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CHARACTERIZATION OF THE GASEOUS AND SOLID PRODUCTS OF DECOMPOSITION OF ALUMINUM SULFATE

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CHARACTERIZATION OF THE GASEOUS AND SOLID PRODUCTS OF DECOMPOSITION OF ALUMINUM SULFATE

Gary F. Knutsen
(M. S. thesis)

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CHARACTERIZATION OF THE GASEOUS AND SOLID PRODUCTS OF DECOMPOSITION OF ALUMINUM SULFATE

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CHARACTERIZATION OF THE GASEOUS AND SOLID PRODUCTS OF DECOMPOSITION OF ALUMINUM SULFATE

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ABSTRACT

Mass spectrometry and effusion weight loss experiments were used to study the gaseous decomposition products of $Al_2(SO_4)_3$. Constant SO_2^+/SO_3^+ ion ratios show that equilibrium is achieved within the effusion cell for three orifice diameters. The H_2O^+/SO_3^+ ion ratio remains constant at about 1/6 until the sulfur oxide content of the effusion cell is essentially exhausted. This result indicates that "anhydrous" aluminum sulfate contains in the lattice about 0.03 moles water per mole of sulfate ion. Experimentally determined decomposition pressures are approximately four times higher than equilibrium pressures calculated from heats and entropies of formation, but agree to within the 5Kcal uncertainty in the measured heat of formation of $Al_2(SO_4)_3$.

The solid decomposition product of $Al_2(SO_4)_3$ is a metastable, amorphous alumina at temperatures below 600°C. The surface area of the alumina is $165M^2/gm$ with particles which contain internal pores which average about 100Å in diameter. These internal pores are not accessable to SO_2 adsorption at room temperature, presumably because reactions of alumina with SO_2 or an impurity block the pore mouths.

INTRODUCTION

Many metal sulfates, when heated, decompose to a solid oxide plus a mixture of SO_3 gas, SO_2 and O_2 in proportions that depend on the temperature necessary to cause decomposition. Very stable sulfates which are formed from refractory oxides yield mainly SO_2 and O_2 as gaseous products. Among reactions investigated in our laboratory in recent years were the decomposition of barium and strontium sulfates.[1,2] These reactions yielded SO_2 and O_2 as primary gas products in both Knudsen (equilibrium) and Langmuir (kinetic) studies. But recently, by a means of a combined weight loss, torsion effusion and mass spectrometry study, Lau and co-workers[3] showed that when $MgSO_4$ is heated in effusion cells, SO_3 is formed at its equilibrium partial pressure, but the equilibrium partial pressures of SO_2 and O_2 were not readily attained. When the orifices of the cells were made sufficiently small or Fe_2O_3 was added as a catalyst a shift toward the equilibrium gas composition was observed.

It appeared of interest to investigate a sulfate decomposition that occurred at a lower temperature than required for $BaSO_4$, $CaSO_4$ or $MgSO_4$, to determine if under conditions for which equilibrium decomposition pressures of SO_2, O_2 and SO_3 are calculated to be nearly equal, the equilibrium concentration of these gaseous products can be obtained. From available data[4,5] it could be predicted that aluminum sulfate decomposition would be suitable for such a study. Furthermore, it appeared of particular interest to investigate the crystal structure, morphology and surface are of the solid product of the reaction sequence:

$$Al_2(SO_4)_3 \cdot 17H_2O_{(s)} \rightarrow Al_2(SO_4)_{3(s)} + 17H_2O_{(g)} \rightarrow Al_2O_{3(s)} + 3SO_{2(g)} + \tfrac{3}{2}O_2(g)$$

Aluminum sulfate has been shown to decompose directly to Al_2O_3 without formation of intermediate basic sulfates, and there are no crystal transformations reported for $Al_2(SO_4)_3$.[4,5,6] Although the most stable form of Al_2O_3 is corundum, designated αAl_2O_3, thermal decomposition of the sulfate in air at temperatures less than 450°C yields an x-ray powder diffraction pattern which indicates that the alumina is amorphous (Ref. 1). A study by Kalintina and Pori-Koshits[6] on aluminum sulfate shows that the sulfate decomposes directly to gamma alumina at approximately 900°C, and then transforms into α-Al_2O_3 at temperatures greater than 1150°C.

Beruto and Searcy[7,8,9] recently showed that the CaO which is produced by decomposition in vacuum of $CaCO_3$ particles less than 30 microns in diameter yields a calcium oxide that is poorly crystalline and has particles with an internal porosity of more than 50%. The oxide is much more reactive towards water vapor than is the oxide produced by decomposition of $CaCO_3$ in air or dry nitrogen.

The molar volume of Al_2O_3 formed from $Al_2(SO_4)_3 \cdot 17H_2O$ can be calculated to be only 10% that of the starting material. Therefore, the alumina from $Al_2(SO_4)_3 \cdot 17H_2O$ decomposition in vacuum might well be highly porous as well as metastable. We have, therefore, studied both the gaseous and solid products of vacuum decomposition of $Al_2(SO_4)$ which in turn was a product of $Al_2(SO_4)_3 \cdot 17H_2O$ dehydration.

Weight loss and mass spectrometry measurements were used to study the gaseous decomposition products. The effusion weight loss method is capable of producing highly accurate decomposition pressure data, once the composition of the vapor is known. Mass spectrometry produce

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information from which the gas composition can be obtained. X-ray diffraction, scanning electron microscopy, surface area analysis and pore-size distribution measurements were applied to obtain a fairly complete characterization of the solid decomposition product.

EXPERIMENTAL

The mass spectrometer used in this study was a 24cm radius, Atlas CH4 magnetic deflection device equipped with a 16 stage, Cu-Be, electron multiplier for use as an ion current detector. Reagent grade aluminum sulfate powder was purchased from the J. T. Baker Co., the only detectable impurities were .010% Cl, .001% Fe and .001% Pb. The powder, a hydrated form of $Al_2(SO_4)_3$, was heated for 24 hours at 350°C to drive the water off. The product then showed the expected powder x-ray pattern for anhydrous $Al_2(SO_4)_3$ (Fig. 1).

