

A PROTECTIVE MATERIAL

TECHNICAL FIELD

[0001] Various embodiments refer to a protective material, such as a ballistic resistant material, and articles formed therefrom. Characterization of the protective material and evaluation of the articles fabricated with the protective material were also carried out according to embodiments, and are detailed herein.

BACKGROUND

[0002] Protective materials refer broadly to substances that may be used to hinder destruction and/or damage to, or exposure of an object, and may find application in a myriad of items ranging from consumer goods such as eyewear and protective cover on watches and electronic gadgets, to construction materials such as windows and shower screens, to parts of vehicles such as windcreens of cars, and to military items such as ballistic resistant materials.

[0003] To render the protective function, the protective materials may be applied on a surface of the object to be protected, such that the protective materials are in direct contact with the object. This may be the case for a protective screen on an electronic device such as a smartphone or watch. In some instances, the protective materials are spaced apart from the object or structure, for example, as an enclosure containing the object or as a shield protecting the object from external elements, such as windscreen of a vehicle or eyewear.

[0004] Depending on the intended application, various materials may be used as the protective material. For example, glass treated with an ion-exchange strengthening process have been used as a protective cover for displays and touch screens in electronic devices such as smart phones, tablet computers, and televisions. Polymeric materials such as poly(methyl methacrylate) have been used as substitutes for glass in applications where transparency, high strength and resistance to shattering is required, such as in windows and aircraft canopies.

[0005] Where military applications are concerned, state of the art bullet-proof materials include armored glass and sapphire single crystals. Armored glass, in particular, is readily available for use in bullet-proof windows. Due to its low hardness and strength, however, thicknesses in the range of about 50 to 150 mm are often necessary for bullet-proof

applications. As such, there is still much room for improvement in terms of weight and volume.

[0006] Sapphire, on the other hand, has improved material hardness and strength over that of armored glass. Accordingly, it may be made thinner and lighter in weight in various applications. Sapphire, however, is an anisotropic crystal and may therefore not be optically uniform. Hence, it cannot be considered to be a general-purpose material. Moreover, it has a very high melting point of 2100 °C, which may lead to high production costs. Hardness of the material may also result in increased processing costs. Further, as strength of the material is dependent on the crystal axes due to its anisotropy, damage may be catastrophic in the weaker crystal planes.

[0007] To address the disadvantages of armored glass and sapphire, transparent ceramics such as Spinel and aluminum oxynitride (AlON) have been developed. Spinel, for example, may be synthesized by adding sintering additives such as LiF followed by hot-pressing. It may be difficult to obtain transparency in Spinel unless sintering additives are used. As this material has a cubic structure, it does not exhibit optical or mechanical anisotropy. Due to the use of LiF additives, grain growth may occur during sintering to result in final average grain sizes of about 30 to 100 microns. Single crystal Spinel has hardness and bending strength of 11 GPa and 270 MPa, respectively. In contrast, polycrystalline Spinel with additives, while having the same level of hardness, has a reduced bending strength of about 90 to 140 MPa. Moreover, using the hot press method to fabricate Spinel is not ideal for production as only one sample may be produced per cycle. This may lead to cost-related issues.

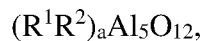
[0008] Aluminum oxynitride (AlON) has a hardness between that of Spinel and sapphire. Its bending strength is about 250 to 300 MPa, which is as good as single crystal Spinel, making it a promising candidate. Synthesis of this material, however, requires solid reaction of the raw materials Al_2O_3 and AlN , which is difficult to achieve. Generally, one has to use γ -alumina under reducing atmosphere while at the same time reacting with nitrogen or ammonia under a temperature of higher than 1800 °C in order to produce AlON powder. As transparency cannot be simply obtained by pulverization, molding and sintering of the raw material, one has to resort to hot pressing at higher than 1600 °C or the use of hot isostatic press (HIP) at higher than 1600 °C. This makes production not economically feasible.

[0009] In view of the above, there exists a need for an improved protective material such as a ballistic resistant material and method of preparing the material that overcome or at least alleviate one or more of the abovementioned problems.

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SUMMARY

[0010] In a first aspect, a protective material comprising a rare-earth garnet ceramic is provided. The rare-earth garnet ceramic has general formula



wherein R^1 is selected from the group consisting of Y, Yb, and combinations thereof, and R^2 is selected from the group consisting of Eu, Gd, Tb, Ho, Tm, Lu, and combinations thereof, R^1 being present in an amount that is more than 90 atomic % of total amount of R^1 and R^2 , and R^2 being present in an amount that is 10 atomic % or less of total amount of R^1 and R^2 , and a is in the range from about 3 to about 3.015.

[0011] In a second aspect, a ballistic resistant article is provided. The ballistic resistant article comprises

- a) a polymeric support, and
- b) the protective material according to the first aspect attached to the polymeric support.

[0012] In a third aspect, use of the protective material according to the first aspect in goggles, safety glasses, personal protective equipment, window, screen, windscreen, panel, optical sensor, imager, windows of aircrafts, windows and bridges of ships, windows of building infrastructure, structural member of a military equipment or a vehicle, vehicles as jet fighter canopies, aircraft windows, helicopter canopies or windows; windows, barriers or doors in police or military installations, jails, schools, sport halls, prisons, or hospitals; protective shields for police or military personnel; lenses and windows in optical devices, goggles, safety glasses, windows, screens, eyeglass lenses, camera lenses, microscope lenses, telescope lenses; LED (light-emitting diode) lenses and windows; protective cover for watches and clocks; diffusers, protective and/or decorative covers and bulb materials for artificial lighting, automotive headlights, highway, parking lot lighting is provided.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

5 [0014] **FIG. 1A** is an optical image showing small cracks covering strike face of an yttrium aluminum garnet (YAG) ceramics tile.

[0015] **FIG. 1B** is an optical image showing back face of the panel depicted in **FIG. 1A** showing no penetration of the bullet.

[0016] **FIG. 2A** is an optical image showing a transparent ceramics armor panel.

