Inorganic Syntheses

Volume III

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INORGANIC SYNTHESSES

Volume III
To

the countless unknown but valiant soldiers of science upon whose labors Inorganic Syntheses are based, this series of volumes is dedicated in the hope that it will ease the toil of future legions.
PREFACE

The Board of Editors of *Inorganic Syntheses* has been more than pleased with the reception accorded to Volumes I and II of this series. The importance of inorganic chemistry as a distinctive branch of chemistry, so clearly defined by developments in the Second World War, has not only encouraged and stimulated the Editorial Board to continue its efforts to make available tried and tested procedures for the preparation of inorganic compounds, but has demonstrated beyond question the need for information of the sort presented in these volumes. The very fact that almost half of the syntheses contained in the present volume were submitted by, or checked in, industrial laboratories is evidence of the usefulness of these volumes.

The policies and practices established as the result of experience gained in assembling Volumes I and II have been continued. Each procedure has been checked carefully at some laboratory other than the one from which the original method was submitted. After checking and revision, syntheses were edited and then returned to the original authors for final approval. No synthesis is published until such approval by the authors has been granted.

As in the past, the syntheses have been arranged on the basis of the Mendeleev periodic classification. An effort has also been made to follow the system of nomenclature adopted in the preparation of Volume II. Trivial and common names, if widely used in the chemical literature, may have been used in a few cases, especially in the index. To make it possible to use all three volumes more satisfactorily, the index has been set up on a cumulative basis.

It has been felt desirable to continue the policy of presenting brief survey articles dealing with specific sub-
jects of interest in the field of inorganic chemistry. It has also been felt desirable to bridge the gap between inorganic and organic chemistry by presenting syntheses of materials which, though organic in nature, are widely used by inorganic chemists.

Contributions are now being accepted for publication in Volume IV of this series. All manuscripts, in triplicate, should be sent directly to Professor John C. Bailar, Jr., of the University of Illinois, who will serve as editor-in-chief of Volume IV. In submitting manuscripts, the authors are specifically requested to adhere to the style employed in the publication of the first three volumes. The procedure should be preceded by an introduction and followed by a discussion of physical and chemical properties of the compound whose method of preparation has been described. Where analytical methods are sufficiently distinctive to warrant a more extended exposition, detailed directions should also be included. Pertinent references should be placed at the end of the synthesis.

The editors take great pleasure in announcing the election of Professor E. G. Rochow of Harvard University and Professor G. Therald Moeller of the University of Illinois to membership on the Editorial Board. Janet Scott has accepted membership on the Board, after having served so faithfully and conscientiously as consultant on nomenclature and indexing for Volumes II and III.

The editor-in-chief is most grateful to his associates on the Editorial Board and to members of the Advisory Board for their help in the preparation of Volume III. It is also a pleasure to acknowledge the help of Patricia Schloesser and Betty Jane Ogg in the preparation of the manuscript.

The editors will be grateful if readers and users of this and previous volumes will call to their attention any errors or omissions.

LUDWIG F. AUDRIETH

URBANA, ILL.
March, 1950
CONTENTS

Preface ........................................ vii

CHAPTER I
1. Sodium Peroxide 8-Hydrate ....................... 1

CHAPTER II
2. Basic Beryllium Derivatives of Organic Acids .................. 4
3. Basic Beryllium Acetate and Propionate .................. 9
4. Strontium Sulfide and Selenide Phosphors .................. 11
   A. Preparation and Purification of Reagents .......... 12
   B. Special Techniques .......................... 16
   C. Preparation of Strontium Compounds .......... 17
   D. Preparation of Infrared-sensitive Phosphors .... 21
5. Barium Thiocyanate ............................. 24

CHAPTER III
6. Boron Chloride and Bromide .................... 27
7. Aluminum Bromide ............................... 30

