Title: LAYERED NON OXIDE CERAMIC MODULE AS THERMOELECTRIC ENERGY SOURCE

Abstract: The invention relates to a layered non oxide ceramic module as thermoelectric energy source. The module built with the body manufactured of a material stable to thermal shocks and corrosion action. The said body comprising at least two adjustment-free resistors. The said resistors made of a mixture of powder metal-like components and a dielectric, have one or several layers with step change of composition inside their bodies and contain a thermoelectric junction between them. The said resistors formed as ceramic bundle conductor embedded in the reservoir hole of the insulating body and supplied with stable to oxidation high-conductive ceramic contacts pick-up co-synthesized with the ceramic material of the body into a ceramic monoblock which is characterized by existence of at least two contact pick-ups, of two intermediate areas for connection the contact pick-ups with the body of ceramic bundle conductor and of the contact junction between them.
"LAYERED NON OXIDE CERAMIC MODULE AS THERMOELECTRIC ENERGY SOURCE"

FIELD OF THE INVENTION
The presented invention relates to a layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device as renewable energy source intended for working at mean and high temperatures, whose readings do not vary in respect of an aggressive medium, duration of performance and the number of temperature cycles; whose body is an insulating ceramic matrix with perfect resistance both to action of an aggressive medium and to thermal shocks, and which may be exploited as an integral part of renewable energy source systems in chemical industry, automobile, aircraft and space engineering, in domestic applications.

BACKGROUND OF INVENTION
Thermoelectric energy generation should possess:
- Stability of time and temperature characteristics;
- Reproducibility of the thermoelectric characteristic;
- Sensitivity that is determined by the ratio of a thermoelectric voltage increment to the corresponding temperature increment;
- Linear dependence of thermoelectric voltage on temperature;
- Resistance to temperature action and to a temperature shock;
- Mechanical strength and resistance to an aggressive medium action;
- Simple procedure of their manufacturing, which provides production of workplaces with the same properties.

Operational principle of thermoelectric devices is founded on the thermoelectric effect. The essence of the phenomenon consists in the fact that in the junction of two conductors from dissimilar materials an electromotive force arises referred to hereinafter as the thermoelectric voltage.
In a closed circuit consisting of two or several dissimilar conductors an electric current flows if at least two junctions of these conductors have different temperatures.

If the simplest circuit is joined from two dissimilar conductors (electrodes) A and B (Fig.2) so that these conductors are connected by their ends and in so doing one of the end has a higher temperature \( t \) and the other a lower one \( t_0 \), and if the number of free current carriers in material is greater than that in material B, then in the junction at temperature \( t \) free carriers will pass (diffuse) into electrode B in a greater amount than in the opposite direction. In consequence, electrode A will charge positively, and electrode B will do negatively, i.e. a difference of potentials \( e \) will arise in the junction at a temperature \( t \). The thermoelectric voltage depends both on temperature \( t \) and on electrode materials.

The thermoelectric voltage of a thermoelectric devices as renewable energy source does not change with providing of a third lead into its disconnected end if temperature of the ends of that one is the same and equal to \( t_0 \). The third lead besides joining into the solder junction may be joined up into the thermocouple (Fig.3). To hold the main equation for thermoelectric voltage

\[
E_{AB} = e_{AB}(t) - e_{AB}(t_0)
\]

in case the third lead is joined, it is necessary that temperature injunctions 3 and 4 be the same (it can change but it must change similarly for the two junctions).

The following conclusions can be made from said above:

- Thermoelectric voltage of a thermoelectric devices as renewable energy source does not change from providing into its circuit a third lead if temperatures of the lead ends are the same.
- The method of the sensing solder preparation does not effect the value of thermoelectric voltage because usually the dimensions of the solder are such that temperature is the same in all its points.
- Any number of conductors whose solders are kept at the same temperature may by joined up into the thermocouple circuits.
Metal wires of high conduction are commonly utilized as thermocouple electrodes in combination with high-resistance wires or dissimilar wires of high resistance: copper-constantan, temperatures from -200°C to +300°C, chromel-alumel, up to 1000°C, tungsten-molibdenum, tungsten-(tungsten+rhenium), vacuum, inert medium up to 2400°C, platinum-(platinum+rhodium), an oxidizing medium, up to 1800°C, iridium-rhodium, vacuum or a weak oxidizing medium, up to 2100°C.

The slightest incidental admixtures at melting, variation of component percentage in an alloy wrong temperature treatment result in significant discrepancy of the thermoelectric voltage. Working time of thermoelectric devices as renewable energy source varies from 2000 hours to 20000 hours. One reason of thermoelectric devices as renewable energy source thermoelectric instability is physicochemical interaction of the thermocouple material with environment, whereby the surface of the electrodes is being oxidized and depleted with alloying elements and admixtures. Another reasons of instability are structural changes in the thermoelectrodes under influence of ambient temperature.

To prolong thermoelectric devices as renewable energy source -working time and to protect the alloy from contact with an aggressive medium, every possible sheaths and cases from insulating or semiconductor materials with high thermo- and corrosion resistance are utilized. Interaction of the thermoelectrode materials with the sheath or environment cannot be eliminated at high temperatures.

