R. Kh. Rakhimov, M. S. Saidov, Development of ceramic coatings and application of their infrared radiation, *Comp. nanotechnol.*, 2016, выпуск 4, 6–9

1. МАТЕРИАЛОВЕДЕНИЕ И ТЕХНОЛОГИЯ МАТЕРИАЛОВ

1.1. DEVELOPMENT OF CERAMIC COATINGS AND APPLICATION OF THEIR INFRARED RADIATION

***Rakhimov Rustam Khakimovich**, PhD, head of laboratory №1. Institute of materials science «Physics-sun». Uzbekistan Academy of sciences e-mail: rustam-shsul@yandex.com*

***Saidov Muhtar Safarbaevich**, Academician Uzbekistan Academy of sciences Physical-Technical Institute «Physics-Sun». Uzbekistan Academy of sciences, e-mail: rustam-shsul@yandex.com*

Abstract: Smelting and sintering of the initial ceramics were performed at the Big Solar Furnace with thermal power of 1000 kW at 2500-2700°C. As the base of some ceramics $CaMgSi_2O_6$ or Al_2O_3 + $CaZrO_3$ were used. The spectrum of the infrared radiation of ceramic coatings changed in depending on the introduced dopant oxides. The ceramics exhibit pulse or pulse – pair infrared (IR) radiation which could be photoluminescence or thermal radiation. The attempt is made to explain pulse radiation supposing the possibility of the presence of the energy barrier on the grain boundary of the ceramics. Many types of narrow range ceramic IR radiators are made and successfully applied in medicine.

Some aspects of the converter of Solar energy into thermal radiation – Solar thermal radiator (STR) are considered.

The efficiency of STR with ceramic coating is considered taking into account the photon thermal conductivity, which takes place when ceramic layer does not absorb thermal radiation of the metal sheet substrate.

Index terms: ceramic materials, the functional ceramics, activation energy, semiconductors, infrared transformers, impulse systems.

Introduction:

Effective realization of the technological potentials of solar furnaces for the development and production of advanced ceramics is the interesting problem of materials sciense. For 1985-2000 years at the Physical Technical Institute and at the Institute of Materials Science of Scientific Production Association "Physics-Sun" of Uzbek Academy of Sciences there have been developed synthesis and solar-radiation treatment of different ceramics. Many types of special ceramics were developed. Part of them are successfully used in physical therapeutics.

In spite of a great deal of effort undertaken in the field of Solar engineering a large scale utilization of Solar energy remains limited. At present the total area of established solar water heaters is ~ 70 Mm^2 (2001) and total power of terrestrial semiconductor solar cells is ~3 GW. However their prices are not acceptable in many countries. In this connection the development of structurally simple high efficient solar units based on available cheap materials is of special interest. In this paper the results on the synthesis of ceramics preparation of ceramic IR radiators and their application in medicine, drying the bilding materials are presented. Prospectives of the use of ceramic coatings in development of effective solar dryers are discussed.

Synthesis and IR radiation of Ceramics

Synthesis of $CaMgSi_2O_6$ and $LnCrO_3$ was completed by smelting at ~2700 °C and ~2500 °C respectively at the Big Solar Furnace with thermal power of 1000 kW. Then $CaMgSi_2O_6$ and $LnCrO_3$ samples were powdered with grain sizes of ~20μ and ~lμ respectively. 99 wt.% $CaMgSi_2O_6$ + 0,8wt.% $LnCrO_3$ powder mixture was sintered at ~1700 °C at the solar furnace. The ingot obtained was again powdered with grain size of ~20μ and grains of $CaMgSi_2O_6$ to be partialy covered by $LnCrO_3$ layers with thickness of $\leq$ 1μ. This powder was mixed with finely divided $CuCrO_2$ (0,2 wt.%) powder with grain size of ~300 Å and was sintered at ~900 °C during one hour in the electric furnace and was slowly cooled there. One can believe that $LnCrO_3$ layers are covered by $CuCrO_2$ layers with thickness of < 300 Å. So $CuCrO_2$ layers prove to be between $LnCrO_3$ layers or between them and $CaMgSi_2O_6$ grains. The final ceramic ingot consisting of 99 wt.% $CaMgSi_2O_6$ + 0,8 wt.% $LnCrO_3$ + 0,2 wt.% $CuCrO_2$ was powdered with grain size of 40-60μ and using the binder additive ~ l00μ thick ceramics was put on the glass of the electric lamp and the surface of quartz tube in which then Ni-Cr alloy heater was placed. The spectrum of radiation of the ceramics induced by the light of the lamp obtained by double-beam method using the device "specord" has shown the presence of the peak with wavelength of ~16μ, (fig. 1). As seen from fig. 1 with increase in intensity of incident beam on the ceramics the intensity of the photoluminescence peak increases and the threshold of its appearance is less than 1 W/cm^2. The ceramics exhibit pulse (fig.2) or pulse-pair (fig.3) infrared radiation, which could be photoluminescence or thermal radiation. The duration of the peak was determined with the help of the pyroelectric joulemeter J-25-HR. According the photoluminescence version accumulation of the photoinduced electrons and holes and their recombinations giving rise to the pulse take place in the intergrain layers of the ceramics if intergrain layer of $CaMgSi_2O_6$ is semiconductor $LnCrO_3$-$CuCrO_2$ – $LnCrO_3$ tunnel hetero-*p-n-p (n-p-n)* or $LnCrO_3$-$CuCrO_2$ *p-n* structure (junction).

