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Short communication

Synthesis of barium silicates by glow discharge electron gun

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Abstract

Barium silicates ($BaSiO_3$, $BaSi_2O_5$) have been synthesized by using the glow discharge electron gun. The melting installation, the sample preparation procedures as well as the experiment results of synthesis together with the crystallographic analysis for the raw materials and the obtained barium silicates are presented. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Due to their special properties barium silicates are used in the ceramics, glaze and glass industry, and more recently in the solar-cell production as an important ingredient. In nature barium silicates are difficult to find as minerals. While $BaSi_2O_5$ is one of just a few barium minerals, called sanbornite and is a rare phyllosilicate, $BaSiO_3$ cannot be found in nature as such, but only in the composition of complex minerals such as benitoite $BaTiSi_3O_9$ (barium titanium silicate), bazirite $BaZrSi_3O_9$ (barium zirconium silicate) and pabstite $Ba(Sn,Ti)Si_3O_9$ (barium tin titanium silicate), all from the cyclosilicate subclass.

Since most of the barium silicate minerals are very rare and even allowable only as mineral specimens, for industrial purposes the barium silicates are obtained from other barium minerals such as witherite $BaCO_3$ (barium carbonate), a carbonate mineral from the aragonite group, having an orthorombic symmetry. To obtain barium silicates, barium carbonate $BaCO_3$ is mixed with silicon dioxide SiO_2 and is heated. During the heating process the following chemical reaction takes place:

$$BaCO_3 + SiO_2 \rightarrow BaSiO_3 + CO_2$$

Because of the melting temperature around 1600 °C of the barium silicate, to obtain a melt use of high performance heat sources is required. As an alternative to the frequently used methods where heating is achieved by electric resistance, high frequency generators, or with oxy-hydrogen flame, we used the glow discharge electron gun (GDEG) [1] as a heat source that ensures quick heating to the melting point and has a higher efficiency in comparison to the above mentioned heating systems.

2. Experimental

For sample heating with the GDEG, an experimental installation was built whose scheme is presented in Fig. 1 [2,3].

It consists in an earthed metallic enclosure, 1, in which an argon pressure of 4×10^{-2} Torr is ensured, its value being indicated by the vacuum-meter 2. At the upper part of the enclosure the proper electron gun is mounted. This is formed by an aluminium cathode, 3, having the emitting surface of a concave spherical shape, the support and the electric feed of the cathode being made by an air proof insulated support, 4.

Around the cathode, the anode, 5 is mounted and the metallic rods, 6 sustain it, thus being electrically earthed (the positive terminal of the high voltage source). The 5 mm anode–cathode distance has been chosen so that it avoids the high-field breakdown in the gas behind and in the lateral parts of the cathode. The graphite crucible,

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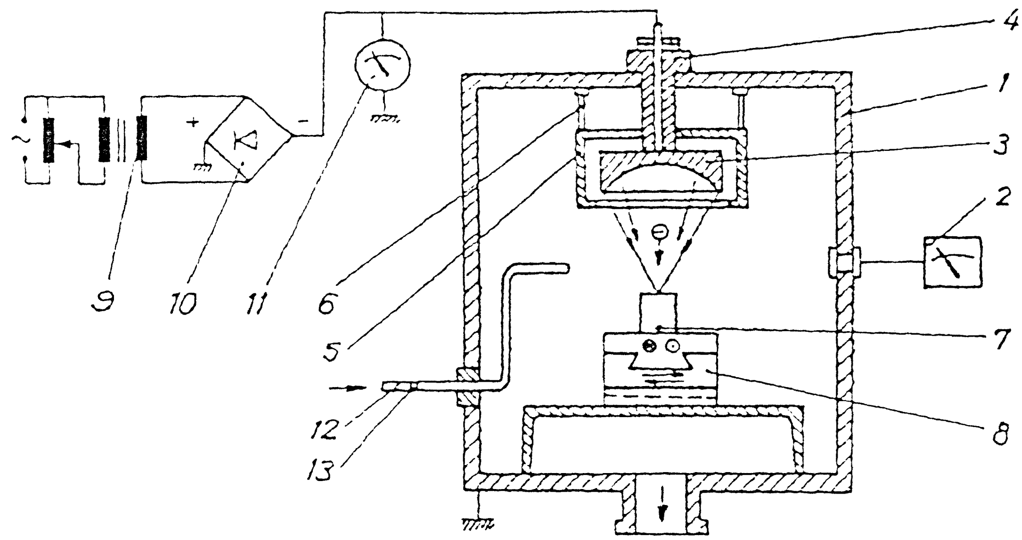

Fig. 1. Scheme of the experimental installation.