DESCRIPTION OF THE PRIOR ART
According to the state of the art the US5696348 patent description makes known a thermocouple structure capable of measurement of a high temperature with a high accuracy is constituted of a protective pipe made of a heat-resistant ceramic; a pair of wires differing in kind and extending in the protective pipe from one end thereof to the other end thereof in the longitudinal direction thereof in a state of being spaced away from each other; a thin film constituting a temperature-sensing portion, made of a
tungsten alloy, disposed on one end portion of said protective pipe, and connected to the wires; and a covering layer made of a heat-resistant ceramic and covering the thin film in such a way as to disallow exterior exposure of the thin film. The protective pipe is made of Si3N4, and a filling member made of a powder mixture of Si3N4 and TiN is filled in the protective pipe. Alternatively, a pair of printed strips differing in kind may be formed as wires in a protective pipe to provide such a thermocouple structure.

The US5092938 patent description makes known a temperature detector for use in a high temperature and high pressure furnace, including thermocouple wires received in a tubular protective sheath for protection against the furnace atmosphere, and characterized by the provision of a pair of rod members of a large diameter serving as a thermocouple pair for the positive and negative sides thereof, a protective sheath having a rod suspending holder portion in an upper portion thereof for supporting the thermocouple rod members therein in a vertically suspended state and arranged to hold the rod members out of contact with each other except at a temperature measuring point and to contact the rod members with the protective sheath only in a region other than a high temperature region of the furnace.

The US4460802 patent description makes known radially activated thermocouple assembly. The lower end of a hollow thermocouple well is removed and replaced by an end cap of a different thermocouple material than the well so that the junction between the end cap and the end portion of the well defines a radially activated thermocouple junction. A wire of the same material as the end cap is affixed to the end cap and electrical connections are made to the wire and to the well to provide a thermocouple output signal indicative of temperature measurement. In another embodiment two end caps are utilized at the end of the thermocouple well with the two end caps being of two dissimilar thermocouple elements and which have the necessary electrical connections made thereof to provide a thermocouple output signal.

The DEI02007063168 patent description makes known thermoelectric module for thermoelectric generator to produce electrical energy, has insulating layer sections that
are separated from one another, where insulating layer electrically insulates electric
guide elements from heat source. The module has electric guide elements arranged in
different positions, respectively, where the position is at a distance from the position. A
set of thermoelectric elements is arranged between the positions, and an insulating layer
electrically insulates the electric guide elements relative to a heat source formed by a
waste gas system of a combustion engine or the electric guide elements relative to a heat
sink. The insulating layer comprises insulating layer sections that are separated from
one another. The insulating layer sections of the insulating layer are composed of a
ceramic material, alumina, or aluminum nitride.

The DEI 02012216043 patent description makes known device e.g. thermo-electric
generator for converting thermal energy of combustion engine into electrical energy, has
frame structure that is arranged between heating channel and cooling channel, so that
enclosure for module is formed. The device has a thermoelectric module that is
provided with an opening that is intended for contact with a heat source planned warm
side and a heat sink planned cold side. A heating channel for flow of hot fluid is
provided in thermal conductive connection with the warm side of the module. A cooling
channel for flow of cooling fluid is provided in heat-conducting connection with the
cold side of the module. A ceramic material frame structure is arranged between the
heating channel and the cooling channel, so that the enclosure for the module is formed.

The WO2015057399 patent description makes known heat exchanger for thermoelectric
power generation with the thermoelectric modules in direct contact with the heat source.
A thermoelectric power generator applied for converting thermal energy into electrical
energy. The thermoelectric power generator includes a heat exchanger configured to
extract thermal energy from an exhaust gas stream. The heat exchanger includes fins in
contact with a boundary of the heat exchanger, where the fins are directly connected to a
first set of thermoelectric modules. A second set of thermoelectric modules are directly
connected to the boundary of the heat exchanger. The first and second sets of
thermoelectric modules are configured to convert the thermal energy to electrical
energy. By eliminating the metal wall that previously existed between the
thermoelectric modules and the fins, the thermoelectric power generator improves the heat transfer between the exhaust gas and the thermoelectric modules, eliminates the thermal fatigue failures at the bond between the metal wall and the thermoelectric modules as well as allows for a higher density of thermoelectric modules.

Nahmok Co. (USA) produces a thermocouple wherein thermoelectrodes from noble metals are flattened out to the thickness of 25 μm and insulated one from the other and from the sheath with mica lamellas of 5 μm thickness. Insulated electrodes are placed between the two halves of a splitted lamina and tightly inserted into the sheath. The hot solder is formed by grinding and polishing of the face part of the sensitive element (Missile-Design and Development, 1960, Ul, V.6).

Thus, to measure high temperatures, thermoelectric devices as renewable energy source made of expensive noble metals or refractory ones are employed. At high temperature changes in physical state of each metal occurs that induces considerable variations of the thermoelectric voltage. This value also changes due to intensive transfer of the substance in the high temperature solder zone. All thermocouples on the basis of refractory metals can be used only in inert gaseous media and in vacuum. To enable said thermocouples to operate in different media, gaslight protective sheaths should be worked out from materials possessing both insulating properties at operating temperatures and high resistance to thermal shocks.