The dried $Al_2(SO_4)_3$ was stored in a vacuum desicator until it was transferred to a 99.5% alumina effusion cell. The cell was heated in the mass spectrometer by radiation from a 0.025cm diameter tungsten wire surrounded by a tantalum heat shield. Temperatures were measured with a Pt - Pt 10% Rh thermocouple inserted in the bottom of a platinum cell holder which contained the alumina cell (Fig. 2).

Experiments were performed with cell lids of three different orifice diameters in order to test whether equilibrium is achieved inside the cells, and to correct for non-equilibrium if necessary.[10] Orifice diameters were 0.31, 0.51, and 0.78mm respectively and the channel length of each lid was 2.13 mm.

Background pressures ranged from 5.0×10^{-8} to 7.0×10^{-8} torr, as measured by an ion gauge, before each run following an overnight bakeout.

The intensities of the SO_3^+ and SO_2^+ ions were followed using both 70 ev and 17ev electrons. In all the decomposition runs the temperature variations were less than 2°C, and the temperatures were stable at the mid-points for long periods of time. The total fluxes of $SO_3 + (SO_2 + H_2O)$

were calculated from the weight changes and the known periods of heating. The relative amounts of SO_2 and SO_3 effused were determined by monitoring the mass 80 peak, which corresponds to $S^{32}O_3^{16}$, and both the mass 64 which corresponds to $S^{32}O_2^{16}\,O_2^{16}$ and the mass peak 66 for $S^{34}O_2^{16}$.

The Al_2O_3 that formed on the decomposition of $Al_2(SO_4)_3$ was examined by the powder x-ray diffraction method to determine its crystal structure. The surface areas of the porous aluminum oxide and the aluminum sulfates were measured using a Quantasorb Surface Area Analyzer. The samples were out-gassed for 1 to 2 hours at 350°C prior to surface area determination to desorb water or other contaminates which may have adsorbed on the samples surface. In this apparatus, mixtures of helium and nitrogen gas are passed through a small cell containing the sample. At liquid nitrogen temperature, helium will not adsorb to a significant extent on any surface, while nitrogen will physically adsorb on all surfaces at that temperature. The quantity of nitrogen adsorbed at various partial pressures can be used to calculate the sample's surface area.

Adsorption and desorption occur when the sample is immersed and then withdrawn from a liquid nitrogen bath. Changes in the ratio of He to N_2 in the flowing stream, due to adsorption and desorption, are sensed by a specially designed thermal conductivity detector. The instantaneous signal height is proportional to the rate of adsorption and desorption and the total area under the signal is proportional to the quantity of gas adsorbed.

Pore size distributions were studied for thoroughly out-gassed samples using a high pressure (60,000 lb.) American Instrument mercury porisimeter.

RESULTS AND DISCUSSION

It has been reported[11] that fragmentation of SO_3 to SO_2^+ is considerable. In order to determine accurate composition data, the ion current ratios were measured at 17eV (about 5eV above appearance potential for both ions[6]). The effective cross-section σ_{eff} for a molecule at less than maximum potential values is given by the equation

$$\sigma_{eff} = \frac{(E-AP)\sigma}{(E_{max}-AP)}$$

where AP is the appearance potential. σ_{eff} for SO_2 is 0.52 and for SO_3 it is 0.54 based on cross-sections by Mann[13] and appearance potentials determined by Hildenbrand. At 17eV, fragmentation of both SO_2 and SO_3 will be minimal and almost equal for both molecules. At 17eV the vapor effused from orifices of diameters 0.31, 0.51, and 0.78 millimeters all showed SO_2^+/SO_3^+ ratios of 1.8/1. The fact that the ratios were independent of orifice area shows that equilibrium was attained. At 70eV the SO_2^+/SO_3^+ ratio was 2.7/1 for both 0.51 and 0.78 millimeter orifices, therefore, the fragmentation of SO_3 to SO_2^+ has a significant effect when 70eV electrons are used in studies of decomposition of aluminum sulfate.

Our early mass spectrometric measurements at 70eV ionizing energy were higher than 2.7/1. Subsequent analysis of the effusing vapor showed that H_2O^+ was present at an intensity approximately 1.1 times that of SO_2^+. After some 20% of the sulfur oxide had been driven out by heating, however, the H_2O^+ intensity decreased in the first hour of decomposition to about 10 to 15% of the SO_2^+ intensity. The relative intensities then remained nearly constant until the sulfate was nearly decomposed (Fig. 3). The initial high water intensity was probably due to adsorbed water, but the subsequent water intensity was probably due to a significant amount of water still in the sulfate lattice.

The ratios of SO_2^+ (from SO_3 and SO_2) and SO_3^+ (from SO_3) measured at 70eV in the mass spectrometer, depended on the previous treatment of the $Al_2(SO_4)_3$. For example, if the powder was exposed to air for more than 20 minutes, a significant amount of water was adsorbed and the SO_2^+/SO_3^+ ratios increased to 5/1. This result suggested that the water vapor reacted with $SO_3(g)$ to form sulfuric acid. In fact, $H_2SO_4^+$ was observed at about 10% of the intensity of H_2O^+ intensity and the SO_2^+/SO_3^+ intensity ratio also decreased. Evidentally, reaction with adsorbed water, significantly reduces the SO_3 partial pressure and leads to a misleadingly high SO_2^+/SO_3^+ ion ratio.

The intensity of SO_2^+, SO_3^+ and H_2O^+ all decreased by about 40% over a period of 6 hours. Since the ion ratios indicated an equilibrium mixture of SO_2 and SO_3, we believe that the electron multiplier was poisoned by the sulfur oxides during the decomposition runs, thus decreasing its sensitivity with time. When nearly 95% of the $Al_2(SO_4)_3$ was decomposed, the SO_2^+/SO_3^+ ratio for 70 volt electrons increased from 1.8/1 to 4.2/1. This change can be attributed to a shift in the equilibrium $SO_3(g) \rightarrow SO_2(g) + 1/2 O_2(g)$ as the total pressure becomes small.

The decomposition pressure P_M for a reaction that yields a metastable solid product should be lower than the pressure P_S that would be found if the stable product is formed by $P_M/P_S = \exp(-\Delta G°/RT)$ where $\Delta G°$ is the free energy difference between the metastable and stable solid. Amorphous alumina which was less stable than γ-alumina was formed at the temperatures of our decomposition pressure measurements. For all orifice sizes, a decomposition pressure approximately 4 times higher than the equilibrium pressure is observed (Fig. 4).

