

AD706924

Final Report

AF-AFOSR/ARPA-68-1609

ARPA Order No. 1184, Amendment No. 2

Start Date: 1 June 1968

End Date: 31 January 1970

**PREPARATION OF CRYSTALS OF ALKALINE EARTH OXIDES
AND RELATED COMPOUNDS**

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31 January 1970

**Research sponsored by the Air Force Office of Scientific
Research, Office of Aerospace Research, United States Air
Force.**

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I. INTRODUCTION

The principal objective of the research supported by this grant was the growth of high quality single crystals of CaO , SrO , and BaO . The program undertaken to accomplish this was pursued in four parts: (1) Purification, (2) Chemical Characterization, (3) Crystal Growth and Improvement, and (4) Physical Characterization. Initially each of the four parts could be pursued almost independently; finally falling into sequence with the production of crystals of assessed quality. During this grant some progress has been made in each of the four parts. The purification and chemical characterization is almost complete. Only very limited success has been achieved in the crystal growth section and the physical characterization has progressed to the point of assembling and checking the conductivity apparatus. The various other apparatus required for study of physical properties was already available at Oregon State University.

In the following sections of this report each of the four parts will be discussed briefly.

II. PURIFICATION

Chemical purification procedures have been developed for BaO , SrO and CaO . These produce relatively clean oxides for initial crystal growth studies.

The impurity problem has been most extensively examined for CaO . In general, previous work^(1,4,6,7,8,9) shows that one of the major sources of

impurities in the alkaline earth oxides is the cross contamination by other members of the group. In addition, contamination from the transition metals, i.e., Fe, Mn, Al, Cu, and Ni, and, almost universally from Si, has been found. This list should not be considered as exhaustive because in most cases the analytical techniques and detection limits were not indicated, so that there are obviously possibilities of impurities being present for which no analysis was attempted or which were present in amounts below the detection limit of the techniques used. In addition, the amounts of each impurity present vary widely, from a few ppm up to several tenths weight per cent, depending upon the source of the material.

There have been several different attacks on the problem of obtaining pure alkaline earth oxides. Ewles and Lee⁽¹⁰⁾ prepared pure CaO for luminescence work by dissolving analytical reagent grade CaCO_3 in doubly distilled HNO_3 , followed by repeated treatment of the solution with ammonium sulfide solution then filtration to precipitate and remove the heavy metal impurities. The $\text{Ca}(\text{NO}_3)_2$ was thermally decomposed to CaO. Gambino⁽⁵⁾ prepared SrO by precipitation SrC_2O_4 from a hot solution of $\text{Sr}(\text{NO}_3)_2$ using $(\text{NH}_4)_2\text{C}_2\text{O}_4$ as the precipitating agent. The oxide was again obtained by thermal decomposition of the oxalate. Sproull, Dash, Tyler, and Moore⁽¹⁾ prepared the oxide by thermal decomposition of C. P. BaCO_3 . Phillips, Nelson, and Kraus⁽²⁾, and Phillips, Kraus, and Carlson⁽¹¹⁾, separated mixtures of the alkali and the alkaline earth ions into various components using Zirconium molybdate or Zirconium phosphate ion exchange resins. The work of the last two groups was not, however, complete in terms of providing a method of purifying the alkaline earths. Finally, Lynch and Lander⁽³⁾ prepared BaO

by the thermal decomposition of the hydroxide.

After considering all the purification processes used previously, the use of ion exchange resins was rejected because the system does not provide a complete, unified method for purifying the alkaline earths. Decomposition of the hydroxides, as used for preparing BaO by Lynch and Lander⁽³⁾ was considered unsatisfactory because the hydroxides only decompose at elevated temperatures and melt before decomposition^(13,p248;14,pp484-485, 496-497,606-607), the highly caustic nature of the melt greatly increasing the possibility of contamination from the decomposition container. There is some evidence that $\text{Ba}(\text{OH})_2$, at least, doesn't completely decompose even at high temperatures^(15,pp765-766). Further, additional problems arise in the handling and storage of the hydroxides. Attempts in this lab to decompose $\text{Ba}(\text{NO}_3)_2$ led to similar problems, i.e., melting and incomplete decomposition, so were discontinued. Therefore, the methods of purification developed have been based, in general, upon the work of Evles and Lee⁽¹⁰⁾, with the carbonates being chosen for decomposition to the oxides, as suggested by Sproull, et. al.⁽¹⁾. The carbonates were chosen since they are relatively insoluble and easy to precipitate out of solution, can be readily dried, and are not deliquescent or caustic so that storage and handling are no problem. Also, they are susceptible to thermal decomposition, with the ease of decomposition depending upon the alkaline earth^(16,p316;14,pp253-254).

1. Purification

Two general procedures for purification have been developed and will be described in detail below. The procedures both involve precipitation of

the heavy metals as sulfides or hydroxides from a solution of a soluble alkaline earth salt by the addition of $(\text{NH}_4)_2\text{S}$ solution, followed by filtration to remove the precipitate. After the excess $(\text{NH}_4)_2\text{S}$ is destroyed, the salt is fractionally recrystallized at least once to remove impurities which do not form insoluble sulfides or oxides, such as the alkali metals and the other alkaline earth metals. The alkaline earth salt is then redissolved and converted to the carbonate by making the solution basic with 15M NH_3 and then bubbling CO_2 through it. This process is essentially a precipitation from homogeneous solution (See any recent quantitative analysis book, such as (12, pp138-141)). As such, it provides a further step in purification, giving a precipitate with fewer occlusions and less co-precipitation of impurities. In addition, as shall be seen below, this type of process can allow more careful control of the purity of the reagents added, than if, say, $(\text{NH}_4)_2\text{CO}_3$ solution itself was made up from the solid salt.

