of dissolving lead from lead-rich titanium compounds. However, in that case one would expect the measured amount of dissolved lead to depend on the EDTA concentration, and this was not observed. Further, no significant amounts of titanium were found in the EDTA extracts.

TABLE III
COMPARISON OF ANALYSES

	<i>Sample identification</i>	<i>Classical methods</i>	<i>Proposed method</i>
Unreacted lead	1	1.25 ± 0.05	1.22 ± 0.02
Unreacted zirconium	1	0.60 ± 0.1	0.65 ± 0.1
Unreacted titanium	1	0.02 ± 0.01	0.03 ± 0.01
Total lead	1	63.7 ± 0.1	63.6 ± 0.1
	4	63.4	63.3
Total zirconium	1	14.78 ± 0.1	14.88 ± 0.04
	2	14.58	14.53
	3	13.80	13.86
	4	13.71	13.69
Total titanium	1	6.97 ± 0.05	6.95 ± 0.02
	2	6.77	6.80
	3	7.50	7.48
	4	7.35	7.30

Not enough samples were analysed for dope content to calculate a standard deviation. From the results so far obtained for magnesium, this deviation is expected to be about 5%; for the other dope elements a standard deviation of less than 2% appeared. In both cases not too low concentrations were present.

The time necessary for the analyses compares very favourably with that of many other methods. The following time requirements do not include the preparation of standards and depend on the length of the series, but include the time necessary for cleaning, calculation and reporting. The simultaneous determination of the three major constituents can be made in about 3 h. Unreacted lead requires about 1.5 h, unreacted zirconium and titanium simultaneously require 3 h. A dope element can be determined in about 1 h, but magnesium requires more time.

Some representative samples were also analysed by chemical methods^{5,6} (dissolution in hydrochloric acid and fusion of the insoluble residue with pyrosulphate). From the results (Table III) a good precision is apparent. The dopes were not analysed by wet chemistry, because of the difficulties encountered.

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SUMMARY

An accurate X-ray fluorescence spectrometric method is described for the determination of lead, zirconium and titanium in lead zirconate-titanate ceramics. Careful matching of samples and standards by a borax fusion method resulted in a relative standard deviation of about 0.2% for the major constituents. The determination, after separation, of the unreacted oxide of lead by atomic absorption spectrometry, and of the unreacted oxides of zirconium and titanium by X-ray fluorescence spectrometry is also described. An X-ray fluorescence spectrometric method is proposed for the determination of dope elements (K, La, Sm, Yb) with internal standards (Ca, Ce, Cr, Ni respectively). The magnesium dope is determined by atomic-absorption spectrometry with standard addition.

RÉSUMÉ

On décrit une méthode spectrométrique de fluorescence aux rayons-X pour le dosage du plomb, du zirconium et du titane dans des céramiques. Un essai précautionneux d'échantillons et d'étalons par voie de la méthode de fusion à borax fournissait une déviation standard relative d'environ 0.2% pour les composés principaux. Après séparation, des dosages ont été effectués pour la partie non-convertie de l'oxyde de plomb à l'aide d'absorption atomique et pour celle respectivement des oxydes de zirconium et de titanium à l'aide de spectrométrie de fluorescence aux rayons-X. On propose également une méthode pour le dosage des éléments de base (K, La, Sm, Yb) au moyen d'étalons internes (respectivement Ca, Ce, Cr et Ni). Le magnésium est dosé spectrophotométriquement par absorption atomique, avec addition d'étalon.

ZUSAMMENFASSUNG

Es wird eine genaue Röntgenfluoreszenz-Methode beschrieben für die Bestimmung von Blei, Zirkonium und Titan in keramischen Werkstoffen auf Blei-Zirkonat-Titanat-Basis. Durch sorgfältige Angleichung der Analysen- und Vergleichsproben mittels eines Borax-Schmelzverfahrens wurde für die Hauptbestandteile eine relative Standardabweichung von etwa 0.2% erzielt. Nach Abtrennung wurden die Oxide bestimmt, die bei der Herstellung nicht reagiert hatten, und zwar Bleioxid durch Atomabsorptionsspektrometrie und die Oxide von Zirkonium und Titan durch Röntgenfluoreszenzanalyse. Für die Bestimmung der zugesetzten Elemente (K, La, Sm, Yb) wird ebenfalls eine röntgenfluoreszenzspektrometrische Methode mit

inneren Standards (resp. Ca, Ce, Cr, Ni) vorgeschlagen. Der Magnesium-Zusatz wird durch Atomabsorptionsspektrometrie nach einer Standard-Zumischmethode bestimmt.

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