

TECHNICAL REPORT No. 1

July 1, 1953

OFFICE OF NAVAL RESEARCH  
Contract No. N-onr-404(02)

N. J. CERAMIC RESEARCH STATION  
RUTGERS UNIVERSITY  
New Brunswick, New Jersey  
John H. Koenig, Director

Investigators:

William H. Bauer  
Irwin Gordon  
Ernest R. Glabau

## TABLE OF CONTENTS

	<u>Page</u>
I. Introduction	1
II. Growth Process	2
A. Equipment and Growth Technique	2
B. Feed Material	3
C. Sample Growth	4
III. Crystal Structure	5
A. Tolerance Factors	9
B. Discussion	10
IV. Melting Point	11
V. Refractive Index	12
A. Technique and Sample Preparation	14
B. Measurements	15
C. Data and Calculations	16
VI. Density	19
A. Calculations	19
VII. Thermal Expansion	20
A. Interferometer Description	20
B. Procedure	21
C. Data and Calculations	22

	<u>Page</u>
VIII. Spectral Transmittance	25
A. Sample Preparation	25
B. Procedure	25
C. Data	26
D. Discussion	26
IX. Electrical Properties	29
A. Procedure	29
B. Data and Calculations	30
C. Discussion	34
X. Discussion of Results	35
XI. Conclusions	38
Bibliography	39

I. INTRODUCTION

This is a technical report based on investigations originated under ONR project N7-cnr-454 /2 and completed under project N-cnr-404 (02). The investigation dealt with the synthesis and study of several rare earth aluminates. Much has been previously reported on the general growth technique used (See Technical Reports I & II under N7-cnr 454/2). Therefore, for the most part, this report will deal with the properties of these aluminates.

Rare earth elements occupy a unique position in the Periodic System. By means of the well known lanthanide contraction, the ions of the series of elements beginning with lanthanum and ending with lutetium undergo a regular decrease in size with increasing atomic number. The reason for this decrease is apparent when the electronic structure of the rare earth atoms is examined. With few exceptions, the normal progression for elements increasing in atomic number consists of the addition of successive electrons to the outermost electron shell.<sup>1</sup> Starting with the rare earths, however, this trend is halted, and subsequent electrons are generally added to the 4f orbital in the N shell. The O and P shells remain constant in their electronic structure, and having correspondingly increased the nuclear charge, the result is a progressive decrease in the ionic radii. We may show the manifestations of this leptonic behavior by examining the ionic radii of the rare earths.<sup>2</sup> Starting with La<sup>+3</sup> which has a radius of 1.22 A, we proceed to Ce<sup>+3</sup> of radius 1.18 A, Pr<sup>+3</sup> of 1.16 A, Nd<sup>+3</sup> of 1.15 A, etc., to Lu<sup>+3</sup> of radius 0.99 A. Further, since the outermost structure, which determines the valence, remains constant, the rare earths are extremely similar in chemical nature.

By synthesizing single crystals of a series of rare earth compounds, the effect of this varying ionic radius on the physical

properties, with constant valence, could be studied. It is on single crystals that fundamental measurements can best be made, unaffected by grain boundaries, extraneous phases, and other discontinuities found in samples of the ceramic type.

The rare earth compounds chosen were of the  $ABO_3$  type in which A is the rare earth element, B is aluminum, and O, oxygen. By this choice it was also hoped to uncover several interesting facts due to the structure of the compound. The structure of  $LaAlO_3$  had been determined by V. N. Goldschmidt as being of the perovskite type.<sup>3</sup> In light of the recent work on  $BaTiO_3$  and other perovskite-structure ferroelectrics,<sup>4-6</sup> it seems reasonable that  $ABO_3$  compounds of the rare earths might also possess a ferroelectric nature.

The choice of the rare earth elements to be studied was governed by their availability. Lanthanum, cerium, and neodymium salts are obtainable in sufficient quantity and desired purity and were therefore utilized.

## II. GROWTH PROCESS

### A. Equipment and Growth Technique

The Verneuil, or flame fusion process was used to grow these refractory compounds. The process, described in previous publications, consists of a feeding device, burner, lowering apparatus and suitable gas controls. While several types of burners are available, the one used chiefly is essentially a modified Verneuil type, consisting of an outer tube carrying the hydrogen and an inner tube carrying the oxygen and feed material.

The technique of forming crystalline boules consists of shaking the finely powdered feed into the oxygen stream which, with the hydrogen, is ignited at the burner tip. A cone-shaped mound of sintered material is formed, the point of which, when sufficiently

small, is melted and then crystallization begins to take place. The resulting foot is allowed to grow upward for a distance and is then widened out into the boule proper.

A more detailed description can be found in the literature and in the previous technical reports. 7-10

#### B. Feed Material

The feed material for flame fusion growth is usually prepared from extremely pure oxides, carbonates, nitrates, alums or gels, thoroughly mixed and calcined to a suitable temperature. The production of feed with the desired homogeneity, purity, and physical characteristics is one of the most difficult problems of the project.

For this investigation various double salts of the rare earths were used which, upon calcination, yielded the desired oxides. The necessary weights of the salts, having been calculated, were weighed and intimately mixed. The mixture was then placed into a covered fused silica dish and calcined through a time-temperature cycle depending upon the composition. The following was the choice of rare earth double salts and the respective optimum calcination treatments:

1. LaAlO<sub>3</sub> - the source of lanthanum was the ammonium nitrate of composition  $\text{La}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ . This salt, of 99.4% purity, was supplied by the Lindsay Light & Chemical Company of West Chicago, Illinois. The optimum calcination for this compound consisted of heating to 2200°F for 1 hr.

2. CeAlO<sub>3</sub> - the cerium component was obtained from ammonium hexanitrate cerate,  $2\text{NH}_4\text{NO}_3 \cdot \text{Ce}(\text{NO}_3)_4$ , which was of 99% purity. The supplier of this salt, the G. Frederick Smith Chemical Company of Columbus, Ohio, specializes in pure cerium chemicals and designates this grade of sample as "Standard or Reference Purity". By

calcining to 2050°F for 1-1/2 hrs., feed with the best possible properties was attained.

3. NdAlO<sub>3</sub> - the ammonium nitrate, 2NH<sub>4</sub>NO<sub>3</sub>.Nd(NO<sub>3</sub>)<sub>3</sub>.4H<sub>2</sub>O was used as the source of neodymium. The 99% pure salt was also purchased from the Lindsay Light & Chemical Company. The calcination procedure for this compound consisted of heating to 2000°F for a period of 1-1/2 hrs.

In the series of three compounds, the ammonium alum, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.24H<sub>2</sub>O, was used as the source of Al<sub>2</sub>O<sub>3</sub>. The high purity product (99.8% pure) was supplied by Baker & Adamson, General Chemical Division of the Allied Chemical & Dye Corporation, New York. It proved to be of sufficient purity to allow the growth of colorless corundum boules, a relatively strict criterion.

### C. Sample Growth

The growth of the lanthanum and neodymium aluminates offered no undue difficulties. In the case of the cerium aluminate, however, a difficulty that can probably be ascribed to the dual valency of cerium manifested itself. The boules persisted in cracking and when cooled by the normal technique of instantly cutting off the flame, were found to be covered with a layer of scum. If, however, the boules were cooled by slowly decreasing the oxygen content of the flame, the scum absented itself from the upper portions of the boules. An experiment was performed in which the same feed was passed through the oxidizing tricone burner of the type used for the growth of rutile. The result was a boules which in no way resembled the cerium aluminate crystals formed with the normal Vernouil burner. The entire boules surface as well as the cone appeared powdery and was of a straw color, as opposed to the transparent lime-green crystals grown

normally.

A chemical analysis\* of the boules coincided with the composition as prepared to within 0.5% indicating negligible, if any, loss by vaporization.

### III. CRYSTAL STRUCTURE

Goldschmidt, in his monumental series of contributions, determined the structure of  $\text{LaAlO}_3$  to be of the perovskite type<sup>3</sup> (Figure 1). The perovskite structure takes its name from the mineral perovskite, a calcium titanate,  $\text{CaTiO}_3$ . As described in Strukturbericht,<sup>12</sup> the structure is cubic with one formula weight per unit cell. In general, compounds of the perovskite type have the formula  $\text{ABO}_3$ ; in this investigation, A = rare earth ion, B = aluminum ion, and O = oxygen ion.

