

## Spectrochemical Determination of Impurities in Barium Titanate and Strontium Titanate Single Crystals

By Jae-young Hwang

Laboratory for Insulation Research, Massachusetts Institute of Technology,

Cambridge, Massachusetts, U. S. A.

### Barium Titanate 및 Strontium Titanate 單結晶中の 不純物の 分光化學分析

黃 在 榮\*

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#### Abstract

A spectrochemical analysis was made to compare the major impurities in  $\text{BaTiO}_3$  single crystals grown from  $\text{KF-BaTiO}_3$  system and  $\text{TiO}_2\text{-BaTiO}_3$  system respectively. The present technique was also extended, without any modifications, to the analysis of  $\text{SrTiO}_3$  crystal.

#### 要 約

$\text{KF-BaTiO}_3$  系와  $\text{TiO}_2\text{-BaTiO}_3$  系에서 각각 成長시킨  $\text{BaTiO}_3$  의 單結晶中の 主要 不純物을 分光化學分析法으로 定量하여 比較 檢討하였다. 이 分析法은  $\text{SrTiO}_3$  의 單結晶의 分光化學分析에도 適用된다.

#### Introduction

Barium titanate, because of its exceptionally high dielectric constant, has been used extensively as a capacitor material<sup>1)</sup>. Various techniques have been attempted to grow the crystals. Among them are the following methods: fluxed melt technique<sup>2)</sup>, pulling technique<sup>3,4,5,6)</sup>, and flame-fusion method<sup>7)</sup>.

For frequency-response measurements in the infrared through the millimeter spectral region, good-quality undoped butterflywing crystals were required. To meet this requirement  $\text{BaTiO}_3\text{-KF}$  system was studied first. No success was obtained in pulling attempts, although one small cube (~5mm on edge) grew on a seed suspended below the surface of the melt.

The  $\text{BaCl}_2\text{-BaTiO}_3$  system appeared more suitable, but growth was very slow. A third system investigated was  $\text{BaTiO}_3\text{-TiO}_2$ <sup>8)</sup>.

The purity requirement of the product made by the process is such that sensitive method of analysis is required for a wide variety of metallic impurities. The emission spectrograph offers a rapid means of ex-

aming materials for many elements with a minimum of sample preparation and better limits of detection. This is the main consideration in choosing this analytical tool for the analysis of the  $\text{BaTiO}_3$  crystals.

#### Experimental

##### Apparatus

A Hilger large quartz spectrograph was used. Microphotometer and step-sector also were needed to read the successive intensities of the analytical lines.

##### Preparation of standards

Since it has been found by analysis that commercially available  $\text{BaTiO}_3$  standards are not sufficiently pure, standards have been prepared by mixing pure  $\text{BaTiO}_3$  powder which was made in this laboratory by thermal decomposition<sup>9)</sup> of  $\text{Ba}[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$  with spectrographically pure oxides of impurity elements of interest (oxides were obtained from Johnson-Matthey Co. through Jarrel Ash Co.).

To minimize sampling error the base material,  $\text{BaTiO}_3$ , and the impurity oxides were screened through a 300-mesh sieve, and thoroughly mixed in a mecha-

\* 美國 M. I. T. 工科大學

nical shaker for 10 minutes for each preparation. Subsequently, the standard samples were mixed with graphite of high quality in a 1:2 ratio, sample-to-graphite, by volume. A tungsten-carbide mortar was used for grinding the samples.

#### Preparation of samples

Samples submitted for analysis were crystal boules. After crushing them in tungsten-carbide mortar, small chips were selected for sampling under microscope. The selected chips of crystals were ground in the same manner as standards preparation.

#### Electrode system

The mixture of sample and graphite was packed into the crater (5mm depth) of the lower electrode. The upper electrode is coneshaped with a planar cross section of 2 mm at the base.

The electrode gap was maintained 5mm throughout the arcing.