10 [0017] **FIG. 2B** is an optical image showing a transparent ceramics armor panel.

[0018] **FIG. 3** is an optical image showing rare earth aluminum garnet ceramics of different size and shape.

[0019] **FIG. 4A** is an optical image showing strike face of a typical transparent armor panel, with multiple shots tested on the panel demonstrating its protection capability.

15 [0020] **FIG. 4B** is an optical image showing back face of the transparent armor panel depicted in **FIG. 4A**, with multiple shots tested on the panel demonstrating its protection capability.

DETAILED DESCRIPTION

20 [0021] A protective material according to embodiments disclosed herein has exhibited excellent scratch resistant properties at almost 3 times harder than glass, as well as excellent energy absorbing performance. The protective material according to embodiments may also possess high optical transparency, which renders their suitability for use in a wide range of applications for land, sea and air platforms, such as, but not limited to, in vehicles as jet
25 fighter canopies, aircraft windows, helicopter canopies and windows; protective windows, barriers and doors, such as for use in police and/or military installations such as prisons, and other installations such as schools, sport halls, hospitals, offices, and factories; protective shields for military and/or police personnel as a ballistic resistant or bullet proof material; lenses and windows in optical devices such as eyeglass lenses, goggles, camera lenses,
30 microscope and/or telescope lenses, LED (light-emitting diode) lenses and windows; protective cover for watches and clocks; diffusers, protective and/or decorative covers and

bulb materials for lightings, such as automotive headlights, highway and/or parking lot lighting.

[0022] The protective material disclosed herein is also suitable as a ballistic resistant material. Conventionally, a high degree of hardness has been considered as a pre-requisite for ballistic resistant materials. Though not having a degree of hardness considered suitable for functioning as a ballistic resistant material, it has been surprisingly found by the inventors that rare-earth garnet type ceramics may function as a ballistic resistant material, as they possess sufficient ballistic resistant properties due to their excellent energy absorbing performance. By attaching tiles of the rare-earth garnet ceramic onto a polymeric support to form a panel, for example, it has been demonstrated herein that the panel comprising the rare-earth garnet ceramic may withstand multiple shots. This compares favorably against conventional hard materials such as sapphire single crystals and spinel ceramics, as they may not be able to achieve such performance, or may demonstrate large area loss of visual clarity upon ballistic impact. The protective material disclosed herein may accordingly be used as a ballistic resistant material or a bullet proof material in various applications, for example, in the fabrication of goggles, safety glasses, personal protective equipment, window, screen, windscreen, panel, optical sensor, imager, structural member of a military equipment or a vehicle, to name only a few.

[0023] With the above in mind, various embodiments refer in a first aspect to a protective material. As used herein, the term “protective material” refers to a material which is able to provide a defense or shield of an object to be protected from harm. For example, the protective material may hinder destruction and/or damage to, or exposure of the object by functioning as a physical barrier to inhibit direct contact between an outer surface of the object and its environment.

[0024] The protective material may comprise a rare-earth garnet ceramic. In various embodiments, the term “rare-earth garnet ceramic” refers to rare earth ceramics having the general formula $(R^1R^2)_aAl_5O_{12}$.

[0025] The term “rare-earth” refers generally to an element of the lanthanide and of the actinide series. Accordingly, in various embodiments, the rare-earth refers to an element selected from the group consisting of yttrium (Y), ytterbium (Yb), europium (Eu), gadolinium (Gd), terbium (Tb), holmium (Ho), thulium (Tm), lutetium (Lu), and combinations thereof.

[0026] As disclosed herein, rare-earth elements Y and/or Yb, and optionally Eu, Gd, Tb, Ho, Tm, and/or Lu are used to form the rare-earth garnet ceramic.

[0027] As the stoichiometric compositions of rare-earth garnet ceramic may have a very narrow solid solution region, a change in chemical composition may have a significant effect on optical and mechanical characteristics of the rare-earth garnet ceramic, and in turn the protective material.

[0028] Referring to the above formula, R^1 may be selected from the group consisting of Y, Yb, and combinations thereof, and may be present in an amount that is more than 90 atomic % of the total amount of R^1 and R^2 . For example, R^1 may be present in an amount that is at least 91, at least 92, at least 93, at least 95, at least 97, or at least 99 atomic % of the total amount of R^1 and R^2 . In various embodiments, R^1 is present in an amount in the range of about 91 atomic % to about 99 atomic %, about 92 atomic % to about 99 atomic %, about 95 atomic % to about 99 atomic %, about 97 atomic % to about 99 atomic %, about 91 atomic % to about 97 atomic %, about 91 atomic % to about 95 atomic %, about 91 atomic % to about 93 atomic %, or about 93 atomic % to about 97 atomic % of the total amount of R^1 and R^2 .

[0029] R^1 and R^2 make up the total amount of R^1 and R^2 , i.e. they add up to 100 atomic %. This means that when R^1 is at x atomic % for example, R^2 is at $(100 - x)$ atomic %. In some embodiments, R^2 is not present, i.e. R^1 is present as 100 atomic % of total amount of R^1 and R^2 . Advantageously, Y and/or Yb may confer stable optical and mechanical characteristics on the protective material, and render the process of manufacturing the protective material economically viable.

[0030] In specific embodiments, R^1 is Y. Accordingly, the rare-earth garnet ceramic may have formula $(YR^2)_aAl_5O_{12}$, with R^2 and a as being defined above. Advantageously, as relative weight of Y is lower than Yb, protective materials comprising Y may be preferred in applications since it is lighter.

[0031] R^2 is optionally present, and may be considered a rare-earth dopant of the rare-earth garnet ceramic. In various embodiments, R^2 is selected from the group consisting of Eu, Gd, Tb, Ho, Tm, Lu, and combinations thereof. When present, amount of R^2 may be 10 atomic % or less of total amount of R^1 and R^2 . For example, R^2 may be present in an amount that is 8 % or less, 6 % or less, 4 % or less, 2 % or less of total amount of R^1 and R^2 . In some embodiments, R^2 is not present in the rare-earth garnet ceramic, i.e. the rare-earth garnet ceramic has general formula $R^1_aAl_5O_{12}$.