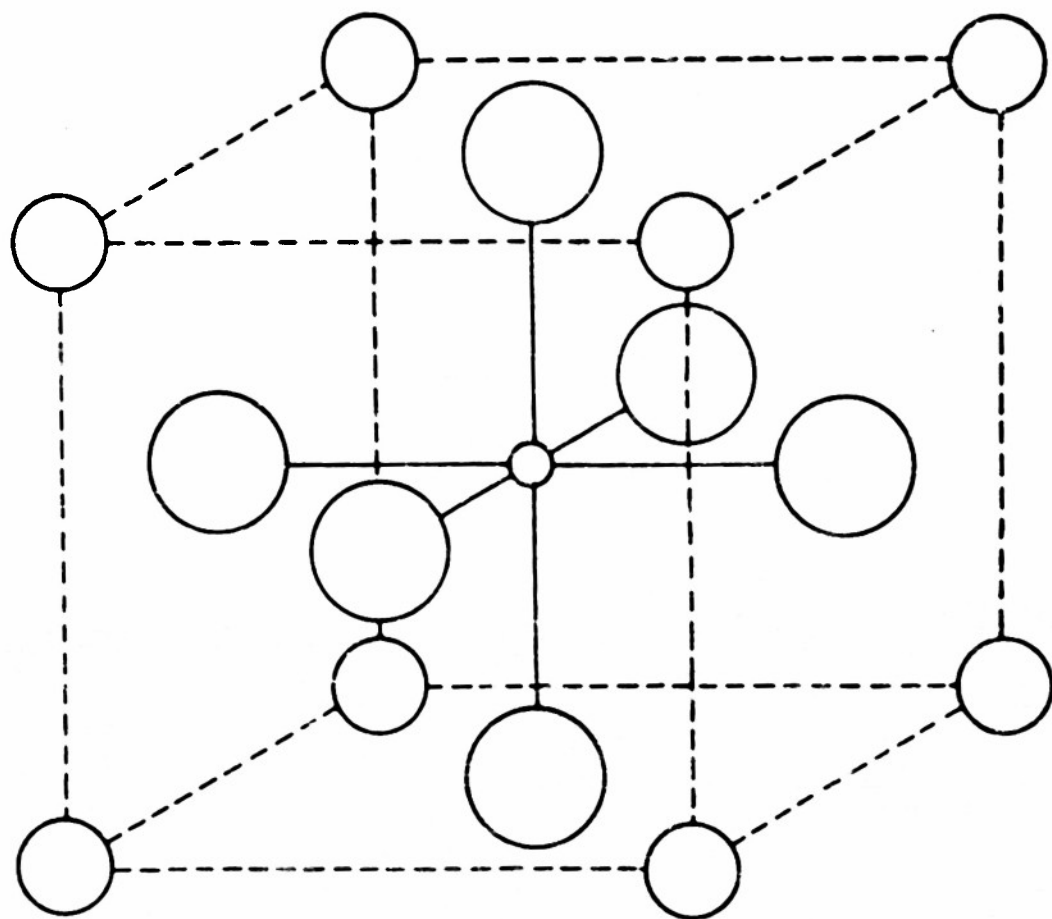
Powder patterns were made of crushed crystalline boules of the series and the results examined. A Norelco recording Geiger-Muller type spectrometer employing nickel-filtered copper  $K\alpha$  radiation was used in obtaining the patterns. The results may be seen in Figure 2.

The data obtained for  $\text{LaAlO}_3$  correspond exactly with the data given by Goldschmidt. Analogous patterns and structures are obtained for  $\text{CeAlO}_3$  and  $\text{NdAlO}_3$ .

By means of the geometric relationship between the cube edge and the crystallographic planes, we may calculate the various distances corresponding to the respective plane separations. The equation for cubic crystals is as follows:

$$d = \frac{a_0}{\sqrt{h^2+k^2+l^2}} \quad (1)$$

6.



○ = La, Ce, or Nd

○ = O

○ = Al

Figure 1  
RELATIVE IONIC POSITIONS IN INVESTIGATED  
PEROVSKITE STRUCTURE



where  $d$  = interplanar distance  
 $a_0$  = cube edge  
 $h, k$  and  $l$  = Miller indices

Upon substituting the appropriate values (3.78 for  $a_0$  in the case of  $\text{LaAlO}_3$ ) and the various Miller indices into equation (1), Table I was constructed. A comparison between Table I and Figure 2 points out the correctness and similarity of the assigned structures.

The nature of the perovskite structure is such that a certain amount of variance from the ideal cube is possible.<sup>13</sup> This variance has been described as a tolerance factor<sup>3</sup> which is based on geometric considerations.

In crystals for which the tolerance factor is close to unity, the ideal cubic structure prevails. As the tolerance factor deviates from unity, structures other than cubic occur. Consequently, the tolerance factors for the investigated compounds were calculated using Goldschmidt's ionic radii and the equation

$$t = \frac{(R_A + R_C)}{\sqrt{2}(R_B + R_O)} \quad (2)$$

where  $t$  = tolerance factor  
 $R_A, R_B$  and  $R_C$  = ionic radii of A, B and C respectively

Table I

<u>(hkl)</u>	<u>LaAlO<sub>3</sub>(G)</u>	<u>LaAlO<sub>3</sub></u>	<u>CoAlO<sub>3</sub></u>	<u>NdAlO<sub>3</sub></u>
100	3.78	3.78	3.76	3.73
110	2.68	2.68	2.66	2.64
111	2.18	2.18	2.17	2.16
200	1.89	1.89	1.88	1.87
210	1.69	1.69	1.68	1.67
211	1.54	1.54	1.53	1.52
220	1.34	1.34	1.33	1.32
221				
300	1.26	1.26	1.25	1.24
310	1.20	1.20	1.19	1.18

LaAlO<sub>3</sub>(G) - Goldschmidt data

Since the ionic radii are given for a coordination number of 6, and the radius varies somewhat with the coordination number, the ionic radius of A must be corrected for its coordination number which is 12. The correction factor used in the following calculations was obtained from Pauling.<sup>14</sup>

A. Tolerance Factors

1. LaAlO<sub>3</sub>

$$t = \frac{(1.30 + 1.32)}{\sqrt{2(0.57 + 1.32)}} \\ = 0.985$$

2. CoAlO<sub>3</sub>

$$t = \frac{(1.26 + 1.32)}{\sqrt{2(0.57 + 1.32)}} \\ = 0.970$$

### 3. NdAlO<sub>3</sub>

$$t = \frac{(1.22+1.32)}{\sqrt{2(0.57+1.32)}} \\ = \underline{0.955}$$

As a result of the values obtained for the tolerance factors, it was felt that more refined X-ray data would be in order. Slight deviations from the cubic system indicated by these tolerance factors could possibly thereby be measured and the structures more closely defined.

The data of Table II, corresponding to a refinement of Figure 2 are the result of measurements made at the Squier Signal Corps Laboratories of Fort Monmouth through the courtesy of Dr. A. E. de Brotteville.

By these more accurate measurements, LaAlO<sub>3</sub> is seen to be truly cubic, whereas CoAlO<sub>3</sub> and NdAlO<sub>3</sub> are tetragonal, the c/a ratios being 1.0001 and 1.006 respectively.

### B. Discussion

E. D. Hogaw,<sup>13</sup> in her discussion of the criteria for the formation of structures different from the ideal cubic, shows that the tolerance factor is a rough guide. That is, the perovskite structure is stable with "t" values greater than 0.80. Having observed cubic structures with "t" values as low as 0.91, a postulate was set up relating the cubic structure to the B-O and A-O distances and the radius sums, rather than the tolerance factors. It was shown that in the cubic structures, the B-O distance is slightly less than, and the A-O distance slightly greater than, the sum of the ionic radii. Upon these considerations, all the rare earth aluminates investigated may be shown to be cubic. The relatively

minute variation from cubic determined by means of the X-ray would not detract from the Megaw postulation. Rather it may be considered that the compounds are, for all practical purposes in the subsequent measurement of physical properties, cubic in nature.

Table II

X-RAY DATA FOR RARE EARTH ALUMINATES AS  
DETERMINED BY DR. A. E. DE BRETTEVILLE

<u>hkl</u>	<u>LaAlO<sub>3</sub></u>	<u>CeAlO<sub>3</sub></u>	<u>NdAlO<sub>3</sub></u>
100	3.774	3.746	3.733
110	2.660	2.651	2.641
111	2.174	2.170	2.163
200	1.883	1.884	1.874
210	1.686	1.687	1.672
211	1.539	1.538	$\alpha_1$ 1.532
			$\alpha_2$ 1.525
220	1.334	1.333	$\alpha_1$ 1.329
			$\alpha_2$ 1.325
300	1.260	1.257	$\alpha_1$ 1.251
221			$\alpha_2$ 1.246
310	1.195	$\alpha_1$ 1.199	1.186
		$\alpha_2$ 1.193	

#### IV. MELTING POINT

In order to learn the melting point of the series of aluminates, it was found necessary to construct a furnace

capable of attaining temperatures of the order of  $2000^{\circ}\text{C}$ . An induction type furnace was decided upon, the source of power being a vacuum-tube generator set manufactured by the Scientific Electric Company of Garfield, New Jersey. This high frequency generator has an output of 10 KW in the range 200 to 600 KC. The furnace consists of an induction coil, graphite susceptor, and appropriate insulation. Samples were prepared by modifying V. Wartenbergs method. Utilizing an optical lever mirror, temperature measurements were made with an optical pyrometer. The mean melting points of lanthanum, corium, and neodymium aluminate were determined to be  $1917^{\circ}\text{C}$ .,  $2017^{\circ}\text{C}$ ., and  $2055^{\circ}\text{C}$ ., respectively. The details of kiln construction, sample preparation, furnace calibration, and the calculations used will be fully reported in a separate technical report in the near future.

#### V. REFRACTIVE INDEX

In determining the fundamental optical property (the refractive index) of the crystals under study, the procedure normally would consist of examining crystal grains by means of the petrographic microscope. The immersion liquids usually employed, however, were found to be of too low a refractive index to be useful. Some idea of the magnitude of refractive index to be uncovered was gained using the empirical relationship of Gladstone and Dale<sup>16a</sup> and the specific refractive energies as given in Larson and Berman.<sup>16</sup> According to Gladstone and Dale, there exists a relationship, unchanged by temperature, between the refractive index, density, and specific refractive energy of a substance. This relationship is

as follows:

$$\frac{n-1}{d} = K \quad (4)$$

where

$n$  = mean refractive index

$d$  = density

$K$  = specific refractive energy

Further,  $K = k_1 \frac{P_1}{100} + k_2 \frac{P_2}{100} + \text{etc.}$  where  $k_n$  and  $P_n$  are the specific refractive energies and weight percents of the elementary or oxide components of the substance.

The component specific refractive energies tabulated in Larsen and Berman were computed and averaged from a number of minerals. Values for "k" are assertedly in agreement within 5% when computed from the properties of the minerals or component oxides.

