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(54) **Folytonos bazaltszálak**

Continuous basalt fibres

DESCRIPTION

[0001] The invention relates to continuous basalt fibres comprising the elements Si, Al, Fe, Mn, Ti, Ca, Mg, K, Na and O, wherein the central Si atom is surrounded by four oxygen atoms and the further elements are likewise surrounded by oxygen atoms with a different coordination or are at least coupled to oxygen atoms and form further structural units, and to a method for producing the basalt fibres in accordance with the invention.

[0002] Basalt fibres are thin fibres formed from basalt and are classified as mineral fibres (MMF - manmade mineral fibres). They are produced from a liquid basalt melt at approximately 1400°C. The fibres have a greenish-brown coloration. The composition of the melt influences the physical properties of the basalt fibres. In contrast to carbon fibres or aramid fibres, basalt fibres are not stretched but are amorphous, like glass fibres. Basalt fibres are used as reinforcing fibres in fibre-plastic composites or as thermal protection materials. The physical properties, and thus the fields of application, are similar to those of glass fibres. However, when in the form of insulating wool, they are thicker than glass fibres and very brittle. However, a clear distinction must be drawn between basalt wool and continuous basalt fibres. Continuous basalt fibres are harmless to health and are primarily employed in composite applications (lightweight constructions in motor vehicles and utility vehicles). However, new technologies have meant that now, very fine fibres with a thickness of less than 0.01 mm can now be produced and processed into textiles.

[0003] The advantages of basalt fibres lie in the larger temperature range for applications (-260°C to +700°C), a

modulus of elasticity which is 20% to 30% higher than with E-glass fibres, and comparable to aramid fibres, a higher thermal and electrical conductivity compared with E-glass, meaning that faster cycle times can be obtained for injection moulding.

[0004] When basalt fibres are used for reinforcement, such as in cement or concrete, they must have a high tensile strength and high chemical resistance in order to be able to compete with alkali-resistant glass fibres, which are known in the art but which are very expensive and complicated to produce, and with aramid fibres or carbon fibres.

[0005] Thus, the object of the present invention is to provide a basalt fibre with improved tensile strength.

[0006] The object of the invention is respectively independently achieved by means of a basalt fibre comprising the elements Si, Al, Fe, Mn, Ti, Ca, Mg, K, Na and O, wherein the central Si atom is surrounded by four oxygen atoms and the further elements are likewise surrounded by oxygen atoms with a different coordination or are at least coupled to oxygen atoms and form further structural units, wherein pre-orientated or orientated molecular structures, in particular domains, are present in an otherwise amorphous X-ray structure, and by means of a method for producing the basalt fibres in accordance with the invention, wherein the raw material comprising 30% to 70% of basalt and/or diabase, 8% to 40% of quartz components, in particular quartz sand, and 5% to 30% of slag, in particular blast furnace slag, is ground into particles, moulds, also named shaped articles, are formed from the particles, which shaped articles pass through a temperature range before melting in which the components of the raw material react with one another and form new mineral phases and molecular

structures and are melted in a melting tank, the melt is fed through a feeder channel via a flow feeder to the die holder or bushing and continuous basalt fibres are drawn, sizing takes place where necessary and they are optionally and subsequently fed to the winder. Advantageously, this means that a high tensile strength can be obtained. By means of the pre-orientated or orientated molecular structures, in particular domains, the mechanical strength of the basalt fibres is substantially higher than that of the starting basalt. The continuous basalt fibres in accordance with the invention are furthermore distinguished by optimized chemical-thermal properties, especially high temperature stability, high tear strength, high chemical resistance, especially in the alkaline pH range, very good insulating and strain properties and good recyclability.

[0007] Preferably, the structural units form a short-range order, wherein the atomic and molecular spacings and angles between the positively charged central atom and the surrounding negatively charged oxygen atoms are irregular and the pre-orientated or orientated molecular structures, in particular domains, form a non-crystalline long-range order, whereupon a higher tensile strength, in particular higher than that of E-glass, can be obtained.