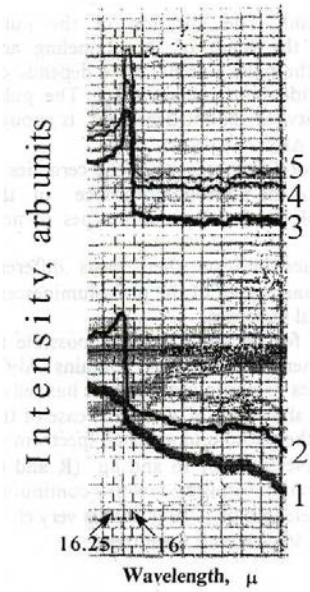

Fig 1. The spectrum of the ceramics at different power of incident light on the ceramics: 1-5 respectively 1;2;3;4;5,3 W/cm^2

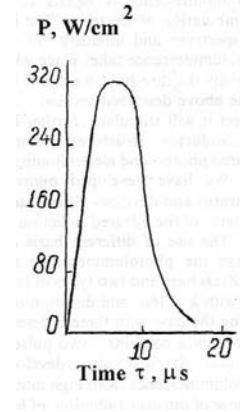

Fig 2. Distribution of the surface density of the power P in the pulse radiation of the ceramics.

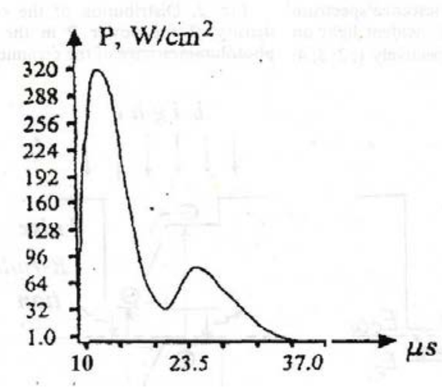

Fig 3. Distribution of the surface density of the power in the pulse-pair IR radiation of the ceramics based on Al_2O_3+$CaZrO_3$.

However, considering the dominance of thermal radiation in the spectrum of ceramic sources, and the effectiveness of pulsed IR radiation application in therapy, sterilization, drying and for other purposes, we try to substantiate the conditions of the pulsed thermal radiation.

In a perfect uniform medium under thermodynamic equilibrium, only stationary thermal radiation is observed. In a material with an energy barrier at the interface of its different kinds of parts, thermally induced free electrons producing thermal radiation can periodically recombine. As an example, we consider the energy band diagrams of the contacts of the dielectric doped with two donor impurities 1 and 2 with the ionization energies E_1 = 0.05 eV and E_2 ~ 0.15 eV, respectively, with the same dielectric highly doped with the impurity 1 only (Fig. 4). In the dielectric with a higher concentration of impurity 1, the Fermi level E_F is closer to the conduction band bottom E_c. This leads to the appearance of the energy barrier at the dielectric-dielectric interface. E_v is the valence band top. As this system is heated, due to the ionization of the atoms of impurity *2,* the thermally stimulated free electrons are carried by the energy barrier and accumulated (Figs. 4*).* As soon as the electric field necessary for backward transitions is attained, the free electrons, which passed to their initial positions, induce the high-intensity radiation in their recombination (Figs. *4).* It could be expected that if a sufficient temperature level is kept throughout the system, the pulsed radiation is repeated. In the dielectric-dielectric system, the synchronous character of the pulsed radiation of all the parts is provided under condition that the highly doped dielectric is coupled by means of the potential relief for the free electrons