[0032] a may be in the range from about 3 to about 3.015, such as about 3.005 to about 3.015, about 3.01 to about 3.015, about 3 to about 3.01, or about 3.005 to about 3.01. In various embodiments, a is 3.

[0033] The rare-earth garnet ceramic may comprise at least one of $\text{Y}_3\text{Al}_5\text{O}_{12}$ or $\text{Yb}_3\text{Al}_5\text{O}_{12}$ having purity of at least 99.8 %. By the term “purity”, this means that at least one of $\text{Y}_3\text{Al}_5\text{O}_{12}$ or $\text{Yb}_3\text{Al}_5\text{O}_{12}$ may constitute at least 99.8 % by weight of the rare-earth garnet ceramic. The at least one of $\text{Y}_3\text{Al}_5\text{O}_{12}$ or $\text{Yb}_3\text{Al}_5\text{O}_{12}$ may constitute at least 99.8 % by weight of the rare-earth garnet ceramic, such as at least 99.9 % or 100 % by weight of the rare-earth garnet ceramic. From the results obtained herein, the protective abilities of $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Yb}_3\text{Al}_5\text{O}_{12}$ are similar. From the perspective of weight, however, relative weight of $\text{Y}_3\text{Al}_5\text{O}_{12}$ is 4.55 g/cm^3 , which is lighter than the relative weight of 6.63 g/cm^3 for $\text{Yb}_3\text{Al}_5\text{O}_{12}$. For this reason, $\text{Y}_3\text{Al}_5\text{O}_{12}$ may be preferred in applications since it is lighter.

[0034] The rare earth garnet ceramic may be made up of multiple grains connected in a continuous network. The term “grain” is used herein to describe an internal structure of the protective material, and refers to individually recognizable crystals or particles that form the continuous matrix of the material. To prepare the protective material, a sintering agent may be added. The term “sintering agent” as used herein refers to a material that is capable of enhancing densification of the rare-earth garnet ceramics. Advantageously, sintering time of the protective material may be shortened by using a sintering agent. Transparency of the protective material may also be improved.

[0035] In some embodiments, the sintering agent is at least one of a metal oxide or a metal fluoride. The sintering agent may, for example, be selected from the group consisting of SiO_2 , MgO , CaO , MgF_2 , CaF_2 , YF_3 , AlF , and combinations thereof.

[0036] In various embodiments, the sintering agent constitutes less than 1000 ppm of the protective material. For example, the sintering agent may constitute less than 900 ppm, less than 800 ppm, less than 700 ppm, less than 600 ppm, less than 500 ppm, less than 400 ppm, less than 300 ppm, less than 200 ppm, or less than 100 ppm of the protective ballistic resistant material.

[0037] Mechanical characteristics of the protective material may be varied by varying grain size of the rare-earth garnet ceramic. This allows tailoring of the protective material to specific requirements of intended application. Advantageously, a decrease in grain size of the rare-earth garnet ceramic may provide improved mechanical characteristics. The grain size

may be affected by composition of the rare-earth garnet ceramic. For example, grain size may be affected by the presence or absence of additives at the same composition. While addition of sintering agent may have effect of shortening the sintering time, average grain size may still be kept to within 20 μm .

5 [0038] As the grains may not be regular in shape and/or be of the same shape, the term “size” as used herein refers to the maximal length of a line segment passing through the centre and connecting two points on the periphery of grains. Average size of the grains may be calculated by dividing the sum of a maximal length of each grain by the total number of grains.

10 [0039] For example, the rare-earth garnet ceramic may comprise grains having an average size in the range of about 1 μm to about 20 μm , such as about 3 μm to about 20 μm , about 5 μm to about 20 μm , about 8 μm to about 20 μm , about 10 μm to about 20 μm , about 12 μm to about 20 μm , about 15 μm to about 20 μm , about 1 μm to about 15 μm , about 1 μm to about 12 μm , about 1 μm to about 10 μm , about 1 μm to about 8 μm , about 5 μm to about 15 μm , or about 8 μm to about 12 μm . In specific embodiments, average grain size of the rare-earth garnet ceramic is in the range of about 1 μm to about 5 μm .

[0040] In various embodiments, grain size of the protective material is closely related to ballistic resistance or bullet-resistance performance. As mentioned above, a protective material according to embodiments disclosed herein may be used as a ballistic resistant material. The term “ballistic resistant material” as used herein refers to a material which is able to absorb or resist impact of a moving object, such as a projectile. Although it may not be completely impenetrable to all types of projectiles under different situations, the ballistic resistant material as described herein is intended to stop, or at least severely retard, the progress of a projectile, such as a bullet. In some embodiments, the ballistic resistant material functions as a bullet-proof material.

25 [0041] In various embodiments, the protective material further comprises one or more pores. Air gaps or voids in and between the grains of the rare-earth garnet ceramic are referred to herein as pores within the rare-earth garnet ceramic.

[0042] As in the case for grains, the pores may not be regular in shape and/or be of the same shape. The term “size” for pores may accordingly refer to the maximal length of a line segment passing through the centre and connecting two points on the periphery of a pore.

Average size of the pores may be calculated by dividing the sum of a maximal length of each pore by the total number of pores.

[0043] In various embodiments, the one or more pores have an average size of about 100 μm or less. For example, the one or more pores may have an average size of about 80 μm or less, about 60 μm or less, about 40 μm or less, about 20 μm or less, or about 10 μm or less. In some embodiments, average pore size of the rare-earth garnet ceramic is about 100 μm or less, preferably less than 5 μm . Size of the pores may be minimized using a pressure compacting process or a high pressure sintering process, such as Hot Press and/or hot isostatic press (HIP) for sintering.

[0044] As pores in the protective material may affect optical characteristics, therefore, from an optics perspective, it is better to have a lesser number of pores. From the perspective of protective performance, however, zero pores may reduce protective performance such as ballistic-resistance as a portion of void or pores may function as crack absorbance band. It has been found by the inventors that an average pore size of about 10 μm or less is the best condition for both optical and mechanical strength aspects.