2. Starting Materials

The starting materials presently used are moderately soluble salts of the alkaline earths which contain as few waters of hydration as possible, since the waters of hydration tend to interfere with obtaining good fractional recrystallizations. The salts used are: barium acetate, strontium nitrate, and calcium acetate. All materials are Reagent Grade. The brand of material may vary for each alkaline earth and from batch to batch of the starting material, depending on the analyzer. However, Fisher & Johnson Reagent Grade seems generally suitable. To point up the fact that Reagent Grade materials

can indeed vary in impurity content, the analyses of Mallinckrodt and Baker & Adamson Reagent Grade barium acetate can be compared (See analytical results). Obviously, the Mallinckrodt salt has a much higher strontium contamination level, and is in fact unsuitable for the preparation of pure BaCO_3 due to the high strontium content in the carbonate. Each of the salts listed above will recrystallize from a hot, concentrated aqueous solution as either the anhydrous salt, or as in the case of $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ as the dihydrate^(17, I, pp304, 615-618, II, pp1509-1511).

The other reagents used in the process are: $(\text{NH}_4)_2\text{S}$ solution, Mallinckrodt Analytical Reagent Grade; 15 N NH_3 , Reagent Grade; CO_2 , C.P. or Commercial Grade, which is 99.5% pure, the main impurities being H_2O , O_2 , and N_2 , which do not interfere with the process. In one of the procedures, 6N HNO_3 is required. This is produced by diluting Reagent Grade 16 N HNO_3 with de-ionized H_2O . In addition, Reagent Grade 16N HNO_3 is also used itself. All H_2O used in the procedures is de-ionized H_2O .

The next step to improve the purity of the carbonates will be to produce our own $(\text{NH}_4)_2\text{S}$ solution and 15 N NH_3 . The Mallinckrodt $(\text{NH}_4)_2\text{S}$ solution apparently contains some polysulfide so that upon decomposition of the excess $(\text{NH}_4)_2\text{S}$, a sulfur precipitate is obtained, which is very fine and difficult to filter out. Local production of the $(\text{NH}_4)_2\text{S}$ solution will do away with the polysulfide problem. The ultrapure NH_4OH will be used in the production of the $(\text{NH}_4)_2\text{S}$ solution and in the carbonate precipitation. Work has already commenced to produce these two reagents.

3. Apparatus

Most of the purification process requires only standard laboratory glassware. Certain steps do, however, require more specialized apparatus. All filtrations done to remove solid impurities, use Millipore filters. The filters are mixed esters of cellulose; the filters are plain, white with a diameter of 47 mm and a mean pore size of $0.45\mu \pm 0.02\mu$. If there are large amounts of precipitate, a Microfiber Glass Prefilter 35 mm in diameter and 0.035 in. thick is used ahead of the millipore filter. A pair of teflon coated tweezers is used to handle the filters and prefilters in order to prevent contamination. The filter holder is a standard Pyrex filter holder modified by adding the female portion of a 55/50 Standard Taper joint and a short sidearm for making a connection to the house vacuum. The filter holder fits on top of 2000 ml. thick-walled Erlenmeyer flasks which are topped with the male portion of 55/50 Standard Taper joints. Teflon sleeves are used on the joints to prevent any contamination from grease. This setup allows the suction filtrations to be done rapidly, efficiently, and cleanly. Caps have also been made for the flasks, again from the female portions of the joints. Thus, if the procedure must be interrupted, the solutions can be safely stored without any fear of outside contamination.

All filtrations involving a solid product that is to be saved are done using Pyrex Buchner funnels.

Finally, a Pyrex wool filter is placed in the CO_2 line to trap any solid or liquid impurities which may be present. So far, there has been no indication of any impurities of the nature, even after several months use.

A gas dispersion tube is used to introduce the CO_2 into the solution in order to break up the gas bubbles and provide more surface area for reaction.

4. Procedures

Outlines of the detailed purification procedures follow, along with comments on certain aspects of the purification.

5. General Acid Prep.

This prep. makes use of a precipitation of the alkaline earth nitrate from a nitric acid solution, followed by a single fractional recrystallization of the nitrate as the means of removing impurities not precipitated out by the $(\text{NH}_4)_2\text{S}$. The prep. was originally designed specifically for the production of BaCO_3 . Later, it was modified to the form below so that it is possible to produce SrCO_3 by this process. The process is unsuitable for making CaCO_3 due to the extremely high solubility of $\text{Ca}(\text{NO}_3)_2$. The prep. can be outlined as follows:

- (1) Dissolve a suitable salt in de-ionized H_2O (Use $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ or $\text{Sr}(\text{NO}_3)_2$). Add $(\text{NH}_4)_2\text{S}$ solution and heat to digest.² (Heavy metals precipitate as sulfides and oxides).
- (2) Cool, filter using Millipore filter, discard residue. Heat filtrate to destroy excess $(\text{NH}_4)_2\text{S}$.
- (3) Cool, filter using Millipore filter. Discard residue.
- (4) Add 16 M HNO_3 to precipitate the alkaline earth nitrate. (For Ba, the first fraction is saved. For Sr, the first fraction, ~10% of the total amount of solid, is discarded and the second fraction is saved.) Heat to digest.
- (5) Cool, filter using Buchner funnel, then wash the crystals with 8 M HNO_3 . Aspirate off as much residual liquid as possible. Discard filtrate.³
- (6) Redissolve the crystals in de-ionized H_2O and fractionally recrystallize.

- (7) Cool, filter using Buchner funnel, discard filtrate.
- (8) Redissolve crystals in de-ionized H_2O , then filter using Millipore filter. Discard residue.
- (9) Make filtrate basic with 15 M NH_3 (the pH must be ~10 for the most efficient conversion), then bubble CO_2 through solution to precipitate the carbonate.
- (10) Digest precipitate.
- (11) Check supernatant liquid for completeness of precipitation and repeat steps (9) and (10) until precipitation is complete, then discard the supernatant liquid.
- (12) Wash precipitate with de-ionized H_2O until filtrate is neutral, filtering using Buchner funnel. Dry precipitate in vacuum oven.

The washing procedure used on the carbonates is essentially the same as used in any standard quantitative analysis procedure, i.e., most of the washing of the precipitate is done in the original container before transferring it to the filter. Approximately three "gross" washings of the carbonate are made with de-ionized H_2O : The H_2O is added and the mixture stirred; then after the solid has settled, the supernatant liquid is decanted off and discarded. As soon as the supernatant from the gross washings is neutral, indicating that all of the remaining base has been removed from the solid, washing with additional portions of de-ionized H_2O with transfer of the carbonate to the filter is commenced. Since the efficiency of washing is better and filtering is faster, the solid is retained in the beaker as long as possible. After all the washings are complete the carbonate is aspirated on for 15 to 30 minutes to remove as much of the residual H_2O as possible.