The most proximate to the present invention is US Patent US 5,696,348 (Dec. 9, 1997) thermocouple structure, according to which two dissimilar metal wires insulated one from the other by a thin insulating film are situated inside a ceramic tube resistant to high temperature action. The wires are finished with a soldered contact at one side and with a connection to a controlling instrument at the other side. The authors of this patent suggest, as an alternative, to employ as thermoelectrodes a covering from two dissimilar film, applied by a printing (temple) technique to the surface of this ceramic tube stable to high temperature action.
THE AIM OF THE INVENTION

The primary aim of the present invention is to create a monoblock ceramic thermoelectric device as renewable energy source with resistance to a thermal shock, with a high value of the thermoelectric voltage, which is able to operate in aggressive media and at high temperatures, which does not contain noble or refractory metals, whose body is made of an insulating material with required characteristics of conductivity.

The associated aim of the presented invention is to create a thermoelectric device as renewable energy source wherein electrodes will be «ceramic bundle conductors» made in the form of adjustment-free ceramic resistors from mixture of metal-like ingredients and a dielectric, wherein the junction between to different materials (positive and negative electrodes) that works at a high temperature will be removed as far as possible from the same junction working at a lower temperature, and wherein a third conductors (for connection of a measuring instrument) will be joined at points 3 and 4 (Fig. 3), wherein the said points have the same temperature and the structure of the said point was formed by step change in composition of «ceramic bundle conductors» inside the ceramic insulating matrix (basic body).

RECOGNITION

When working out the solution according to the invention it was recognized, according to the primary aspect of the invention, creation of an insulating ceramic basic body of a thermoelectric device wherein the said body is set-up from layers of green ceramic sheets, wherein specially prepared recesses (the resistors reservoir hole of the insulating body) exist in the said sheets for placing of thermoelectrodes and formation of a junction between positive and negative thermoelectrodes and attaching of contact pickups at the ends of the said thermoelectrodes to connect a multipoint joint is provided.

To prepare the ceramic sheets, non-metal refractory nitrides in combination with oxide additives selected from refractory oxides are utilized, whereby a monoblock ceramic
product with exclusively high resistance to thermoshocks, to aggressive medium action and with a required level of electric conductivity is being fabricated in the course of synthesis.

According to the associated aspect of the invention, creation of a thermoelectric instrument which includes a ceramic multilayer-body with recesses (the resistors reservoir hole) in the said basic body, with specially prepared ceramic thermoelectrodes and contact pick-ups embedded in the said recesses to join an electrical measuring instrument, with the said thermoelectrodes and contact pick-ups fabricated as adjustment-free resistors from a mixture of powder ingredients of the insulating body material and additives of metal-like component of the selected group is provided.

To provide equality of temperatures in the contact areas serving connection and to form round them a zone with a temperature as low as possible, step change of the thermoelectrodes inside the basic body is employed, and the electrodes themselves are manufactured as «ceramic bundle conductors» that are placed inside the said ceramic body in several layers. To provide high conduction of the contact pick-ups in combination with their corrosion resistance, ceramic resistors containing in addition additives of tantalum nitride and of boron silicide are utilized.

STATEMENT
The invention is a layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, wherein a thermoelectric device as renewable energy source with the body manufactured of a material stable to thermal shocks and corrosion action, with the said body manufactured from a corrosion resistant material with the required characteristics of electric conduction with the said body comprising at least two adjustment-free resistors, with the said resistors made of a mixture of powder metal-like components and a dielectric, with the said resistors that have one or several layers with step change of the composition inside their bodies and contain a thermoelectric junction between them, with the said junction at heating of which a thermovoltage is being generated and the other ends of the said resistors electrical voltage appears with the
value proportional to the temperature of the contact junction; the said adjustment-free resistors, formed as ceramic bundle conductor embedded in the resistors reservoir hole of the insulating body and supplied with stable to oxidation high-conductive ceramic contacts pick-up co-synthesized, over the whole surface together, with the ceramic material of the body into a ceramic monoblock which is characterized by existence of at least two contact pick-ups, of two intermediate areas for connection of the contact pick-ups with the body of ceramic bundle conductor - thermoelectrodes and of the contact junction between these thermoelectrode.

In a preferred embodiment of the solution according to the invention ceramic adjustment-free resistors, ceramic contacts, ceramic junction and the insulating body contain one and the same ceramic insulating matrix from the selected materials and providing required characteristics of electric conduction.

In another preferred embodiment of the solution according to the invention the ceramic matrix of insulating materials makes from 0.5% to 98.5 vol. % of its body.

In a further preferred embodiment of the solution according to the invention the ceramic resistive leads of the thermoelectrode, of ceramic conductive junctions and of ceramic conductive contact pick-ups make all together from 0.5 to 98.5 vol.% of the ceramic material of the basic body.

In a further preferred embodiment of the solution according to the invention the main body and resistive ceramic materials contain the mixture of $Si_3N_4:Al_2O_3:Si_2ON_2:La_2O_3$ in the volume ratio of: from 30:1:1:1 to 23:3:5:2.

In a further preferred embodiment of the solution according to the invention the main body and resistive ceramic materials contain the mixture of $Si3N4:AlN:Al2O3:Si20N2$ in the volume ratio of: from 1:2:14:4 to 2:1:1:6.
In a further preferred embodiment of the solution according to the invention the main body and resistive ceramic materials contain the mixture of BN:MgO:SiC:B₄C:B₄Si:C in the volume ratio of: from 2:1:2:2:3:1:1 to 8:2:2:3:1:4.