The  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ , and  $\text{Ce}_2\text{O}_3$  values are given as 0.193, 0.149, and 0.16, respectively.  $\text{LaAlO}_3$  consists of 23.83%  $\text{Al}_2\text{O}_3$  and 76.17%  $\text{La}_2\text{O}_3$ ;  $\text{CeAlO}_3$  contains 23.67%  $\text{Al}_2\text{O}_3$  and 76.33%  $\text{Ce}_2\text{O}_3$ . A value of "k" for  $\text{Hf}_2\text{O}_3$  was not given.

For  $\text{LaAlO}_3$ , then, by equation (4).

$$\frac{n-1}{d} = K = k_1 \frac{P_1}{100} + k_2 \frac{P_2}{100} = (0.149) (0.762) + (0.193) (0.238)$$

$$\frac{n-1}{6.59} = K = 0.160$$

$$n-1 = (0.160) (6.59)$$

$$n = 1 + 1.054$$

$$n = \underline{2.05}$$

By like calculations, the refractive index of  $\text{CeAlO}_3$  was expected to be 2.13.

Though the empirical Gladstone and Dale formula was employed to gain some idea of the refractive index to be encountered, the theoretically correct Lorentz-Lorenz relation could have been used equally as well. Consequently, two methods of attack were considered; namely, immersion melts and the preparation of crystal prisms. A preliminary investigation of melts showed them to be relatively difficult to prepare homogeneously, as well as possessing increased opacity with increasing refractive index. Furthermore, once a grain is identified with a melt as to like index, it becomes necessary to prepare a prism of the melt and measure its refractive index on a spectrometer. Rather than prepare a series of melts, which would be necessary for ease of operation, it was decided to proceed with the preparation of crystal prisms since suitable samples were available.

#### A. Technique and Sample Preparation

A Gemlap faceting device, of the type commonly used by lapidaries, was procured for the purpose of grinding the prism samples. The device consists of a vertical standrod which is mounted on the lap housing (parallel to the lap axis). An engraved quadrant rides on the standrod and indicates the angle between the dop arm and the standrod. The dop stick, to which the crystal is cemented, is chucked into the dop arm. The dop arm also is provided with a scale enabling a crystal face to be set in any one of thirty-two positions radially about the axis of the arm. This latter feature was not employed.

The angle which the prism faces should contain for optimum conditions of accuracy and light transmission when employing the method of minimum deviation depends upon several factors. 17.

Foremost among these factors are the refractive index and optical density of the material. Though the angle should be as large as possible for greatest accuracy, in practice such is not the case, for the transmission of the light must be considered. As a result, angles are used which are considerably lower than those indicated. All things considered, a prism angle of  $30^\circ$  was decided upon.

Utilizing the faceting equipment described above, it was relatively simple to grind the sample to the desired angular relationship and to obtain the necessary polish.

A spectrometer was made available by the Physics Department of the University. The particular instrument used was manufactured by the Societe' Genevoise D'Instrumente de Physique, of Geneva, Switzerland. By means of a vernier, the angular scale could be read to ten seconds. A two circle goniometer was an integral part of the spectrometer table and proved indispensable in aligning the prism.

#### B. Measurements

A determination of refractive index by the method of minimum deviation involves the measurement of two angles. These two angles are the prism angle and the angle of minimum deviation of the refracted light. In order to specify the refractive index, monochromatic light must be used, for refractive index varies with the wavelength. Upon examining the transmission data for the crystals, it was found that  $\text{NdAlO}_3$  absorbed quite strongly in many regions of the visible spectrum. In the region of the sodium D line, the wavelength most often used for index determinations, absorption was almost complete. Rather than report the index for dissimilar wavelengths, the mercury green line was chosen for use in

this investigation. A mercury arc lamp was employed with a Wratten mercury green filter No. 62 to isolate the line at  $5460.7 \text{ \AA}$ .

The prism angle,  $A$ , was measured by observing the position of the vertical slit as reflected from each face. If the prism edge is directed toward the collimator, the beam of light is split, a portion being reflected from each face. This reflection position was noted three times alternately for each face. The difference between the mean of the readings for each face represents twice the prism angle.

Having determined the prism angle, the angle of minimum deviation was observed as follows. By rotating the spectrometer table, a prism face was presented to grazing incident light from the collimator. The deviated ray was observed and the position of minimum deviation noted, the table and telescope being displaced and readjusted between each reading. This mean position of minimum deviation forms one side of the angle being measured. By moving the telescope to a position directly opposed to the collimator, the complete angle of minimum deviation is determined. All the data are now obtained for calculating the refractive index from the relationship

$$n = \frac{\sin \frac{1}{2} (A + \delta)}{\sin \frac{1}{2} A} \quad (5)$$

where  $n$  = refractive index  
 $A$  = prism angle  
 $\delta$  = angle of minimum deviation

### C. Data and Calculations

#### 1. LaAlO<sub>3</sub>

##### a. Prism angle, A

	<u>a</u>	<u>b</u>	<u>c</u>	<u>Mean</u>
face (1)	310°35'00"	310°35'00"	310°36'00"	<u>310°35'20"</u>
face (2)	250°4'30"	250°4'40"	250°4'30"	<u>250°4'33"</u>

$$310^{\circ}35'20'' - 250^{\circ}4'33'' = 60^{\circ}30'47'' = 2A$$

$$A = \underline{30^{\circ}15'24''}$$

b. Angle of Minimum Deviation,  $\delta$

	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>
234 <sup>o</sup>	13'30"	-15'00"	-15'00"	-16'00"
	<u>e</u>	<u>f</u>	<u>Mean</u>	
	-14'30"	-15'30"	<u>234<sup>o</sup>14'55"</u>	

$$\text{Telescope position} = 269^{\circ}20'00''$$

$$\text{Angle of minimum deviation} = 269^{\circ}20'00'' - 234^{\circ}14'55''$$

$$\delta = \underline{35^{\circ}4'55''}$$

c. Refractive Index, n

$$n = \frac{\sin \frac{1}{2}(A + \delta)}{\sin \frac{1}{2}A}$$

$$= \frac{\sin \frac{1}{2}(30^{\circ}15'24'' + 35^{\circ}4'55'')}{\sin \frac{1}{2}(30^{\circ}15'24'')}$$

$$= \underline{2.068}$$

2. CeAlO<sub>3</sub>

a. Prism Angle, A

	<u>a</u>	<u>b</u>	<u>c</u>	<u>Mean</u>
face (1)	299 <sup>o</sup> 53'30"	299 <sup>o</sup> 53'20"	299 <sup>o</sup> 53'40"	<u>299<sup>o</sup>53'30"</u>
face (2)	238 <sup>o</sup> 58'00"	238 <sup>o</sup> 58'00"	238 <sup>o</sup> 58'00"	<u>238<sup>o</sup>58'00"</u>

$$299^{\circ}53'30'' - 238^{\circ}58'00'' = 60^{\circ}53'30'' = 2A$$

$$A = 30^{\circ}27'45''$$

b. Angle of Minimum Deviation,  $\delta$

	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>
233 <sup>o</sup>	36'00"	35'30"	36'00"	37'00"
	<u>e</u>	<u>f</u>	<u>Mean</u>	
	36'30"	35'50"	<u>233<sup>o</sup>36'8"</u>	

$$\text{Telescope position} = 269^{\circ}20'00''$$

Angle of minimum deviation =  $269^{\circ}20'00'' - 233^{\circ}36'8''$

$$\delta = 35^{\circ}43'52''$$

c. Refractive Index, n

$$n = \frac{\sin \frac{1}{2} (A + \delta)}{\sin \frac{1}{2} A} = \frac{\sin \frac{1}{2} (30^{\circ}27'45'' + 35^{\circ}43'52'')}{\sin \frac{1}{2} (30^{\circ}27'45'')}$$

$$n = \underline{2.079}$$

3. NdAlO<sub>3</sub>

a. Prism Angle, A

	<u>a</u>	<u>b</u>	<u>c</u>	<u>Mean</u>
face (1)	$321^{\circ}2'20''$	$321^{\circ}2'20''$	$321^{\circ}2'20''$	<u><math>321^{\circ}2'20''</math></u>
face (2)	$262^{\circ}29'00''$	$262^{\circ}30'00''$	$262^{\circ}29'30''$	<u><math>262^{\circ}29'30''</math></u>

$$321^{\circ}2'20'' - 262^{\circ}29'30'' = 58^{\circ}32'50'' = 2A$$

$$A = \underline{29^{\circ}16'25''}$$

b. Angle of Minimum Deviation,  $\delta$

	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>
	$303^{\circ}27'10''$	$26'00''$	$27'40''$	$27'10''$
	<u>e</u>	<u>f</u>	<u>Mean</u>	
	$26'30''$	$26'10''$	$303^{\circ}26'47''$	

Telescope position =  $269^{\circ}20'00''$

Angle of minimum deviation =  $303^{\circ}26'47'' - 269^{\circ}20'00''$

$$\delta = 34^{\circ}6'47''$$

c. Refractive Index, n

$$n = \frac{\sin \frac{1}{2} (A + \delta)}{\sin \frac{1}{2} A} = \frac{\sin \frac{1}{2} (29^{\circ}16'25'' + 34^{\circ}6'47'')}{\sin \frac{1}{2} (29^{\circ}16'25'')}$$

$$n = \underline{2.079}$$

VI. DENSITY

In view of the presently known structure of the rare earth aluminates, it was decided to determine the density of the crystals by calculation. All the data necessary for the calculation are known, assuming a value of  $6.02 \times 10^{23}$  for Avogadro's number. Table III has been constructed, containing the beforementioned data. Since the unit cell contains one molecule, the molar volume is equal to the product of Avogadro's number and the volume of the unit cell. The unit cell volume was obtained by cubing the value for the respective unit cell edge. The slight departure from cubic symmetry reported under "Crystal Structure" is of small enough consequence to leave these data unaffected.