[0045] The protective material may have a pore volume in the range of about 10 ppm to about 1000 ppm, such as about 50 ppm to about 1000 ppm, about 100 ppm to about 1000 ppm, about 200 ppm to about 1000 ppm, about 500 ppm to about 1000 ppm, about 800 ppm to about 1000 ppm, about 10 ppm to about 800 ppm, about 10 ppm to about 600 ppm, about 10 ppm to about 400 ppm, about 10 ppm to about 200 ppm, about 100 ppm to about 800 ppm, about 200 ppm to about 600 ppm, or about 300 ppm to about 500 ppm.

[0046] As mentioned above, both mechanical and optical characteristics are important parameters for the protective material disclosed herein. In various embodiments, the protective material disclosed herein has the same level of mechanical strength as single crystal for high bullet-resistance.

[0047] For example, the protective material may have a three-point bending strength in the range of about 150 MPa to about 450 MPa, such as about 200 MPa to about 450 MPa, about 300 MPa to about 450 MPa, about 350 MPa to about 450 MPa, about 150 MPa to about 400 MPa, about 150 MPa to about 350 MPa, about 150 MPa to about 300 MPa, about 150 MPa to about 250 MPa, about 250 MPa to about 350 MPa, or about 300 MPa to about 400 MPa.

[0048] For optical applications, surfaces of the protective material may be mirror polished so that the protective material may have an optical transmittance of more than 65 %. This

may be measured on a sample of the protective material having a thickness of about 1 cm and using a radiation having a wavelength of about 550 nm. Depending on the composition of the protective material, for example, 80 % to about 84 % may be a theoretical limit regarding optical transmittance of the protective material. As such, optical transmittance of the protective material disclosed herein may be in the range of about 65 % to about 84 %, such as about 65 % to about 80 %, or about 65 % to about 75 %, as measured on a sample of the protective material having a thickness of about 1 cm and using a radiation having a wavelength of about 550 nm. At these linear optical transmittances, an end user may be able to see through the protective material.

[0049] As mentioned above, the protective material according to embodiments disclosed herein has exhibited excellent scratch resistant properties and energy absorbing performance, and may also possess high optical transparency. These attributes may render their suitability for use in applications such as, but not limited to, in vehicles as jet fighter canopies, aircraft windows, helicopter canopies and windows; protective windows, barriers and doors, such as for use in police and/or military installations such as prisons, and other installations such as schools, sport halls, hospitals, offices, and factories; protective shields for military and/or police personnel as a ballistic resistant or bullet proof material; lenses and windows in optical devices such as eyeglass lenses, goggles, camera lenses, microscope and/or telescope lenses, LED (light-emitting diode) lenses and windows; protective glass for watches and clocks; diffusers, protective and/or decorative covers and bulb materials for lightings, such as automotive headlights, highway and/or parking lot lighting.

[0050] In various embodiments, the protective material disclosed herein may be used as a ballistic resistant material in the fabrication of goggles, safety glasses, personal protective equipment, window, screen, windscreen, panel, optical sensor, imager, structural member of a military equipment or a vehicle.

[0051] Accordingly, various embodiments refer in a further aspect to a ballistic resistant article. The ballistic resistant article may comprise a polymeric support attached to the protective material disclosed herein.

[0052] Choice of the polymeric support is not particularly limited, and may comprise a polymer selected from the group consisting of acrylic, perspex, butyrate, polycarbonates, copolymers thereof, and combinations thereof.

[0053] One or more tiles comprising the protective material may be attached to the polymeric support. As used herein, the term “tile” refers to a relatively thin and substantially planar object having two principal sides lying in planes that are substantially parallel. The sides may be joined together by at least three and usually four, sides or peripheral sides which are small in relation to the areas of the principal sides.

[0054] In various embodiments, the one or more tiles has a shape capable of tessellation. Although tiles are generally rectangular or square in shape, they may have more or less than four peripheral faces and may have shapes such a square, a rectangle, or a hexagon. Generally, a regular polygon shape such as a square, a rectangle or a hexagon is preferred as this may provide flexibility in arrangement of the tiles on the polymeric support to form the ballistic-resistant article. In some embodiments, a circular tile of the protective material may be attached to the polymeric support and used singularly.

[0055] Depending on the size and type of the bullets, it is possible to adjust the tile thickness to raise or lower the protection level. A thickness of less than 10 mm, for example, may be good enough to protect against 7.62 mm rounds. Transparency requirements, however, may limit material thickness to less than 25 mm, hence it may be preferable to use a thickness that is less than 25 mm.

[0056] Accordingly, the one or more tiles comprising the protective material may have a thickness that is less than 25 mm, such as about 0.1 mm to about 25 mm, about 0.5 mm to about 25 mm, about 5 mm to about 25 mm, or about 10 mm to about 25 mm.

[0057] Although tile size of the protective material is not particularly constrained, in practice, probability of bullets hitting the same tile may be higher for a tile having an area greater than $10 \times 10 \text{ cm}^2$. As such, it may be difficult for the same tile to protect against multiple shots. Furthermore, the fabrication yield and cost may become problematic. By using relatively small area tiles of the protective material and attaching them to a polymeric support to form the ballistic resistant article, the bonding of multiple tiles into a single panel allows multi-shot protection, though the shots may not be on the same point.

[0058] Accordingly, in various embodiments, the one or more tiles comprising the protective material have a cross-sectional area in the range of about 16 cm^2 to about 100 cm^2 and an aspect ratio of 2 or less. Advantageously, the specified cross-sectional area and aspect ratio may avoid damage to surrounding tiles due to ballistic impact, which may otherwise take place for a tile area smaller than 16 cm^2 and aspect ratio greater than 2.

[0059] As mentioned above, the one or more tiles comprising the protective material may be attached to the polymeric support. In various embodiments, the one or more tiles comprising the protective material are attached to the polymeric support by an adhesive. Any suitable adhesives that are within the knowledge of the person skilled in the art may be used, so long as the adhesive holds the protective material and the polymeric support together. Examples of such adhesives may include, but are not limited to polyurethane, polyvinyl acetate, epoxy, cyanoacrylate or combinations thereof. In some embodiments, epoxy or polyurethane may be used to bond the protective material to the polymeric support.