CHAPTER IV
8. Carbon Tetraiodide ............................. 37
9. Cyanamide ....................................... 39
10. Dicyanodiamide (Cyanoguanidine) ................. 43
11. Aminoguanidonium Hydrogen Carbonate (Aminoguanidine Bicarbonate) .................. 45
12. Ammonium Dithiocarbamate ....................... 48
13. Organosilicon Compounds ....................... 50
14. Dimethyldichlorosilane (Dimethylsilicon Dichloride) ....... 56
15. Vinylchlorosilanes ................................ 58
16. Diphenylsilanediol .............................. 62
17. Germanium(II) Iodide (Germanium Diiodide) ........... 63
18. Methylgermanium Triiodide (Methyltriodogermaine) ........ 64
19. The Extraction of Hafnium and Zirconium from Cyrtolite 67
   A. Extraction .................................... 68
   B. Analytical Methods ........................... 69
   C. Precipitation of Zirconium-Hafnium Phosphates .... 71
   D. Conversion of the Phosphates to Acid-soluble Compounds 72
   E. Fractionation of Zirconium and Hafnium ........... 74
   F. The Preparation of Low-hafnium Zirconia .......... 76
CONTENTS

CHAPTER V
20. Nitrogen(V) Oxide (Nitrogen Pentoxide, Dinitrogen Pentoxide, Nitric Anhydride) .................................. 78
21. Hydroxylammonium Salts ......................................................... 81
   A. Hydroxylammonium Phosphate ............................................ 82
   B. Hydroxylammonium Arsenate .............................................. 83
   C. Hydroxylammonium Oxalate .............................................. 83
22. The Poly- and Metaphosphates and the Strong Phosphoric Acids 85
23. Pyrophosphoric Acid (Diphosphoric Acid) ............................... 96
24. Sodium Pyrophosphates (Sodium Diphosphates) ....................... 98
   A. Disodium Dihydrogen Pyrophosphate .................................... 99
   B. Tetrasodium Pyrophosphate ............................................... 100
25. Sodium Triphosphate (Sodium Tripolyphosphate) ....................... 101
26. Sodium Metaphosphates ....................................................... 103
   A. Sodium Trimetaphosphate ................................................ 104
   B. Sodium Polymetaphosphate (Graham's Salt) .......................... 104
27. Sodium Monofluophosphate ................................................... 106
28. Silver Monofluophosphate .................................................... 109
29. Hexafluophosphates of Sodium, Ammonium, and Potassium .......... 111
30. Ammonium Metavanadate ...................................................... 117

CHAPTER VI
31. Sulfur(VI) Fluoride (Sulfur Hexafluoride) ................................ 119
32. Disulfur Pentoxydichloride (Pyrosulfuryl Chloride) .................. 124
33. Selenium(IV) Oxide (Selenium Dioxide) ................................ 127
34. Selenium(IV) Oxychloride ................................................... 130
35. Crystalline Selenic Acid ..................................................... 137
36. Tellurium(IV) Chloride (Tellurium Tetrachloride) .................... 140
37. Tellurium(IV) Oxide (Tellurium Dioxide) ............................... 143
38. Telluric Acid ........................................................................ 145
39. Chromium(II) Acetate (Chromous Acetate) ............................... 148
40. Anhydrous Chromium(II) Chloride (Chromous Chloride) ............ 150
41. Hexamminechromium(III) Nitrate .......................................... 153
42. Chromium Hexacarbonyl ....................................................... 156
43. Potassium Octacyanomolybdate(IV) 2-Hydrate (Potassium
    Molybdocyanide Dihydrate) .............................................. 160
44. Tungsten(VI) Chloride (Tungsten Hexachloride) ....................... 163
45. Uranium(IV) Oxalate ........................................................... 166
46. Potassium Tetraoxalatouranate(IV) ...................................... 169

CHAPTER VII
47. Anhydrous Metal Fluorides .................................................... 171
   A. Nickel(II) Fluoride ........................................................... 173
   B. Cobalt(III) Fluoride ....................................................... 175
CONTENTS

C. Silver(II) Fluoride .............................................. 176
D. Carbon Tetrafluoride ........................................... 178
E. Tantalum(Niobium)(V) Fluoride [Tantalum (Niobium)
   Pentfluoride] .................................................... 179
F. Tungsten(VI) Fluoride (Tungsten Hexafluoride) ........... 181
48. Bromine(III) Fluoride (Bromine Trifluoride) ............... 184
49. Rhenium(VI) Oxide (Rhenium Trioxide) ....................... 186
50. Rhenium(VII) Oxide (Dirhenium Heptoxide) ................. 188

CHAPTER VIII

51. Anhydrous Iron(III) Chloride (Ferric Chloride) .......... 191
52. Hexamminenickel(II) Bromide and Hexamminenickel(II)
   Iodide ............................................................ 194
53. Bis(N,N’-Disalicylalethylene diamine)-µ-Aquodicobalt(II)
   (Bis[N,N’-bis(0-hydroxybenzylidine)ethylenediamine]-µ-
   aquodicobalt(II)) ............................................... 196