It has been found that it is much better to carefully transfer the entire mass, carbonate and filter paper, to a covered beaker and dry it in

the vacuum oven for about 12 hours at 60° - 65°C. Then, the filter paper can be easily separated from the solid. Drying of the solid is completed at 90° - 100°C under vacuum. A soft, fairly powdery product results. This is a much better product than obtained when the carbonate is dried in a drying oven.

There are three problems connected with this prep. in addition to the nuisance and danger of working with large quantities of fairly concentrated HNO_3 solutions. One is that CaCO_3 can not be produced by this procedure. Secondly, it is hard to judge just how much $\text{Sr}(\text{NO}_3)_2$ should be precipitated and discarded before collecting the second fraction. Finally, it is impossible to remove all of the nitric acid from the crystals in step (5). The solution obtained upon redissolving the crystals is still acidic. Thus, the recrystallization of step (6) must be done on a hotplate, rather than in the cleaner, more contamination free, atmosphere afforded by a vacuum oven. Originally, the nitrate crystals were rinsed with portions of de-ionized H_2O to try to remove additional amounts of the acid. However, the procedure was not effective and led to losses of solid due to dissolution, so was discontinued.

There was some fear that more impurities would be introduced than were being removed by the precipitation from the HNO_3 solutions due to the large quantities of acid necessary and the number of operations necessary. However, these fears proved unfounded. The BaCO_3 produced by this process is as pure or purer than that produced by the second procedure.

6. General Non-Acid Prep.

In order to circumvent the problems encountered with the Acid Prep., to make the procedure somewhat simpler and have a purification system that could be used for all three of the alkaline earths, the following prep. has been developed. It is similar to the Acid Prep. described above, except the precipitation from nitric acid has been deleted and a second fractional recrystallization added. As before the heavy metals are removed as sulfides or oxides by precipitation upon the addition of $(\text{NH}_4)_2\text{S}$ solution. The two recrystallizations remove the cross-contamination of the other alkaline earths along with other impurities which weren't precipitated by the $(\text{NH}_4)_2\text{S}$. An outline of the procedure follows:

- (1) Dissolve a suitable salt in de-ionized H_2O (use $\text{Ba}(\text{ClO}_4)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, H_2O ; rough concentrations: ~50 ml./100 g. substance) and heat to digest (heavy metals precipitate as sulfides and oxides).
- (2) Cool, filter using Millipore filter. Discard residue. Wash filtrate to destroy excess $(\text{NH}_4)_2\text{S}$.
- (3) Cool, filter using Millipore filter. Discard residue.
- (4) Fractionally recrystallize (rough final values of supernatant liquids: 100-150 ml. solubility of salts in gms./100 g. saturated solution at 25°C; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$: 26 (17.1g-100); $\text{Sr}(\text{NO}_3)_2$: 45 (17.11g-100-150); BaCl_2 : 43 (17.1g-100)).
- (5) Cool, filter using Buchner funnel. Discard filtrate. Recrystallize crystals in de-ionized H_2O .
- (6) Repeat steps (4) and (5) at least once.
- (7) After recrystallizing crystals for last time, filter using Millipore filter. Discard residue.
- (8) Make filtrate basic with 15 % NaOH (the pH must be >10 for most efficient conversion), then bubble CO_2 through solution to precipitate carbonates.

- (9) Sieve precipitate.
- (10) Wash supernatant liquid for completeness of precipitation and repeat steps (8) and (9) until precipitation is complete, then discard the supernatant liquid.
- (11) Wash precipitate with de-ionized H₂O until filtrate is neutral, filtering using Buchner funnel. Dry precipitate to vacuum oven.

The same cautions and precautions involving washing and drying of the carbonates in connection with the General Acid Prep. are applicable here.

In addition, since there are no carbonates whose low-boiling, the vacuum oven is used for carrying out the recrystallizations in this procedure. While recrystallization is as facile in the vacuum oven the temperature is more uniform and there is less chance of atmospheric contamination. During the recrystallizations the vacuum oven is operated at approximately atmospheric pressure with the chamber being constantly purged by drawing filtered air through it. The recrystallizations are carried out at 85° - 95°C.

In terms of laboratory work, this prep. is easier than the Acid Prep., but whether the final product is as pure as obtainable with the other procedure depends on the salt. For BaCl₂, the other procedure probably works best, but is not applicable to CaCl₂. For SrCl₂, both procedures give about the same results. Such procedures should improve greatly if some fractional recrystallizations are used. Due to its ease, fewer external sources of contamination, and applicability to all three alkaline earths, this prep. appears to be preferable to the Acid Prep.

7. Purification of the Carbonates

Prior to use, the carbonates are decomposed in the oxidizer by heating

III. CHEMICAL CHARACTERIZATION

The most difficult part of any purification program is providing convincing evidence of the purity of the substance. Frequently the purity of a material is expressed as an assay. Usually the numerical fraction given in an assay report represents the fraction of the material which is the desired substance as measured by quantitative test unique to that substance. In practice it often means the fraction of the material which passes a particular test in the same way as the desired substance. Assayable assays become very difficult on materials with particles exceeding millions. However, for the purpose of developing purification techniques assays provide an indication concerning the nature of the impurities. Thus an knowledge of the effectiveness of various purification procedures on specific impurities or on sources of contamination. For these reasons we choose to analyze for specific impurities. Of course this approach can not prove the substance pure unless all elements except those of the compound are shown not present, obviously an impossibility. However, the advantage of knowing the effectiveness of various purification procedures on specific impurities and the ability to watch sources of contamination far outweigh the negative proof aspect of this approach. By careful choice of the analyzed impurities one can obtain a reasonable degree of confidence about the sample's purity. Judged from literature reports and the nature of our purification process we choose to analyze for H, N, O, S, P, Na, Cu, Cr, Br, Fe, Zn, Si, C and S. Thus far, we have useful analysis for all but the Si, C, and S.

