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Inventor <u>John M. Jewell</u> <u>Barry B. Harbison</u> <u>Ishwar D. Aggarwal</u>

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2		Accesion For		
3	GERMANATE GLASS CERAMIC	DTIC TAB		
4		Justification		
5	Field of Invention			
6	This invention relates to the field of germanate	glass		
7	ceramics.	Availability Cor		
8		Dist Special		
9	Background of Invention	r		
10	Requirements for infrared domes and similar applic	ations		

include hardness, infrared transparency, fracture toughness, and thermal shock resistance. There are currently three commercially available materials for use in applications such as infrared domes which can transmit in the infrared region of about 3-5 microns: SnS, spinel, and sapphire. Although these materials are excellent in some respects, they all have important limitations.

17 ZnS has excellent transparency and is readily formed into the specific shapes required for windows and domes. 18 However, this 19 material is very soft and is abraded under normal operating 20 conditions. The abrasion limits both the useful scope and the 21 lifetime of products made from ZnS. Some improvement of the abrasion resistance is possible through the application of 22 23 protective coatings, but the high temperatures which are rapidly generated during high speed acceleration leads to delamination. 24 For instance, a speed of Mach 4, or about 2800 mph, generates a 25

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1 temperature of about 600°C.

Spinel has a slightly diminished transparency as compared to ZnS, i.e., the 5-micron radiation is partially absorbed. Since this material is about ten times harder than ZnS, it has greater erosion resistance. It is also better at resisting thermal shock because of higher fracture toughness than ZnS. However, difficulty in the fabrication of required shapes makes windows and domes of this material slightly more expensive than those made from ZnS.

9 Sapphire has a transparency about equal to that of spinel and 10 has hardness and fracture toughness properties that are about 40% 11 greater than those of spinel. Thus, windows or domes produced from 12 sapphire are highly abrasion resistant and can be used for super-13 sonic applications. However, this material is very expensive to 14 produce and even more expensive to fabricate into the required 15 configurations.

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Summary of Invention

18 It is an object of this invention to produce a germanate glass19 ceramic with improved physical properties.

Another object of this invention is a germanate glass ceramic with improved thermal shock, improved erosion resistance, and improved fracture toughness, which glass ceramic can transmit in the infrared region of about 3-5 microns at a transmission above 80% for a 0.5 cm thick sample.

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Another object of this invention is a germanate glass ceramic

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that can be produced at a small fraction of the cost of the
 commercially available materials currently used for infrared domes
 and other related applications.

Another object of this invention is a germanate glass ceramic that can be produced cheaply pursuant to conventional glass-forming procedures and that can be formed into intricate configurations.

7 These and other objects of this invention can be accomplished 8 by an infrared-transmitting germanate glass ceramic article processing germanate glass ceramic components, 9 prepared by including phase separating and/or nucleating agents, pursuant to 10 conventional glass forming procedure to form a solid glass article, 11 12 annealing the glass article, and subsequently nucleating and crystallizing the article to form the germanate glass ceramic. The 13 14 resulting product is nearly all crystalline, maintains a high 15 infrared transparency and has improved thermal and mechanical 16 properties.

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Detailed Description of Invention

19 This invention pertains to a novel non-silicate germanate 20 glass ceramic article and to a method for making same.

The article is a glass ceramic that is crystalline to a level of above 98%, is made from a germanate glass and has improved thermal and physical properties. The following Table A compares an average of improved properties of the novel glass ceramic with the properties of competing materials.