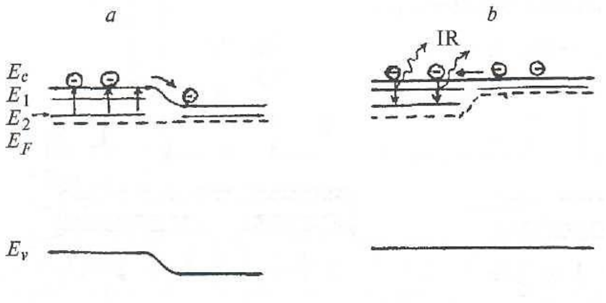

Fig. 4. Energy band diagram of the n-dielectric – n$^+$-dielectric junction: (a) thermal ionization of impurities and accumulations of free electrons; (b) back-ward transitions and recombination of electrons with IR radiation.

Therapeutic ceramic IR radiatiors

In 1982—1997, technologies for the manufacture of new ceramic materials were developed. Some of them served as the basis of therapeutic IR sources implemented in two variants (Fig. 5).

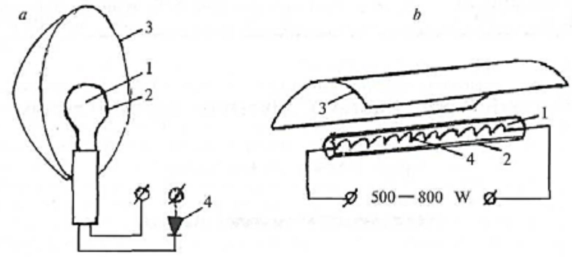

Fig 5 Schematic diagram of ceramic IR radiator for (a) local and (b) overall irradiation

1. The IR sources for local action on an ailing organ are comprised of a 100-W light bulb with the ceramic layer *2* deposited on its glass part (Fig. 5*a).* The bulb is attached to the handle of reflector *3* and connected to the circuit through the diode *4* which reduces the consumed power to 50 W. The efficiency of conversion of this power to IR radiation is approximately 60-70%, while the power of the ceramic layer's IR radiation is 30-35%. Usually during the therapy the distance between the bulb and the patient's ailing area is about 20 cm. In this case, the exposed surface area is 400-500 cm^2. The IR radiation intensity on the skin is 0.09-0.07 W/cm^2 which is about 50% higher than man's own radiation intensity.

2. The key component of the IR source as a whole intended for irradiation of the ailing body is the quartz tube *1* (Fig. 5*b).* It is about 1 cm in diameter and 2 m long and fully coated with the ceramic layer *2.* The tube is placed under the reflector *3.* The Ni-Cr alloy spiral heater *4* with 500-800 W power consumption is placed inside the tube. The therapeutic equipment has 1-4 pairs of quartz elements. In the therapy, one such pair with 1.6 kW power consumption is frequently used. The distance between the quartz tubes and the patient's body is about 80 cm.

At the efficiency of conversion of consumed energy into IR radiation of 60-70%, its intensity is about 0.03 W/cm at the patient's skin level. This is lower than the intensity of man's own radiation by a factor of 1.5. About 90% of the integral intensity of the ceramic IR sources under discussion lies within the wavelength range 8-20 μ. At present, some of the developed ceramic IR sources are successfully applied in many hospitals.

In the table are presented the types, some peculiarities of the radiation of the ceramic radiators and some diseases to be cured.

At present in Uzbekistan, Germany, Malaysia and Korea a number of the private clinics are equipped with the radiators given in the table and their long-term physical therapeutic tests are completed. R & D for the improvement of the ceramic IR radiators and activities to start their large-scale applications are sponsored by several private companies.

Table

Type of radiators	Base of ceramics	Some features of radiation	Application in medicine
TLI	R_2O_3+Al_2O_3+ +$CaMgSi_2O_6$	Pulse with $\lambda=16\mu$, duration $\tau\sim10\mu s$.	
RC	R_2O_3+$CaZrO_3$	Pulse-pair $\lambda=16\mu$, $\tau\sim23\mu s$.	Cancer and free radical diseases Antiviral
RV	R_2O_3+Al_2O_3+$CaZrO_3$	Two pulse-pair $\lambda_1=16\mu$, $\lambda_2=8\mu,\tau_1\sim20\mu s$.	
	Contain RC or RV ceramics:		
GI	0,5 wt.%	Pulse-pair or Two pulse-pair	
GL	1 wt.%		
GM	2 wt.%		
AF	4 wt.%		Inflammation antibacterial antifungi
GH	5 wt.%		
		continuous radiation with:	
KL		$\lambda=9,17\mu$	
KH		$\lambda=9,53\mu$	
KS		$\lambda=9,36\mu$	
		Continuous radiation with $\lambda=10\mu$ and defferent intensity I	Status of hormon immune and nervous systems
ZB		I_o	
ZC		I_o	
AK		~10 I_o	
AV		~100 I_o	Anticollagen