[0008] The pre-orientated or orientated molecular structures, in particular domains, may have a long-range order of chain and/or band molecules, also named ribbon molecules, similar to a pyroxene structure, which again explains the high tensile strength. In addition, the basalt fibres in accordance with the invention are resistant to UV light, non-toxic and are completely chemically inert in behaviour.

[0009] Advantageously, the proportion of chain molecules similar to the pyroxene structure is selected from a range with a lower limit of 20% and an upper limit of 80%, whereupon improved values for the tensile strength are obtained, and thus the application possibilities for the basalt fibre in accordance with the invention are broadened.

[0010] The modulus of elasticity of the basalt fibres has a value with a lower limit of 60000 MPa and an upper limit of 150000 MPa, whereupon a high stiffness is obtained and in particular, the suitability of the basalt fibres for reinforcement purposes is improved.

[0011] Preferably, the tensile strength of the basalt fibres has a value with a lower limit of 1500 MPa and an upper limit of 8000 MPa, whereupon the mechanical load on the basalt fibres can be very high without tearing.

[0012] The value for the density is in a range with a lower limit of 2.0 g/cm^3 and an upper limit of 3.0 g/cm^3, in particular 2.3 g/cm^3, whereupon advantageously, a slight increase in the density can substantially increase the tensile strength and the stiffness.

[0013] In one variational embodiment, the shaped articles are melted in a melting tank, the melt is fed through a feeder channel via a flow feeder which in particular projects into the melt to the bushing and the continuous basalt fibres are drawn and they are subsequently fed to the winder; by this means, a production method which is already extant can be used for the production of the basalt fibres in accordance with the invention, and thus the costs for evaluating a completely novel production method can be saved. Only the parameters of the method need to be adjusted.

[0014] The shaped articles pass through a temperature range from room temperature to 1200°C prior to melting, whereupon on the one hand, better physical properties such as higher abrasion resistance and less spalling can be obtained and on the other hand, there is no further need for the provision of space for storage while drying. Furthermore, the basalt and/or diabase, quartz components, in particular quartz sand and the slag, in particular blast furnace slag, can react together and form new mineral phases and molecular structures. The new mineral phases which are formed in this manner melt completely in the melting furnace, whereupon molecular structures which are already present are retained or are formed afresh upon cooling. In this manner, the material is reminiscent of its original state.

[0015] For a better understanding, the invention will now be explained in more detail with the aid of the accompanying drawings.

[0016] In the figures, which are all highly simplified and diagrammatic in nature:

Fig. 1 shows an X-ray diffraction diagram of a basalt fibre in accordance with the invention;

Fig. 2 shows an X-ray diffraction diagram of the basalt fibre in accordance with the invention at different temperatures;

Fig. 3 shows an X-ray diffraction diagram of a mineral fibre (glass fibre) from the prior art at different temperatures.

[0017] Firstly, it should be noted that in the various embodiments which are being described, identical parts are provided with identical references, whereupon the

disclosures in the description as a whole are applicable analogously to identical parts with the references. Similarly, the positional details provided in the description, for example top, bottom, side etc. refer to the embodiment being described at that instant and should be transferred analogously to the new position when the original position is changed. Furthermore, individual features or combinations of features from the various exemplary embodiments which are described and illustrated may also represent independent or inventive solutions or solutions in accordance with the invention.

[0018] All of the details in the present description regarding ranges should be understood to mean that they encompass any and all part-ranges; as an example, the statement "1 to 10" should be understood to mean that all part-ranges are included, starting from the lower limit of 1 to the upper limit of 10, i.e. all part-ranges beginning with a lower limit of 1 or higher and ending with an upper limit of 10 or lower, for example 1 to 1.7 or 3.2 to 8.1 or 5.5 to 10.

[0019] The basalt fibres in accordance with the invention, which contain the elements Si, Al, Fe, Mn, Ti, Ca, Mg, K, Na and O and optionally B, P, S, Cr, Zr and Li, form structural units and comprise orientated or pre-orientated molecular structures, in particular domains, in an otherwise X-ray amorphous structure. The orientated or pre-orientated domains are in the form of chain and/or ribbon molecules similar to a pyroxene structure, such as ortho- and clinopyroxenes. The clinopyroxenes are primarily present as augite and diopside.