In a further preferred embodiment of the solution according to the invention the sum of the oxide additives \( Al_2O_3 - SiON2 - La_2O_3 \) makes from 3% to 50% of its body volume.

In a further preferred embodiment of the solution according to the invention the sum of the oxide additives \( Al_2O_3 - \frac{3}{4}N \) \_2 makes from 30 to 70 vol. % of its body, and the ratio of \( SiN4 - AlN \) takes values from 1:1 to 3:1.

In a further preferred embodiment of the solution according to the invention the sum of the additives \( SiC - B4C - B4S1 \) \_C makes from 0.5 to 45% of the volume of basic body and ratio of \( BN: MgO \) is defined in the limits from 10:1 to 4:1.

In a further preferred embodiment of the solution according to the invention the ceramic bundle conductor of the positive thermoelectrode and the corresponding portion the contact and the ceramic junction contain current conducting powder inclusions of boron carbide or lanthanum hexaboride or carbides hafnium, niobium, zirconium, tungsten or nitrides of tantalum, vanadium, zirconium, hafnium in volume content from 2.5 to 97.5%, the said inclusions determine the value of electric resistance of the said part and the value of thermoelectric voltage with the «+» sign.

In a further preferred embodiment of the solution according to the invention the resistive lead of the active zone and the corresponding portion of the contact have the value of thermoelectric voltage of one junction from 0.2 to 200 \( \mu V/\text{grad} \) and quantity of junction from 1 till 5000.

In a further preferred embodiment of the solution according to the invention the ceramic bundle conductor of the negative thermoelectrode and the corresponding part of the
contact and the ceramic junctions contain current conducting inclusions of carbon, carbides of silicon, hafnium, niobium, zirconium, tungsten or nitrides of tantalum, vanadium, zirconium, hafnium from 2,5 at 97,5% by volume that determines the value of their electric resistance and the value of thermoelectric voltage with the «» sign.

In a further preferred embodiment of the solution according to the invention the ceramic bundle conductor of the negative thermoelectrode and the corresponding portion of the contact and the ceramic junctions have the value of thermoelectric voltage from «» 0.2 to 85 μV/grad.

In a further preferred embodiment of the solution according to the invention the ceramic bundle conductor of contact pick-ups contain current conduction powder inclusions of the mixture $SiC - B_4 Si - TaN$ in the ratio 2:1:10 in value content from 15 to 99,5%, determining the value of electric resistance and stability to oxidation of the said ceramic bundle conductors.

In a further preferred embodiment of the solution according to the invention the green ceramic elastic sheets with the thickness from 0,1 to 3,0 mm, mainly from 0,85 to 1,25 mm and relative density from 0,51 to 0,64, mainly from 0,52 to 0,56 are fabricated by methods of pressing, rolling, casting, injection molding and others.

In a further preferred embodiment of the solution according to the invention to making the green ceramic elastic sheets, bulk stuff is prepared by adding to the mixture the powders of the basic body, resistive materials of the thermoelectrodes, of the contact, of the ceramic junctions and of the contact pick-ups of organic binders and softening agents wherein the mass ratio of the elements C:0:H makes from 22:0:3 to 19:1 1:4.

In a further preferred embodiment of the solution according to the invention the total mass content of the binder and softening agent additives to the mixture to produce the basic body, resistive materials of the thermoelectrodes, of the contact, of the ceramic junctions and the contact pick-ups makes from 1,5 to 15 mass.%. 
In a further preferred embodiment of the solution according to the invention profiled parts with the precisely defined dimensions, with the ratio of the said profile to its thickness varies from 2 to 12, are cut out of the green ceramic sheets of ceramic bundle conductors: of the thermoelectrodes, of the contact, of the ceramic junctions and of the contact pick-ups.

In a further preferred embodiment of the solution according to the invention the resistors reservoir hole of the basic body that correspond exactly to the profiles cut out from the ceramic bundle conductors are punched out in precisely defined method from the green sheets of the basic body.

In a further preferred embodiment of the solution according to the invention its basic body (the insulating matrix) is formed from at least two sheets put on each other in such a manner that the resistive ceramic bundle conductors fabricated and placed in to the resistors reservoir hole of the basic body must make an electric circuit and provide formation of a junction in the area of the contact between the resistive conductor of the positive thermoelectrode and the resistive conductor of the negative electrode and the said body synthesized together with the adjacent conductors presents a monoblock ceramic device.

In a further preferred embodiment of the solution according to the invention the contact pick-ups are placed on one side of the basic body, on one face (cartridge A), on one side of the basic body on different faces (cartridge B) or on different sides of the basic body on one face (tube A) or on different faces (tube B).

In a further preferred embodiment of the solution according to the invention each of the said devices has its contact pick-ups and each of the said devices can act either as an independent on or as a constituent element of a complex device.
In a further preferred embodiment of the solution according to the invention the ceramic resistive bundle conductors have a lot of contact pick-ups, which of the said conductors is placed in the bulk of the basic body (of the insulating matrix) in its recesses, produced in the layers of the green ceramic sheets of the insulating matrix in the precisely defined sites.

In a further preferred embodiment of the solution according to the invention the contact pick-ups are manufactured from a ceramic resistive bundle conductors by means of their punching out of the green ceramic sheets to obtain details of precisely defined dimensions, which are set in a green state in the recesses (holes) of the insulating matrix of the body and sintered in such a way that they create in combination with the ceramic resistive bundle conductors and in combination the insulating matrix a single whole.

