

## Impurity control with the precise measurement of alumina powders synthesized by hydrolysis method

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The boehmite precursors with high surface area have been obtained using aluminum isopropoxide (AIP) and deionized water as starting materials and have been transformed into  $\alpha$ -alumina after annealing at 1200°C for 2 hrs. Aluminum isopropoxide was purified with hydrolysis reaction with isopropyl alcohol for 1 hr by stirring at 120 rpm at 80°C. A highly selective and very sensitive spectrophotometric method was used to determine the trace amounts of each element in the synthesized alumina samples.

**Key words:** Alumina, Aluminum isopropoxide, Boehmite precursor, Sol-gel method, Interfering effect.

### Introduction

During last decades, the utilization of sapphire has dramatically grown for electronics and all branches of technology. Furthermore, sapphire has gradually taken the functions of silicon substrate for use in research laboratories and industries. Consequently, making high quality sapphire in an economical way has become an issue for material scientists. The appropriate quality and purity of the starting materials is necessary to grow high quality sapphire single crystal.

Generally, boehmite, which has been widely used as a starting material for the preparation of alumina, can be obtained by the hydrolysis of aluminum isopropoxide (AIP) [1, 2]. And  $\alpha$ -alumina can easily be synthesized by the calcination of the boehmite [3]. It is not only the most economical way, but it is also easy to handle the purity of  $\alpha$ -alumina among the various aluminum alkoxides.

There are many impurities such as Fe, Ti, V, Ca, Mg, Si, Mn, Cu, Pb, Na, Cr and Zn in AIP and  $\alpha$ -alumina. Among the impurities, Fe is the key trace impurity in AIP, which dramatically affects the optical properties of alumina-containing materials [8]. Also, the increase of Fe content in AIP causes the agglomeration of alumina particles prepared by hydrolysis of AIP, which limits the preparation of nano-sized alumina [9]. Furthermore, the other impurities can lead to various disadvantages when using alumina in the above mentioned applications [10]. Therefore, it is important to precisely measure the impurities quantitatively and to remove trace impurities from AIP or from  $\alpha$ -alumina.

Several methods are widely used currently to quantify the impurities in the alumina, such as atomic absorption spectroscopy (AAS), inductively coupled plasma - atomic emission spectrometry (ICP-AES), spark source mass spectroscopy (SSMS), and spectrophotometry. Although ICP-AES method is generally used currently, its sensitivity varies with the kind of elements and the accuracy strongly dependent on the sample preparation method. While the SSMS can detect the impurities with better resolution than ICP-AES up to 0.1 ~ 3 ppm level, the sampling region is so small that it is difficult to obtain the overall impurity level of the sample. The spectrophotometric method [4, 5, 6] used in this study is a relatively simple but showed high sensitivity and accuracy to detect the impurities in the alumina synthesis processes. The high purity alumina can be obtained after repeated vacuum distillation at a controlled temperature and pH together with filtration.

### Experimental

Aluminum isopropoxide (AIP) was purified by hydrolysis with isopropyl alcohol. The concentrated aluminum isopropoxide containing impurities was charged with isopropyl alcohol in the reactor (Fig. 1) and maintained for 1 hr by stirring at 120 rpm at 80°C to hydrolyze the AIP. The purified AIP was obtained by the filtration and vacuum distillation at 10 mmHg and at ~ 140°C.