The water loss throughout the decomposition would raise the weight loss probably less than 10%, and therefore, does not account for the discrepancy. The fact that an H_2O^+ peak persisted at some 3% of the $SO_2^+ + SO_3^+$ intensity throughout sample decomposition appears to mean that water, perhaps as HSO_4^- and OH^-, is a significant component of "anhydrous aluminum sulfate," as usually prepared. This agrees with the report by Young[15] that he was unable to lower the water content below 0.3 wt%, or about 2.4 mole%, of the sulfur oxide content. The formation of such ions presumably would lower the SO_2 and SO_3 partial pressures. It appears that the reported heat of formation of $Al_2(SO_4)_3$, on which the calculated pressure to which we compared our measured pressure depends, may be too negative by about 5 Kcal/mole, a conclusion consistent with the 5 Kcal/mole estimated uncertainty in the calorimetric data.

Decomposition of $Al_2(SO_4)_3$ in vacuum of 450°C produced only an amorphous x-ray pattern (Fig. 5). Decomposition in vacuum at 750°C produced a somewhat crystalline x-ray pattern, with only the three major peaks of γAL_2O_3 present (Fig. 6). Decomposition in vacuum at 1100°C produced α-Al_2O_3. These results are consistent with earlier results for $Al_2(SO_4)_3$ decomposition in air.[6]

Scanning electron micrographs of $Al_2(SO_4)_3 \cdot 17\ H_2O$, $Al_2(SO_4)_3$ and Al_2O_3 show the particles to be of the same shape and dimensions, approximately 20μ in overall cross-section (Fig. 8). Molar volume calculations indicate that the alumina particles must have in excess of 85% internal porosity. The fact that the pores could not be resolved in SEM pictures shows that their diameters must be less than 0.1μ.

Surface areas were obtained using the dynamic BET method on $Al_2(SO_4)_3 \cdot 17H_2O$, $Al_2(SO_4)_3$ and Al_2O_3. The results are as follows:

Material	Surface Area (M^2/gram)
$Al_2(SO_4)_3 \cdot 17H_2O$	1.5
$Al_2(SO_4)_3$	35
Al_2O_3	165

These results coupled with the scanning electron micrographs prove that the alumina particles have very high internal surface areas.

The average pore sizes were obtained with a high pressure mercury porisimeter. The distribution for Al_2O_3 is given in Fig. 9. The average pore size is about 100 Å.

Because the surface area of 165 M^2/g is nearly as high as those of catalyst supports,[16] we were encouraged to test the possibility that this alumina would adsorb a larger volume of sulfur dioxide per volume of solid than will other sulfur oxide adsorbants. Unfortunately, we found the apparent surface area of the alumina when measured with SO_2 at room temperatures to be less than 35 M^2/g. Presumably reaction of SO_2 or an impurity gas blocked the entrances of internal pores.

Hartman and Coughlin,[17] report that pore size distributions of unsulfated calcines of $CaCO_3$ and sulfated samples are remarkably different. They concluded that pores with radii greater than 0.4μm are probably responsible for the reaction with SO_2 and that incomplete sulfation results from the strong diffusional resistance developed in the interior of the particles due to reduction in porosity as the sulfation reaction proceeds. These results appear inconsistent with an unpublished experiment by D. Beruto. He showed that a calcium oxide which has a very small pore size reacts with SO_2 much more rapidly at 450°C than does calcium oxide that has 1μm pores.

It is potentially of great practical importance to clarify the influence of morphology of high surface area oxides on their reactivities toward SO_2 and SO_3. We hope to carry out such studies with this objective in this laboratory.

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FIGURES

Fig. 1. X-ray pattern of amorphous alumina.

Fig. 2. X-ray pattern of $Al_2(SO_4)_3$.

Fig. 3. Knudsen cell assembly.

Fig. 4. Plot of ion intensity vs. time.

Fig. 5. Plot of equilibrium decomposition pressures with respect to αAl_2O_3, γAl_2O_3 vs. 1/T. 5 Kcal error bar is included on γAl_2O_3 line.

Fig. 6. X-ray pattern of γAl_2O_3.

Fig. 7. X-ray pattern of αAl_2O_3.

Fig. 8. SEM photographs of $Al_2(SO_4)_3$ and Al_2O_3.

Fig. 9. Pore size distribution of Al_2O_3.