In a further preferred embodiment of the solution according to the invention the contact pick-ups of the ceramic resistive bundle conductors contain a metallic covering.

In a further preferred embodiment of the solution according to the invention metal contact wires are joined to the contact pick-ups of a ceramic resistive bundle conductors by means of mechanical clamping, soldering or welding.

In a further preferred embodiment of the solution according to the invention conducting powder inclusions, which are added to the material of the insulating matrix (basic body) to obtain required sign of the thermoelectric voltage and the defined value of electric resistance of the resistive ceramic bundle conductors of the thermoelectrodes of the contact, of the ceramic junctions and of the contact pick-ups consist of a mixture of coarse (3-15 µm) :middle (1-3µm) : fine (less than 1 µm) particles in the ratio of 5:4:8.

In a preferred application of the solution according to the invention a constituent unit of control-and-measuring systems in food and light industries, in production of metals and alloys, in chemical industry, in automobile, aircraft and space engineering in instrumentation for scientific researches.
BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the three-dimensional projection, explaining mutual disposition of the one from more thermoelectrodes, of the contacts between them and of the contact areas for connection of the device inside the ceramic matrix, manufacturing from layers (green ceramics sheets).

Fig. 2 shows a diagram according to the state of the art illustrating the reasons of thermovoltage arising at the contact of two materials with different amount of free carriers in the case when one contact has a temperature higher than the other.

Fig. 3 shows a diagram according to the invention illustrating the conditions under which a third lead may be joined up into a disjunction of one electrode to connect a measuring instrument.

Fig. 4 shows an application a multilayer non oxide ceramic module as thermoelectric energy source.

DETAILED DESCRIPTION OF THE DRAWINGS

In a preferred embodiment of the solution according the invention, as seen in the Fig. 1-4 in the layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, a thermoelectric device as renewable energy source with the body 7 manufactured of a material stable to thermal shocks and corrosion action, with the said body manufactured from a corrosion resistant material with the required characteristics of electric conduction with the said body comprising at least two adjustment-free resistors 1,2, with the said resistors made of a mixture of powder metal-like components and a dielectric, with the said resistors that have one or several layers with step change of the composition inside their bodies and contain a thermoelectric junction 6 between them, with the said junction at heating of which a thermovoltage is being generated and the other ends E₁, E₂ of the said resistors electrical voltage appears with the value proportional to the temperature of the contact junction 6.
The said adjustment-free resistors, formed as ceramic bundle conductor 1,2 embedded in the resistors reservoir hole of the insulating body 7 and supplied with stable to oxidation high-conductive ceramic contacts pick-up co-synthesized, over the whole surface together, with the ceramic material of the body into a ceramic monoblock which is characterized by existence of at least two contact pick-ups 3,4, of two intermediate areas for connection of the contact pick-ups 5,52 with the body of ceramic bundle conductor - thermoelectrodes 1,2 and of the contact junction between these thermoelectrode 6.

The ceramic adjustment-free resistors 1,2, ceramic contacts 3,4, ceramic junction 6 and the insulating body 7 contain one and the same ceramic insulating matrix from the selected materials and providing required characteristics of electric conduction.

In the monoblock ceramic as renewable energy source being the subject of the present invention such embodiment is suggested when this device consists of several semiconducting components or other ones, each, in its turn, consisting of several components disposed inside the whole ceramic matrix which we will call a thermocouple body. This body is built up of the materials specifying objective conductance characteristics, high thermal shock or environmental resistance.

Base materials of the body are ALONs, SIALONs or BORANes having excellent thermal shock and corrosion resistance.

Improved thermal resistance of as renewable energy source basic body materials is provided due to creation of ceramic matrix which consists of materials having bending strength high values (Si3Ni4, SiC, B4C), reinforced with oxynitride phases with low density and thermal capacity.

Reinforcing phases appear in the process of thermal treatment of green blank due to chemical reactions between insulation matrix components and sintering environment.
Basic body conductance is a critical characteristic. With certain conductance value in a contact layer between thermoelectrode and basic body «junction» generating false signal can develop. Thereby body conductance in the direct electrode contacting area is to be at most than $1 \times 10^{-2}$ l/Ohm*cm in the whole category temperature range. The process of the basic body sintering is to be performed so that ceramic matrix microcrystallines should have the size more than 3 µ and the phase on grain boundary should be in fine-grained state.

Inside the ceramic body described we place thermoelectrodes from two different adjustment-free resistors consisted of the same ceramic matrix as the basic body comprising organic whole with it so that there is no physical boundary between thermoelectrodes and the matrix.

Thermoelectrodes, ceramic junctions and bonding sites differ from the body only in inclusions additionally introduced in their composition as contacting conducting ceramic particles forming «bundle ceramic conductor» which looks like a multicore cable. The number of cores in such «bundle ceramic conductor» is determined by thermoelectrode size, namely its thickness and width-to-thickness ratio. With small thickness possibility of «bundle» development is excluded. Only several solid conductors parallel to each other develop. With big width two «bundles» can appear alongside each interfering in other's work.

To develop positive thermoelectrode additives from the series: carbides of silicon, hafnium, niobium, zirconium, wolfram or nitrides of tantalum, vanadium, zirconium, hafnium are used in the volume content from 2.5 to 98.5% predetermining their electrical resistance value and thermoelectric voltage value.