Highly selective and sensitive spectrophotometric methods were used for the determination of each impurity element in the synthesized alumina. Samples were analyzed spectrophotometrically for Fe by forming the reddish-orange complex of iron(II) and 1,10-phenanthroline ( $C_{12}H_8N_2$ ). This complex absorbs light in the visible region rather strongly with a

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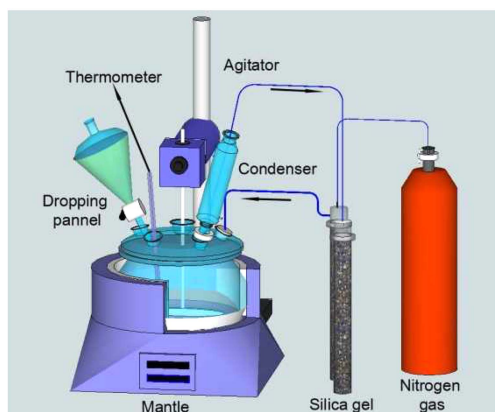


Fig. 1. Schematic diagram of AIP purification apparatus.

maximum absorbance occurring in 510 nm. The method for the determination of trace amounts of titanium(IV) is based on the catalytic effect of titanium(IV) with methylene blue-ascorbic acid redox reaction. The reaction was followed spectrophotometrically by measuring the change in absorbance of methylene blue at 665 nm, 5 minutes after the initiation of the reaction. For the determination of vanadium(V), 2, 3, 4-trihydroxyacetophenonephenylhydrazone (THAPPH) was used as an analytical reagent. This method utilized the catalytic effect of vanadium on oxidation of THAPPH by hydrogen peroxide in hydrochloric acid - potassium chloride buffer (pH = 2.8). For the spectrophotometric determination of calcium, sodium rhodizonate was used as a reagent.

The crystallinity of alumina was measured with X-ray diffractometer (Rigaku with copper  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and  $5^\circ/\text{min}$  scanning speed, 0.01 step size). The morphology of the synthesized samples was observed using the scanning electron microscopy (JSM-6400) with an accelerating voltage of 20 kV. The determination of impurity metal ion concentration was carried out by T-60 UV - VIS spectrophotometer equipped with 1.0 cm quartz cell and the pH of the solution was controlled with a Thermo, Orion 920A + digital pH meter.

## Results and discussion

### Synthesis of aluminium isopropoxide

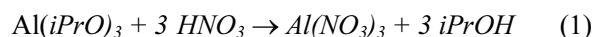
We have used  $\text{HgCl}_2$  or pre-synthesized AIP as a catalyst for the reaction between Al and isopropyl alcohol to obtain AIP. There were no big differences in the XRD patterns (Fig. 2) of the samples with  $\text{HgCl}_2$  or pre-synthesized AIP as a catalyst except the peak and background intensities, both showing the standard reflections of AIP at  $d = 9.77 \text{ \AA}$ ,  $8.79 \text{ \AA}$ ,  $8.03 \text{ \AA}$  (PDF # 30-1508). The only difference is the reaction time of the synthesizing process of AIP and the average particle size of AIP.

### Synthesis of boehmite precursor and $\alpha\text{-Al}_2\text{O}_3$

The stoichiometric amount of deionized water were used for the hydrolysis of AIP to obtain boehmite. The synthesized boehmite precursor after the aging and peptization processes showed partially amorphous structure as shown in Fig. 3 and transformed into  $\alpha\text{-Al}_2\text{O}_3$  by calcination at  $1200^\circ\text{C}$  for 2 hrs with the major peaks at  $3.4891 \text{ \AA}$ ,  $2.5504 \text{ \AA}$ ,  $2.3833 \text{ \AA}$ ,  $2.0891 \text{ \AA}$ ,  $1.7423 \text{ \AA}$ ,  $1.6303 \text{ \AA}$ ,  $1.4048 \text{ \AA}$  and  $1.3754 \text{ \AA}$ .

### Determination of impurity level of synthesized $\alpha\text{-Al}_2\text{O}_3$

One of the main purpose of this study is to determine impurity level of the synthesized  $\alpha\text{-Al}_2\text{O}_3$  such as Fe, Ti, Ca and V by simple spectrophotometric method. The samples were prepared by the hydrolysis of an AIP with 10 - 20% nitric acid, boiling down of the resultant isopropyl alcohol and decomposition of the excess nitric acid, and dilution of the resultant solution with an appropriate amount of deionized water [7].