[0060] As the ballistic resistant article may have a refractive index of around 1.80, in specific embodiments, the one or more tiles comprising the protective material are attached to the polymeric support by an adhesive having a refractive index in the range of about 1.7 to about 1.9. In so doing, this may avoid refractive index mismatch at the bonding interfaces, which may be the case for normal adhesives having refractive index of around 1.4. Such adhesives may, for example, have a main composition of organic materials or a mixture of organic material and inorganic particles with refractive indices greater than 2.0 and sizes smaller than 100 nm. In this way, problem(s) relating to visual discomfort due to the joints may be mitigated.

[0061] In various embodiments, the adhesive has a refractive index in the range of about 1.7 to about 1.9, about 1.7 to about 1.8, or about 1.75 to about 1.85. Examples of an adhesive that may have a refractive index in this range may include cyanoacrylates and/or nanoparticles doped adhesives. Accordingly in some embodiments, the adhesive is selected from the group consisting of cyanoacrylates, nanoparticles doped adhesives, and combinations thereof.

[0062] The one or more tiles comprising the protective material may be arranged to form a panel. By the term “panel”, it is meant an arrangement of the one or more tiles comprising the protective material such that they are placed adjacent to each other so as to cover a larger area for various applications.

[0063] In various embodiments, the ballistic resistant article is a goggle, a safety glass, personal protective equipment, window, screen, windscreen, panel, optical sensor, imager, structural member of a military equipment or a vehicle, such as a helicopter, an airplane, a car, a tank, a boat, a ship, to name only a few.

[0064] Various embodiments refer to a method of preparing the protective material disclosed herein, which is provided herein for purposes of illustration only.

[0065] The method may comprise preparing a mixture comprising aluminum oxide and an oxide of R^1 in a suitable solvent, where R^1 is as defined above. In various embodiments, the oxide of R^1 is selected from the group consisting of Y_2O_3 , Yb_2O_3 , and combinations thereof. In some embodiments, the oxide of R^1 comprises Y_2O_3 .

[0066] Examples of suitable solvent include, but are not limited to, alcohol based solvents such as methanol, ethanol, and/or propanol, to name only a few.

[0067] The aluminum oxide and the oxide of R^1 may independently have a size in the range of about 1 μm to about 10 μm , such as about 3 μm to about 10 μm , about 5 μm to about 10 μm , about 7 μm to about 10 μm , about 1 μm to about 8 μm , about 1 μm to about 5 μm , about 1 μm to about 3 μm , about 3 μm to about 8 μm , or about 4 μm to about 6 μm .

[0068] In various embodiments, the mixture further comprises an oxide of R^2 , where R^2 is as defined above. In various embodiments, R^2 is selected from the group consisting of Eu, Gd, Tb, Ho, Tm, Lu, and combinations thereof. As mentioned above, R^2 is optionally present, and may function as a rare-earth dopant of the rare-earth garnet ceramic.

[0069] In various embodiments, the mixture further comprises a sintering agent. Examples of suitable sintering agent have already been discussed above.

[0070] The method may include physically working the mixture to form a slurry. Physically working the mixture may be carried out by any suitable technique, such as milling, ball milling, and/or grinding.

[0071] In various embodiments, physically working the mixture is carried out by ball milling. The ball milling may be carried out, for example, at a speed in the range of about 10 to about 100 rpm, and for a time period in the range of about 1 hour to about 48 hours.

[0072] The slurry may be dried to form a powder. Drying the slurry may be carried out using any suitable techniques, such as by oven drying or spray drying.

[0073] A pressure in the range of about 100 MPa to about 200 MPa, such as about 100 MPa to about 150 MPa, about 120 MPa to about 180 MPa or about 140 MPa to about 160 MPa, may be applied to the powder to form a compact, which may be carried out using a cold isostatic pressed (CIP) process.

[0074] Upon forming the compact, it may be heated in two steps by calcining the compact at a temperature in the range of about 500 °C to about 1000 °C, and sintering the compact

following calcination at a temperature in the range of about 1600 °C to about 1800 °C in vacuum to obtain the protective material.

[0075] The calcination step may be carried out for a time period sufficient to burn off organic constituents, and may be in the range of about 1 hour to about 12 hours. Sintering the compact following calcination, on the other hand, may be carried out for a time period sufficient to obtain transparency in the protective material, such as in the range of about 1 hours to about 50 hours.

[0076] Following sintering, a pressure in the range of about 100 MPa to about 200 MPa may be applied to the protective material at a temperature in the range of about 1600 °C to about 1800 °C to reduce the pore size within the ceramics. Advantageously, a smaller pore size within the ceramics may enhance mechanical strength of the protective material.

[0077] A surface of the protective material may be polished so as to improve transparency of the protective material. The polishing may be carried out using commercially available grinder and polisher as would be understood by a person of average skill in the art.

[0078] Various embodiments refer in a further aspect to use of the protective material according to the first aspect in goggles, safety glasses, personal protective equipment, window, screen, windscreen, panel, optical sensor, imager, windows of aircrafts, windows and bridges of ships, windows of building infrastructure, structural member of a military equipment or a vehicle, vehicles as jet fighter canopies, aircraft windows, helicopter canopies and windows; windows, barriers and doors in police and/or military installations, jails and prisons, hospitals; protective shields for police and/or military personnel; lenses and windows in optical devices, goggles, safety glasses, windows, screens, eyeglass lenses, camera lenses, microscope lenses, telescope lenses, LED (light-emitting diode) lenses and windows, protective glass for watches and clocks, diffusers, protective and/or decorative covers and bulb materials for artificial lighting, automotive headlights, highway, parking lot lighting and combinations thereof.