[0020] The structural units form a short-range order, wherein the atomic and molecular spacings and angles

between the positively charged central atom and the surrounding negatively charged oxygen atoms are irregular and the orientated or pre-orientated (part-crystalline) molecular structures, in particular domains, form a non-crystalline long-range order.

[0021] The short-range order of the melt is built up from structural units which also characterize the configuration of the corresponding amorphous phases. The basic constructional unit for the melt for the production of basalt fibres is the $[SiO_4]^{4-}$ tetrahedron. The oxygen which binds two neighbouring $[SiO_4]^{4-}$ tetrahedra is described as the bridging oxygen or bridge-forming oxygen. By depositing alkali and alkaline-earth oxides which function as lattice-modifying oxides (Na_2O, K_2O, Li_2O etc.) and intermediate oxides (such as bivalent metals or metal oxides such as CaO, MgO, BaO, FeO etc.), the lattice is depolymerized. An opposite effect is caused by the additional presence of aluminium in the lattice. The $[SiO_4]^{4-}$ tetrahedron is an almost rigid unit irrespective of the degree of polymerization. The modifications to the structure are determined by the Si-O-Si bonding angle (bridging angle) as well as the Si-O bond lengths (bridging oxygen).

[0022] The basalt fibres in accordance with the invention are characterized by a tensile strength which is 30% to 40% higher compared with prior art basalt fibres. This is accomplished because of the presence of or the fresh formation of pre-orientated molecular structures, in particular with a chain or ribbon structure. The higher tensile strength is obtained by means of the non-crystalline long-range order of the molecules.

[0023] The basalt fibres primarily consist of distorted $[SiO_4]^{4-}$ tetrahedra. By means of heat treatment, chains

and/or ribbon molecules are formed which resemble a pyroxene structure. Controlled seed and crystal growth cycles and also partial crystallinity can be obtained by exploiting the temperature- and time-dependent homogeneous and heterogeneous seed and crystal formation mechanisms.

[0024] A possible variation of the production of the basalt fibres in accordance with the invention comprises pre-treating the raw material before it reaches the melting furnace. The raw material, in particular rock, is ground during the pre-treatment then formed into shaped articles and finally, the shaped articles undergo a heat treatment which is carried out in a range from room temperature to 1200°C, whereupon in this step of the method, structures are pre-formed in a pre-reaction which are precursors for the pre-orientated or orientated (part-crystalline) molecular structures, in particular domains. By being compacted into shaped articles, the individual particles are brought so close together that they can react more quickly compared with loosely packed particles which have voids between them. In addition, a pre-reaction occurs in the melting furnace prior to complete melting of the starting materials, resulting in higher strengths than with the usual glass and basalt fibre materials.

[0025] The chain and/or band molecular structure is already present in the melt at approximately 1500°C and during the course of the cooling procedure, it builds up further from the melt along the melt flow path. The melt flow path comprises the following steps:

a) partial melting during the charging, pre-heating and melting procedure;

b) complete melting in the melting furnace at approximately 1500°C or higher;

c) melt flows in the feeder channel → below 1500°, or lower than in the melting tank;

d) further cooling occurs in the flow feeder in order to accommodate the limits of the demands on the platinum or platinum alloy;

e) further cooling occurs in the bushing or the die holder to approximately 1250-1350°C;

f) during the fibre drawing process and optional sizing, cooling occurs from 1250-1350°C to temperatures below 100°C.

[0026] Heat treating the basalt fibres in accordance with the invention causes the fresh formation of mineral with crystallinity and partial crystallinity. In particular, clinopyroxenes and orthopyroxenes are formed afresh or its peaks are strengthened in an X-ray diffractometric analysis. This brings about an increase in the crystallinity. In addition, plagioclase is also generated.