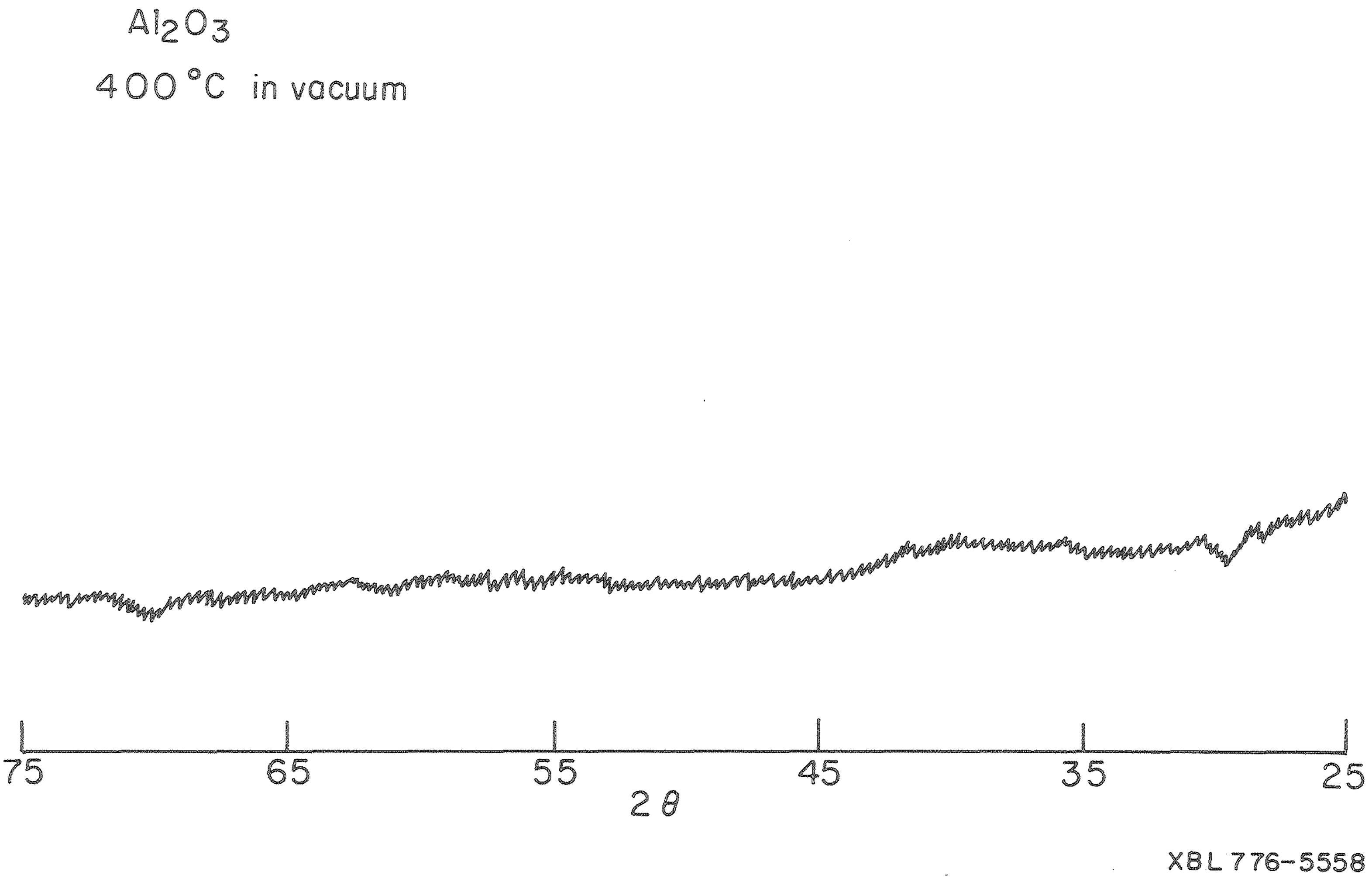
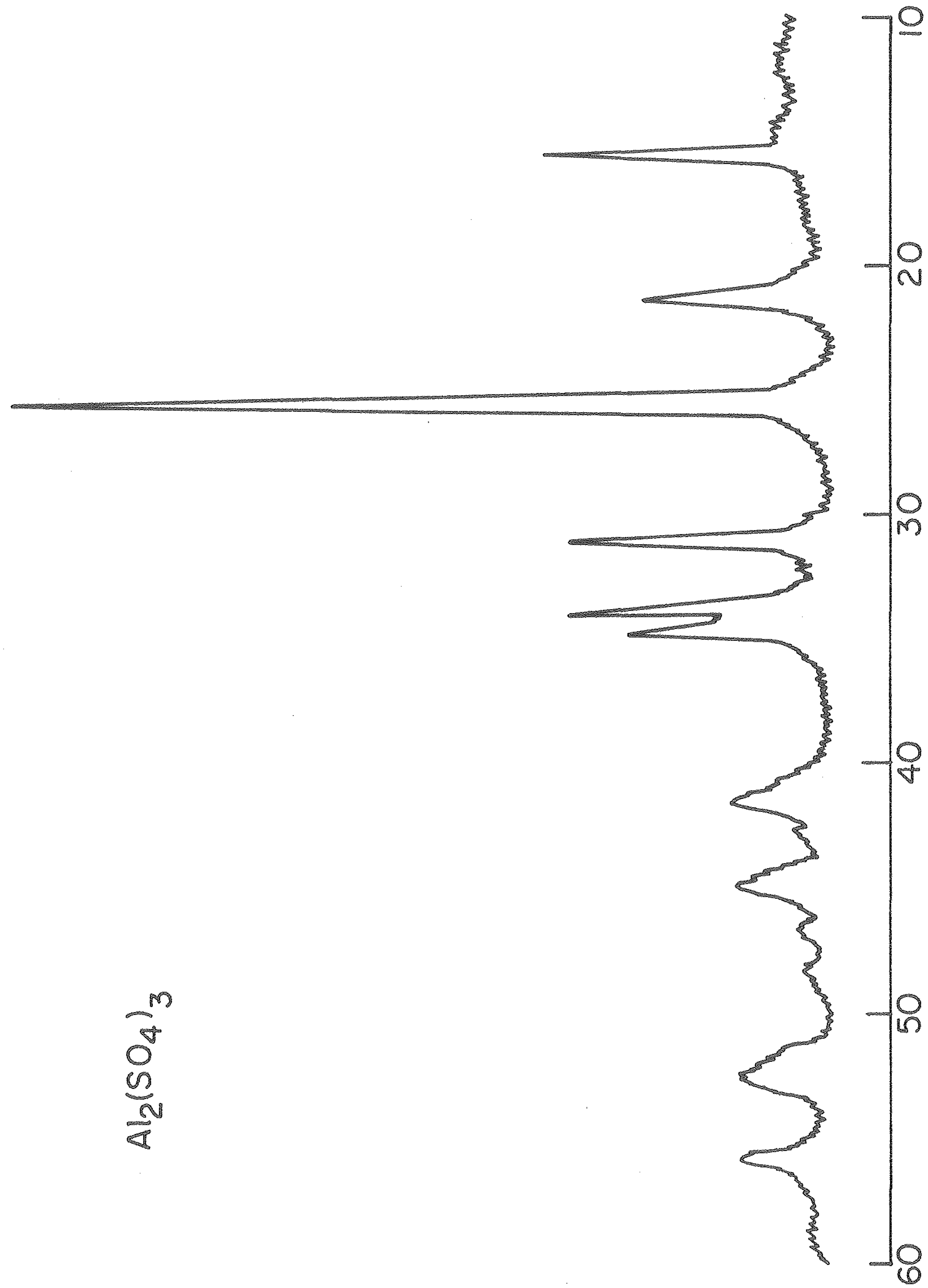