7 is placed in the curvature center of the spherical cathode, on a support, 8. To the cathode, 3 a continuous high voltage of up to 10 kV from a transformer, 9 is supplied, through the rectifier equipment, 10, the voltage value being indicated by a kilo-voltmeter, 11. In order to facilitate the start of the glow discharge and the gas ionisation in the enclosure we introduced argon, as a plasmatic medium, through the pipe, 12, the pressure, in a dynamic regime being of 4×10^{-2} Torr, the governor for the pressure floating control being a needle valve, 13.

The electrons emerging from the cathode are accelerated in the cathodic fall space and they pass through the anode aperture, being thus focused in the curvature center of the concave spherical surface, where the crucible, 7 is placed, heating the pastille. The target temperature was measured with an optical pyrometer using the filament disappearance method. We indicate that the glow discharge electron gun has the following dimensions:

- cathode diameter: 130 mm;
- curvature radius of the cathode spherical surface: 130 mm;
- cathode height: 60 mm.

To obtain barium silicates, a mixture of barium carbonate $BaCO_3$ and silicon dioxide (amorphous silica) SiO_2 was prepared by mixing the reactants in a 1:1 molar proportion. It followed a homogenization process by manual mixing in a mortar and then the obtained powder was humified with a watery solution of 4% polyvinilic alcohol, in an adequate quantity for an easy powder aglomeration at finger pressing, and shaped into pellets using a manual press and moulds with an 8 mm diameter.

The pellets were dried for 48 h at 120 °C in order to eliminate all humidity, and after drying they were calcinated in an electric furnace with silicon carbide bars at 1200 °C for 320 min in order to eliminate all the polyvinilic alcohol and to obtain an appropiate mechanical resistance of the pastilles for their maneuvering and heating with the GDEG. After calcination the pellets were cooled down to ambient temperature in the same furnace for around 7 h.

The pellets obtained after the above procedure were introduced into a crucible made of spectrally pure graphite, placed within the curvature center of the spherical surface of the cathode. When the argon pressure of 4×10^{-2} Torr was reached, the supply voltage was progressively augmented to 3.5 kV and a current of 275 mA, thus resulting an increase in the target temperature up to the melting point of the pellet surface layer. The pellet heating lasted for 210 s. The cooling down was also progressively made, afterwards the pellet being extracted from the crucible in order to be analyzed.

3. Results and discussion

The X-rays diffractograms were achieved with a DRON 3 diffractometer at $U = 30$ kV and $I = 30$ mA, using the Cu K_α radiation with $\lambda = 1.542$ Å, 2θ between 10 and 80°, at a detector moving speed of 1°/min, in order to increase the results relevance concerning the transformations in the initial mixture after heating with the GDEG at 1600 °C.

The diffractograms for the initial pellet, prior to the GDEG heating are presented in Fig. 2. The X-ray spectrum, indexed with the help of the ASTM file confirms the initial state structure of the specimen as a powder mixture of barium carbonate ($BaCO_3$) and silicon dioxide (SiO_2).