To develop «negative» thermoelectrode semiconducting additives with low concentration of free and slightly bound carriers which contain «trap levels» and which are able to «catch» a part of free carriers drawn from «positive» thermoelectrode to
these levels. «Negative» thermoelectrode like «positive» one is to be characterized with exactly defined ratio between content of fine, middle and large particles: 3:4:10. To develop negative thermoelectrode additives from the series: boron carbide, silicium carbide or lanthanum diboride or titanium diboride in the volume content from 2.5 to 98.5% predetermining their electrical resistance value and thermoelectric voltage value are used.

Junction between two different materials (positive and negative thermoelectrodes) develop in ceramic body volume so that at least 25% of bonding sites square should fall on «ceramic bundle conductors». The thermoelectric devise as renewable energy source consist from 1 till 5000 thermoelectric junction inside of one ceramic body (Fig.4).

Thermostable area for the third conductor connection (to positive or negative electrode break) which will connect a measuring device with thermoelectrodes develop due to step change of ceramic resistor composition inside ceramic insulation matrix. Through step junction bonding site temperature is stabilized due to heat exchange with the environment.

To provide increased bonding ceramic contact pick-up (3,4) resistance to oxidation for electric signal pickup from heated ceramic junction between positive and negative thermoelectrode, materials TaN:B₄Si in 3:1 ratio are additionally infused in ceramic resistor composition.

To provide safe bonds between the third conductor for the measuring device attachment and thermoelectric device ceramic bonding sites, methods of pressing, soldering or welding by known manners is used. To reduce signal loss in the place of connection of the third conductor on ceramic bonding sites metal coating is additionally applied.

According to the first aspect of the invention creation of ceramic insulation body of thermoelectric device that built up of ceramic type layers, which have specially prepared voids inside for thermoelectrodes distribution, provided. High-strength and
flexible ceramic types are prepared by pressing, rolling, casting, injection molding or other methods.

The profiles accurate in geometric dimensions to hole shapes are carved by exactly defined manner out of ceramic types of resisting materials of thermoelectrodes 1 and 2, ceramic multipoint junctions 51, 52 and contacts. Resisting materials carved profiles are installed in adequate ceramic insulation basic body layer holes so that each ceramic insulation basic body layer should have one or several insertions of some resisting material. In exceptional cases as an assembling base ceramic insulation body layer which do not contain holes with insertions out of resisting materials can be used.

Ceramic insulation body layers with profiles of ceramic resisting materials inserted into their holes are assembled by overlay method in conformity with thermoelectric converter scheme. Overlaid layers under slight pressure (several Newton) are saturated with moisture to provide homogeneity in layer bonds.

Thermoelectric device can be constructed in way the third conductor attachment points to the measuring device can be located:

- From one side (at the left or on the right) of the basic body in one plain (top or bottom);
- From one side (at the left or on the right) of the basic body in different plains (top and bottom);
- From different sides (on the left and on the right) of the basic body in one plain (top or bottom);
- From different sides (on the left and on the right) of the basic body in different plains (top and bottom).

The invention allow for the creation of several thermoelectric converters each built up owing to its principal wiring circuit. As thermoelectrode ceramic resistors have certain resistance value while connecting them to external circuit with current passage in ceramic uncontrolled resistors heat will be evolved in proportion to dissipation (Joule-
Lenz effect). Thus, the invention allows for possibility of combined thermoelectric device creation. Such device will consist of ceramic insulation basic body with adjustment-free ceramic resistors generating heat while connecting them to external electric circuit in its one part and with thermoelectric converter, hot «junction» of which will be located close to thermal generation zone and bonding site voltage will be in proportion to thermal generation zone temperature in another part adjacent to the first one and comprising the organic whole.

Green assemblies composed of overlaid ceramic layers are subject to thermal treatment (sintering) so that as a result of sintering monoblock (one-piece) ceramic article consisted of ceramic insulation basic body with ceramic «bundle conductors » of thermoelectrodes and ceramic junctions inside and minimum two ceramic contact pick-ups for conductor attachment to external electric circuit on the basic body surface should be obtained.

EXAMPLE
Green «ceramic bundle conductors») of thermoelectrodes, ceramic junctions and ceramic contact pick-ups were tightly installed into adequate holes in green sheet of ceramic basic body. Ceramic body layers with installed «ceramic bundle conductors » were overlaid one on another in sandwich-like manner in order to develop junction between thermoelectrodes (Fig.1) and ceramic junctions should connect thermoelectrodes with ceramic contact pick-ups for the third conductor connection and provide temperature equality in the area of these ceramic contact pick-ups. Sandwich body was subject to slight pressure and then thermally treated according to sintering, pressure sintering, hot pressing or hot isostatic pressing method until monoblock ceramic thermoelectric device was obtained.