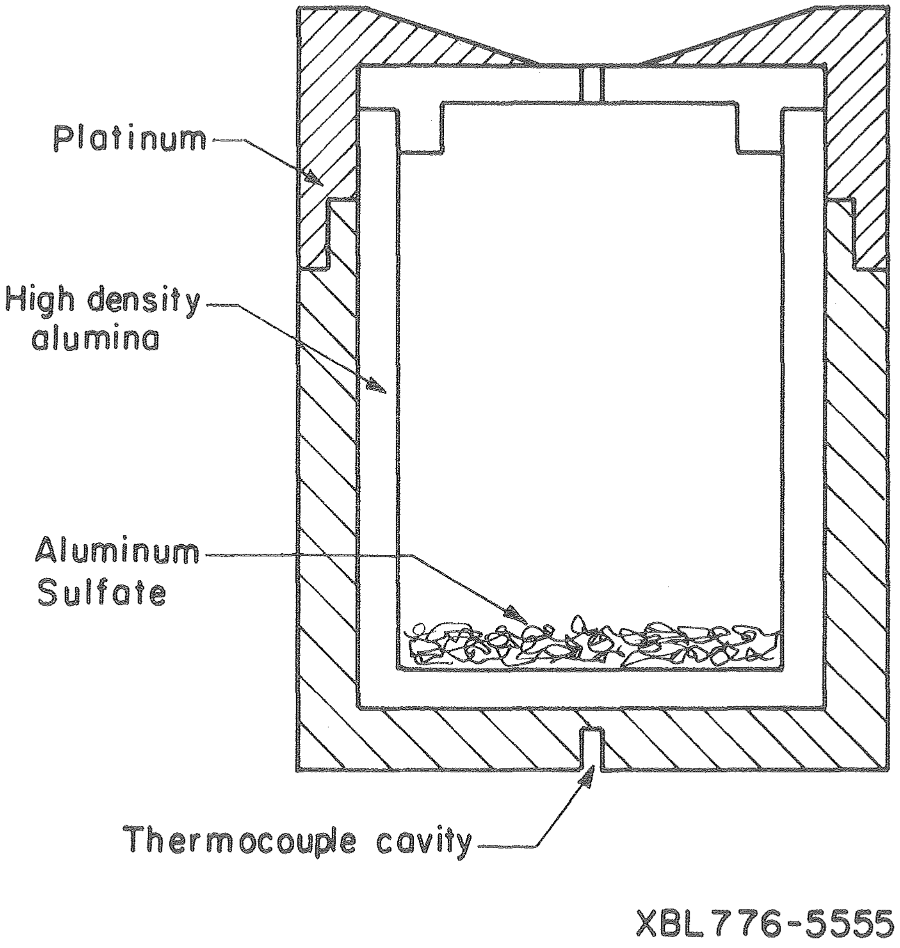