Table III

	<u>LaAlO<sub>3</sub></u>	<u>CeAlO<sub>3</sub></u>	<u>NdAlO<sub>3</sub></u>
Unit cell edge, Å	3.78	3.76	3.73
Unit cell volume, $\times 10^{-24}$ cc	54.01	53.16	51.90
Molecular weight, g./mole	213.89	215.11	219.25
Molar volume, $\frac{\text{cc}}{\text{mole}}$	32.51	32.00	31.24

It is now a simple matter to calculate the density from the following relation:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\text{Molecular Weight}}{\text{Molar Volume}} \quad (6)$$

A. Calculations

<u>LaAlO<sub>3</sub></u>	<u>CeAlO<sub>3</sub></u>	<u>NdAlO<sub>3</sub></u>
$D = \frac{213.89}{32.51}$	$D = \frac{215.11}{32.00}$	$D = \frac{219.25}{31.24}$
$= \underline{6.58}$	$= \underline{6.72}$	$= \underline{7.02}$

### Discussion

Density as derived from X-ray data usually represents the upper limit attainable for that substance. The density obtained is that of the unit cell whereas any other method, i.e. pycnometric, Archimadean, etc., gives the density of an aggregate of unit cells. Since the normal crystal rarely, if ever, consists of perfectly aligned and composed unit cells, values derived from X-ray data represent the limit approached by other measurement methods.

As an experimental check on the reliability of the data employed, the density of  $\text{LaAlO}_3$  was also determined pycnometrically. The mean of eight determinations on three samples gave a value of 6.58. It would seem that the calculated values are reasonably accurate, not only for  $\text{LaAlO}_3$ , but also by analogy for the cerium and neodymium aluminates.

### VII. THERMAL EXPANSION

The determination of the thermal expansion of a crystal normally allows the presence of a phase transition to be made known within the temperature range covered. In order to learn of the existence of polymorphous inversions in any of the crystals studied, as well as for the knowledge of the thermal expansion itself, dilatation data were obtained.

An interferometric method was chosen, being more amenable to the samples at hand as well as being capable of greater sensitivity and accuracy than other dilatometric methods.

#### A. Interferometer Description

The interferometer consists of a pair of fused silica plates, the upper one of which is polished on both faces. These plane faces

are 20' from parallel with each other. The upper surface of the lower plate is likewise polished and bears a reference target at its center; the lower surface of this plate is unpolished to eliminate reflections. In use, the three pyramidally shaped elements comprising the sample are equilaterally placed on the lower plate. The upper plate, with reference notch appropriately placed to allow the 20' angle to act in deflecting unwanted reflections away from the telescope, is supported on the apices of the elements. The result is two parallel faces separated by the known sample height. Monochromatic illumination, the 5460.7 Å line of mercury vapor, is caused to be reflected from the upper surface of the lower plate and the lower surface of the upper plate. If these two reflected waves are in phase, maximum brightness results; if they are in opposition, there is no light and consequently we see a "fringe". It is the apparent movement of these fringes past a reference line which is observed. The movement is caused by the thermal expansion of the sample which in turn causes the distance between the plates to increase. The increase in distance between the plates is manifested by the movement of fringes past a reference line. A movement of one fringe is equal to one-half the monochromatic wavelength used, since the optical path is twice the distance between the plates. Since, with the apparatus at hand, the experiment is performed in air, the change of refractive index of the air must be considered and is accounted for with an "air correction".<sup>18</sup>

#### B. Procedure

Suitable samples were chosen and flat bases lapped on each element, using the forementioned faceting device. The elements were then ground by hand on abrasive paper to an approximately pyramidal

shape until they were of equal height when measured with a micrometer ( $\pm 0.0001$  in.). When this condition was fulfilled, the sample was arranged in the interferometer and usually a convenient number of interference fringes, from seven to fourteen, were visible in the telescope field.

After setting up and aligning the interferometer within the furnace, the entire system was allowed to reach thermal equilibrium. The current thru the furnace and a stop-watch were activated simultaneously. An approximate  $3^{\circ}\text{C}$  rise per minute was followed by adhering to a previously determined time-ampere schedule. Lest any discontinuities in the expansion go by unnoticed, the time and temperature was recorded for every fringe. In order to conserve the fused silica interferometer plates, the current was shut off at  $650^{\circ}\text{C}$ .

Having previously recorded the height of the sample, and knowing the wavelength of the light being used, all the data are known for the calculations.

### C. Data and Calculations

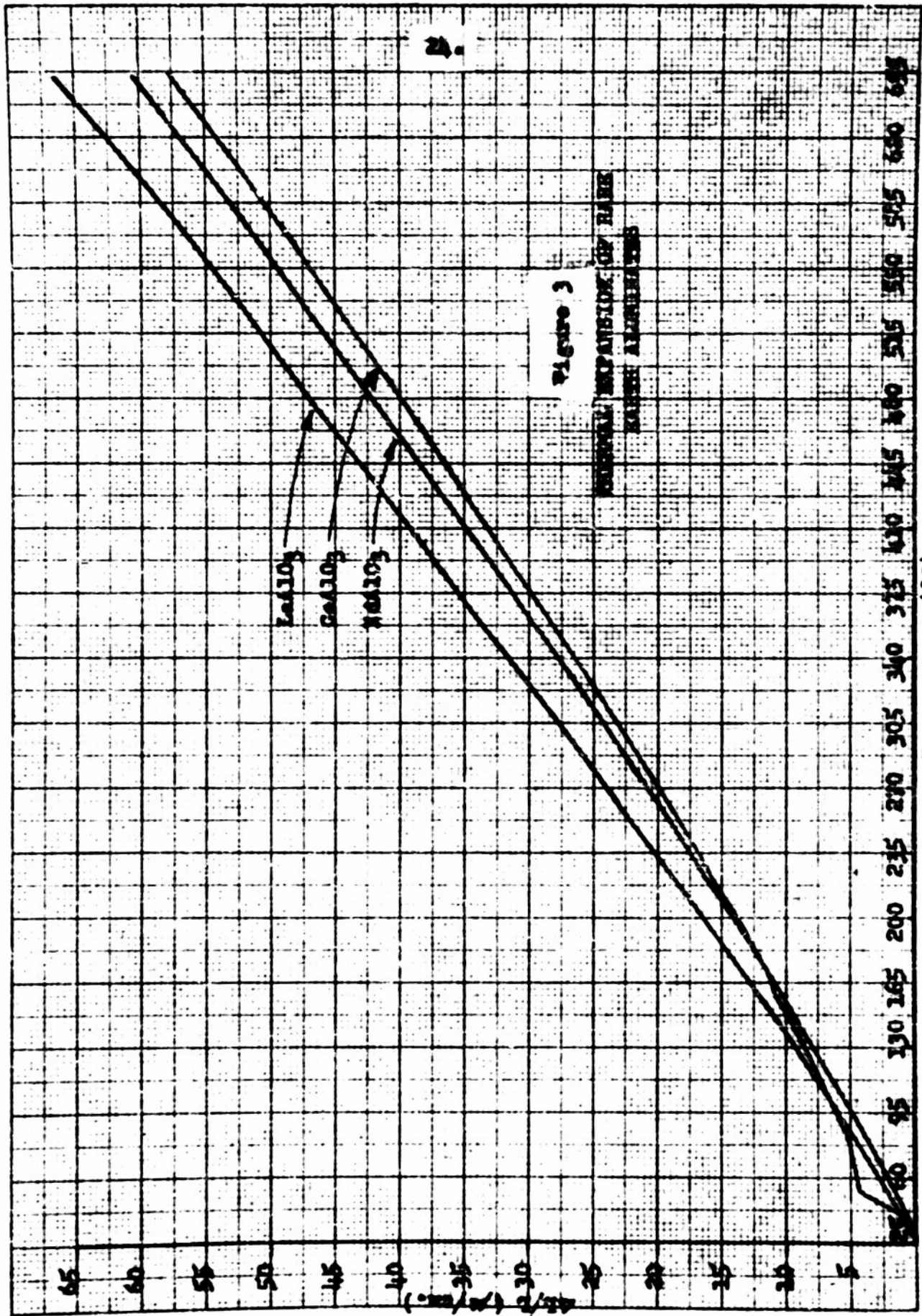
The data, as observed, are recorded as fringe number and temperature. From the sample dimensions ( $L_0$ ), and the wave length of light employed ( $\lambda$ ), a change in length ( $\Delta L$ ) is determined for each fringe number ( $N$ ).  $\left[ \Delta L = \frac{N \lambda}{2L_0} \right]$  To this value of  $\Delta L$  is added an air correction ( $A$ ) to compensate for the change in the refractive index of the air for the temperature at which the fringe is observed. It is this sum of  $\Delta L$  and  $A$  (the corrected change in length per unit length) which is plotted against the temperature at which the particular fringe is observed.

For reasons of convenience, the average coefficient of expansion is expressed in parts per million, or, as plotted as the ordinate of Figure 3, in hundredths of a per cent ( $\mu/cm$ ). Due to the discontinuous nature of the expansion of  $CeAlO_3$  and the slight increase in coefficient with increasing temperature in the other two compounds, a mean coefficient would not be as meaningful as the graph. However, for purposes of general comparison, the mean coefficient of thermal expansion for  $LaAlO_3$  and  $UdAlO_3$  from room temperature to  $650^\circ C$  is 10.66 and 9.70 times  $10^{-6}/^\circ C$ , respectively. For the form of  $CeAlO_3$  prevailing above  $150^\circ C$ , the coefficient is  $9.10 \times 10^{-6}/^\circ C$  between 150 and  $654^\circ C$ .