Then, we have determined the amount of impurities including Fe, Ti, Ca and V using the selective reagent for each element and the spectrophotometer. The color of the sample changed linearly with the concentration

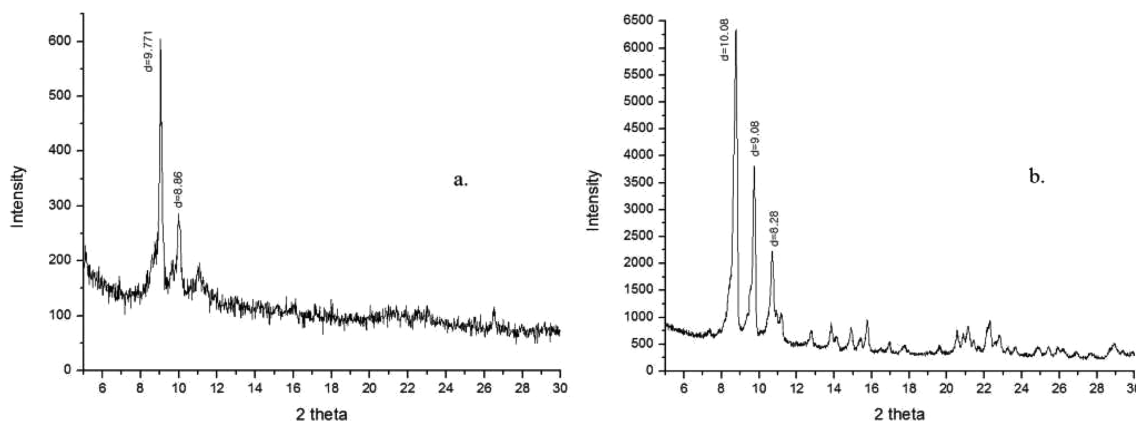


Fig. 2. X-ray diffraction patterns of synthesized AIP (a) with  $\text{HgCl}_2$  and (b) AIP as a catalyst.

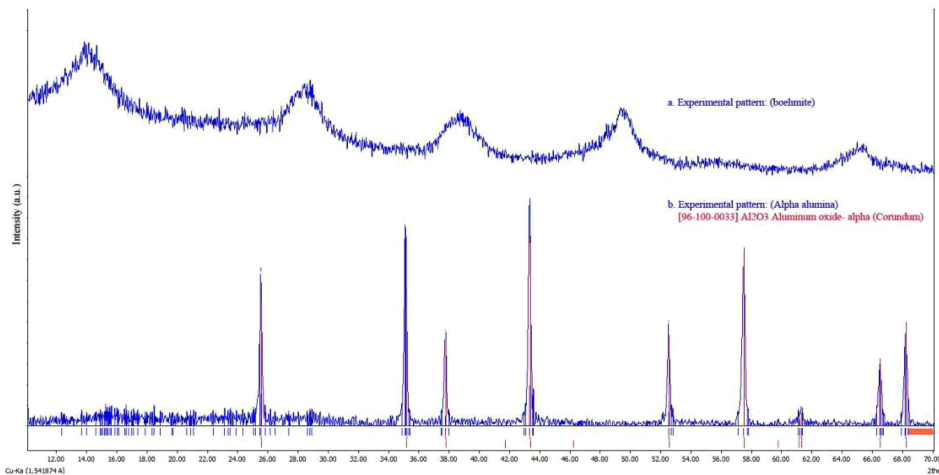


Fig. 3. X-ray diffraction patterns of synthesized (a) boehmite precursor and (b) alumina.