Fig. 1



XBL776-5554

Fig. 2.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High density alumina
Aluminum Sulfate
Thermocouple cavity
XBL776-5555

Fig. 3

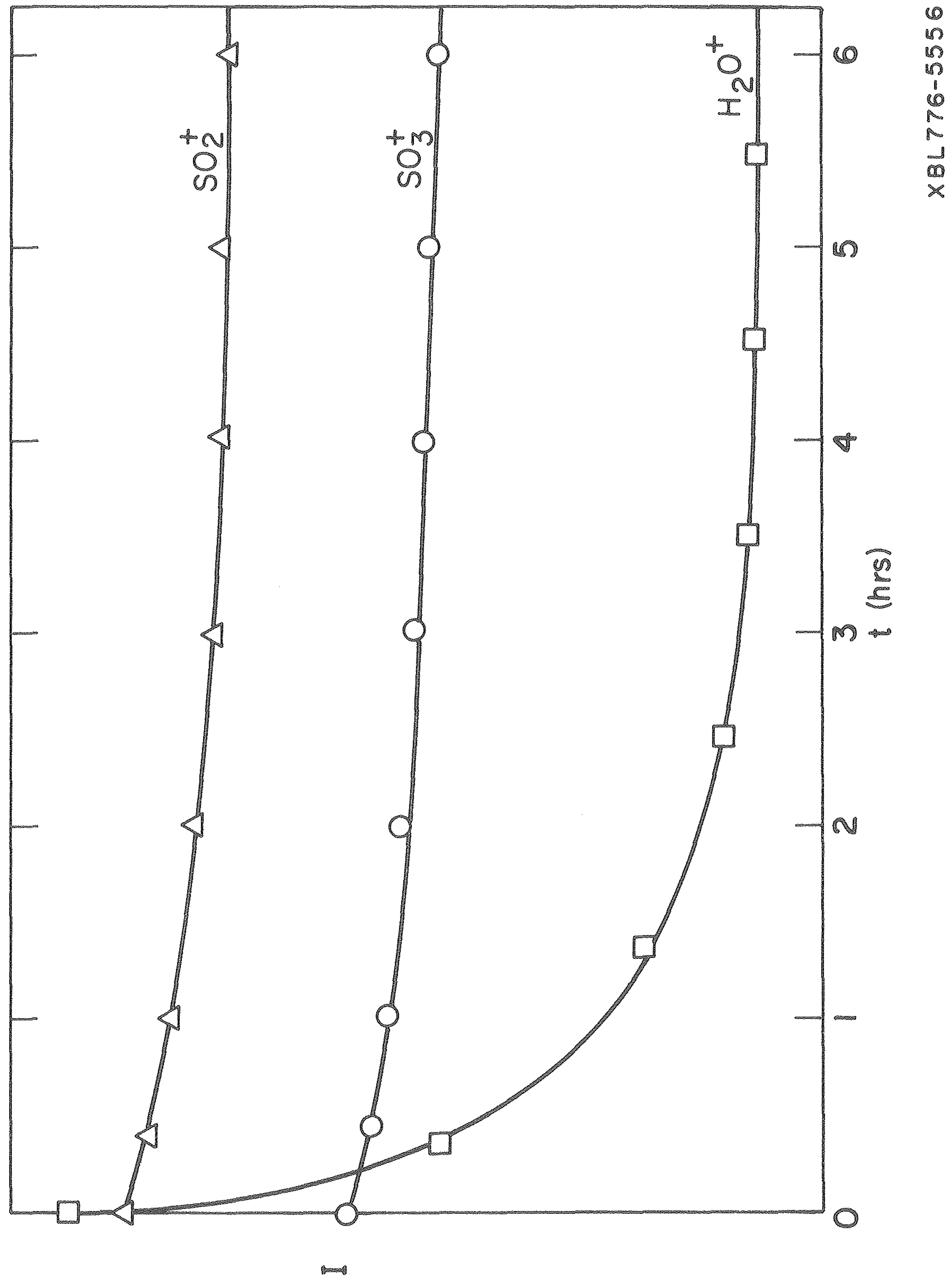

Fig. 4

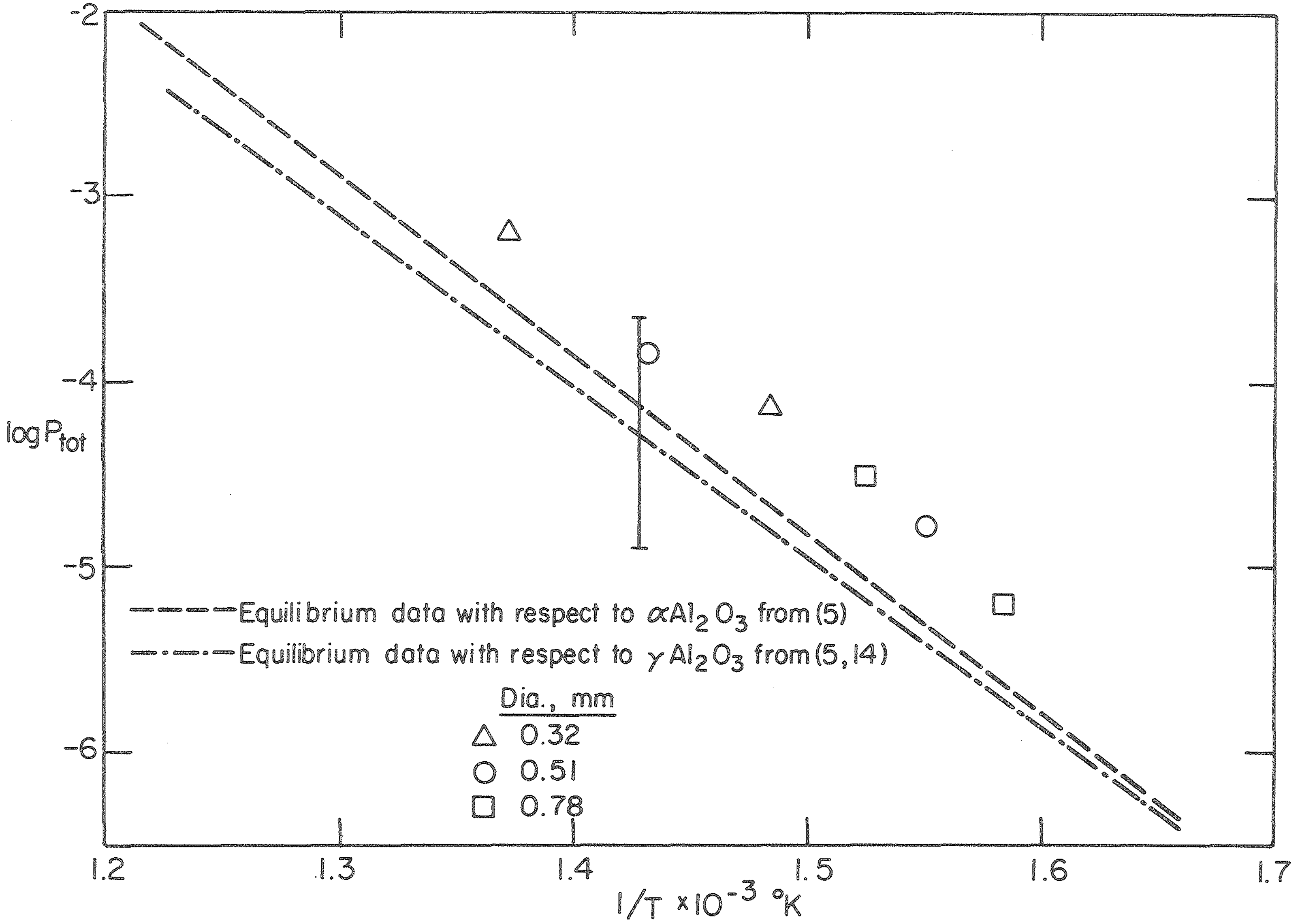