The ideal analytical technique would require an additional sampling of the purified material, could give quantitative results by comparison with

infinite sensitivity of a large number of elements in a single operation. Emission spectroscopy appears to have many of the desired characteristics. However, it was quickly found that it lacks sufficient sensitivity for boron in alkaline earth salts to be useful. The two analytical methods which have been most useful are atomic absorption spectroscopy (AAS) and neutron activation analysis (NAA). We have avoided wet chemical methods of analysis largely because of the many operations required and to a greater degree of contamination and because of the large amount of time required in their use.

The major analytical tool in our program has been the atomic absorption technique. It has been used to determine the concentration of the following ions: Na, Mg, Ca, Sr, Ba, Pb, and Cr. The analyses have been carried out at the U.S. Bureau of Mines, Albany, Oregon, under the direction of R. F. Farrell. All standard solutions and sample solutions were prepared at BML and analyzed at the Bureau of Mines using standard atomic absorption techniques. The sample and standard solutions contain 1% by weight solids. The samples and standards must be as nearly identical as possible. We attempt to allow only the "background" ion concentration to differ in the standard to vary between the standards and samples. The standards are prepared with industrial security concentrations over the range of 0 to 10 mg/ml and all other concentrations constant. One of the purified substances is used as the entire solution except salt for the standards and the boron concentration determined by extrapolation to zero boron addition. This was necessary because all salts enter from other sources sufficient enough boron to mask the effect of the boron.

impurity addition. Immediately after preparation the sample and standard solutions are transferred from the Pyrex volumetric vials to polyethylene vials to not only minimize the possibility of contamination but also to reduce the effects of preferential absorption of the ions on the container. At these impurity levels this is a detectable effect in glass containers over a few weeks period.

The carbonates are insoluble in water, so they must be dissolved in 3 M HCl. To make sure that all solutions have about the same composition, the same amount of acid is used for dissolving all solids, and acid is also added to the samples of the starting reagents when these are made up for analysis even though the reagents are water soluble. The amount of acid used is adjusted so that for a given series of solutions, both samples and standards, all have the same acid content. Then, the impurity level of the acid can be corrected for by running a acid blank of the same concentration.

The sample solutions are made up directly by weighing out the solid, either dissolving it in acid or adding acid, then diluting volumetrically with de-ionized H_2O to the desired volume. The standards are made up by taking aliquots of a more concentrated stock solution, pipetting in a known volume of a stock solution which contains the impurity ions of interest and diluting volumetrically to the desired volume. The stock solution itself is made up by weighing out the carbonate, dissolving in acid, and diluting volumetrically. The stock solution is made from primary standard materials which are dissolved and diluted up volumetrically. The primary standards are solids of known

results to allow determining which starting reagents were used to produce the various carbonates and indicate what prep. procedure was used. Many of the first batches of carbonates were entirely experimental in nature, being produced before standard prep. procedures were developed and starting materials determined.

As a further indication of the purity of our product materials, Dr. J. C. Kemp, the co-investigator, and co-workers at the University of Oregon, have measured the IR spectra of samples of BaCO_3 , Batch #11, BaO produced from BaCO_3 , Batch #1, and SrCO_3 , Batch #11. None of the samples showed any IR spectra. BaCO_3 , Batch #1, was never analyzed, being immediately converted instant to the oxide for crystal growth attempts.

The analytical results are very encouraging. They indicate that our products are much better than previous materials^(1,4,6,7,8,9). Also, they show the continual improvement in purity obtained as prep. procedures evolved to their present standardized form and the general consistency of the purity, which indicates the product purity is fairly easily controlled and is relatively insensitive to minor changes or problems in the prep. The crystals grown from the carbonates should have even lower impurity levels since most of the impurities will volatilize during the growth process. The only real source of contamination left is the cross-contamination by the other alkaline earths. However, even here the products are much improved over previous materials. Further improvements in purity in this respect can be obtained by more judicious choice of the source of starting materials and by increasing the number of fractional recrystallizations.

Finally, one of the most nagging problems connected with our analytical work has been the lack of a good, accurate method for determining the presence of Si impurity in the matrices with which we are working. The chemical methods available necessitate the use of concentrated H_2SO_4 , which will, of course, precipitate out the alkaline earths. Thus much of the Si could be lost by co-precipitation. However, just recently facilities became available at the OBN Radiation Center for determination of Si by fast neutron activation. Therefore, work is now in progress on obtaining Si analyses.

Table I Resume' of Salts

BaAc ₂ , Mall., Electronic grade:	Run for comparison only
BaAc ₂ , B & A, Regt.:	Starting material for all batches of BaCO ₃
BaCO ₃ , 8/21	Small test batches run to test BaCO ₃ prep.
BaCO ₃ , 9/10	Used TA and NH ₃ to ppt. sulfides; only used distilled H ₂ O; No Millipore filters.
BaCO ₃ , #2	1st large scale production batches of BaCO ₃ .
BaCO ₃ , #3	Batch #1 all used to prepare BaO so was not analyzed. Used TA and NH ₃ and only used distilled H ₂ O; No Millipore filters.

It should be pointed out that the above batches were made without benefit of the use of the (NH₄)₂S solution or the Millipore filters.

BaCO ₃ , #4:	1st batch made using (NH ₄) ₂ S solution and Millipore filters; still used only distilled H ₂ O.
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All of the above batches were made with only the HNO₃ ppt'n and no recrystallization, i.e., similar to the general acid prep., but without the recrystallization.

BaCO ₃ , #5:	1st batch made using deionized H ₂ O and recrystallization of the nitrate, i.e. essentially General Acid Prep.
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BaCO ₃ , #A1:	Batch made using General Acid Prep.
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SrCl ₂ ·6H ₂ O, B & A, Rgt:	Used to prepare batches #1, #1', and #2 of SrCO ₃ .
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Sr(NO ₃) ₂ , B & A, Rgt.:	Used to prepare batches #A1 and #A1' of SrCO ₃ .
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NOTE: The prime of a batch number indicates that it is a batch prepared from the supernatant or 2nd fraction of the previous batch.