#### Discussion

Since the expansion of  $CeAlO_3$  was found to be discontinuous, the sample was examined several times at lower heating rates. There was no difference noted in any of the successive runs with respect to the location or amplitude of the discontinuity.

In view of the attainability of temperatures involved, an attempt was made to learn the nature of the high temperature form. An electric heater coil was mounted to radiate directly on the sample holder of the previously mentioned X-ray unit. The temperature of the sample holder was adjusted by means of a Powerstat to remain at about  $95^\circ C$ . The X-ray powder pattern obtained did not vary from the room temperature pattern indicating that the inversion was not sufficiently drastic to visibly alter the structure. A more accurate camera would probably show the structure change, however.



### VIII. SPECTRAL TRANSMITTANCE

The compounds investigated display interesting differences in color. That of lanthanum is orange, cerium is green, and neodymium, brown violet. In order to more closely describe the colors of the crystals, plates were prepared and spectral transmittance data obtained using a spectrophotometer. A Beckman Model DU Photoelectric Quartz Spectrophotometer was used in this investigation in the spectral range from 380 to 770 millimicrons. Transmittance readings were made every two millimicrons in the region from 380 to 600 millimicrons. From 600 to 770 millimicrons, observations were made every five millimicrons. These relatively small increments were found necessary in order that no absorption bands be overlooked.

#### A. Sample Preparation

The samples were prepared by lapping suitable boule fragments to two approximately plane and parallel faces. This operation was accomplished with the aid of the faceting device described previously in the section on "Refractive Index".

#### B. Procedure

The sample holder for transmission measurements requires an exposed sample area of approximately  $1/4 \times 3/4$  inches. Since it would be extremely difficult to prepare samples of that size in suitable quality, an investigation was undertaken to compare spectral sensitivity with sample area.

A sample of AKLO\* glass  $7/32$  in. thick, was observed, first with the normal area exposed, and then with the area decreased to  $7/32 \times 5/16$  in. The two curves were identical, the curve obtained from the smaller area being approximately 1% lower in transmittance

\* Blue Ridge Glass Corp., Kingsport, Tennessee.

(Figure 4). When the normal area was employed but the glass surfaces were roughened with 150 mesh SiC, the same shape of transmittance curve was obtained. On observing this roughened sample with an exposed area of  $1/16 \times 1/16$  in., the curve showed the same general form as with the clear sample using the normally exposed area. The transmittance was greatly decreased, however.

In view of this sensitivity even with a small sample area, reasonably accurate data could be expected on available crystal plates. Consequently two like masks were prepared, one to be used as the standard blank and the other to support the sample. The masks were clamped together and a  $1/8$  inch diameter hole was drilled thru them. In that way, the monochromatic light beam would strike both masks in a like manner. The sample was cemented to one of the masks, both of which were placed and spring held in the transmission cell holder. Data were then obtained by following the standard operating procedure for the instrument. The instrument was also balanced for dark current between each reading.

#### C. Data

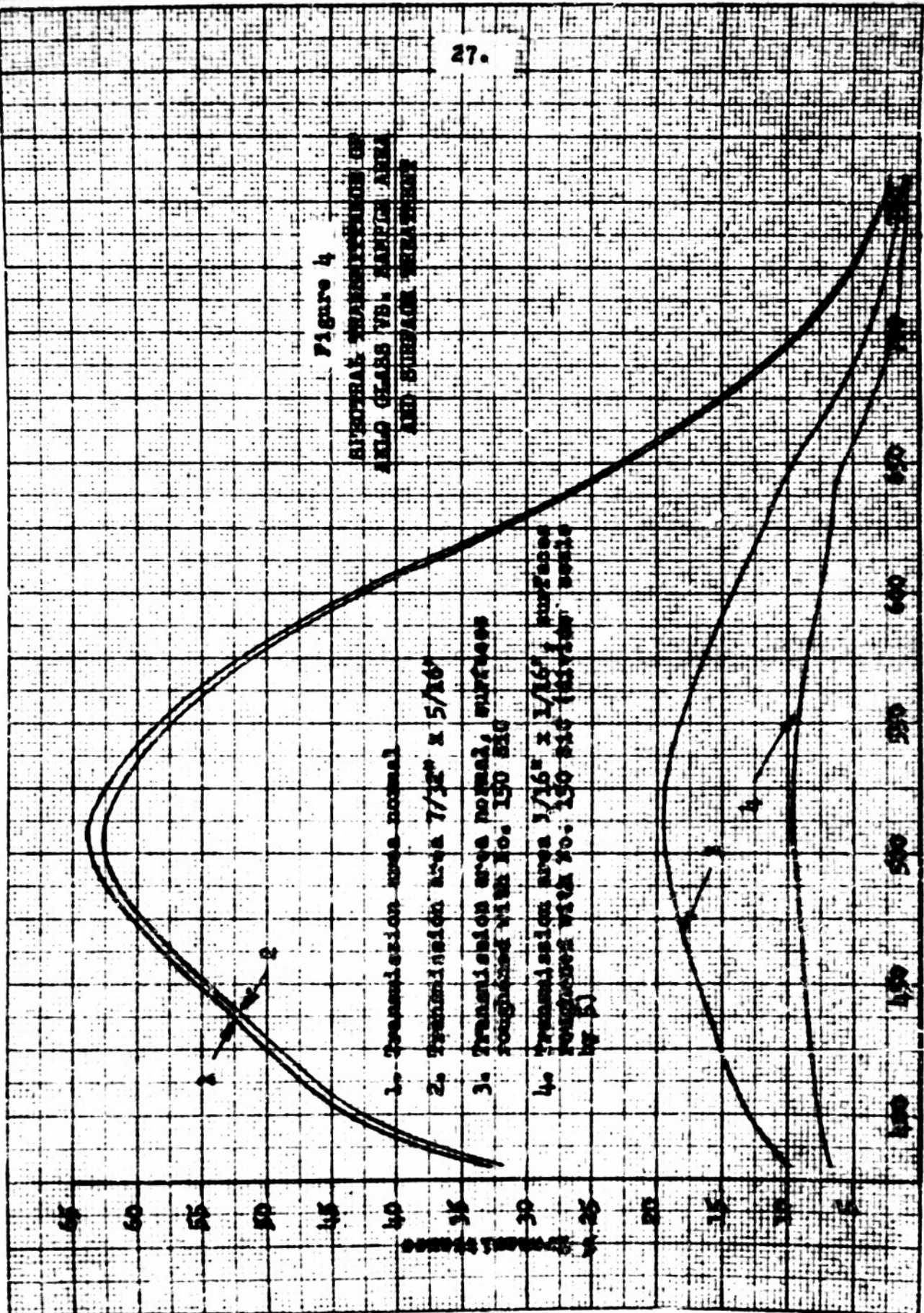
Fig. 5, shows the transmittance values for these single crystal samples. The sample thicknesses were .0394, .0243, and .0145 inches, respectively, for the lanthanum, cerium, and neodymium aluminates.

#### D. Discussion

Insofar as the color of the investigated compounds is concerned, little can be said regarding any preliminary predictions. Color in rare earth salts is due primarily to the incomplete  $4f$  sub-shell, causing characteristic absorptions. Such is the case with neodymium,

Figure 4

**SPECTRAL TRANSMISSION OF  
K10 GLASS VS. SAMPLE AREA  
AND SURFACE TREATMENT**



- 1. Transmission area normal
- 2. Transmission area  $7/32" \times 5/16"$
- 3. Transmission area normal, surface roughened with No. 150 SiC
- 4. Transmission area  $1/16" \times 1/16"$ , surface roughened with No. 150 SiC (division scale 1/2)

Wavelength (microns)