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Fig. 5

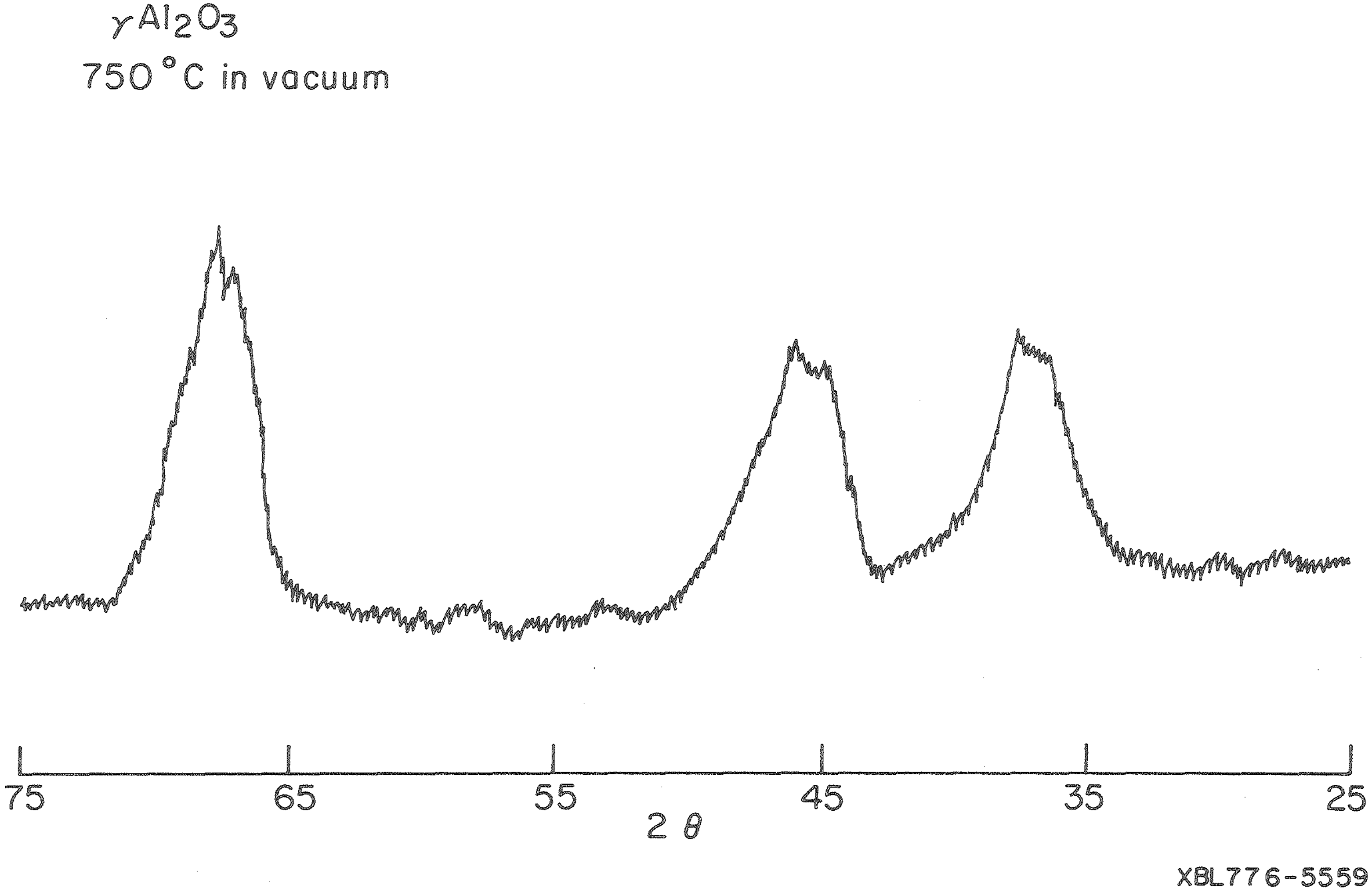

Fig. 6

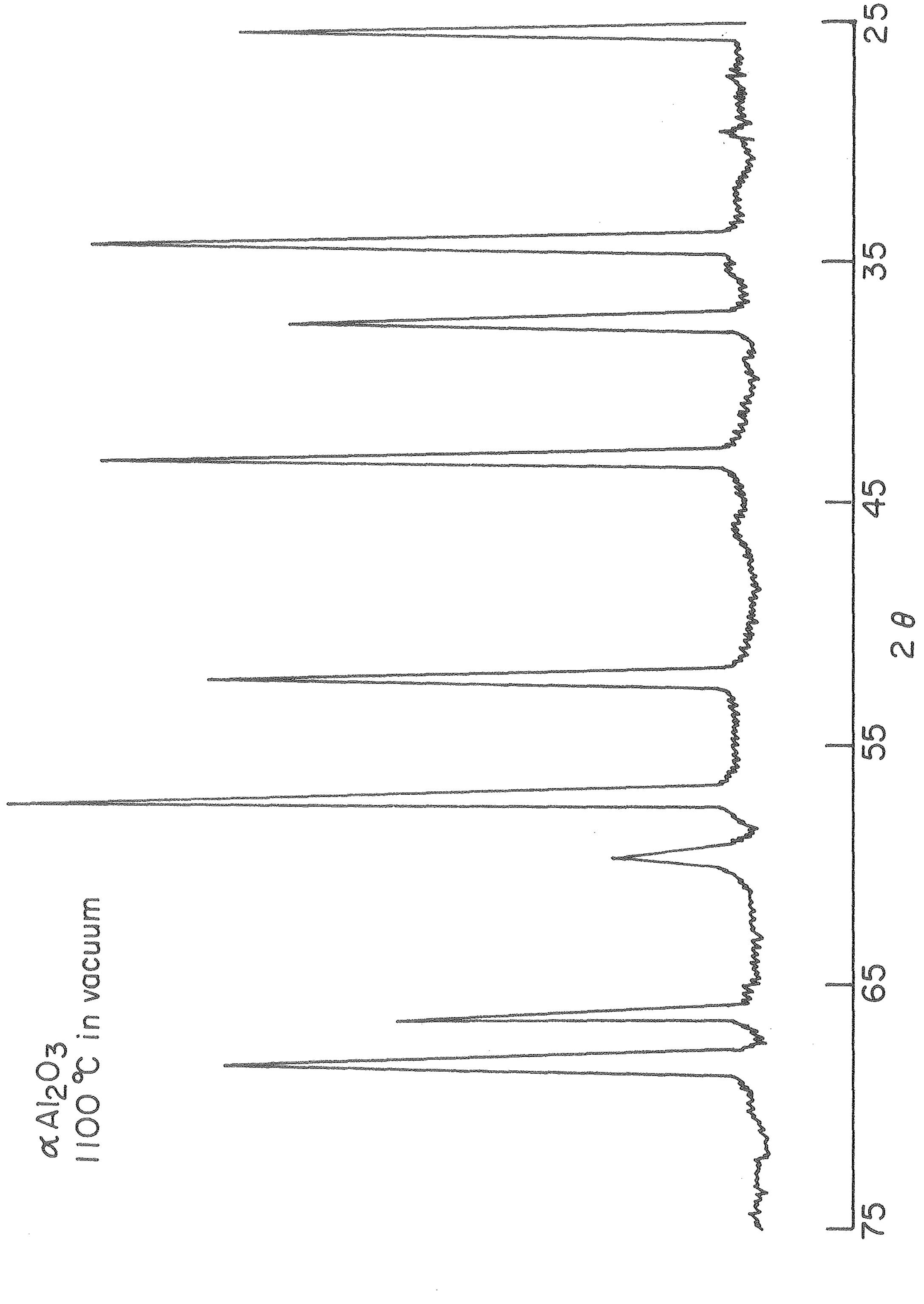

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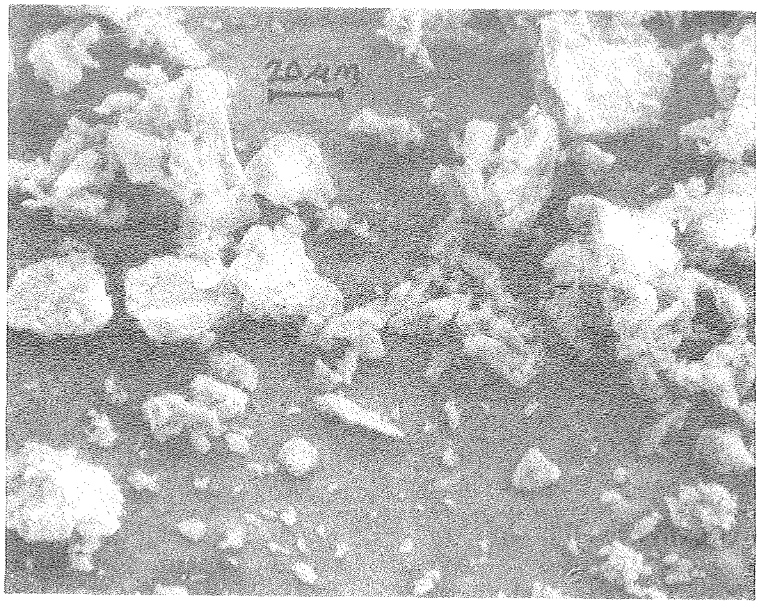
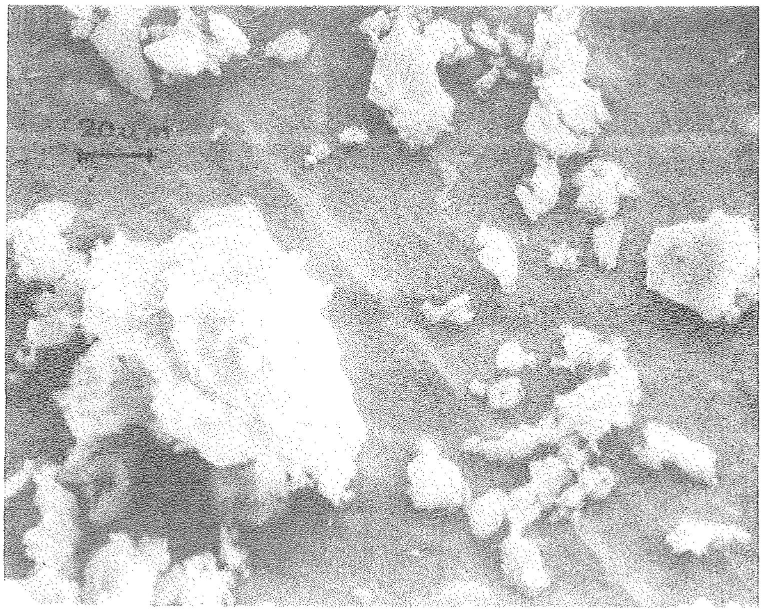