(Table I continued)

SrCO_3 , #1	1st large production batch of SrCO_3 . Used $(\text{NH}_4)_2\text{S}$ solution and Millipore filters; but no deionized H_2O ; only 1 recrystallization. Batch #1' prepared from the supernatant of the recrystallization.
SrCO_3 , #1'	
SrCO_3 , #2	1st batch using deionized H_2O ; used two recrystallizations of the SrCl_2 , i.e. essentially the same as General Non-Acid Prep.
SrCO_3 , #A1	Produced using $\text{Sr}(\text{NO}_3)_2$ as starting material and General Acid Prep. Batch #A1' prepared from the 2nd fraction of the nitric acid ppt'n.
SrCO_3 , #A1'	

Table 11 Results of Analysis of Alkaline
Earth Sulfate Ions (ppm wt. H_2O)

Salt	Mg	I.A.							Act. Anal.		Mg
		Na	K	Ca	Fe	Mn	Co	Cr	Na	Fe	
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	3.04	220	24	<870		54			0.18	<3.8	
MAA., Pct.	$(\frac{246.0}{87.6})$	198	15	>1520			24				
$\text{Sr}(\text{NO}_3)_2$	2.41	31	<2.4	7		193	29	<24	$\frac{0.0002}{0.0007}$	<2.4	
MAA., Pct.	$(\frac{211.6}{87.6})$								0.014	<0.31	<0.096
$\text{SrCO}_3 \cdot \text{H}_2\text{O}$	1.68	15	1.7	84		50			0.013	<3.4	
	$(\frac{147.0}{87.6})$										
#1		69	5.2	290		130			0.034	<1.7	
#2		18.5	1.7	280			<8.4		0.010	4.7	
		30	<1.8	240		55	<10	<18			
#A1		17	<1.7	5		620	<7	<15	$\frac{0.0009}{0.0012}$	<2.2	
#A1'		8	<1.7	5		67	<8	<17	$\frac{0.0002}{0.0012}$	<1.5	
#B1		5	<1.7	5		202	<8	<17	0.0067	<1.5	<0.057

Ball	L	A.A.							Act. Amal.		As
		As	As	As	As	As	As	As	As	As	
Ball ₂	1.06								7.1	2.7	
Electronic grade, Ball.	$(\frac{215-11}{137.36})$										
Ball ₂	1.06								0.39	<1.9	
Ball., Reg.	$(\frac{215-11}{137.36})$	17	<1.7	6.9	370				<0.011	<3.6	
		22	1.9	<2.0	330	<9.5					
Ball., A.R.		30	<1.9	32	3070	<23	<23	<0.0007	0.74	<0.11	
Ball ₃ , 8/23	1.44								<0.006	<4.3	
	$(\frac{137-37}{137.36})$										
9/20									<0.017	<2.9	
02		<1.4	<1.4	<1.4	3.0	<7.2			<0.014	<2.9	
03		0.6	1.4	<1.4	1.2	<7.2			<0.019	<2.9	
04		4.3	<1.4	1.4	1.5				<0.0086	<3.6	
05		14	1.4	<1.4	3.0	<7.2			<0.019	<2.9	
011					1.2				<0.003	<1.6	
		<1.4	<1.4	2.9	2.9	<14	<14				<0.019
012		<1.4	<1.4	2.9	1.20	<14	<14	<0.0003	0.43		

Salt	Lb	A.A.						Art. Anal.		As
		Na	Na	Ca	Cr	Na	Ca	Cr	Na	
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	3.30	150	100		400	350	50	<30	0.035	0.50
Dist. H ₂ O	$(\frac{234-16}{40.08})$									
$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	1.40	40	120		400	200	70	<20	0.035	0.80
Dist. H ₂ O	$(\frac{174-16}{40.08})$									
$\text{Ca}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	2.30	5	20		550	125	25	<12	0.010	<0.75
	$(\frac{180-16}{40.08})$									
H ₂ O		20	27		220	120	30	<12	0.030	1.0
H ₂ O*		37	35		400	120	25	<12	0.030	1.0

IV. CRYSTAL GROWTH

The OGU crystal growth program has been directed toward the growth of BaO from melts, BaO, SrO and CaO by the Verneuil method in a plasma torch, and by vapor transport techniques. This part of the program required much equipment design and development as well as assembling it into functioning systems. This report will include only brief descriptions of the present apparatus and techniques.

1. Growth of BaO from Melts

The apparatus presently used for this experiment consists of a pulling mechanism of local design with a rotating water cooled pulling rod. This rod holds the seed and enters the growth chamber through an O-ring seal in water cooled top cover of the chamber. The chamber itself is a 2 inch diameter quartz tube approximately 18 inches long; the middle 12 inches are surrounded by a Pyrex tube such that a 1/4 inch annulus is formed. Through the annulus water is circulated from a tangential inlet at the bottom and an outlet at the top. The iridium crucible which holds the BaO is supported by a graphite rod. The graphite rod is carried by an aluminum rod through an O-ring seal in the bottom cover. The graphite rod is insulated from the aluminum by a Vycor tube. At the upper end the graphite rod is screwed into a larger graphite rod. The larger rod can be machined to fit the crucible or shaped to provide various coupling configurations to the R.F. induction coil used to heat the sample. The induction coil is approximately 5 turns of flattened 1/4 inch copper tubing coupled to a 2 level DF-207 generator through a 6:1 transformer. The

BF-30T is operated in the Kilohertz range.

The growth chamber can be either evacuated or flushed with argon or helium. All metal surfaces exposed to the growth chamber are aluminum or monel and are water cooled. When required the inside of the growth chamber can be coated with a reflecting oxide (MgO for example) to cut heat losses. All surfaces in the growth chamber are kept below 100°C except the crucible and the graphite support on which the crucible rests. All graphite is baked at temperatures well above the 1950-2000°C region used for BaO growth experiments.