Index of Contributors ............................................. 203
Subject Index ..................................................... 205
Formula Index .................................................... 221
CHAPTER I

See also: Pyrophosphoric acid, synthesis 23
Crystalline selenic acid, synthesis 35
Telluric acid, synthesis 38
Disodium dihydrogen pyrophosphate, synthesis 24A
Tetrasodium pyrophosphate, synthesis 24B
Sodium triphosphate, synthesis 25
Sodium trimetaphosphate, synthesis 26A
Sodium polymetaphosphate, synthesis 26B
Sodium monofluophosphate, synthesis 27
Sodium hexafluophosphate, synthesis 29
Potassium hexafluophosphate, synthesis 29
Potassium octacyanomolybdate (IV) 2-hydrate, synthesis 43
Potassium tetraoxalatouranate (IV), synthesis 46
Silver monofluophosphate, synthesis 28
Silver(II) fluoride, synthesis 47C

1. SODIUM PEROXIDE 8-HYDRATE

Submitted by R. A. Penneman*
Checked by A. D. F. Toy†

Hydrates of sodium peroxide may be prepared by (1) the slow evaporation of a cold aqueous solution of sodium peroxide;¹ (2) the slow action of water vapor on solid sodium peroxide;² (3) the electrolysis of aqueous sodium hydroxide at temperatures between −10 and 0⁰;³ and (4) precipitation from a cold solution of sodium hydroxide and hydrogen peroxide by means of alcohol.⁴

The method outlined below is a modification of the last mentioned of these procedures and yields a chemically pure product. The success of this method depends upon the use of an excess of sodium hydroxide, since no precipitate is

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obtained when hydrogen peroxide is present in excess. However, it was found that the amount of water in the hydrate depends upon the temperature at which precipitation is carried out. The directions that follow give the 8-hydrate consistently, whereas a product analyzing almost exactly for Na$_2$O$_2$·11H$_2$O is formed when hydrogen peroxide is added to a saturated sodium hydroxide solution at 0°.

**Procedure**

Ten grams of carbonate-free sodium hydroxide is dissolved in 25 ml. of water in a stoppered Erlenmeyer flask and cooled to 15°. Ten grams of a 30 per cent solution of hydrogen peroxide (corresponding to a mol ratio of NaOH: H$_2$O$_2$ = 2.83:1) is added slowly with constant stirring at a rate such that the temperature does not rise above 18°. Sixty milliliters of 95 per cent alcohol (cooled to 15°) is added; the flask is then stoppered and shaken vigorously. The solution is allowed to stand about 44 hour, the supernatant liquid is decanted, and the washing is repeated with two 60-ml. portions of cold alcohol. The white crystals are filtered with suction on a hardened filter paper and washed with ether. The compound is transferred quickly to a desiccator containing sulfuric acid (not in vacuo) and kept in a cold chest for 10 hours at a temperature not above 15°. The yield is 18 g. (92 per cent based on H$_2$O$_2$). The product may be preserved for a limited period of time in the ice chest.

**Analysis**

Sodium (reported as Na$_2$O) was determined by hydrolysis of a sample and titration with a standard acid. Peroxide oxygen was determined by dissolving a weighed sample in an excess of standard cerium(IV) nitrate solution and titrating the excess cerium(IV) ion with iron(II) sulfate using o-phenanthroline as indicator. Anal. Calcd. for Na$_2$O$_2$·8H$_2$O: Na$_2$O, 27.88; O (peroxide) 7.2. Found: Na$_2$O, 27.92; 0, 7.11.
Properties

The 8-hydrate is a white, crystalline powder which reacts readily with carbon dioxide, hence must be kept from contact with the atmosphere. It melts in its own water of crystallization at 30° and decomposes to yield oxygen. If kept for a long period over sulfuric acid in a vacuum desiccator, the 8-hydrate loses 6 molecules of water to form the 2-hydrate, \( \text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O} \).²

References

3. German patent 245531 (1911).
An apparently unique property of beryllium is its tendency to form so-called "basic" derivatives of a number of organic acids. These compounds correspond in composition to the general formula \( \text{Be}_2\text{O}(\text{RCOO})_6 \) (\( \text{R} \) = hydrogen or organic radical) and are, in general, remarkably stable. In fact, the tendency toward their formation is so pronounced that the corresponding "normal" beryllium salts can be prepared only with difficulty or not at all. Best known of these compounds is the basic acetate, a material that was first discussed critically by Urbain and Lacombe in 1901. A number of other compounds of the series have been described by Lacombe, Tanatar and Kurowski, Glassmann, Bragg and Morgan, Morgan and Astbury, and Feild. A comprehensive summary of the preparation and properties of these substances is given in Gmelin's "Handbuch der anorganischen Chemie."