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Germanate Germanate ZnS Spinel Sapphire Parent Glass Property **Glass Ceramic** Fracture Toughness (MPa-m 72) 0.7 1.0 1.9 2.0 2.6 Thermal Expansion (ppm/K 8.0 5.6 6.0 5.6 6.6 Hardness (kg/mm²) 1880 390 570 160 1600 Erosion Resistance --Threshold Velocity (m/S) 460 190 390 490 • • • Thermal Shock 2.1 Figure of Merit (W/m) 3.4 0.8 1.4 ... Normalized Cost 0.1-0.2 1 2.5 1

Table A

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22 In Table A, above, the term "Germanate Parent Glass" refers to 23 the precursor glass for the glass ceramic material of the present 24 invention. The term "Germanate Glass Ceramic" refers to glass ceramic material of the present invention. In the above table, the 25 2.6 MPs- $m^{1/2}$ fracture toughness for the glass ceramic of this 26 invention exceeds the 0.7 MPa- $m^{1/2}$ fracture toughness of the 27 germanate parent glass. Thus, subjecting a germanate glass to 28 nucleation and crystallization can increase the fracture toughness 29 of a germanate glass several fold. 30

The germanate glass ceramic of this invention has thermal shock in terms of figure of merit in the approximate range of 2.5-4.5W/m, preferably 3-4W/m; erosion resistance in terms of threshold velocity is in the approximate range of 350-1000 m/s, preferably 500-800 m/s; fracture toughness is 1.5-4.5 MPa-m^{1/2}, typically 2-4 MPa-m^{1/2}.

The method of the present invention includes the steps of mixing germanate glass ceramic components; melting the components

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1 to form a molten mass; cooling the molten mass to form a solid 2 glass article; annealing the glass article; nucleating the solid 3 article by heating it to an elevated temperature for a period of several hours to develop nuclei in the article; and crystallizing 4 the nucleated article by heating it, after nucleation, at an 5 elevated temperature for a period of at least one minute to grow 6 7 the crystallites to an average diameter of less than about 1000 nanometers (nm); and cooling to form the glass ceramic with 8 improved thermal and physical properties. Phase separation may be 9 needed to allow nucleation to proceed. Phase separation can be 10 11 effected by addition of a phase separation agent or by heating or 12 upon cooling the parent glass to cause phase separation. When phase 13 seaparation takes place, nuclei form on the separated phase 14 followed by crystallization.

15 The germanate glass ceramic composition includes germanate 16 glass components, nucleating agents, and, optimally, phase 17 separation components. There can be at least three, preferably at 18 least four germanate glass components although the glass ceramic 19 article can contain more components than specified herein.

The primary germanate glass components include germanium oxide (GeO₂); barium oxide (BaO), which is uaually initially in the form of barium carbonate (BaCO₃), which converts to an equivalent mol amount of barium oxide (BaO) on heating, and gallium oxide (Ga₂O₃). The secondary germanate glass components include calcium oxide (CaO), zinc oxide (ZnO), alumina (Al₂O₃), gadolinium oxide (Gd₂O₃),

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lead oxide (PbO), indium oxide (In_2O_3) , bismuth oxide Bi_2O_3), 1 2 lanthanum oxide (La₂O₃), and yttrium oxide (Y₂O₃). The amount of germanium oxide is 25-80, preferably 35-70 mol percent; amount of 3 barium carbonate is 10-60, preferably 15-45 mol percent; and amount 4 of gallium oxide is 5-30, preferably 10-20 mol percent. These 5 6 amounts are based on total number of mols of germanium oxide, 7 barium carbonate, and gallium oxide used in making the glass ceramic. The secondary germanate glass components can be used in 8 conventional amounts. 9

10 To avoid crystallization when forming the glass, the mole 11 ratio of barium carbonate to gallium oxide should be in the range 12 of about 4:1 to 1:1.

13 The germanate glass ceramic composition includes about 0.1-20, preferably 2-10 mole percent, based on the germanate glass 14 components, of at least one nucleating agent. If an insufficient 15 amount of a nucleating agent is used, nucleation will be 16 insignificant and an insufficient number of crystals will be 17 18 produced to significantly improve the properties of the germanate ceramic. If too much nucleating agent is used, glass will not be 19 formed from the germanate glass ceramic composition. 20 Typical nucleating agents include arsenic oxide (As₂O₃), bismuth oxide 21 (BiO₃), phosphorus pentoxide (P₂O₅), hafnium oxide (HfO₂), indium 22 oxide (In_2O_3) , antimony oxide (Sb_2O_3) , tantalum oxide (Ta_2O_5) , 23 titanium oxide (TiO₂), and zirconium oxide (ZrO₂). A combination 24 of the nucleating agents can constitute a nucleating agent. 25

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1 The germanate glass ceramic composition includes about 0.1-20 2 mole percent of a phase separation agent such as indium oxide 3 (In_2O_3) , phosphorus oxide (P_2O_3) , antimony oxide (Sb_2O_3) , and bismuth 4 oxide (Bi_2O_3) . The amount of the phase separation agent is based 5 on the total of the germanate glass components and the phase 6 separation agent.