The third conductor was connected by vacuum soldering, mechanical pressing or other method to ceramic bonding sites through metallized layer or directly. Potential measurement device was connected to this conductor.
Additional stabilization of thermoelectric voltage changes coefficient if Si$_2$ON$_2$ develop through heterophase reactions when sintering all-ceramic thermocouple with the assistance of moisture which additionally saturate sandwich-like assembly. Minimum moisture amount inserted into assembly should be 2, maximum 25 wt.%.
CLAIMS:

1. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, wherein

a thermoelectric device as renewable energy source with the body (7) manufactured of a material stable to thermal shocks and corrosion action, with the said body manufactured from a corrosion resistant material with the required characteristics of electric conduction with the said body comprising at least two adjustment-free resistors (1,2), with the said resistors made of a mixture of powder metal-like components and a dielectric, with the said resistors that have one or several layers with step change of the composition inside their bodies and contain a thermoelectric junction (6) between them, with the said junction at heating of which a thermovoltage is being generated and the other ends (E₁, E₂) of the said resistors electrical voltage appears with the value proportional to the temperature of the contact junction (6); the said adjustment-free resistors, formed as ceramic bundle conductor (1,2) embedded in the resistors reservoir hole of the insulating body (7) and supplied with stable to oxidation high-conductive ceramic contacts pick-up co-synthesized, over the whole surface together, with the ceramic material of the body into a ceramic monoblock which is characterized by existence of at least two contact pick-ups (3,4), of two intermediate areas for connection of the contact pick-ups (5₁,5₂) with the body of ceramic bundle conductor - thermoelectrodes (1,2) and of the contact junction between these thermoelectrode (6).

2. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claim 1, wherein ceramic adjustment-free resistors (1,2), ceramic contacts (3,4), ceramic junction (6) and the insulating body (7) contain one and the same ceramic insulating matrix from the selected materials and providing required characteristics of electric conduction.
3. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claim 2 wherein the ceramic matrix of insulating materials makes from 0.5% to 98.5 vol. % of its body.

4. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-3 wherein the ceramic resistive leads of the thermoelectrode, of ceramic conductive junctions and of ceramic conductive contact pick-ups make all together from 0.5 to 98.5 vol. % of the ceramic material of the basic body.

5. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-4 wherein the main body (7) and resistive ceramic materials (1,2,3,4,5 1, 5 2,6) contain the mixture of $Si_3N_4:A_2O_3:Si_2ON_2:La_2O_3$ in the volume ratio of: from 30:1:1:1 to 23:3:5:2.

6. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-4 wherein the main body (7) and resistive ceramic materials (1,2,3,4,5 1, 5 2,6) contain the mixture of $Si_5N_4:AlN:Al_2O_3:Si_0N_2$ in the volume ratio of: from 1:2:1:4:4 to 2:1:1 1:6.

7. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, by claims 1-4 wherein the main body (7) and resistive ceramic materials (1,2,3,4,5 1, 5 2,6) contain the mixture of BN:MgO:SiC:B 4 C:B 4 Si:C in the volume ratio of: from 21:2:2:3:1:1 to 8:2:2:3:1:4.

8. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claim 5 wherein the sum of the oxide additives $Al_2O_3$ – $Si_2ON_2$ – $La_2O_3$ makes from 3% to 50% of its body volume.

9. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claim 6 wherein the sum of the oxide additives
$\text{ABO}_3 - \text{SiON}_2$ makes from 30 to 70 vol. % of its body, and the ratio of $\text{SiN}_4 - \text{AlN}$ takes values from 1:1 to 3:1.

10. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claim 7, wherein the sum of the additives $\text{SiC} - \text{B}_4\text{C} - \text{B}_4\text{Si} - \text{C}$ makes from 0,5 to 45% of the volume of basic body and ratio of $\text{BN} : \text{MgO}$ is defined in the limits from 10:1 to 4:1.

11. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-10, wherein the ceramic bundle conductor of the positive thermoelectrode (1) and the corresponding portion the contact (6) and the ceramic junction ($5_1$) contain current conducting powder inclusions of boron carbide or lanthanum hexaboride or carbides hafnium, niobium, zirconium, tungsten or nitrides of tantalum, vanadium, zirconium, hafnium in volume content from 2,5 to 97,5%, the said inclusions determine the value of electric resistance of the said part and the value of thermoelectric voltage with the «+» sign.

12. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-11, wherein the resistive lead of the active zone (1) and the corresponding portion of the contact (6) have the value of thermoelectric voltage of one junction from 0.2 to 200 $\mu$V/grad and quantity of junction from 1 till 5000.

13. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-10, wherein the ceramic bundle conductor of the negative thermoelectrode (2) and the corresponding part of the contact (6) and the ceramic junctions ($5_2$) contain current conducting inclusions of carbon, carbides of silicon, hafnium, niobium, zirconium, tungsten or nitrides of tantalum, vanadium, zirconium, hafnium from 2,5 at 97,5% by volume that determines the value of their electric resistance and the value of thermoelectric voltage with the «-» sign.
14. Layered non-oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-10 and 13, wherein the ceramic bundle conductor of the negative thermoelectrode (2) and the corresponding portion of the contact (6) and the ceramic junctions (5_2) have the value of thermoelectric voltage from «_» 0.2 to 85 µV/grad.

15. Layered non-oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-14, wherein the ceramic bundle conductor of contact pick-ups (3,4) contain current conduction powder inclusions of the mixture SiC — B_4Si — TaN in the ratio 2:1:10 in value content from 15 to 99.5%, determining the value of electric resistance and stability to oxidation of the said ceramic bundle conductors.