**Preparation.** Listed methods of preparation are most extensive for the basic acetate. Methods for the preparation of this compound, however, are generally applicable to the other members of the series.

1. **Action of Organic Acid on Beryllium Oxide or Hydroxide.** This method has been used for the preparation of the majority of the basic derivatives, the most notable exception being the formate. Usually, it amounts to treatment of the hydroxide with the appropriate acid, heating until reaction is complete, evaporating to a solid or oily product,
extracting the basic beryllium compound with a solvent such as chloroform or petroleum ether, and crystallizing from that solvent.

2. Action of Organic Acid on Beryllium Carbonate or Basic Carbonate. This method is similar in all respects to the above procedure. While it has been used most extensively for only the simpler members of the series, there is no apparent reason why it should not be equally effective for the preparation of other members as well. The procedure is one of the few claimed to give the basic formate. Directions given for the preparation of the basic acetate (synthesis 3) and basic propionate (synthesis 3) represent modifications of this general procedure.

3. Action of Organic Acid or Anhydride on Anhydrous Beryllium Chloride. This method apparently yields only the normal formate but gives basic beryllium derivatives of such acids as acetic, propionic, butyric, benzoic, and o-chlorobenzoic. It amounts to refluxing anhydrous beryllium chloride with the corresponding acid or anhydride, adding benzene, toluene, or petroleum ether, and distilling to remove the hydrogen chloride and acid chloride by-products. Under strictly anhydrous conditions normal beryllium derivatives are said to result, but in the presence of water, added either with the original acid or as moist benzene, the basic derivatives are formed.

4. Action of Organic Acid Chloride on a Basic Beryllium Compound. This method is useful for the preparation of mixed basic beryllium derivatives. Thus, refluxing basic beryllium isobutyrate with acetyl chloride yields a mixed compound, the composition of which may be represented by the formula $\text{Be}_4\text{O}((\text{CH}_3\text{COO})_2'[\text{(CH}_3)_2\text{CHCOO}]_4$. A mixed acetate propionate of composition $\text{Be}_4\text{O}((\text{CH}_3\text{COO})_3-(\text{CH}_3\text{CH}_2\text{COO})_3$ has been prepared from the basic propionate by the same procedure.

5. Miscellaneous. Preparations of the basic formate by heating the normal formate under reduced pressure (30 to 35 mm.) and by boiling the normal formate with a water
suspension containing the calculated amount of beryllium carbonate have been described.\(^3\)

In addition to the compounds listed in Table I, corresponding basic derivatives of the following acids have been reported: crotonic; isocrotonic; levulinic; succinic; cyanoacetic; mono-, di-, and trichloroacetic; monobromoacetic; monochloro- and monobromopropionic; lactic; glycic; ethyl- and phenylglycolic (α-hydroxybutyric and mandelic, respectively); and salicylic. Confirmatory evidence for the identities of most of these is completely lacking.

**Properties.** The basic beryllium compounds are non-electrolytes and possess all of the properties of purely covalent substances. They are low-melting, low-boiling materials that generally sublime or distill without decomposition. They are usually insoluble in water but soluble in such organic solvents as chloroform, ether, petroleum ether, benzene, toluene, and the alcohols. Physical constants, where known, are given in Table I. Molecular weights, as determined by vapor density\(^1\) and cryoscopic\(^2\) measurements, correspond to those of monomolecular compounds of composition Be\(_2\)O(RCOO)\(_6\).

Chemically, the basic beryllium compounds are stable toward heat, toward oxidation except under very drastic conditions (e.g., boiling with nitric acid), and toward cold water. Treatment with boiling water usually effects hydrolysis slowly; treatment with mineral acids normally yields the corresponding beryllium salt and the free organic acid.