5. Ceramic IR dryer and prospectives of Solar thermal radiators.

We have developed several types of the dryers with ceranic coatings and realized their production on a small scale. Here note the results of the test of the dryers in reconditioning the damp walls of the buildings after the flood happened in Germany. One of the models of the dryer is shon on the fig.6.

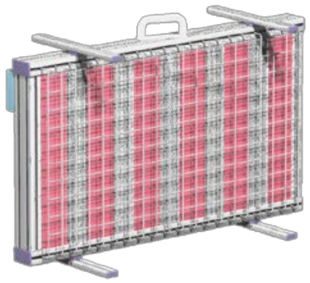

Fig.6. InfraRed Dryer for the wall «Zebra»

Voltage 230V

Power 2,0kW

Square of surface 0,5 m^2

Dimensions 1035x620x120 mm

Weight 22 kg

The operation temperature of the ceramic coating of the steel sheet of the dryer was 200^{o}C. In using our dryer the thickness of the wall dryed for twenty-four hours reached 100 cm. At the same time the thickness of the layer of the wall dryed by check dryer was 10 cm. only. Therefore the drying method based on ceramic coatings developed by Dr.R.Rakhimov was awarded with Grand Prize “Simply Genius” of Germany in 2003.

Abovestated results on IR radiators and their application as well as the importance of the utilization of solar energy are good reason to consider the prospectives of the converter of solar radiation into thermal one – Solar thermal radiator (STR), which is very simple. Its base to be thin metal sheet 1 front surface layer of which 2 with absorption coefficient α>0,9 and emissivity ε<0,2 and back one 3 with ε~0,9 (fig.7a).

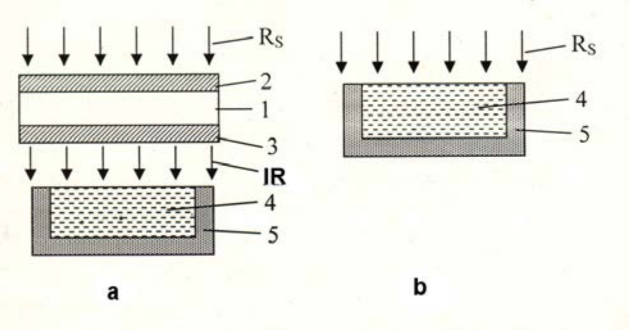

Fig7. Transparent vessel 5 with water 4 under STR (a) and without it (b)

We believe that STR is a ready solar dryer. 90% of the power of solar radiation is the share of the photons with energy of >0,7 eV., which are not absorbed by water. STR heated up to 60-80^{o}C by Solar radiation R_s converts each of incident photons with energy of 1,5-2,0 eV into 10 IR photons with energy of 0,15-0,2 eV, which are absorbed by the upper layer of the water 4 filled in the transparent vessel 5 and cause its intensive evaporation (fig 7a). R_s does not essentialy change the state of the transparent vessel with water (fig.7b). To improve the efficiency of STR it is reasonable to use the difference of the spectrum of thermal radiation of the materials. Our idea concerning the solution of this task is the realization of photon thermal conductivity when in transfering the heat in solids share of not absorbed thermal radiation is essential.

So suppose that ceramic coating does not absorb the thermal radiation of steel sheet with ε~0,9 and increases the intensity of IR radiation of STR.

To check the idea the effect of ceramic coating on the heating of water with electric stove 2 at power = 60; 200; 1000 W was determined.

Water 4 was boiled in the tea-pot 1 without and with ceramic coating 3 of the outer surface of its bottom. (fig.8). The presence of the coating reduced the boiling time from 130 min to 70 min and the transport of the heat increased ~35% (fig.9) though the additional lost of the energy took place due to thermal resistance of the ceramic layer and the higher temperature of the tea-pot.