In operation the BaO is placed in the iridium crucible and heated below red heat for several hours under vacuum to remove absorbed gases. On occasion the BaCO₃ is directly decomposed in the iridium crucible under vacuum. The chamber is then filled with helium and a slight flow of helium out a small exhaust port in the bottom cover is maintained. The crucible is then quickly heated to above 1100°C. The purpose of this operation is to remove as much adsorbed oxygen from the BaO as possible at temperatures below red heat where iridium oxide forms. Then to get the temperature above 1100°C, where the free energy of formation of iridium oxide becomes possible, as quickly as possible. This technique works reasonably well so long as the BaO is free of Ba(OH)₂. The Ba(OH)₂ melts around 1250°C and rapidly attacks the iridium crucible. A similar technique can be used to decompose BaCO₃ directly in the growth chamber. Care must be taken to completely decompose the carbonate before getting the temperature above 1450°C at which the carbonate melts because it attacks the iridium when molten.

The graphite crucible must be designed such that it provides the necessary auxiliary coupling but does not come into contact with the BaO. Near the melting point BaO reacts with the graphite to form Barium Carbide which is quite volatile. The controlled atmosphere not only provides a clean environment for the BaO but also provides a stream of gas to remove BaO vapors from the immediate growth region. It would be better to use a gas with a lower thermal conductivity than helium, but the high temperature and electric field tend to cause ionization of gases such as argon. This leads to a catastrophic arc and the rebuilding of the growth chamber.

The present problems with the system involve reducing the heat loss and increasing the RF coupling to the crucible. The system will reach 1950°C at the crucible wall but the heat transfer into the BaO charge is very inefficient and a melt forms on the crucible wall which is wet by molten BaO. This causes the molten portion to pull away from the major mass of BaO. The problem will be solved if we can increase the coupling or decrease heat losses. Slight changes in the coupling coil and the crucible holder are being made. An additional change that may improve the temperature will be to use argon helium mixtures as the flushing gas.

Samples taken from the wall of the container show the melt contains Iridium. This appearance suggests that this is the form of small free metal particles. Whether these particles will be incorporated in pulled crystals will depend on the agitation of the melt caused by the induction field. The quantity of the Iridium particles formed appears to depend on the amount of OH^- or O_2 remaining in the BaO powder at temperatures above red heat.

2. Feasibility - Plasma Torch Crystal Growth

The plasma torch presently in use consists of an 8 1/2 inch quartz tube that forms the main portion of the torch enclosure. This 30 inch long tube has water jackets above and below the center. The top closure forms the torch head. It holds a 30 inch quartz tube approximately 10 inches long centered in the 8 1/2 inch tube. At the center of the torch head a 2 inch heavy walled quartz tube enters the torch chamber. This tube is adjustable in the depth it extends into the plasma region. Its external end is 3 inch diameter quartz and connects to one of the two powder delivery systems. The head itself is aluminum and water cooled. All tubes seal to it by O-ring compression fittings. The bottom closure is also an aluminum, water cooled cap with an O-ring seal to the 8 1/2 inch tube and the exact support passing through its center. A side port from the cap is connected to a powder trap and also holds an orifice used to regulate total gas pressure in the torch chamber. It is necessary to trap the effluent powders because of their corrosive nature, and toxicity. The powder delivery systems are of two types. One is the screw drive and tapper type. The other is a fluidized powder type. The screw and tapper are stainless steel with a plastic cone as the funnel and cap. The fluidized powder system consists of a brass case with the gas entry at the bottom through a side orifice tunnel and the gas-powder exit two-thirds up the case from the bottom. The entire case is 3 inches diameter by 5 inches long. The seal is held in the plasma by a 12 inch Al_2O_3 rod 1/8 inch in diameter and held by the pulling rod of a transport mechanism identical to the one used for the pulling experiments.

The induction coil is 1/4 inch diameter and the voltage across it is about 1000 volts. The coil is wound on the core of the 1/4 inch tube. The coil is directly coupled to the input of the 10-200 generator and operates in the magnetic region.

In operation there are three distinct regions. The highest velocity flow occurs in the annulus between the 1/4 inch and 3/8 inch tubes through a set of orifices perpendicular to the axis of the tube. This set of orifices can be rotated through 180° in the flow direction from 11 o'clock to 1 o'clock from directly against the 1/4 inch tube through longitudinal flow to against the 3/8 inch tube. The usual position is approximately longitudinal. This produces a stream of gas which extends down the tube producing a lower pressure region near the axis of the tube. The annulus between the 3/8 inch tube and the powder fuel tube is fed at a much lower rate and constitutes the annulus of the combustion chamber by the spray stream. The gas flow through the center powder fuel tube flows through the slot and taper at the bottom of the fuel tube chamber into the powder to the flame. The height of the end of this tube above the flame and the velocity of the gas through it determine the density and hence molecular weight of the powder stream fed into the flame. The pressure at which the flame operates is controlled by the size of the slot orifice.

The various flows required by the tube are supplied through low-pressure regulators and a flow meter manifold. The spray flow and the direct flow streams are given approximately 12 to 20 p.s.i. and 10 to 20 cubic feet per hour and 1 to 10 cubic feet per hour respectively. These pressures and rates are very small and the volume flow is very low. The powder flow is about 10 to 20 p.s.i. and 10 to 20 cubic feet per hour.

and flows of 8 to 15 cubic feet per hour. A plasma of this size will operate with power inputs of 6 to 9 KW depending on flow rates, oxygen content, the powder feed rates, and the composition of the powder.

We have grown small boules of SnO but they are polycrystalline. The problem appears to be lack of uniformity of particles in the feed which leads to fluctuations in the rate at which powder enters the plasma. An ingot printer was ordered to produce more uniform powders. However, it has just arrived and the effect of particle size has not yet been examined. Otherwise the system has the stability and heat capacity necessary to grow SnO , CaO and InO if the powder delivery problems can be overcome.

3. Vapor Phase and Chemical Transport

Vapor phase and chemical transport growth studies were the last technique in which we started experimental work and the assembly of equipment. This technique offers the best possibility of getting mechanically good crystals of high purity. The basic experimental requirement is the provision of a precisely controlled furnace with at least one variable temperature gradient. The furnaces constructed for these studies are of the three zone design. The two outside zones are held at equal temperatures which are higher than the middle zone. The raw materials are placed in one of the end zones and growth takes place in the center zone. This arrangement allows growth to occur in a region where the fewest external constraints are on the crystal. This reduces the tendency to form polycrystals and of spontaneous nucleation.