[0027] An X-ray diffraction diagram of a basalt fibre in accordance with the invention is shown in Figure 1. The measurement parameters for generating the X-ray diffractogram are as follows: radiation source: Cu K alpha, at a temperature of 25°C, at an angle 2-theta of 5°. The peaks with a square indicate anorthite, $Ca(Al_2Si_2O_8)$, triclinic - a 8.18400 - b 12.89000 - c 14.21400 - □ 93.220 - □ 115.9 □ 91.13; the peaks with a diamond indicate clinopyroxene, $Ca_{0.970}Co_{0.030}(Mg_{0.831}Co_{0.169})(Si_2O_6)$, monoclinic - a 9.7527 - b 8.9261 - c 5.2486 - □ 90 - □ 105.856 - □ 90; and the

peaks with a circle indicate orthopyroxene, $Mg_{1.12}Fe_{0.88}Si_2O_6$, orthorhombic - a 18.224 - b 8.775 - c 5.179 - □ 90 - □ 90 - □ 90.

[0028] Figure 2 shows an X-ray diffraction diagram for the fibres in accordance with the invention, wherein the curves show, from bottom to top, an analysis of the continuous basalt fibres for a heat treatment at 800°C, 900°C and 1000°C. Time and temperature-dependent reinforced regular tetrahedra, complex silicates and regular mineral structures, in particular pyroxenes, are formed from the SiO_4 tetrahedra distorted at the beginning in the pre-orientation phase, whereupon the crystallinity in the fibres also increases.

[0029] In comparative fibres (glass fibres) from the prior art, the crystallinity increases in the temperature range under investigation much less than in the basalt fibres in accordance with the invention. Figure 3 shows an X-ray diffraction diagram of a mineral fibre (glass fibre) from the prior art at different temperatures, wherein, from bottom to top, firstly the untreated fibre is shown, followed by heat treatments at 800°C, 900°C and 1000°C.

[0030] The intensity of the pre-orientation, i.e. the proportion of the chain molecular structure which resembles the pyroxene structure, is selected from a range with a lower limit of 20% and an upper limit of 80%, preferably 40% to 60%, in particular 45% to 55%, whereupon by means of a longer heat treatment and also a higher temperature, an increased formation of fresh mineral, in particular pyroxene formation, occurs. The diameter of the fibre also plays a role. Thus, thinner fibres have a higher proportion of pyroxene than thicker continuous basalt fibres for the same temperature and duration of treatment.

[0031] The basalt fibres in accordance with the invention have a diameter selected from a range with a lower limit of 5 µm and an upper limit of 40 µm, preferably 7 µm to 25 µm, in particular 9 µm to 16 µm.

[0032] The mixing and grinding charge for the raw material may be based on approximately 50% basalt, approximately 20% blast furnace slag, approximately 30% quartz sand and clay. In alternative variational embodiments, the starting material may also comprise only basalt or only selected additives such as only blast furnace slag, quartz sand or clay. It is also possible to admix other materials into the starting material. Other compositions which also form the basis of the basalt fibres in accordance with the invention are disclosed in the Applicant's patent application WO 2012/083334 A2 entitled "Raw material for producing basalt fibres" dated 28/06/12. The shaped articles may be produced with the aid of various methods; these are also disclosed in one of the Applicant's patent applications, WO 2012/083335, entitled "Pre-treatment of raw material for producing basalt fibres" dated 28/06/12.

[0033] Prior to melting, the shaped articles are subjected to a range of temperatures from room temperature to 1200°C for a period of 2 to 15 minutes. Preferably, the temperatures are approximately 300°C ± 50°C.

[0034] The method in accordance with the invention comprises the following steps of the method: a) the shaped articles are melted in a melting tank, b) the melt is fed through a feeder channel via a flow feeder to the die holder or bushing, where the basalt fibres are drawn, and optionally c) sizing is carried out, and subsequently d) fed to the winder. The heat treated