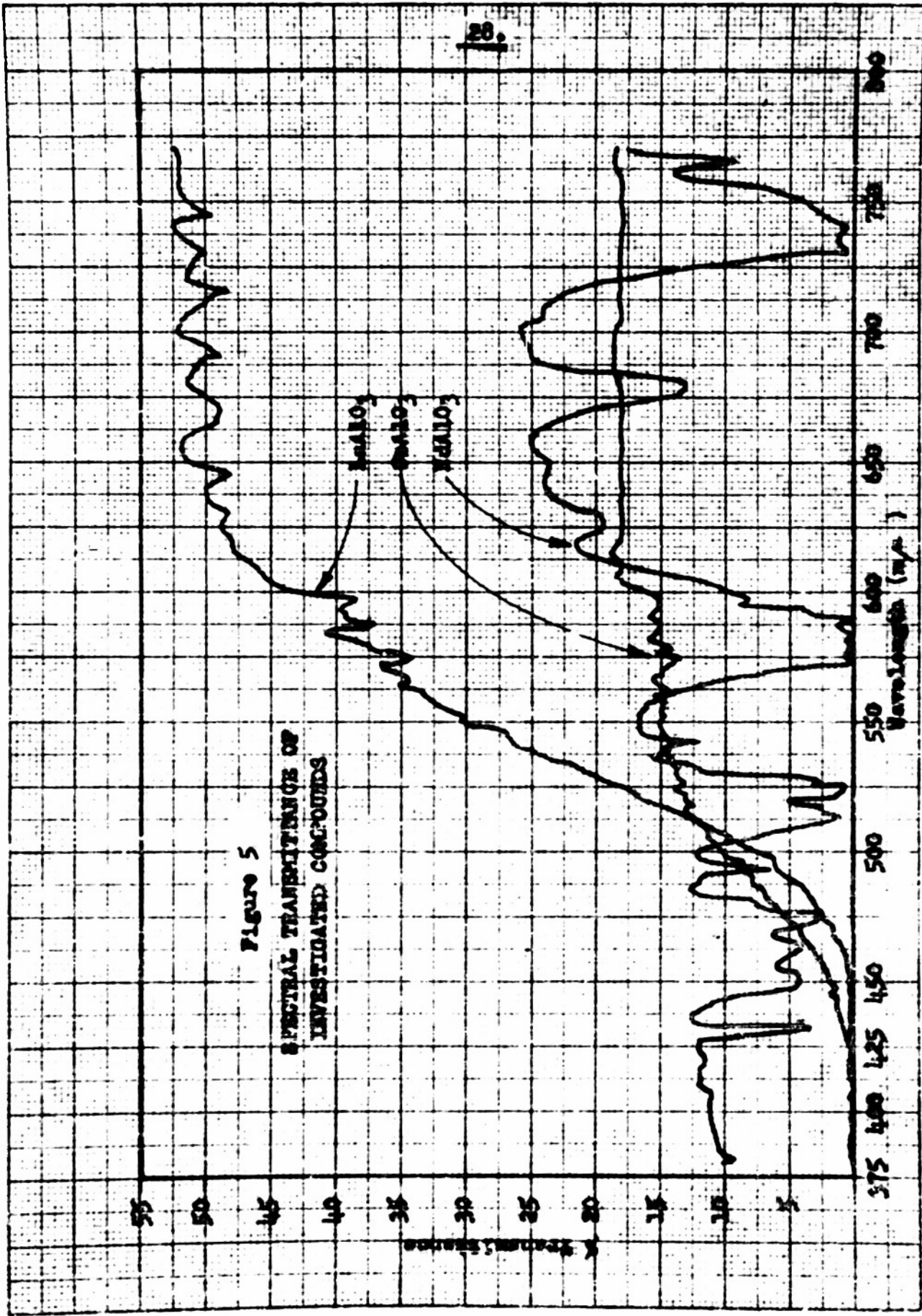


Figure 5  
SPECTRAL TRANSMITTANCE OF  
INVESTIGATED COMPOUNDS

where the absorption bands are markedly apparent over the visible spectrum. Lanthanum and cerium have absorption bands, for the most part, in the ultraviolet. This strong absorption of cerium in the ultraviolet finds application in the manufacture of eye-protective glasses. In the visible range of the spectrum, however, cerium and lanthanum display little of the typical absorption of neodymium. It is interesting to note that lanthanum has rarely, if ever, been described as a colorant. It is possible, as Weyl<sup>19</sup> points out, that "certain impurities or accessory constituents often impart intensive colours to minerals and synthetic crystals but not to glasses." If lanthanum had been added in the usual small amounts as a colorant, perhaps the orange color would not have developed in glasses and therefore remain unreported.

#### IX. ELECTRICAL PROPERTIES

Through the courtesy of Dr. A. E. De Bretteville, arrangements were made for the measurement of the electrical behavior of the investigated crystals. In order to learn whether or not the crystals are ferroelectric, the measurement of dielectric constant was undertaken. Resistance measurements were also made on the same samples.

##### A. Procedure

Suitable samples were chosen and lapped to parallel plates as previously described. In order to allow the calculation of the dielectric constant, the area of the samples was measured using a projection microscope fitted with a micrometer stage. The thickness of the plates was measured by means of a vernier micrometer. Gold electrodes were evaporated on to the crystal, the edges having

previously been lacquered. After the electrodes were deposited, the lacquer was dissolved away leaving the sides of the sample free of conducting material. Connecting wires were then soldered to the center of each electrode.

The sample was mounted in an oven and dielectric constant and loss factor determined at a frequency of one megacycle over the temperature range of 25° to 250°C. In making these measurements, a Boonton Q meter\* was used, corrections being applied for the capacitance of the leads and edge effects.

Resistance was measured on the same samples using a 20 million Megohmmeter.\*\* The area and thickness of the samples having been previously measured, the resistivity is easily calculated.

#### B. Data and Calculations

The data observed from the dielectric measurements are plotted in Figures 6, 7, and 8; resistance data and the calculated resistivity appear in Table IV.

Table IV

	<u>LaAlO<sub>3</sub></u>	<u>CeAlO<sub>3</sub></u>	<u>NdAlO<sub>3</sub></u>
Area-cm. <sup>2</sup>	0.101	0.077	0.105
Thickness-cm.	0.0470	0.0724	0.0318
Resistance-ohms	4.78x10 <sup>10</sup>	2.1x10 <sup>7</sup>	2.02x10 <sup>10</sup>
Resistivity-ohm-cm.	10.2x10 <sup>10</sup>	2.25x10 <sup>7</sup>	6.67x10 <sup>10</sup>

A sample calculation follows, using the relation

$$R = \sigma \frac{l}{A} \quad (7)$$

\*Boonton Radio Corp., Boonton, New Jersey.  
\*\*Electronic Instruments, Ltd., Richmond, Surrey, England.

300 91. SURVEY & TEST CO.  
Semi-conducting, 4 1/2 inch X 10 to the inch.  
File Times specified.  
1954

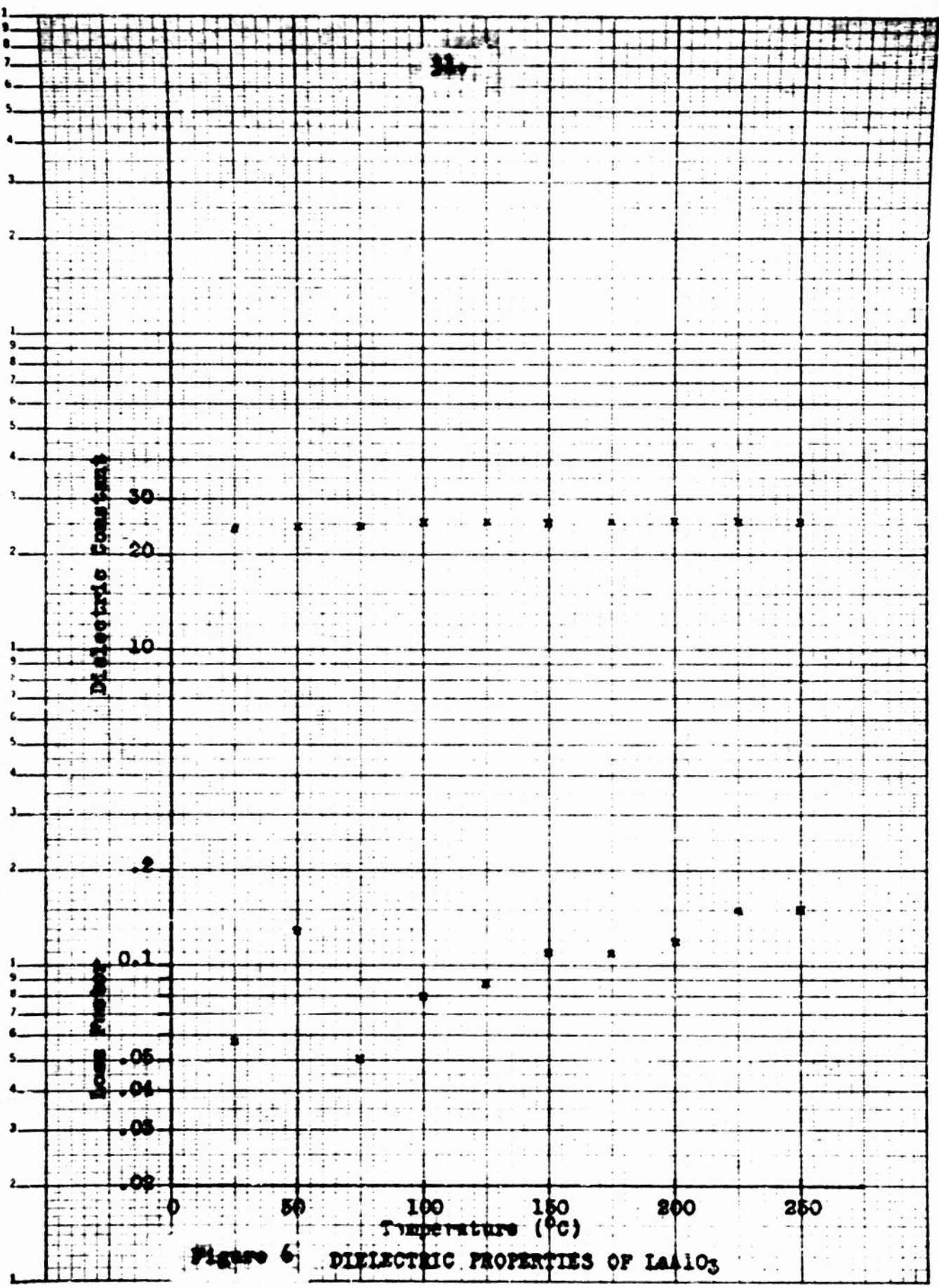


Figure 6 DIELECTRIC PROPERTIES OF LaAlO<sub>3</sub>

339-51 SUPP. & SEER CO.  
 Semi-Logarithmic, 1 Cycle X, 10 to the Inch.  
 513 lines across.  
 1947 N. Y. S. A.