The present element is 40 mil Mo wire wound on a pure Al_2O_3 core 1 3/4 inch in diameter and each section is 7 inches long. This element will operate up to 1700°C. The vapor pressure data available suggest that this is a reasonable temperature range for material transport of a useable rate for BaO , SrO and possibly CaO . However, the uncertainty of the highest temperature required for vapor phase growth forced us to design furnace cases that could also use heavy, free-standing elements. The cases are designed for use up to about 2200°C. They are water-cooled, vacuum-tight Al cases. To change to free standing elements will only require relatively minor changes in the installation. The elements are mounted such that it can freely expand. Access to the growth chamber is through quartz windows on the end of the furnace.

The control system is of a master-slave design. Master Control is by a Barber-Coleman 541B at the center zone. It slaves Barber-Coleman 359 differential drive 620 SCR power controllers which couple through variable transformers to the furnace elements. The variable transformers allow considerable freedom in element design.

Two three zone systems have been constructed. They were completed at the end of this contract period due to delays in construction of the furnace cases. Initial vapor phase experiments are underway in one. The other will be used for chemical transport growth studies on the system CaO in HCl .

4. Crystal Improvement

The apparatus for annealing CaO, SrO and BaO is available and operational. It consists of a Brev 466 Tungsten Vacuum furnace with programable controls. The containers for packing crystals in pure powder of the same oxides have not been constructed as we have as yet to get suitable crystals for annealing, and their assembly is simple. All other equipment for cutting and polishing is available.

V. PHYSICAL CHARACTERIZATION

The majority of equipment that will be used to survey the physical properties of these crystals was already available at Oregon State University. We have facilities for optical absorption studies from 33 wave numbers to 1650 Angstroms (Perkin Elmer Model 450, Beckman IR-7 and IR-11), for fluorescence excitation and emission (Perkin-Elmer Model 450 spectrofluorescence attachment), for light scattering (Biochemistry, Dr. I. Isenberg), for electron and optical microscopy, and for X-ray diffraction (G.E. XRD-5).

A facility for ionic conductivity in the temperature range necessary for CaO, BaO, and SrO was assembled under this grant. This system supplements equipment used at OSU for D.C. conductivity of insulating crystals and the data output of the new apparatus is compatible with existing equipment. Because of the length of time required to measure conductivity versus temperature when the temperature range is large (approximately 300 to 1600°C) and at least duplicate runs must be made sequentially some type of automation is required. The system constructed is a.c. to

avoid electrode problems. The conductance and capacitance are measured by a General Radio Model 1680 bridge. The temperature is measured by a thermocouple and its output converted to a frequency by a Hewlett-Packard voltage to frequency converter Model 2212A. This frequency is counted by a Monsanto preset counter. The preset feature allows the voltage to be converted from frequency to temperature. Of course, the temperature presented in this device must be later converted to an accurate temperature with higher order corrections, but the rough correspondence makes for easy set up with fewer errors. The outputs of the devices are fed into an interface of local construction which sequences measurements and shifts all output levels to be compatible with a Monsanto printer Model 511. The system will take an excessive amount of data if left to run freely. The rate of data calculation is controlled by a second preset counter which instructs the machine to measure at a specific time interval or temperature interval. The temperature control system (Barber-Coleman Model 541B and 621 SCII) increases temperature at a preset constant rate until the maximum set temperature is reached, then decreases the temperature until it reaches the initial temperature. At this time the entire apparatus shuts down. To make similar measurements by hand requires 16 to 18 hours of continuous attention.

VI. SUMMARY

A chemical method of purification of BaO , SrO and CaO has been developed. It produces oxides of greater purity than previously available.

The method would be even more effective if an atomic absorption spectrometer were available in our laboratory to provide quality control as the purification was in progress. It is our prime aim to better the process. There seems little requirement for better welds until we can grow crystals of controlled quality. Then direct reaction methods will be tried.

Crystal growth studies have reached the critical stage in the melt and plasma torch technique. Both systems are functioning correctly and the major problem remaining is to get the parameters of the system properly adjusted, i.e. powder feed, heat losses etc. This is largely a process of trial and error. It appears at the moment the systems should grow crystals shortly. The vapor phase and chemical transport experiments are just getting underway. We will need to systematically search for correct growth conditions. This can be a slow process because the time required to investigate each set of parameters is the order of a week to ten days.

The apparatus for measurement of various physical properties is available or in the final stage of test.

VII. EQUIPMENT AT OSU

During this grant the major equipment in use at OSU that was acquired under this grant is the following:

1. D. F. Generator, Lepel Model DF-200 and accessories	1 each
2. High Vacuum Tungsten Furnace, Bree Model 446	1 each
3. Optical Pyrometer, Leeds and Northrup Model 8636-C	1 each
4. Zone Refiner Unit, Materials Research Corp. Model Z 83 1A	1 each
5. Crystal Saw, Materials Research Corp. Model 1051	1 each
6. Precision Controllers, Barber-Colman, Model 341B	3 each
7. Differential Controller, Barber-Colman Model 359	4 each
8. Power Controller, Barber-Colman Model 621	7 each
9. Preset Counter, Monnaco Model 107A	2 each
10. Printer, Monnaco Model 511	1 each
11. Bridge, General Radio Model 1620	1 each
12. Forepump, Precision Model 85	2 each
13. Voltage to Frequency Converter, Hewlett-Packard Model 2012A	1 each

VIII. PERSONNEL

During the course of this program V. J. Fredericks was principal investigator. Mr. Robert Tanner was senior technician concerned with operation of crystal growing equipment and Mr. V. A. Fropp, research assistant, was concerned with the purification and analysis of the oxides.

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Final Report: J. C. Kemp, University of Oregon

I. General Description.

The period covered by this grant is from July 1968 through January 1970. This was divided for funding purposes into an initial 6 months, followed by a 12 month period, plus a two month no-cost extension.

The program was a joint one, with separate but complementary projects carried on by the two principal investigators, J. C. Kemp at the University of Oregon, and W. J. Fredericks at Oregon State University. The two efforts divided into chemistry and crystal growth (Fredericks); and trace-impurity and similar studies (Kemp). This section of the Report covers the latter work.