This result can be explaned on the base of photon thermal conductivity of the ceramic layer and its pulse IR radiation and shows the possibility of the improving of the efficioncy of STR, which is of special interest to develop Solar dryers, water distillers and theroperlic means.

As to fulure of R&D, concerning the STR based Solar units it is advisable to find out the laws of the photon thermal conductivity in multilayer converters of solar energy into thermal radiation using the available and cheep substrate materials and ceramics.

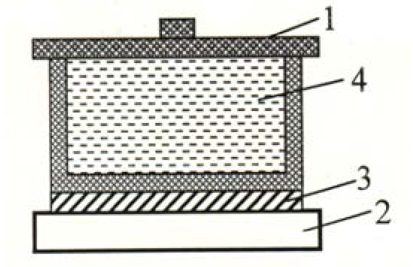

Fig.8. 1-teapot, 2-elcetric stove, 3-ceramics, 4-water

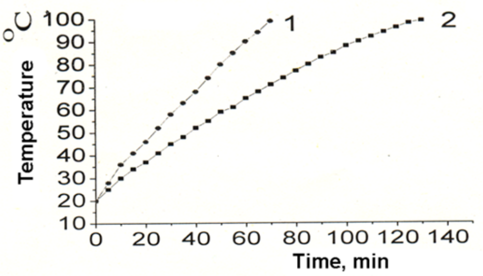

Fig.9. Dependence of temperature of water on duration of heating through ceramics (1) without it (2)

References:

1. Becker M. IEA, Solar PACES. Annual Report 1997. Ed. W. Grasse, DLR Koln/Germany, May 1998. P.4.1-4.39.

2. Riskiev T.T., Abdurakhmanov A.A., Akbarov R.U. Renewable Energy. Moscow. InterSolarCemtre. 1997. №1.P47-48.

3. Rakhimov R., Tikhonova N., Resonance Therapy, Ceramic Materials and Methods of their use in Medicine, Part I. Printing House of Publishing and Printing Centre Yangi asr avlodi. Uzbekistan, Tashkent, 2000.

4. V.A. Butuzov, Industrial Energy, 2001 №10 p. 54-61

5. L.Kazmerski and T.Surek, OE magazine 2003 april.

6. R.Kh. Rakhimov, M.S. Saidov, Applied Solar Energy (Geliotekhnika), 2001 №2, p.65-68

7. R.Kh.Rakhimov, M.S. Saidov, Applied Solar Energy (Geliotekhnika), 2002, №3, p.71-74

8. M.V. Kharchenko, Individial Solar Units, Moscow, Energyatom publisher, 1991

9. Р. Х. Рахимов, М. С. Саидов, В. П. Ермаков, «Особенности синтеза функциональной керамики с комплексом заданных свойств радиационным методом. Часть 5. Механизм генерации импульсов функциональной керамикой», *Comp. nanotechnol.*, 2016, № 2, 81–93

10. Р. Х. Рахимов, «Синтез функциональной керамики на БСП и разработки на ее основе», *Comp. nanotechnol.*, 2015, № 3, 11–25

11. Э. З. Имамов, Т. А. Джалалов, Р. А. Муминов, Р. Х. Рахимов, «Теоретическая модель новой контактной структуры «нанообъект-полупроводник», *Comp. nanotechnol.*, 2015, № 4, 51–63

12. Р. Х. Рахимов, «Особенности синтеза функциональной керамики с комплексом заданных свойств радиационным методом. Часть 1», *Comp. nanotechnol.*, 2016, № 2, 9–27

13. Имамов Э. З., Джалалов Т. А., Муминов Р. А., Рахимов Р. Х., Отличительные особенности контактных структур с наноразмерными включениями полупроводниковых фотодиодов. Журнал «Computational nanotechnology», №3, 2016, 196-203.

14. Imamov E. Z., Djalalov T. A., Muminov R. A., Rakhimov R. Kh., The difference between the contact structure with nanosize inclusions from the semiconductor photodiodes. Журнал «Computational nanotechnology», №3, 2016, 203-208

15. Рахимов Р. Х., Ермаков В. П., Рахимов М. Р., Латипов Р. Н. Особенности синтеза функциональной керамики с комплексом заданных свойств радиационным методом. ЧАСТЬ 6. Журнал «Computational nanotechnology», №3, 2016, 6-35

16. Рахимов Р. Х., Особенности синтеза функциональной керамики с комплексом заданных свойств радиационным методом. часть 7. природа электромагнитного излучения. Журнал «Computational nanotechnology», №3, 2016, 35-183