#### Excitation and exposure

##### Electrical parameters

Discharge type	A d-c arc, anode excitation
Voltage, v.	220
Current, amp.	6

##### Exposure conditions

Spectral region, Å	2700-4400
Slit width, $\mu$	30
Arc preburn period	none
Arc exposure period	complete arcing

##### Emulsion calibration

Emulsion calibration was made by step sector using

iron spectrum which was taken for 5 seconds under the same experimental conditions applying 3 ampere of current instead of 6 ampere.

#### Preparation of analytical curves

The intensity of the analytical lines and the internal standard lines, titanium lines, was converted to log. intensity ratio versus the log. concentration for each of the respective elements.

In determining the residual impurities in the starting material of barium titanate, the addition method of Harvey<sup>10</sup> was followed.

#### Results

Analytical lines employed in the present experiment for both BaTiO<sub>3</sub> and SrTiO<sub>3</sub> are listed in Table I. Titanium line, 3349.88 Å was used as an internal standard line.

Table II shows the analysis of the two types of BaTiO<sub>3</sub> crystals together with the feed material.

The analysis of the light and dark-colored SrTiO<sub>3</sub> crystals grown from flame-fusion method is shown in Table III.

Table I Analytical lines for BaTiO<sub>3</sub> and SrTiO<sub>3</sub>.

Element line, Å		Element line, Å	
Al	3092.71	Si	2881.58
Fe	3020.64	Pt	3064.71
Mg	2852.13	Sr	4077.71
Mn	2794.82	Ca	3968.47
Pb	2833.14	Cr	4254.35

Table II Impurities in various BaTiO<sub>3</sub> crystals.

Sample No.	Impurity elements(% by weight)										
	Al	Fe	Mg	Mn	Pb	Sr	Ca	Si	Pt	K	F*
1	.004	.02	.003	.003	.003	.01	.003	.04	ND	ND	ND
	.002	.01	.001	.001	.001	.005	.001	.02			
2	.003	.006	.001	.001	.001	.005	.002	.02	.05	.02	.4
	.002	.003	.0002	.0005	.0008	.002	.001	.01	.03	.01	.2
3	.003	.005	.001	.001	.001	.008	.003	.04	ND	ND	ND
	.001	.002	.0006	.0005	.0006	.004	.001	.01			

ND-not detected.

No. 1—BaTiO<sub>3</sub> powder; No. 2—butterfly-wing grown with sample No. 1 and KF; No. 3—pulled crystal with sample No. 1 and TiO<sub>2</sub>.

\* Fluoride was determined by colorimetric method<sup>11</sup>.

Ta, Nb, Ni, Co, Mo, Sn, Sb, and Cu were sought but not detected.

Ranges of triplicate results are shown throughout the experiment.

**Table III** Impurities in various SrTiO<sub>3</sub> crystals.  
Impurity elements (by weight %)

Sample	Al	Fe	Mg	Mn	Na	Si	Cr	Ca	Ba
Feed	.004 .001	.009 .004	.003 .001	.003 .001	.002 .001	.005 .003	.002 .001	.003 .001	.002 .001
Dark crystal	.003 .001	.005 .003	.002 .001	.002 .001	ND .002	.003 .002	ND .001	.002 .001	ND .001
White crystal	.003 .002	.002 .001	.002 .001	.003 .002	ND .001	.004 .001	ND .001	.002 .001	ND .001

ND-not detected.

#### Summary

From Table I, it is obvious that the purity of crystal grown by pulling technique in TiO<sub>2</sub>-BaTiO<sub>3</sub> system is better than that of the butterfly-wings. The system also has the advantage that no foreign ions from flux are present.

The main impurities in the pulled crystals are iron and silicone from the TiCl<sub>4</sub> feed stock. A simple distillation<sup>12)</sup> procedure was therefore used. Significant improvement in the transition element content of the feed was noted by spectrochemical analysis, but a considerable amount of silica was picked up from the glass column.

With SrTiO<sub>3</sub> analysis, the present analytical condition proved to be satisfactory. No significant difference in impurity content was found between the dark and white crystals except iron.

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