16. Layered non-oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-15, wherein the green ceramic elastic sheets with the thickness from 0.1 to 3.0 mm, mainly from 0.85 to 1.25 mm and relative density from 0.51 to 0.64, mainly from 0.52 to 0.56 are fabricated by methods of pressing, rolling, casting, injection molding and others.

17. Layered non-oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-16, wherein to making the green ceramic elastic sheets, bulk stuff is prepared by adding to the mixture the powders of the basic body (7), resistive materials of the thermoelectrodes (1,2), of the contact (6), of the ceramic junctions (5_1, 5_2) and of the contact pick-ups (3,4) of organic binders and softening agents wherein the mass ratio of the elements C:H makes from 22:0:3 to 19:1:4.

18. Layered non-oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-17, wherein the total mass content of the binder and softening agent additives to the mixture to produce the basic body (7),
resistive materials of the thermoelectrodes (1,2), of the contact (6), of the ceramic junctions \((5_i, 5_2)\) and the contact pick-ups (3.4) makes from 1.5 to 15 mass.\%.

19. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-18, wherein profiled parts with the precisely defined dimensions, with the ratio of the said profile to its thickness varies from 2 to 12, are cut out of the green ceramic sheets of ceramic bundle conductors: of the thermoelectrodes (1,2), of the contact (6), of the ceramic junctions \((5_i, 5_2)\) and of the contact pick-ups (3.4).

20. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-18, wherein the resistors reservoir hole of the basic body (7) that correspond exactly to the profiles cut out as set forth in to claim 19 from the ceramic bundle conductors are punched out in precisely defined method from the green sheets of the basic body (7).

21. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-20, wherein its basic body (the insulating matrix 7) is formed from at least two sheets put on each other in such a manner that the resistive ceramic bundle conductors fabricated as set forth in to claim 19 and placed in to the resistors reservoir hole of the basic body, the produced by claim 20, must make an electric circuit and provide formation of a junction in the area of the contact (6) between the resistive conductor of the positive thermoelectrode (1) and the resistive conductor of the negative electrode (2) and the said body synthesized together with the adjacent conductors presents a monoblock ceramic device.

22. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-21, wherein the contact pick-ups (3.4) are placed on one side of the basic body, on one face (cartridge A), on one side of the basic body on different faces (cartridge B) or on different sides of the basic body on one face (tube A) or on different faces (tube B).
23. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-22, wherein one or several devices can be placed in one basic body as set forth in claims 1 and 2, each of the said devices has its contact pick-ups (3,4) and each of the said devices can act either as an independent on or as a constituent element of a complex device.

24. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-23, wherein the ceramic resistive bundle conductors (1,2) have a lot of contact pick-ups (3,4), which of the said conductors is placed in the bulk of the basic body (of the insulating matrix 7) in its recesses, produced in the layers of the green ceramic sheets of the insulating matrix in the precisely defined sites.

25. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-24, wherein the contact pick-ups (3,4) are manufactured from a ceramic resistive bundle conductors by means of their punching out of the green ceramic sheets to obtain details of precisely defined dimensions, which are set in a green state in the recesses (holes) of the insulating matrix of the body and sintered in such a way that they create in combination with the ceramic resistive bundle conductors and in combination the insulating matrix (7) a single whole.

26. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-25, wherein the contact pick-ups (3,4) of the ceramic resistive bundle conductors contain a metallic covering.

27. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-26, wherein metal contact wires are joined to the contact pick-ups (3,4) of a ceramic resistive bundle conductors by means of mechanical clamping, soldering or welding.
28. Layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-27, wherein conducting powder inclusions, which are added to the material of the insulating matrix (basic body) to obtain required sign of the thermoelectric voltage and the defined value of electric resistance of the resistive ceramic bundle conductors of the thermoelectrodes (1,2) of the contact (6), of the ceramic junctions (5_1,5_2) and of the contact pick-ups (3,4) consist of a mixture of coarse (3-15 \( \mu m \)) :middle (1-3 \( \mu m \)) : fine (less than 1 \( \mu m \)) particles in the ratio of 5:4:8.

29. Application of an all layered non oxide ceramic module as thermoelectric energy source, built with a thermoelectric device, as set forth in claims 1-28 as a constituent unit of control-and-measuring systems in food and light industries, in production of metals and alloys, in chemical industry, in automobile, aircraft and space engineering in instrumentation for scientific researches.
Fig 4
A. CLASSIFICATION OF SUBJECT MATTER

H01L 35/28 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01L 35/00-35/34

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PatSearch (RUPTO internal), USPTO, PAJ, Esp@ccnet, DWPI, EAPATIS, PATENTSCOPE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>US 2001/0002201 A1 (ISUZU CERAMICS RESEARCH INSTITUTE CO., LTD.) 31.05.2001</td>
<td>1-4, 29</td>
</tr>
<tr>
<td>A</td>
<td>JPH 02237177 A (MURATA MFG CO LTD) 19.09.1990</td>
<td>1-4, 29</td>
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</tbody>
</table>

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search: 18 April 2016 (18.04.2016)

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Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993

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Form PCT/ISA/210 (second sheet) (January 2015)
**INTERNATIONAL SEARCH REPORT**

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.:
   - because they relate to subject matter not required to be searched by this Authority, namely:

2. □ Claims Nos.:
   - because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. X Claims Nos.: 5-28
   - because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. □ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

□ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

□ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

□ No protest accompanied the payment of additional search fees.