[0079] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0080] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

5

EXPERIMENTAL SECTION

[0081] Various embodiments relate generally to a rare-earth garnet ceramic, such as a transparent aluminum garnet ceramics with Y and/or Yb as the main composition, with high optical transmittance in the visible to infrared wavelength range and possessing excellent mechanical strength.

10

[0082] For example, the rare-earth garnet ceramic may comprise or consist of a transparent garnet material $(R^1R^2)_aAl_5O_{12}$, wherein R^1 is Y and/or Yb, and R^2 is one or more types of rare-earth selected from the group consisting of Eu, Gd, Tb, Ho, Tm, Lu, and combinations thereof, R^1 being present in an amount that is 90 % or more of total amount of R^1 and R^2 , R^2 being present in an amount that is 10 % or less of total amount of R^1 and R^2 , and a is in the range from about 3 to about 3.015.

15

[0083] The transparent garnet ceramic material may be $Y_3Al_5O_{12}$, $Yb_3Al_5O_{12}$, or their solid solution with purity of 99.8 % or higher.

20

[0084] The transparent garnet ceramic material may have average grain size within a range of 1 to 20 microns.

[0085] The transparent garnet ceramic material may have a residual pore amount in the range of 10 ppm to 1000 ppm and average pore size of smaller than 100 micron, or preferably, smaller than 5 microns.

25

[0086] The transparent garnet ceramic material may have a three-point bending strength in the range of about 150 MPa to 450 MPa.

[0087] The transparent garnet ceramic material may have an optical transmittance of more than 65 % for a thickness of 1 cm at 550 nm.

[0088] The transparent garnet ceramic material may be used as a transparent armor material.

30

[0089] The transparent garnet armour material may be made of transparent garnet ceramic tiles with an area in the range of about 16 cm² to 100 cm². The tiles may be bonded in a horizontal manner to form a plate, and be bonded into one piece of panel using a polymeric

backing material for application as a composite bullet-proof panel. For example, the bullet-proof panel may be made of tiles having a thickness of less than 25 mm, an area of between 16 cm² to 100 cm², and an aspect ratio of smaller than 2. The tiles may be bonded using transparent adhesives, which may be commercially available, and in combination with
5 polymeric material as a backing to form the whole transparent ceramics armor panel.

[0090] The transparent garnet ceramics tiles may have a shape structure that is not limited to just 4 sides like a square, and may include other tessellation structures such as hexagon, and rectangle. It can be used singularly as a circle. The tiles may be bonded using commercially available transparent adhesives, and may be bonded to a suitable polymeric
10 backing material to form the bullet-proof panel. The bullet-proof panel may have excellent bullet-resistance even in the case of two or more shots fired on the same panel.

[0091] The transparent garnet ceramic tiles disclosed herein may further be used in military systems that feature the application of bullet-proof protective screens such as protection for optical sensors and imagers, windows, windcreens, and panels; for platforms
15 which include but is not limited to various land, air and sea platforms such as for e.g. fighter jets, helicopters, airplanes, cars, armored vehicle windows, windows of boats and ships etc.

[0092] While naturally occurring garnets may be composed of oxides of Ca, Si, Al, Fe, etc., garnets may be prepared using various other elements from the periodic table. Amongst them, although rare-earth aluminum garnets may be used as materials for laser devices, they
20 cannot be applied as bullet-resistant materials. The reasons are:

[0093] (1) Material hardness is only half that of sapphire, and it lacks the ability to deform the bullet shot at its surface.

[0094] (2) It is widely believed that YAG single crystal and ceramics do not possess sufficient mechanical strength for bullet resistance. This is evident from the fact that the
25 development of bullet-resistant transparent ceramics has centered on spinel and AlON, while garnet materials have been excluded. The basic characteristics of bullet-resistant materials are in order of priority, (1) hardness (for eroding the bullet near the surface of the bullet-resistant material), followed by (2) mechanical strength and fracture toughness.

[0095] **Example 1: Mechanical Impact Test**

30 [0096] To understand the behavior of rare-earth aluminum garnet material in a mechanical impact test, an experiment was carried out as described below. AlON material was excluded from this study as it is not easily available.

[0097] When a steel ball with diameter of 5 cm was dropped from a height of 5 m onto Spinel, YAG ceramic, and single-crystal sapphire of sizes of $10 \times 10 \times 0.5$ cm, the inventors observed that all the materials were easily destroyed, and it was not possible to quantitatively determine the merits of the materials. Despite so, it was observed that the number of cracks created by the impact differed. Listing in ascending order from least amount of cracks to most amount of cracks, sapphire had the least amount of crack followed by Spinel, and YAG. The length of crack was longest for sapphire. It was observed that for YAG, the cracks were concentrated around the centre portion where impact with the steel ball occurred. The inventors determined that the propagation of the cracks was the least for YAG as it was hard for cracks to spread to the surrounding.

[0098] As it was not possible to obtain an accurate assessment on the bullet resistance characteristics via measuring the mechanical characteristics of material or low energy destruction test such as dropping a steel ball, a ballistic test was performed on a single tile encapsulated in a polymeric backing of 300×300 mm (the two sides of the tiles were mirror polished). At the rear-side of the tile, a polycarbonate was used as a backing material. The ballistic test was performed using a 7.62 mm bullet with the impact velocity at a speed of 800 m/s in a direction perpendicular to the tile surface. **TABLE 1** describes the results observed.

[0099] **TABLE 1:** Effect of a 7.62 mm bullet on the different materials tested.

	Sapphire Crystal	Spinel Ceramics	YAG Ceramics
Bullet penetration	No	No	No
Effect on tile	Long cracks cover tile area	Large cracks cover entire tile area	Small cracks cover tile area.

[00100] For all three materials, there is no penetration of the material. However, the lengths of cracks in the order of longest are Sapphire (longest), followed by Spinel and YAG. For YAG, the cracks were concentrated near the impact region, and it was characteristic that the cracks were smaller at the peripheral as shown in **FIG. 1A** and **FIG. 1B**.