연결 습과법

7 It should be understood that other components can be included 8 in making the glass ceramic article disclosed herein as long as 9 they do not significantly change the physical properties of the 10 article.

11 Components of the germanate glass ceramic composition are 12 typically powders that are mixed sufficiently in a suitable 13 receptacle to distribute the components. Mixing time can be on the 14 order of about one-half hour if a mixing tumbler is used.

15 After mixing the components, the resulting mixture is 16 transferred to a vessel that can withstand high germanate glass 17 melting temperatures. Such a vessel is typically a platinum boat 18 that can be preheated before the mixture is transferred thereto. To melt the glass ceramic composition disposed in a platinum boat, 19 a furnace is heated to about 1350-1600°C, an inert atmosphere is 20 provided in the furnace, and the boat is placed in the furnace for 21 about 1/2-3 hours until the contents of the boat melt. 22 Once 23 contents of the boat are melted, the boat is removed from the furnace and conventional techniques can be used to produce a glass 24 article of any size or shape. A typical technique of preparing an 25

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article involves pouring the molten germanate glass into a mold,
 forming the glass into the desired shape, and cooling to solidify
 the molten glass.

The solidified glass in the form of an article is then 4 annealed to relieve inherent stresses therein. This can be done by 5 6 heating the glass article to about the glass transition temperature (T_{a}) of the glass and holding it at that temperature for an amount 7 of time sufficient to substantially relax the glass, typically 8 about 10 minutes to 4 hours followed by slow cooling. 9 At this point, the glass is amorphous and not a glass ceramic. Annealing of 10 11 the glass can be avoided by cooling the melt directly to the 12 nucleation temperature. Stresses develop in the solid glass upon 13 cooling the melt to below T.

14 To convert the glass from amorphous to essentially all 15 crystalline, i.e., to convert the glass to glass ceramic, the glass 16 is subjected to nucleation followed by crystallization.

17 Nucleation throughout the germanate glass can be accomplished 18 by heating the germanate glass article to a temperature range of 19 about 600-900, preferably 650-750°C in a time period of 1-16, preferably 2-10 hours. The glass transition temperature (T_a) for 20 21 the germanate glass is above about 600°C and for nucleation to 22 occur, the glass is heated above T_a. Nucleation can be represented as a bell-shaped curve with nucleation starting at about 600°C and 23 terminating at about 900°C, with the maximum nucleation rate taking 24 place at the maximum point on the nucleation curve, about 750°C. 25

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1 It is believed that a minimum of about 10¹¹-10¹² nuclei/cm³ may be 2 needed to realize significant property improvements after 3 crystallization in the germanate glass ceramic article. The nuclei 4 are below 1 micron, typically below 100 nanometers in average 5 diameter.

6 It may be necessary to cause phase separation to take place in 7 the glass to provide a phase on which nuclei can form. Phase 8 separation can be induced by adding to the germanate glass ceramic 9 composition a phase separation agent which causes phase separation 10 to take place when the glass is subjected to an energetic force. 11 Phase separation appears to facilitate nuclei formation on the 12 separated phase.

It is possible for a nucleation agent to function as a phase 13 14 separation agent, depending on the combination and amounts of the 15 components used. If a nucleation agent can function as a phase 16 separation agent, then its phase separation function preempts its nucleation function and the agent functions as a phase separation 17 18 agent. In such a case, two or more nucleation agents should be used to allow one to function as a phase separation agent and 19 20 another to function as a nucleation agent.

In order to induce phase separation, it may be necessary to heat or cool the glass. Application of an energetic force, apparently facilitates or expedites phase separation. Energetic force can be heat treatment above T_a of the glass.