Fig. 7



$Al_2(SO_4)_3$ 500X



Al_2O_3 500X

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Fig. 8

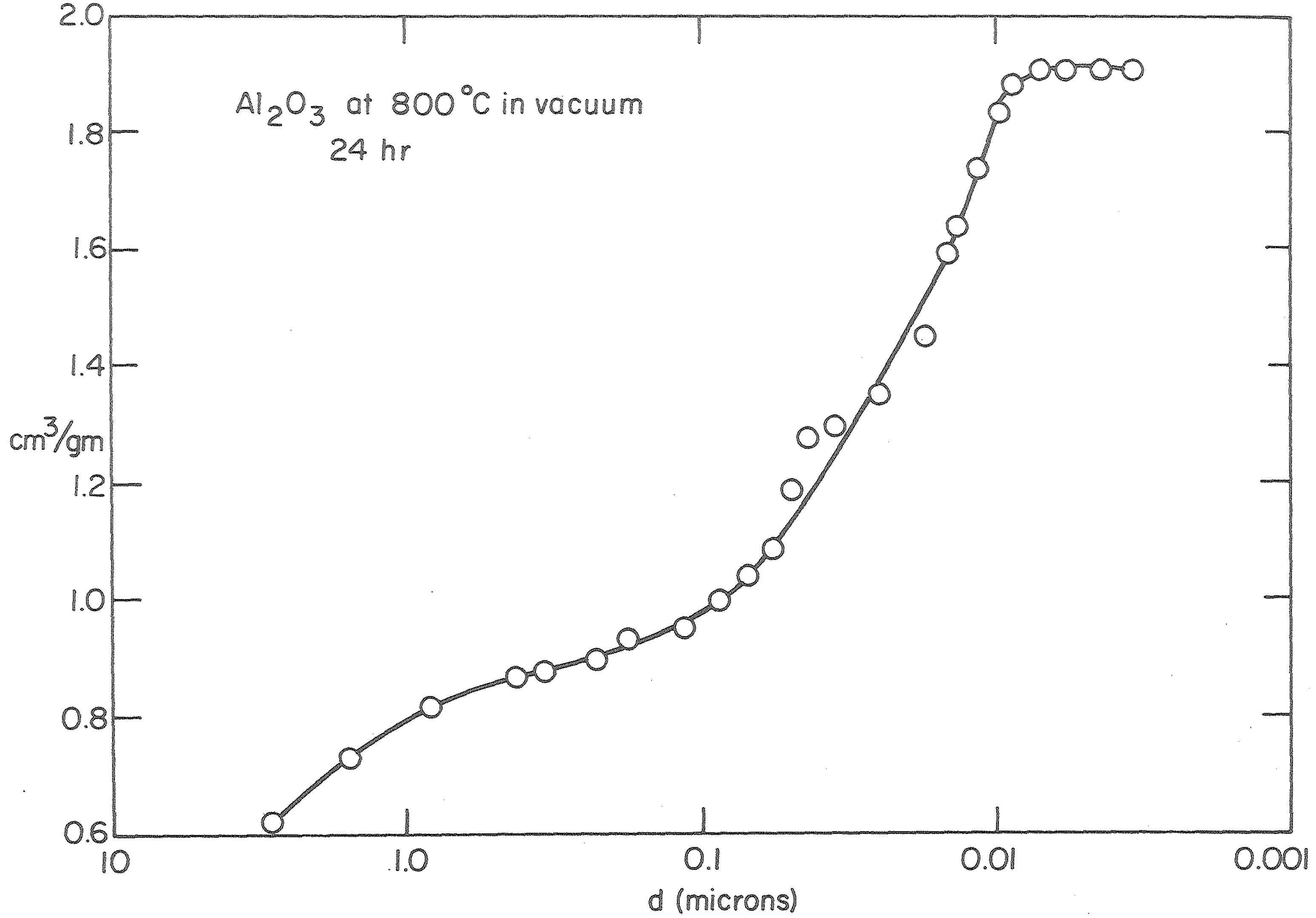

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Fig. 9

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