[00101] Next, multiple tiles (all sides mirror polished) forming a 300 mm x 300 mm panel was tested. They were bonded at the 4 edges using commercially available adhesives. This was further bonded to a polymeric backing. The ballistic test was performed using a 7.62-mm round at a speed of 800 m/s in a perpendicular direction to the panel surface. The bullet was shot at the ceramic strike face and the observations are described in **TABLE 2**.

[00102] **TABLE 2:** Effect of a 7.62 mm round on a bonded panel comprising of different materials.

	Sapphire Crystal	Spinel Ceramics	YAG Ceramics
Bullet penetration	No	No	No
Effect on surrounding material	Long cracks cover surrounding tiles	Big cracks cover surrounding tiles	Small cracks on surrounding tiles.

[00103] Firing again at a neighboring damaged sapphire tile, the bullet penetrated. There were similar findings for Spinel. For YAG, the first shot had minor effects on surrounding tiles, and a bullet fired at an adjacent tile was blocked in the same way as the first bullet.

[00104] Conventional understanding regards hardness as the most important characteristic for bullet-resistance, but the actual shooting test did not align with conventional understanding, as unlike hard materials such as sapphire, AlON or Spinel, YAG is not a particularly hard material. Although rare-earth-doped aluminum garnet is not as hard as other materials, it has exhibited excellent energy absorbing performance as demonstrated herein. Various embodiments disclosed herein relate to rare-earth-doped aluminum garnet containing aluminum element being an extremely effective bullet-resistant material.

[00105] It may not be the case that any transparent rare-earth-doped aluminum garnet is good as a bullet-resistant material. In various embodiments disclosed herein, rare-earth elements Y and/or Yb were to form the garnet ceramics as a basic/principle composition. The rare-earth elements Y and/or Yb may confer ability to obtain stable optical and mechanical characteristics, and to render the process economically viable.

[00106] **FIG. 2** shows a panel made by bonding 16 pieces of tiles of 80 mm × 80 mm using adhesives. The joints are visible but it is not a problem practically.

[00107] **Example 2: General preparation method**

[00108] To achieve the desired characteristics economically, one could mix oxides with the targeted composition, followed by sintering.

[00109] In examples to fabricate $Y_3Al_5O_{12}$, Y_2O_3 powder (particle size ≥ 1 micron) and Al_2O_3 (particle size ≥ 1 micron) in right weight proportion were used for forming garnet. Milling balls with suitable quantity of solvents as pulverization and mixing media, were mixed together with additives, and milled from a few hours to tens of hours depending on the mixing requirements. Sintering agents such as MgO, CaO, MgF_2 , CaF_2 , AlF, and/or SiO_2

with weight% of less than 1000 ppm may also be added. The slurries obtained were spray-dried to form powders.

[00110] The powders were molded into desired green compact forms, and finally cold isostatic pressed (CIP) in the pressure range of about 100 MPa to about 200 MPa.

5 [00111] To burn off organic constituents, the compacts were first calcined using temperatures in the range from a few hundred degrees up to a 1000 degrees Celsius. After that, they were sintered in vacuum from a few hours to tens of hours under a temperature in the range of about 1600 °C to about 1800 °C to obtain transparency. HIP was applied at a pressure of 100 MPa to 200 MPa between 1600 °C to 1800 °C for another few hours.

10 [00112] Transparent tiles were obtained by polishing the surface of the sintered body, which were carried out using commercially available grinder and polisher. Transparent panels were obtained by bonding the polished tiles on the edges with adhesives to form a flat transparent ceramics panel and then bonding the ceramics panel to a polymeric support.

[00113] Notwithstanding the above, it should be noted that as long as the characteristics of the ballistic resistant material as presently claimed are fulfilled, there are no particular restrictions imposed on the fabrication method.

[00114] **Example 3: Characterization**

[00115] To inspect the material disclosed herein, the material composition was analyzed with X-ray fluorescence (XRF), or for the case of powder, X-ray diffraction (XRD), to
20 quantify the garnet or rare-earth amounts.

[00116] Average grain size of the ceramic was measured by thermal etching of mirror polished material to expose the grain boundary part, and then using scanning electron microscopy (SEM) to observe 10 random positions to obtain the grain size via image analysis.

25 [00117] Amount of residual pores was measured either by visually observing the size and number of voids or by image analysis of a two-side mirror-polished sample under an optical microscope.

[00118] The bending strength was measured in accordance to ASTM (American Standard Testing Method), and may be measured using any relevant international standard.

30 [00119] The transmittance was measured by preparing a 10 mm thick mirror-polished sample and using a commercially available UV-vis spectrophotometer.

[00120] **Example 4: Implementation examples**

[00121] To verify the effect of embodiments exemplified herein, the inventors fabricated materials as illustrated in **FIG. 3**, and having different characteristics as listed in **TABLE 3** to **TABLE 8** (the inventors used test samples where each piece is 40 X 40 mm with both faces mirror polished).

5 [00122] **TABLE 3:** Vacuum Sintered rare-earth aluminum garnet ceramics

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Chemical composition	$(\text{Eu}_{0.15}\text{Y}_{.85})_3\text{Al}_5\text{O}_{12}$	$(\text{Gd}_{0.15}\text{Y}_{.85})_3\text{Al}_5\text{O}_{12}$	$(\text{Ho}_{0.15}\text{Y}_{.85})_3\text{Al}_5\text{O}_{12}$	$(\text{Tm}_{0.05}\text{Y}_{.95})_3\text{Al}_5\text{O}_{12}$	$(\text{Lu}_{0.30}\text{Y}_{.70})_3\text{Al}_5\text{O}_{12}$
Average grain size (micron)	7	4	6	3	5
Residual air pore volume (ppm)	500	400	100	150	700
Average air pore diameter (micron)	50	30	80	90	80
Bending strength (MPa)	250	270	280	290	260
Transmittance %/cm@550 nm	66	68	73	76	71
Bullet penetration	No	No	No	No	No