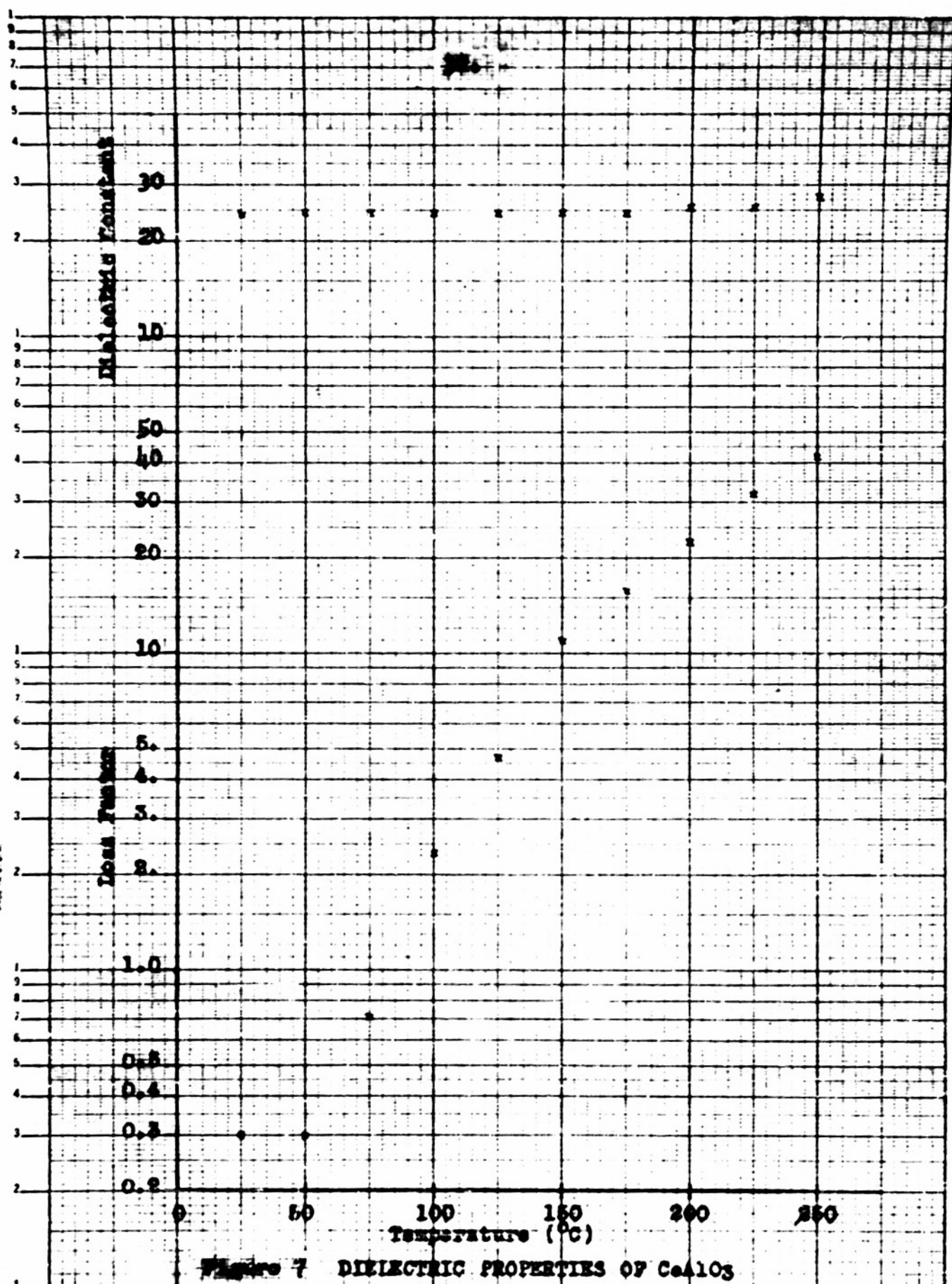


Figure 7 DIELECTRIC PROPERTIES OF Ca<sub>10</sub>O<sub>3</sub>

100-81 NEUFEL & SOBER CO.  
 2 mil. Graphite, 4 Cycle X 10 to the Inch.  
 (18 lines omitted)  
 MADE IN U.S.A.

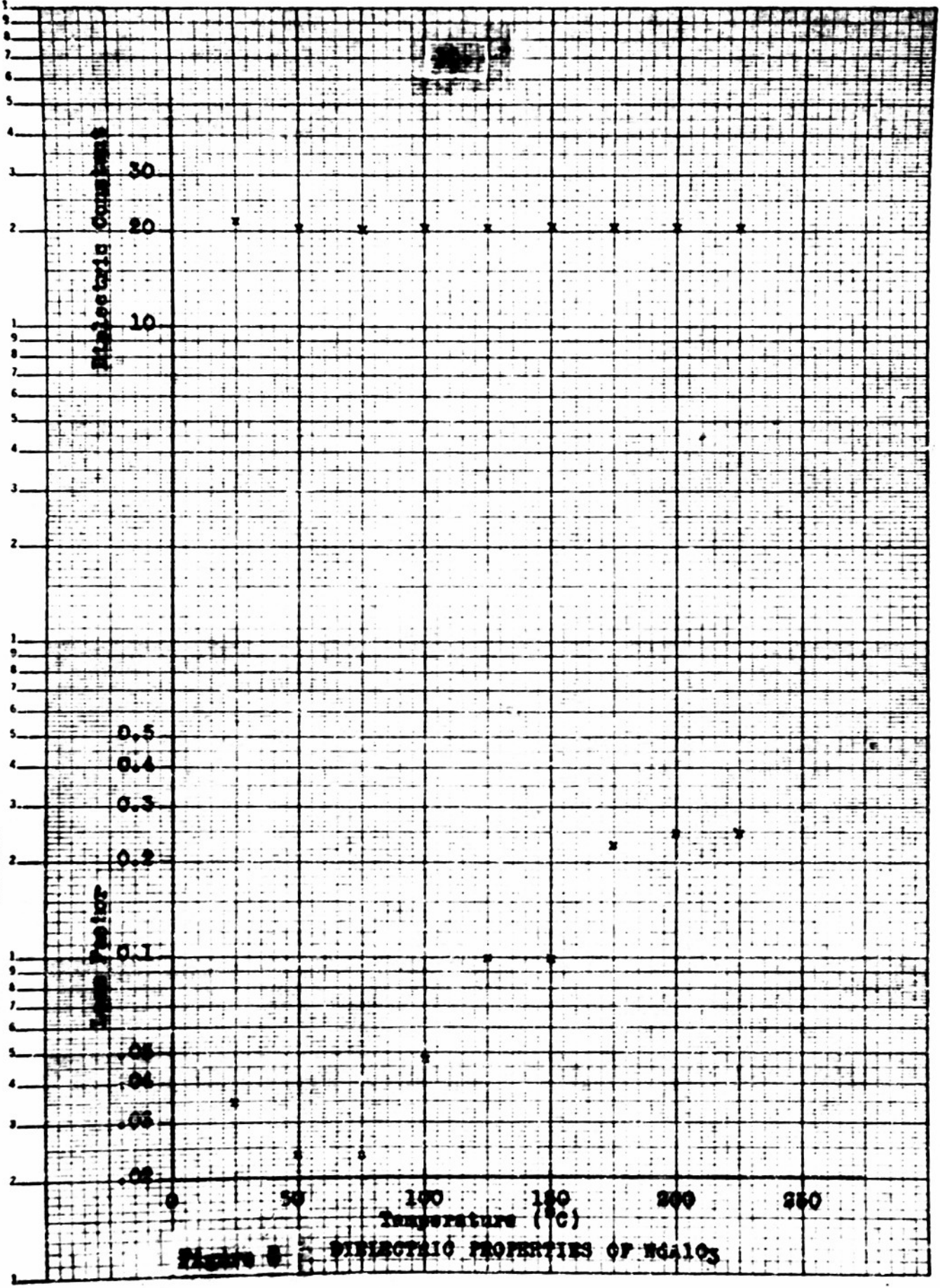


Figure 5 DIELECTRIC PROPERTIES OF MgAlO<sub>3</sub>

where            R = resistance  
                    $\sigma$  = resistivity  
                   l = thickness  
                   A = area

$$4.78 \times 10^{10} = \sigma \frac{(.0470)}{(.101)}$$

$$\sigma = 10.2 \times 10^{10} \text{ ohm-cm.}$$

### C. Discussion

On a basis of the measurements of dielectric constant, it is apparent that the crystals, at least over the temperature range investigated, are not ferroelectric. A ferroelectric material is one which possesses a spontaneous polarization, shows nonlinearity of dielectric constant vs. temperature, and has a Curie point. Probably the best known ferroelectric is  $\text{BaTiO}_3$  in its tetragonal modification.

The conditions for a ferroelectric are quantitatively established for  $\text{BaTiO}_3$ . On heating the tetragonal form through  $120^\circ\text{C}$ , i.e. the Curie point, the dielectric constant increases from approximately 300 at  $80^\circ$ , to 500 at  $100^\circ$ , and to 10,000 at  $120^\circ\text{C}$ .<sup>20</sup> Above  $120^\circ\text{C}$ , the dielectric constant declines almost as steeply. The spontaneous polarization (displacement of the  $\text{Ti}^{4+}$  ion) shows a like precipitous change, decreasing to zero above  $120^\circ\text{C}$ .<sup>21</sup> It is obvious that the spontaneous polarization should be zero above the Curie point, for the tetragonal  $\text{BaTiO}_3$  then becomes cubic. Since  $\text{LaAlO}_3$  has been shown to be cubic, it would not be expected to be ferroelectric. The similarity of dielectric constant data indicates that the cerium and neodymium aluminates are also not ferroelectric.

## X. DISCUSSION OF RESULTS

The choice of the method of crystal growth proved to be suitable in all respects. Having prepared feed materials embodying optimum characteristics, single crystals of  $\text{LaAlO}_3$ ,  $\text{CeAlO}_3$ , and  $\text{NdAlO}_3$  were grown of size and quality suitable for all the measurements undertaken.

