

NO DRAWINGS.

Date of Application (No. 20366/68) and filing Complete Specification: 30 April, 1968.

Complete Specification Published: 26 Nov., 1969.

1,171,875



Index at acceptance:—CI A(D53, D62, D63, DX, G12, G46, G47, G48, G51) AG12D53, AG12D62, AG12D63, AG12DX, AG46D53, AG46D62, AG46D63, AG46DX, AG47D53, AG47D62, AG47D63, AG47DX, AG48D53, AG48D62, AG48D63, AG48DX, AG51D53, AG51D62, AG51D63, AG51DX.

International Classification:—C 01 f 1/00.

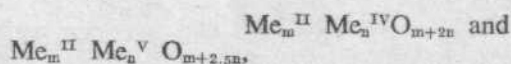
COMPLETE SPECIFICATION.

Method of Producing Salts of Alkaline Earth Metals.

We, SERGEI ALEXEEVICH KUTOLIN of Ulitsa Demiana Bednogo, 58, Kvartira 19, ALEXANDR ILICH VULIKH of Ulitsa Demiana Bednogo, 58-a, Kvartira 36 and ANNA EGOROVNA SHAMMASOVA of Ulitsa Dostoevskogo, 22, Kvartira 75 all Novosibirsk, Union of Soviet Socialist Republics, all citizens of the Union of Soviet Socialist Republics, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of producing salts of alkaline earth metals, which are often employed as ferroelectrics in electrical and radio engineering and as heat resistant materials for refractory articles and coatings.

A method is known of producing salts of alkaline earth metals of the general formulae



where

$Me^{II}$  = the alkaline earth metals Mg, Ca, Sr and Ba or combinations thereof,

$Me^{IV}$  = the transition metals Ti, Zr and Hf or combinations thereof,

$Me^V$  = the transition metals Nb and Ta or a combination thereof,

m and n = numbers expressing the amount of gram-atoms of the metals in a gram-molecule of the salt,

[Price 4s. 6d.]

by thermal treatment of a charge containing carbonates of alkaline earth metals and oxides of said transition metals in the air at a temperature of 1300—1400°C (I. A. Glzman "Ferroelectrics", Moscow, 1967, pp 25—27).

A disadvantage of said known method is the high temperature at which the charge is treated which complicates the construction of plant for the process.

Another disadvantage of this known method is the necessity for very lengthy heat treatment of the charge for its complete conversion. In practice the process is not continued until the charge is completely converted and as a consequence the final product as a rule contains substantial amounts of free alkaline earth metal oxides and transition metal oxides. In the synthesis of barium salts the product often contains 0.5—1% BaO.

It is an object of the present invention to eliminate the above disadvantages.

It is a further and more specific object of the invention to provide a method of producing salts of alkaline earth metals of the above general formulae enabling a substantial lowering of the temperature of the process and ensuring quantitative conversion of the charge in a shorter time.

These objects have been accomplished by the provision of a method of producing salts of alkaline earth metals, wherein a charge containing carbonates of alkaline earth metals and oxides of the above mentioned transition metals is heated at a temperature of 700—900°C in a stream of ammonia and

then in the air at a temperature of 600—750°C.

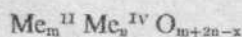
The present method of producing salts of alkaline earth metals may be carried out as follows.

The charge containing carbonates of alkaline earth metals and oxides of transition metals (titanium, zirconium, hafnium, niobium and tantalum) is comminuted to minus 200 mesh per sq. cm. and charged directly into a tube furnace or into vessels placed in a furnace. The lining of furnace and vessels may be graphite, porcelain or other ceramic materials.

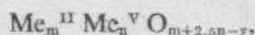
During the first stage of the process the charge is treated in a stream of ammonia fed through the furnace at a linear velocity of 5 cm/sec, at a temperature of 700—900°C over a period of 2—3 hours.

In these conditions reduction of the oxides of the transition metals and their reaction with the carbonates of the alkaline earth

metals is not complete. Intermediate compounds are formed having the general formulae:



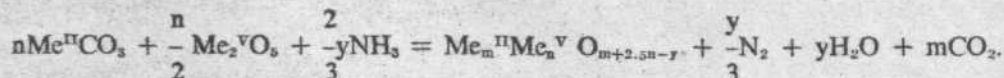
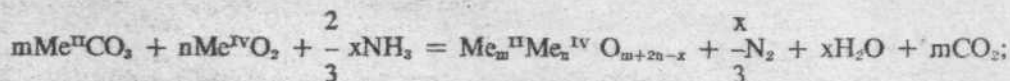
and



where x and y are numbers expressing the number of gram atoms of oxygen lost by a gram-molecule of oxide of transition metal when it is not completely reduced.

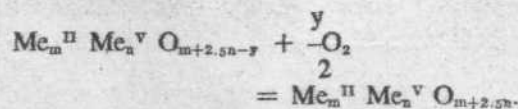
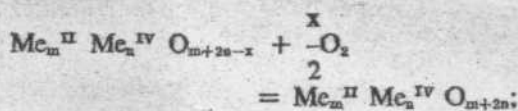
For instance, when preparing compounds having the formulae  $\text{BaMe}^{\text{IV}}\text{O}_3$  and  $\text{BaMe}_2^{\text{V}}\text{O}_6$ , the intermediate products in the first stage of the process have the composition  $\text{BaMe}^{\text{IV}}\text{O}_{2.5-2.8}$  and  $\text{BaMe}_2^{\text{V}}\text{O}_{1.5-3.0}$ , x being equal to 0.2—0.5 and y to 1.0—1.5.