shaped articles are introduced into a melting tank where the upper furnace temperature is up to 1750°C and the melting temperature is up to 1600°C. The internal furnace pressure is from 0.5 to 3 mm WC (1 mm WC = 0.09807 mbar). Preferably, 2 burners with a gas/O_2 supply are used for heating. The upper furnace temperature in the feeder channel is up to 1550°C and the melting tank temperature is up to 1500°C, produced by means of 9 burners with gas/O_2 heating. At all times, the temperature in the feeder channel is lower than that in the melting furnace. The flow feeder has a diameter of approximately 15 to 23 mm and is at a temperature of up to 1450°C. An output of 80 kg/h per spinneret is obtained. In the bushing with up to 2000 tips, the temperature is up to 1500°C and again, the output obtained is up to 80 kg/h per spinneret. In this manner, the basalt fibres are substantially cooled. Subsequently, sizing of the continuous basalt fibres may be carried out. The winder may have an output of 0 to 3600 m/min.

[0035] It is also possible to employ methods for the production of the continuous basalt fibres in accordance with the invention with improved tensile strength other than that described.

[0036] The embodiments illustrate possible variational embodiments of the basalt fibres, and it should be pointed out at this juncture that the invention is not restricted to the exemplary embodiments which have been specifically illustrated but rather, various combinations of the individual variational embodiments are possible and this variability lies within the purview of the person skilled in this technical field given the disclosed technical teaching. Thus, it is possible to use any other envisageable variational embodiment which is obtained by combining individual

details of the variational embodiments which have been described and illustrated. Accordingly, all conceivable variational embodiments which can be obtained by combining individual details of the variational embodiments described are possible and fall within the scope of the invention.

[0037] The individual inventive solutions forming the subject matter of the present invention may be discerned from the description.

Folytonos bazaltszálak

Szabadalmi igénypontok

1. Folytonos bazaltszál, amely tartalmaz Si, Al, Fe, Mn, Ti, Ca, Mg, K, Na és O elemeket, amelynél az Si központi atom négy oxigén atommal van körülvéve és a további elemek szintén oxigén atomokkal vannak különböző koordinációban körülvéve vagy legalább kapcsolódnak oxigén atomokhoz és további strukturális egységeket képeznek, **azzal jellemezve, hogy** pre-orientált vagy orientált molekuláris struktúrák, különösen domének, vannak jelen az egyébként röntgen-amorf struktúrában.

2. Az 1. igénypont szerinti folytonos bazaltszál, **azzal jellemezve, hogy** a strukturális egységek rövidtávú rendezettséget képeznek, amelynél a pozitív töltésű központi atom és a körülvevő negatív töltésű oxigén atomok közötti atomi és molekuláris távolságok és szögek szabálytalanok és a pre-orientált vagy orientált molekuláris struktúrák, különösen domének, nem-kristályos hosszú távú rendezettséget képeznek.

3. A 2. igénypont szerinti folytonos bazaltszál, **azzal jellemezve, hogy** a pre-orientált vagy orientált molekuláris struktúrák, különösen domének, piroxén struktúrához hasonló lánc- és/vagy szalagmolekulák hosszú távú rendezettségét tartalmazzák.

4. A 3. igénypont szerinti folytonos bazaltszál, **azzal jellemezve, hogy** a piroxén struktúrához hasonló láncmolekuláknak az aránya a 20 % alsó határú és 80 % felső határú tartományból van kiválasztva.

5. Az 1-4. igénypontok bármelyike szerinti folytonos bazaltszál, **azzal jellemezve, hogy** a bazaltszál E-modulja olyan értékkel rendelkezik, amelynek alsó határa 60000 MPa és felső határa 150000 MPa .

6. Az 1-5. igénypontok bármelyike szerinti folytonos bazaltszál, **azzal jellemezve, hogy** a bazaltszál olyan húzószilárdság-értékkel rendelkezik, amelynek alsó határa 1500 MPa és felső határa 8000 MPa.

7. Az 1-6. igénypontok bármelyike szerinti folytonos bazaltszál, **azzal jellemezve, hogy** a sűrüség értéke olyan, amelynek alsó határa 2,0 g/cm^3 és felső határa 3,0 g/cm^3.