Results obtained from many of the measurements were roughly predictable on a crystallochemical basis. The compounds examined are of similar structure, differing only in the rare earth element present. This difference is manifested by a decreasing interionic distance in the crystal lattice with increasing atomic number of the rare earth ion. Starting with lanthanum of ionic radius 1.22 Å, the crystal unit cell has an edge length of 3.774 Å. Upon replacing lanthanum with cerium, (ionic radius of 1.18 Å), the cell edge decreases to 3.746 Å. A further replacement by neodymium of ionic radius 1.15 Å gives a cell edge of 3.733 Å.

As a consequence, the density of the crystals increased successively from 6.53 for the  $\text{LaAlO}_3$  to 6.72 and 7.02 for the  $\text{CeAlO}_3$  and  $\text{NdAlO}_3$  respectively.

Similarly, by increasing the number of highly refractive oxygen ions per unit volume, the effect can be observed in the refractive index. Values of the refractive index for the mercury green line were found to increase from 2.068 in lanthanum aluminate to 2.079 in the neodymium aluminate, the more dense crystal.

A shortening of distances in ionic crystals produces an increase in the stability of the crystal. Therefore, any property which is dependent upon the stability of the crystal (melting point, for example) is directly influenced by the size and valence of the

lattice ions. Since the valence of the rare earth ions remains constant, any change in the above mentioned property is due basically to the changing ion size. The experimental results described in the sections on Melting Point and Thermal Expansion may be cited as supporting these statements. The melting point of  $\text{LaAlO}_3$ , i.e. involving the largest rare earth ion is  $1917^\circ\text{C}$ ; upon substituting the smaller cerium ion for lanthanum, the melting point was increased to  $2017^\circ\text{C}$ . A still further substitution of neodymium for lanthanum produced an increase in the melting point to  $2055^\circ\text{C}$ .

Similar concepts to the above could be employed in part in examining the thermal expansion data. As mentioned previously, the stability of the crystal is increased by replacing the larger lanthanum ion with neodymium. As a result, the mean coefficient of thermal expansion of  $\text{LaAlO}_3$  ( $10.7 \times 10^{-6}/^\circ\text{C}$ ) is greater than that of the  $\text{NdAlO}_3$  ( $9.7 \times 10^{-6}/^\circ\text{C}$ ). The break in the thermal expansion curve of  $\text{CeAlO}_3$ , evidently a second order transition, merits further discussion.

A differential thermal analysis examination had been made in an effort to learn more about the nature of the change. There was no heat effect evident indicating that if a new form came into existence its thermal properties were the same as those of the room temperature form. The X-ray results, previously described, obtained at the higher temperature were also such that no differentiation could be made between the two forms. The X-ray apparatus employed, however, was that which indicated that all the investigated crystals were cubic. A more precise X-ray unit working at the appropriate temperature would doubtless throw more light on the situation.

The well known spectral transmittance curve of neodymium-bearing glass is contained in the absorption bands shown by  $\text{NdAlO}_3$ . The transmittance of the lanthanum and cerium aluminates, on the other hand does not possess the fine structure and absorption bands generally associated with rare earths. Nevertheless, a fine structure does exist, though much weaker and present to a lesser extent than that of  $\text{NdAlO}_3$ . This structure appears in the lanthanum compound in the red, while in  $\text{CeAlO}_3$  in the green region of the spectrum there is an indication of the rare earth nature of the crystals.

The presence of the previously mentioned second order transition in  $\text{CeAlO}_3$  was viewed with much interest, for the onset of ferroelectricity is marked by just such a condition. Though no thermal effects could be observed by means of thermal analysis, the change in heat capacity at the Curie point of  $\text{BaTiO}_3$  is of the order of  $3 \times 10^{-3}$  cal/g°C. This very small change could easily have been overlooked or unresolved on the differential equipment used. For these reasons, the results of dielectric measurements were eagerly awaited. The dielectric constants as reported, range between 20 and 28, and are of a magnitude displayed by many substances. It would appear, then, that the crystals are not ferroelectric, in spite of the marked similarities to  $\text{BaTiO}_3$  with respect to a second-order transition (possible Curie point) and tetragonality of its perovskite structure.

In the crystals examined,  $\text{LaAlO}_3$  with the highest resistivity ( $10.2 \times 10^{10}$  ohm-cm) has the lowest change in loss between 25 and 250°C (from 0.058 to 0.15). On the other hand,  $\text{CeAlO}_3$  with a

resistivity of  $2.1 \times 10^7$  ohm-cm has a loss change of 0.30 to 41.5. Neodymium aluminate has intermediate values of  $2.02 \times 10^{10}$  ohm-cm and a loss change of 0.035 to 0.25. Though the resistivity is referred to D.C., it appears that the conductivity mechanism is closely linked to that producing the loss with increasing temperature. Loss and resistivity data indicate some correlation of this sort.

#### XI. CONCLUSIONS

1. Single crystals of  $\text{LaAlO}_3$ ,  $\text{CeAlO}_3$ , and  $\text{NdAlO}_3$  were grown successfully using the Verneuil technique.
2. Substitution of cerium and neodymium for lanthanum disturbed the cubic nature of the latter aluminate and produced tetragonal structures, which nevertheless retained the perovskite form.
3. The molar volume of the aluminates decreased upon substituting cerium for lanthanum or neodymium for cerium.
4. Density, refractive index, and melting point of the crystals increased with increasing atomic number of the rare earth ion.
5. The thermal expansion of  $\text{CeAlO}_3$  displays what appears to be a second-order transition.
6. Spectral transmittance curves of the rare earth aluminates possess, in varying degree, fine structure typical of rare earth spectra.
7. On the basis of the electrical data, the investigated compounds are apparently not ferroelectric.
8. The mechanism producing loss in the crystals appears to be associated with conductivity.

BIBLIOGRAPHY

1. Yost, D. M., Russel, H. Jr., and Garner, C. S. "The Rare Earth Elements and Their Compounds, p. 3, 1st edit., John Wiley & Sons, Inc., N. Y. (1947), 92 pp.
2. Goldschmidt, V. M., "Crystal Structure and Chemical Constitution," Transactions Faraday Society, 25, 253-83 (1929).
3. Goldschmidt, V. M., "Geochemische Verteilungsgesetze der Elemente, VII," Skrifter Det Norske Videnskaps-Akademi i Oslo I Matematisk-Naturvidenskapelig Klasse, Vol. I (1926).
4. von Hippel, A., "Ferroelectricity, Domain Structure, and Phase Transitions of Barium Titanate," Rev. Mod. Phys., 22 221-37 (1950).
5. Matthias, E. T., "Ferroelectricity," Science, 113, 591-6 (1951).
6. Wood, S. A., Acta Crystallographica, 4, 353-61 (1951).
7. Vorneuil, A. V. L., "Artificial Production of Rubies by Fusion," Compt. rend., 135, 791-4 (1902).
8. Moore, C. H., Jr., "Formation and Properties of Single Crystals of Synthetic Rutile," Am. Inst. Min. Met. Eng. Transactions, 184, 194-9 (1949).
9. Bauer, W. H., Gordon, I., and Moore, C. H., "Flame Fusion Synthesis of Mullite Single Crystals" J. Am. Ceram. Soc. 33 140-143, 1950  
 & Bauer, W. H., and Gordon, I., "Flame Fusion Synthesis of Several Types of Silicate Structures" J. Am. Ceram. Soc. 34 250-254, 1951.
10. Seoman, A. K., "American Synthetic Crystals-Sapphire to Titania," Gems and Gemology, p. 151-9, Spring (1949).
11. Ephraim, F., "Inorganic Chemistry," p. 595, 5th edit., revised, Interscience Publishers, Inc., N. Y. (1948) 939 pp.
12. Ewald, P. P. and Hermann, C., "Strukturbericht I. 1913-28," p. 303, Akademische Verlagsgesellschaft, Leipzig, 1931.
13. Hegaw, H. D., "Crystal Structure of Double Oxides of the Perovskite Type," Proc. Phys. Soc. London, 58, 133-52 (1946).
14. Pauling, L., "The Nature of the Chemical Bond," p. 368, 2nd edit., Cornell University Press, Ithaca, N. Y. (1945) 450 pp.

15. V. Martenberg, H., and Reusch, H. J., "Schmelzdiagramme Höchstfeurfester Oxyde IV (Aluminium oxyd)," Z. anorg. u. allg. chem., 207, 1-20 (1932)
16. Larson, L. S., and Berman, H., "The Microscopic Determination of the Opaque Minerals," p. 30, 2nd edit., U. S. Geological Survey, Bull. 848, (1934), 266 pp.  
  
a. Gladstone, J. W. and Dale, T. I., "Researches on the Refraction, Dispersion, and Sensitiveness of Liquids," Roy. Soc. London Philos. Trans., 153, 337 (1864).
17. Fairbairn, H. W., and Sheppard, C. W., "Maximum Error in some Mineralogic Computations," Am. Mineral. 30, 673-703 (1945).
18. Merritt, G. W., "The Interference Method of Measuring Thermal Expansion," J. Res., Nat'l. Bur. Stds., 10, 59-76 (1933), Pl. P. 515.
19. Weyl, H. W., "Coloured Glasses - Part I. The Constitution of Coloured Glasses," J. Soc. Glass Tech. 27, 133-206 (1943).
20. Herz, J., "The Dielectric Behavior of BaTiO<sub>3</sub> Single Domain Crystals," Phys. Rev., 75, 687 (1949).
21. Mason, P. and Matthias, J. T., Phys. Rev., 74, 1622-36 (1948).