**Structure.** Older concepts picturing the basic beryllium compounds as derivatives of condensed acids or as structural analogs of the true basic salts of the other elements have been discarded in favor of unitary structures comparable with those ascribed to other strictly covalent compounds.

The x-ray studies of Bragg and Morgan\(^4\) on the basic acetate indicate a central oxygen atom surrounded tetrahedrally by the four beryllium atoms, each edge of the
<table>
<thead>
<tr>
<th>Derivative</th>
<th>Formula</th>
<th>Melting point, °C</th>
<th>Boiling point, °C</th>
<th>Density, g./ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formate</td>
<td>Be₂O(HCOO)₄</td>
<td>Sublimes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetate</td>
<td>Be₂O(CH₃COO)₄</td>
<td>285-286</td>
<td>330-331</td>
<td>1.39</td>
</tr>
<tr>
<td>Propionate</td>
<td>Be₄O(CH₃CH₂COO)₄</td>
<td>137.5-138</td>
<td>339-341 (19 mm.)</td>
<td>1.25</td>
</tr>
<tr>
<td>Triacetate Tripropionate</td>
<td>Be₄O(CH₃COO)₄(CH₃CH₂COO)₃</td>
<td>140-142</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>Butyrate</td>
<td>Be₄O(CH₃CH₂CH₂COO)₄</td>
<td>25-27</td>
<td>239 (19 mm.)</td>
<td></td>
</tr>
<tr>
<td>Isobutyrate</td>
<td>Be₄O(CH₃CH₂COO)₆</td>
<td>88-89</td>
<td>336-337</td>
<td>1.14</td>
</tr>
<tr>
<td>Diacetate Tetraisobutyrate</td>
<td>Be₄O(CH₃COO)₄(CH₃CH₂CH₂COO)₄</td>
<td>-15</td>
<td>351</td>
<td></td>
</tr>
<tr>
<td>Isovalerate</td>
<td>Be₄O(CH₃CH₂CH₂COO)₆</td>
<td></td>
<td>254 (19 mm.)</td>
<td>1.05</td>
</tr>
<tr>
<td>Pivalate</td>
<td>Be₄O(CH₃CH₂C₆H₄COO)₄</td>
<td>163</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoate</td>
<td>Be₄O(C₆H₅COO)₄</td>
<td>317-318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Chlorobenzoate</td>
<td>Be₄O(ClC₆H₄COO)₄</td>
<td>255-256</td>
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</tr>
</tbody>
</table>
tetrahedron being occupied by an acetate group acting as a bridge between two atoms of beryllium. This structural arrangement may be depicted graphically in the following manner:

![Diagram](image)

The data of Morgan and Astbury are in agreement with this picture. Pauling and Sherman indicate the structure to amount to four BeO$_4$ tetrahedra with one oxygen atom common to all four and the remaining oxygen atoms being supplied by the acetate groups. This is essentially the same concept.

X-ray studies also indicate that the same type of structure may be assigned to the basic propionate, triacetate tripropionate, isobutyrate, butyrate, and pivalate. It may therefore be assumed as general for all members of the series. In the basic formate and acetate, complete crystal symmetry is predicted by structures of this type. Replacement of the hydrogen or methyl with radicals such as ethyl and propyl should induce dissymmetry. That this is true is shown by the crystal habits of these compounds. The basic acetate crystallizes in the cubic system, but the basic propionate, triacetate tripropionate, and pivalate are monoclinic in form, and the basic isobutyrate crystallizes in the triclinic system. The low melting point of the basic butyrate made a complete x-ray investigation difficult, but the crystals were shown to be of very low symmetry.
3. BASIC BERYLLIUM ACETATE AND PROPIONATE

\[ x\text{BeO} \cdot y\text{BeCO}_3 + \frac{3}{2}(x + y)\text{RCOOH} \rightarrow \]
\[ \frac{x+y}{4}\text{Be}_4\text{O}(\text{RCOO})_6 + y\text{CO}_2 + \frac{3}{4}(x + y)\text{H}_2\text{O} \]

Submitted by THERALD MOELLER,* ALVIN J. COHEN,* AND ELLIOT MARVELL*

Checked by P. S. BAKER† AND D. F. SMITH†

The basic acetate and propionate of beryllium are prepared most conveniently from a reactive form of the basic carbonate. The composition and the reactivity of the starting material are variable, and it may therefore be necessary to prepare the so-called "basic" carbonate from some convenient source of beryllium, especially if the available "carbonate" dissolves with difficulty in either hot acetic or propionic acid. For properties of these compounds see page 7.