Essentially the first stage of the process may be expressed by the following equations:



The nitrogen, water vapour and carbon dioxide formed in the first stage are carried away by the ammonia stream.

In the second stage of the process the intermediate compounds formed are held in air or in a stream of air at a temperature of 600—750°C for 1—2 hours, during which period said intermediates are oxidized by atmospheric oxygen, this being expressed by the following equations:



The invention is further illustrated with reference to the following Examples.

#### EXAMPLE 1

Preparation of barium metatitanate,  $\text{BaTiO}_3$

86.3 g of barium carbonate and 34.8 g of titanium dioxide are placed in a porcelain boat and held in a stream of ammonia fed in at a rate of 5 cm/sec at a temperature of

800°C for 3 hours. The flow of ammonia is thereupon stopped and the product held in air at 700°C for 2 hours.

Yield 98.5 g or 98.5% of theory.

Found % by weight:

BaO 65.55;  $\text{TiO}_2$  34.05.

Calculated for  $\text{BaTiO}_3$  % by weight:

BaO 65.74;  $\text{TiO}_2$  34.26.

According to X-ray phase analysis the product consists entirely of the phase  $\text{BaTiO}_3$ .

#### EXAMPLE 2

Preparation of barium metaniobate,  $\text{BaNb}_2\text{O}_6$

48.0 g of barium carbonate and 63.2 g of niobium pentoxide are placed in a porcelain tube furnace and held in a stream of ammonia fed in at a rate of 5 cm/sec at a temperature of 800°C for 3 hours. The flow of ammonia is thereupon stopped and the product held in air at 650°C for 2 hours.

Yield 98 g or 98% of theory.

Found, % by weight:

BaO 36.5;  $\text{Nb}_2\text{O}_5$  63.3.

Calculated for  $\text{BaNb}_2\text{O}_6$ , % by weight:

BaO 36.58;  $\text{Nb}_2\text{O}_5$  63.42.

According to X-ray phase analysis the product consists entirely of the phase  $\text{BaNb}_2\text{O}_6$ .

## EXAMPLE 3

*Preparation of calcium metazirconate,  
CaZrO<sub>3</sub>*

5 55.9 g of calcium carbonate and 68.8 g of zirconium dioxide are placed in a tube furnace and held in a stream of ammonia fed in at a rate of 5 cm/sec at a temperature of 900°C for 3 hours, and then in a stream of air at 700°C for 2 hours.

10 Yield 99 g or 99% of theory.

Found, % by weight:

CaO 31.45; ZrO 68.3.

Calculated for CaZrO<sub>3</sub>, % by weight:

CaO 31.28; ZrO<sub>2</sub> 68.72.

15 According to X-ray phase analysis the product consists entirely of the phase CaZrO<sub>3</sub>.

## EXAMPLE 4

*Preparation of calcium barium metatitanate,  
CaBaTi<sub>2</sub>O<sub>6</sub>*

20 27.1 g of calcium carbonate, 53.5 g of barium carbonate and 43.3 g of titanium dioxide are placed in a tube furnace and held in a stream of ammonia fed in at a rate of 5 cm/sec at a temperature of 900°C for 3 hours, whereupon the flow of ammonia is stopped and the product is held in air at a temperature of 750°C for 2 hours.

30 Yield 98.5 g or 98.5% of theory.

Found, % by weight:

CaO 15.25; BaO 41.4; TiO<sub>2</sub> 43.2.

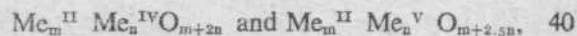
Calculated for CaBaTi<sub>2</sub>O<sub>6</sub>, % by weight:

CaO 15.19; BaO 41.53; TiO<sub>2</sub> 43.28.

35 According to X-ray phase analysis the product consists entirely of the phase CaBaTi<sub>2</sub>O<sub>6</sub>.

## WHAT WE CLAIM IS:—

1. A method of producing salts of alkaline earth metals of general formulae



where

Me<sup>II</sup> = the alkaline earth metals Mg, Ca, Sr and Ba or combinations thereof,

Me<sup>IV</sup> = the transition metals Ti, Zr and Hf or combinations thereof, 45

Me<sup>V</sup> = the transition metals Nb and Ta or a combination thereof,

and  
m and n = numbers expressing the amount of gram-atoms of the metals in a gram-molecule of the salt, 50

by heating an alkaline earth metal carbonate with an oxide of a said transition metal at a temperature of 700—900°C in a stream of ammonia and then at a temperature of 600—750° in air. 55

2. A method according to claim 1, substantially as hereinbefore described. 60

3. A salt of an alkaline earth metal, when prepared by the method of claim 1 or claim 2.

MARKS & CLERK,  
Chartered Patent Agents,  
Agents for the Applicants.