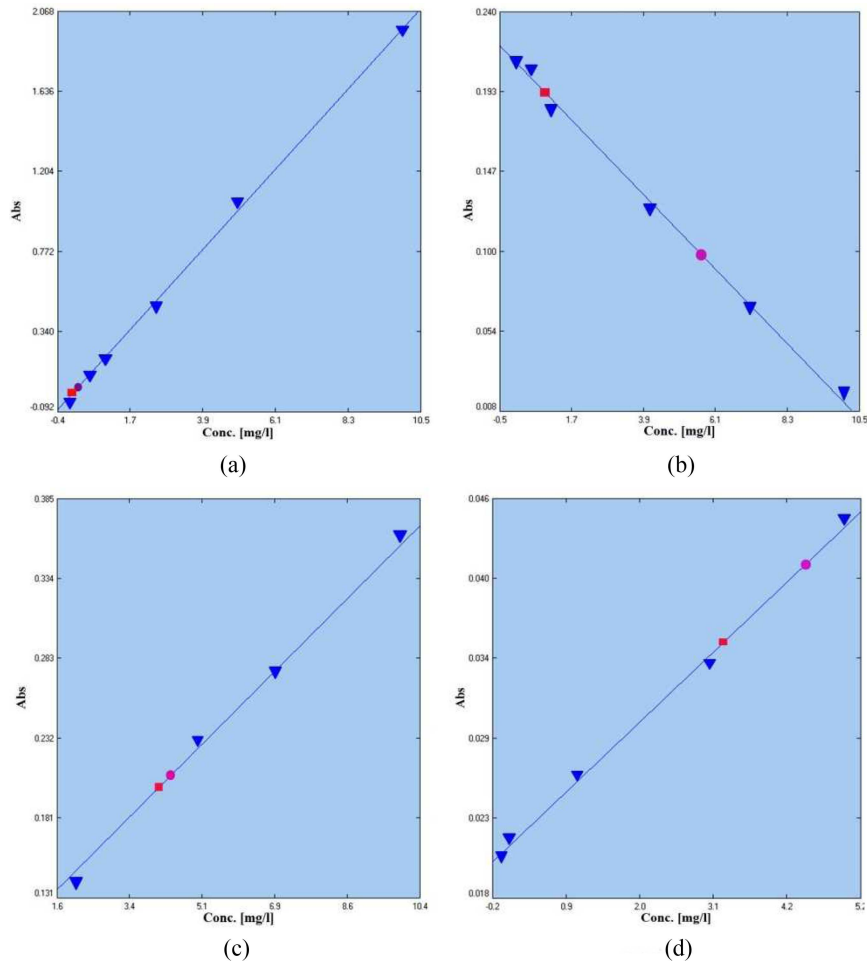


Fig. 4. Determination results of Fe (a), Ti (b), Ca (c) and V (d) in the synthesized alumina:

▼ Calibration curve, ● before purification, ■ after purification.

of each impurity element. The spectrophotometric determination of the sample in this study showed Fe = 0.032 ppm, Ti = 5.666 ppm, Ca = 4.121 ppm and V = 4.506 ppm, respectively (Fig. 4) using the standard calibration lines which have been obtained with the known impurity concentrations of each

elements.

After the purification of AIP by the repeated hydrolysis reaction with isopropyl alcohol and distillation process mentioned above, the impurity level could be reduced as follows; Fe = 0.012 ppm, Ti = 1.3630 ppm, Ca = 3.964 ppm and V = 3.335 ppm, respectively.

## Conclusion

In comparison with the high cost techniques such as ICP-AES or SSMS for metal ions determination, the spectrophotometric method used in this study proved its potential to determine the trace impurity level precisely. It is a low-cost, very simple, selective and highly sensitive method for the determination of metal ions in the range of 0.001 to 10 mgL<sup>-1</sup> with a detection limit of 0.6 ng mL<sup>-1</sup> using a simple spectrophotometer. The procedure is not laborious, easily eliminates all interfering ions and can be easily adopted in the high purity alumina industry. Also, the purification of AIP by the repeated hydrolysis and vacuum distillation in this study was effective for synthesizing extremely high purity alumina, e.g. at least 5N or higher.

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