Procedure

A. BASIC BERYLLIUM ACETATE

\[ \text{Be}_4\text{O}(\text{CH}_3\text{COO})_6 \]

Forty grams of basic beryllium carbonate is stirred with 80 ml. of glacial acetic acid on the hot plate until carbon

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dioxide is no longer evolved.* When reaction is complete, some of the basic acetate may separate as white, semitransparent crystals. If reaction is incomplete, an amorphous-appearing white residue remains. The solution is cooled to room temperature, and the crude basic beryllium acetate that crystallizes is removed by suction filtration and air-dried. The product is treated with 60 to 80 ml. of chloroform and any undissolved material removed by filtration. The chloroform solution is evaporated on the steam bath. The colorless octahedra of the basic acetate are freed of residual solvent in a vacuum desiccator. The product melts at 284° (uncorr.) and sublimes without residue under reduced pressure. The yield is 28 g. (65 per cent, based upon a basic carbonate containing 26.6 per cent beryllium oxide).† Anal. Calcd. for Be₄O(CH₃COO)₆: C, 35.46; H, 4.46. Found: C, 35.70; H, 4.82.

B. BASIC BERYLLIUM PROPIONATE

Be₄O(CH₃CH₂COO)₆

Twenty-five grams of basic beryllium carbonate is treated with 125 ml. of propionic acid in a 400-ml. beaker. When evolution of carbon dioxide has ceased, the solution is transferred to a porcelain evaporating dish and evaporated on a

* If the basic carbonate used does not react completely with acetic acid or if only beryllium oxide is available as starting material, conversion to freshly precipitated basic carbonate by the following procedure must precede treatment with acetic acid. Ten grams of beryllium oxide or 40 g. of the basic carbonate is dissolved in 50 ml. of concentrated sulfuric acid and the solution diluted to 500 ml. with distilled water. Aqueous ammonia (5N) is added until the solution is basic to litmus. The resulting suspension is clarified by digestion on the steam bath, and the precipitated hydroxide is removed by suction filtration and air-dried. The product is powdered in a mortar and suspended in 200 ml. of water containing 5 ml. of 5 N ammonia. The suspension is saturated with carbon dioxide either by addition of a few pieces of solid carbon dioxide or by bubbling in the gas. The container is stoppered and allowed to stand overnight. The resulting basic carbonate is removed by suction filtration and air-dried. It is then powdered and dried further in a desiccator.

† Calculation of percentage yield must be based upon the analytically determined beryllium content of the basic carbonate.
hot plate at 130 to 140°. When the cooler portions of the liquid begin to deposit crystals, the dish is allowed to cool. The solid cake of crude product is broken up and ground to a fine powder in a mortar. The powder is dissolved in 300 ml. of hot petroleum ether (b.p. 80 to 100°), and the filtered solution allowed to crystallize overnight in the refrigerator. The colorless crystals are removed by suction filtration and dried in the air. The yield is 45 g. (85 per cent, based on a starting material containing 15.4 per cent beryllium). The crystals melt at 137.5 to 138°, with preliminary softening at 134°. Anal. Calcd. for Be₄O-(CH₃CH₂COO)₆: C, 44.07; H, 6.17. Found: C, 44.18; H, 6.31.

4. STRONTIUM SULFIDE AND SELENIDE PHOSPHORS

Submitted by R. Ward,* R. K. Osterheld,* and R. D. Rosenstein*
Checked by D. W. Lyon† and E. L. Poor†

The alkaline earth sulfides were among the earliest known synthetic phosphorescent materials. Recent work by Urbach¹ has shown that some of these substances exhibit the property of energy storage to a phenomenal degree and that this property may be developed by the addition of small quantities of two impurity cations or "activators." One of the activators serves to furnish electrons that may be promoted to higher energy states in the lattice by absorption of short-wave-length visible or ultraviolet light. This process is called "excitation." The other activator introduces potential wells in which some of the excited electrons are trapped. The potential barriers opposing the liberation of the electrons from these traps are high enough so that very few electrons are released by thermal energy at room temperature. Exposure to infrared radiation (about 1 μ), however, effectively releases the trapped electrons with

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