8. Eljárás az 1-7. igénypontok bármelyike szerinti folytonos bazaltszál előállítására, **azzal jellemezve, hogy** 30 % - 70 % bazaltot és/vagy diabázt, 8 % - 40 % mennyiségben kvarckomponenseket, különösen kvarchomokot és 5 % - 30 % salakot, különösen kohósalakot, tartalmazó nyersanyagot részecskékké őrölünk, a részecskékből formatesteket állítunk elő, a formatesteket már a megolvasztás előtt átvezetjük olyan hőmérséklettartományon, amelynél a nyersanyag komponensei egymással reakcióba lépnek és új ásványfázisokat és molekuláris struktúrákat képeznek, és olvasztó kádban megolvasztjuk, az olvadékot bevezető csatornán keresztül folyadék adagolón át fúvóka tartóhoz vagy perselyhez vezetjük és folytonos bazaltszálat húzunk, adott esetben méretre vágjuk és a továbbiakban adott esetben feltekercselőhöz vezetjük.

9. A 8. igénypont szerinti eljárás, **azzal jellemezve, hogy** a formatesteket a megolvasztás előtt átvezetjük szobahőmérséklet - 1200°C hőmérséklettartományon.

Fig.1

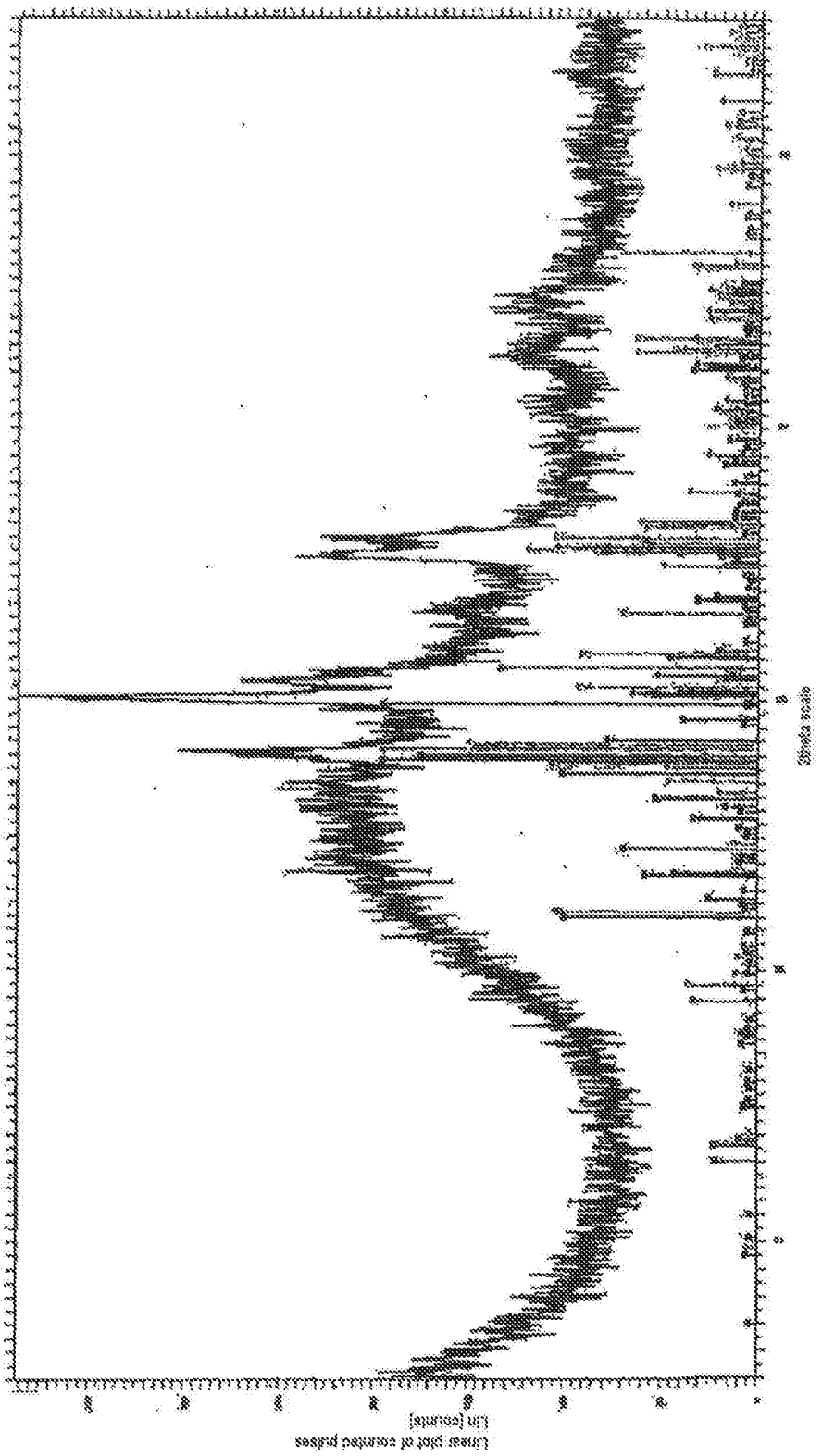

Fig.2

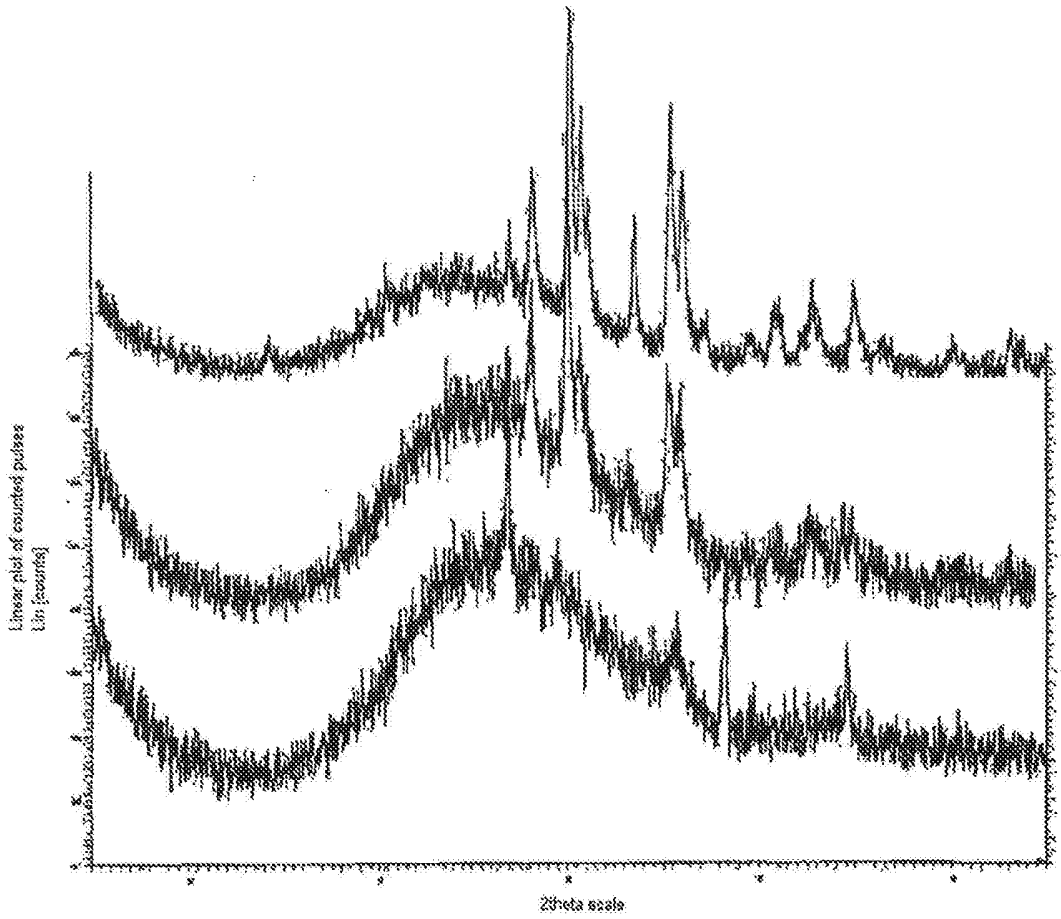

Fig.3