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Neither nucleation nor phase separation need to commence at

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room temperature but can commence at any temperature as long as the
 objectives of nucleation or phase separation are achieved.

Crystallization or growth of nucleated crystals is typically 3 carried out by heating nucleated glass to a temperature in the 4 approximate range of 750-1200°C for a period of 1/2 minute to 8 5 hours, preferably 900-1100°C for a period of 1 minute to 2 hours. 6 7 The crystal growth rate can be represented as a bell-shaped curve with crystallization starting at about 750°C and terminating at 8 about 1200°C, with the maximum crystal growth rate taking place at 9 10 the maximum point on the growth rate curve, about 975°C. Melting of the germanate glass commences at about 1200°C. Although the 11 12 crystal growth rate curve is generally at a higher temperature range than is the nucleation curve, the upper temperature range of 13 the nucleation curve overlaps the lower temperature range of the 14 15 crystallization curve. The overlap means that at the overlapping temperatures, nucleation and crystallization proceed simultaneously 16 17 although at different rates, depending on the location on the respective curves. 18

19 The crystals in glass ceramic are typically different 20 chemically from the nuclei although they can be the same as the 21 nuclei. In a glass ceramic containing germanium oxide, barium 22 oxide and gallium oxide, the crystals are germanium, barium, and 23 gallium oxide and their average size is typically less than about 24 1000 nanometers and larger than about 20 nanometers. The crystals 25 should not be too large since the crystal oversize can lead to

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diminished infrared transparency of the glass ceramic. The size of 1 2 the crystals should be less than the wavelength of the transmitted If the crystal size exceeds the wavelength of the 3 light. transmitted light, light will be scattered and/or absorbed and 4 transparency will diminish. Additionally, regardless of crystal 5 6 size, improvement in the thermal and physical properties in the glass ceramic typically requires that the glass ceramic be in 7 excess of 98% by volume crystalline, and preferably essentially 8 100% crystalline. 9

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10 After crystallization, the glass ceramic is in the solid state 11 and is cooled slowly to about room temperature. Since a germanate 12 glass is essentially solid at about 1100°C as it is cooled from a 13 higher temperature, it is possible to carry out nucleation and 14 crystallization while the glass is in the solid state. In fact, 15 typically, nucleation and crystallization are carried out on a 16 germanate glass that is in a solid state.

The invention having been generally described, the following examples are given as particular embodiments of the invention to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit in any manner the specification or any claims that follow.

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Example I

This example demonstrates preparation of a germanate glass

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1 ceramic from a germanate glass wherein nucleation was achieved without phase separation. 2

The following batch of germanate glass ceramic was prepared, as summarized in Table I, below:

Oxide	Weight Percent	Mole Percent	Batch Materials	Weight (grams)
Base Gla	ass			
BaO	47.12	42.9	BaCO3	24.260
Ga ₂ 03	22.33	17.0	Ga ₂ O3	9.131
Ge0 ₂	30.05	40.1	GeO ₂ 1	2.019
Addition	าร			
Sb ₂ O ₃	5.22	2.5	Sb ₂ O ₃	2.088
TiO,	1.72	3.0	TiO,	0.688

25 The batch was mixed in a tumbler for about one-half hour and 26 then melted in a platinum crucible at about 1400°C over a period of about one hour. As the batch was melted, dry nitrogen gas was 27 flown over the batch to keep the water interaction therewith to a 28 29 minimum. The melted batch was then quenched to about room 30 temperature by dipping the bottom of the crucible in water, whereby a solid, amorphous glass was formed. For annealing, the glass was 31 reheated to about 675°C for about one hour and then slowly cooled 32 at about 1°C/min to 400°C followed by furnace cooling to about room 33 34 temperature.

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The glass was then nucleated by reheating to about 710°C and

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holding at 710°C for about four hours and then crystallized by
 heating the glass at about 10°C per minute to about 1000°C and
 holding at 1000°C for about one minute.