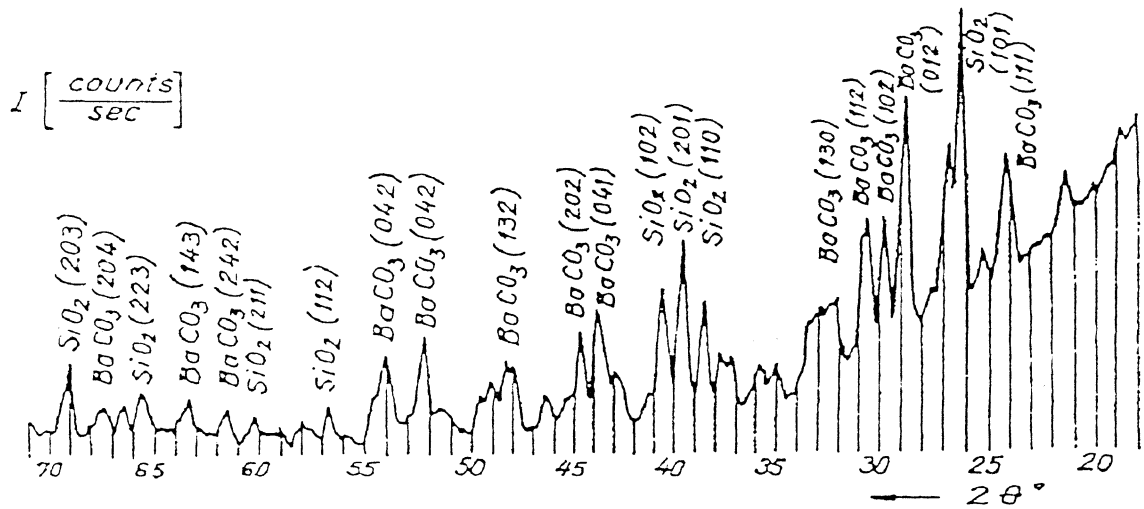

Fig. 2. Diffractogram of the powder mixture of $BaCo_3$ and SiO_2.

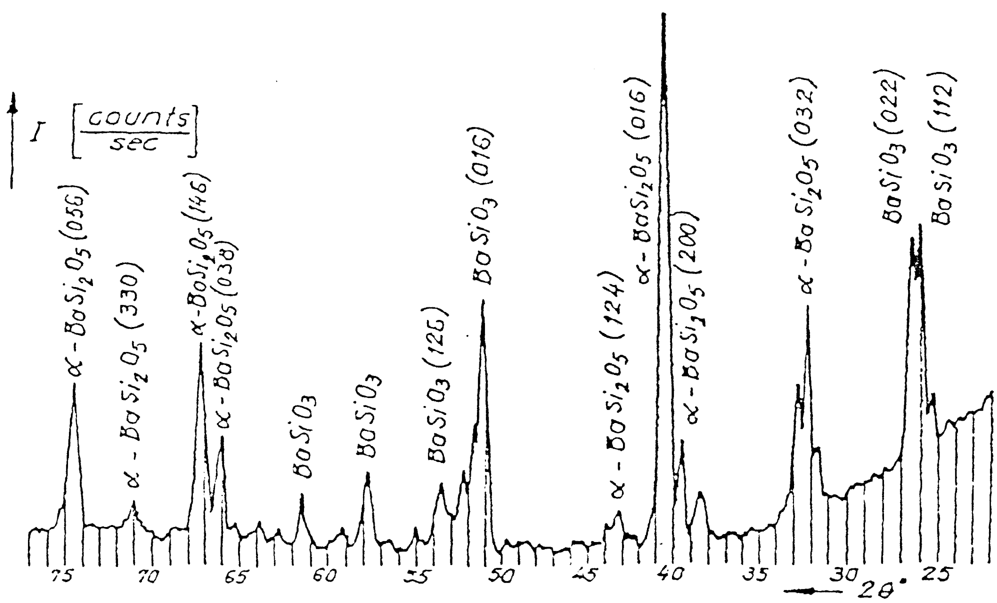

Fig. 3. Diffractogram of the barium silicates $BaSiO_3$, $BaSi_2O_5$.

The pellets heated with GDEG until the melting of the superficial layer followed by its solidification, from the macroscopic point of view, present the formation of a superficial layer of polycrystalline barium silicate, equigranulated, having a white colour and between 0.5 and 4 mm thickness. The surface layer has a glassy aspect that indicates the vitrification of the barium silicate. Fig. 3 presents the diffractogram corresponding to the surface layer of polycrystalline barium silicate.

Following the X-ray diffraction spectrum indexation using the ASTM files, we obtained the confirmation of the fact that the surface layer obtained after the solidification of the melted part of the $BaCO_3$ and SiO_2 pellet, heated with the glow discharge electron gun, consists of polycrystalline $BaSiO_3$ and α-$BaSi_2O_5$. The comparison between the diffractogram corresponding to the powder mixture of $BaCO_3$ and SiO_2 and the diffractogram of the barium silicate confirms the increase of the crystallized state.

4. Conclusions

The synthesis of barium silicate in polycrystalline state using the GDEG as a thermal source of high efficiency has been achieved. The carbon dioxide releasing process during heating is very important in order to verify to what extent the presence of the gasous phase influences the material transformation quality.

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