Our aims were to carry on ESR (electron spin resonance) and optical absorption analyses of starting powders and crystals produced in Fredericks' laboratory; to develop new, highly specific methods for detecting the important trace impurities in the oxide materials; and to apply annealing, doping, and oxidation-reduction techniques to crystals grown by Fredericks and by other groups participating in the ARPA oxides program. This work dovetailed with my other program, funded on a separate AFOSR grant through December 1969, concerned with color centers in the alkaline earth oxides.

Samples of BaCO_3 and SrCO_3 powders, prepared with high chemical purity by Fredericks for use as starting materials for growing the oxide crystals, were monitored for transition metal traces in our K-band ESR spectrometer. Extremely low levels of Fe^{2+} and Fe^{3+} , at or below our detection limit ($< 1 \text{ ppm}$), were demonstrated.

A critical problem with all alkaline earth oxide crystals available to date is that of the Fe content. Iron, in one or another of the valence states +2, +3, or +4, is believed responsible for the well-known optical absorption bands in the near- to middle-u.v. in these materials; these bands inhibit the usefulness of these materials as optical materials, and also as hosts for other impurities. In addition, such as ferric iron, is a source of the intrinsic photoconductivity. We therefore determined to identify these strong Fe optical

bands, using a powerful ESR-magneto-optical method we have developed. Since these bands are easily seen, even in samples with Fe concentrations near or below 1 ppm, establishment of their identity would permit rapid monitoring of Fe levels in new crystals with greater sensitivity and ease than by nuclear activation analysis or similar methods.

Our first experiments with MgO:Fe showed that both the two familiar bands at 4.3 and 5.7 e.v. have strong MCD (magnetic circular dichroism) patterns, with the characteristic temperature dependences (essentially at $1/T$) of paramagnetic species, as of iron-group ions. Through our double-resonance method, in which the changes in the MCD strength are produced by simultaneous excitation of an ESR line, we have identified the 4.3 e.v. band with, specifically, Fe^{3+} . Further tentative results, not definitive at this writing, suggested that the 5.7 e.v. band is also due to Fe^{3+} . A paper reporting these experimental results will be prepared, although a great deal remains to be understood. For example, the location of the Fe^{2+} absorption, which must include one or more strong bands in the u.v., becomes something of a mystery; presumably most of that absorption lies beyond 5.7 e.v. The work on the Fe bands is being actively continued into the period beyond the end of the present grant; and parallel work on at least one other transition-metal impurity is planned.

Apparatus for high-temperature modification and vapor-phase doping of samples was constructed as part of the program, making use of the 1000 watt induction heater and the Centorr tungsten furnace. A precise electronic temperature stabilizer, allowing samples to be held within a one or two degree temperature range, was built for the 1000.

Successful vapor-phase doping of Fe, and later of Cr and Co, into MgO crystals, was accomplished. The main purpose was to furnish a range of controlled samples for the iron-group impurity detection program above. Along with this, studies of the changes in the $\text{Fe}^{3+} : \text{Fe}^{2+}$ ratio due to heating and oxidation-reduction, via ESR, were also carried out.

II. Personnel.

A full-time technician, J. C. Foster, was employed on this project. His main job was to run the high-temperature facilities, including building up apparatus.

One graduate student, E. E. Iann, was assisted as research assistant, working mainly on the high-temperature experiments and on IR and optical absorption.

During the latter portion of the grant period, two other graduate students, J. C. Chung and F. A. Hoffman, were also paid on the grant. They had previously been supported on my other AFOSR grants. They went on the Raman experiments aimed at identification of the Fe and cobalt absorption bands.

III. Publications.

No papers have as yet appeared on the University of Oregon portion of this program. However, material for a preliminary report of the Raman IR results is on hand; and a more complete paper, with theoretical explanation of the nature of the Fe³⁺ bands, is planned.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) University of Oregon Department of Physics Eugene, Oregon 97403		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
J. REPORT TITLE PREPARATION OF CRYSTALS OF ALKALINE EARTH OXIDES AND RELATED COMPOUNDS		2b. GROUP	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Scientific-----Final			
5. AUTHOR(S) (First name, middle initial, last name) J. C. Kemp, W. J. Fredericks, W. A. Propp, and R. Tanner			
6. REPORT DATE 31 January 1970	7a. TOTAL NO. OF PAGES 40	7b. NO. OF REFS 17	
8a. CONTRACT OR GRANT NO. AFOSR-68-1609 (ARPA)	9a. ORIGINATOR'S REPORT NUMBER(S)		
b. PROJECT NO. 9542	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFOSR 70-0445 TR		
c. 6144501F			
d. 681301			

J. DISTRIBUTION STATEMENT

1. This document has been approved for public release and resale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES TECH., OTHER	12. SPONSORING MILITARY ACTIVITY Air Force Office of Scientific Research (SRP) 1400 Wilson Boulevard Arlington, Virginia 22209
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13. ABSTRACT

Processes developed during the period of the project for the purification of BaO, SrO, and CaO are described. These involve, with some variations, dissolution, precipitation of heavy metals and transition metals with $(\text{NH}_4)_2\text{S}$, filtration upon a millipore filter, recrystallization of the alkaline earth nitrates from HNO_3 solution, precipitation of the carbonates with CO_2 and thermal decomposition to the oxides. Analysis by atomic absorption spectrometry and nuclear activation analysis demonstrates that, except for the presence of other alkaline earths, the purity of the starting material for crystal growth is markedly improved by this treatment.

Apparatus for crystal growth from the molten oxides, by the Czochralski method, and from oxide powders by the Verneuil method using a plasma torch, has been constructed. Experiments to ascertain the correct parameters for successful growth of single crystals are incomplete; the probability of early success appears higher for the melt-growth method.

By means of a double-resonance method in which the magnitude of the magnetic circular dichroism is changed by simultaneous ESR excitation, the 4.3 eV optical absorption band in MgO has been definitely shown to be due to Fe^{3+} .

DD FORM 1473

UNCLASSIFIED

Security Classification

14.

KEY WORDS

LINK A

LINK B

LINK C

ROLE

WT

ROLE

WT

ROLE

WT

Alkaline earth oxides

Barium oxide

Strontium oxide

Calcium oxide

Oxide crystals