The nucleation and crystallization heat treatments produced 4 5 germanate glass ceramic that was over 98% by volume crystalline. The resulting glass ceramic showed infrared transmission beyond 5 6 7 microns; its fracture toughness over the base glass increased from 0.7 to 2.6 MPa- $m^{1/2}$; its thermal shock was 3.4W/m, exceeding even 8 that of sapphire; its erosion resistance was 460m/s, which was 9 below that for sapphire but above that of zinc sulfide and spinel; 10 its thermal expansion over the base glass decreased from 8 to 5.6 11 12 ppm/K; its Vicker's hardness over the base glass increase from 390 to 570 kg/mm²; and its normalized cost was 0.1-0.2 compared to 1 13 and 2.5 for the competing materials. 14

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Example II

17 This example demonstrates preparation of a glass ceramic from 18 a germanate glass wherein nucleation was achieved after phase 19 separation by using a phase separation agent as a component of the 20 germanate glass ceramic composition.

The following batch of germanate glass ceramic was prepared,
as summarized in Table II, below:

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Oxide	Weight Percent	Nole Percent	Batch Materials	Weight (grams)	
<u>Base Glass</u> BaO	17.00	15.0	BaCO3	9.032	
Ga203	10.72	7.5	Ga203	4.289	
1n203	15.88	7.5	1n203	6.354	
GeO2	55.85	70.0	GeO2	22.339	
Additions Ti0 ₂	5.0	8.2	TiO2	2.101	

Table II

21 The batch was mixed in a tumbler for about one-half hour and 22 then melted in a platinum crucible at about 1600°C over a period of about one hour. During melting of the batch, nitrogen flush was 23 used to minimize water interaction with the batch. 24 The melted batch was then guenched to about room temperature by dipping the 25 26 bottom of the platinum crucible in water, whereby a solid, 27 amorphous glass was formed. For annealing, the glass was reheated to about 675°C for about one hour and then slowly cooled at about 28 1°C/min to 400°C followed by furnace cooling to about room 29 temperature. 30

Nucleation herein was preceded by phase separation of an indium-rich phase of BaO - 10.7 %, $Ga_2O_3 - 10.0$ %, $In_2O_3 - 28.9$ %, and $GeO_2 - 50.4$ % from original glass composition of BaO - 17.3 %, $Ga_2O_3 - 10.8$ %, $In_2O_3 - 13.5$ %, and $GeO_2 - 58.4$ %, all in mol percent, by heating the glass above its T_g to abut 725°C and holding it there for about two hours. About 10-20% by volume of the In_2O_3 -

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phase in the form of solid droplets of about 0.1-0.5 microns in size dispersed in a solid parent matrix of BaO-Ga₂O₃-GeO₂. The phase-separated glass was then heated to about 1000°C and held there for about 1 minute for crystallization to be carried out.

The resulting germanate glass ceramic was more than 98% by 5 volume crystalline, transmitted in the infrared region of 3-5 6 7 microns at a transmission in excess of 80%, had thermal shock of 8 3.6 W/m, erosion resistance of 470 m/s, thermal expansion of 5.8 ppm/K, hardness of 590 kg/mm², fracture toughness of 2.3 MPa/m^{1/2}, 9 10 and was produced at a small fraction of the cost compared to a competing material. For infrared window and dome applications, the 11 more important parameters are thermal shock and cost. 12

Many modifications and variations of the present invention are possible in light of the above techniques. It is, therefore, to be understood that the invention may be practiced otherwise than as specifically; described.

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Abstract

A germanate glass ceramic article which has better thermal and 2 physical properties than the competing materials of zinc sulfide, 3 spinel, and sapphire is made by mixing germanate ceramic glass 4 components; melting the components to form a molten mass; cooling 5 the molten mass to form a solid glass article; nucleating the solid 6 article by heating it in the range of about 630-790°C for about 1-7 16 hours to develop nuclei in the article; and crystallizing the 8 nucleated article by heating it, after nucleation, in the range of 9 10 about 1/2 minute to about 8 hours to grow the nuclei to crystallites having an average diameter of less then about 1000 11 12 nanometer (nm); and cooling to form the glass ceramic.

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