[00123] **TABLE 4:** Vacuum sintered YAG, YbAG and YAG-YbAG ceramics

	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Chemical composition	$\text{Y}_3\text{Al}_5\text{O}_{12}$	$\text{Yb}_3\text{Al}_5\text{O}_{12}$	$\text{Y}_{2.40}\text{Yb}_{0.60}\text{Al}_5\text{O}_{12}$	$\text{Y}_{1.50}\text{Yb}_{1.50}\text{Al}_5\text{O}_{12}$	$\text{Y}_{0.60}\text{Yb}_{2.40}\text{Al}_5\text{O}_{12}$
Average grain size (micron)	18	10	10	11	12
Residual air pore volume (ppm)	380	620	100	280	440
Average air pore diameter (micron)	95	80	70	30	15
Bending strength (MPa)	260	250	270	260	250
Transmittance %/cm@550nm	69	69	71	72	70
Bullet	No	No	No	No	No

penetration					
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[00124] **TABLE 5:** Sintered (Samples 11 and 12) and HIP sintered (Samples 13 to 15) YAG ceramics

	Sample 11	Sample 12	Sample 13	Sample 14	Sample 15
Chemical composition	$\text{Y}_{3.005}\text{Al}_5\text{O}_{12}$	$\text{Yb}_{3.015}\text{Al}_5\text{O}_{12}$	$\text{Yb}_{3.005}\text{Al}_5\text{O}_{12}$	$\text{Yb}_{3.010}\text{Al}_5\text{O}_{12}$	$\text{Yb}_{3.015}\text{Al}_5\text{O}_{12}$
Average grain size (micron)	8	6	3	2	1
Residual air pore volume (ppm)	120	150	10	20	10
Average air pore diameter (micron)	90	50	1	1	1
Bending strength (MPa)	290	280	390	400	420
Transmittance %/cm@550 nm	70	71	82	80	79
Bullet penetration	No	No	No	No	No

5 [00125] **TABLE 6:** HIP YAG ceramics

	Sample 16	Sample 17	Sample 18	Sample 19	Sample 20
Chemical composition	$\text{Y}_3\text{Al}_5\text{O}_{12}$	$\text{Yb}_3\text{Al}_5\text{O}_{12}$	$\text{Yb}_3\text{Al}_5\text{O}_{12}$	$\text{Yb}_3\text{Al}_5\text{O}_{12}$	$\text{Yb}_3\text{Al}_5\text{O}_{12}$
Average grain size (micron)	3	1	1	1	1
Residual air pore volume (ppm)	10	15	20	10	25
Average air pore diameter (micron)	1	1	1	1	1
Bending strength (MPa)	360	450	370	360	450
Transmittance %/cm@550 nm	79	82	83	84	81
Bullet penetration	No	No	No	No	No

[00126] **TABLE 7:** Test panels made from tiles of different sizes (4×4 pieces)

	Sample 21 Material of Sample 16	Sample 22 Material of Sample 16	Sample 23 Material of Sample 16	Sample 24 Material of Sample 16
Tile size (cm)	4×4	5×5	10×10	3×3
Bonding 16 pieces of the above tiles, and firing at centre area				
Bullet penetration	No	No	No	Yes
Effect on surrounding material	Cracks on 5 pieces of surrounding tiles	Some cracks on surrounding tiles	Mild cracks on surrounding tiles	Full destruction of 8 surrounding tiles (the rest of the tiles damaged)
	Sample 25 Material of Sample 16	Sample 26 Material of Sample 16	Sample 27 Material of Sample 16	Sample 28 Material of Sample 16
Tile size (cm)	10×5 (AR = 2.0)	6×4 (AR = 1.5)	10×3 (AR = 3.3)	8×3 (AR = 2.7)
Bonding of 16 pieces of the above tiles, and firing at centre area				
Bullet penetration	No	No	Yes	Yes
Effect on surrounding material	Mild cracks on surrounding tiles	Mild cracks on surrounding tiles	Full destruction of 4 surrounding tiles (the rest of the tiles damaged)	Full destruction of 4 surrounding tiles (the rest of the tiles damaged)

[00127] **TABLE 7** lists panels that were formed by bonding 16 pieces of fabricated tiles using adhesives, where the tiles have different sizes. The panels were all bonded to polymeric backing and their bullet resistance were evaluated under conditions the same as those in **TABLE 3** to **TABLE 6**.

[00128] For panels that are made of 16 pieces of tiles ($t = 6$ mm), bullet-resistance may only be possible for tile sizes of greater than 3×4 cm. For tile sizes smaller than this, it may be difficult for a tile to absorb all the energy and therefore surrounding tiles may either be fully destroyed or extensively damaged. Even for the exact same material, the extent of damage may depend on the tile size.

[00129] **TABLE 8:** Vacuum Sintered YAG ceramics

Chemical composition	$\text{Y}_3\text{Al}_5\text{O}_{12}$	$\text{Yb}_3\text{Al}_5\text{O}_{12}$	$\text{Y}_3\text{Al}_{5.02}\text{O}_{12}$	$\text{Y}_3\text{Al}_{5.05}\text{O}_{12}$	1 % excess Al_2O_3 -YAG
Average grain size (micron)	25	5	30	60	3
Residual air	900	1100	20	800	1500

pore volume (ppm)					
Average air pore diameter (micron)	6	4	110	1	50
Bending strength (MPa)	240	250	140	360	450
Transmittance %/cm@550 nm	65	65	37	44	81
Bullet penetration	Yes	Yes	Yes	Yes	Yes

[00130] The shooting test followed the procedure described earlier. The panel is 4×4 pieces of test tiles bonded with adhesives and with a polymeric backing material similar to that illustrated in **FIG. 1**.

5 [00131] Through application of various embodiments disclosed herein, not only is it possible to provide bullet-proof panel with high energy absorbing ability unavailable from conventional materials, the panel that is obtained by bonding relatively small tiles is furthermore able to withstand multiple shots and hence provides much higher probability of protecting lives. Moreover, the fabrication of rare-earth aluminum garnet tiles is much less
 10 costly compared to the fabrication costs of sapphire single crystal, AlON, Spinel ceramics, etc., and hence, it is also highly advantageous economically.

[00132] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing
 15 from the spirit and scope of the present invention as defined by the following claims.

CLAIMS

1. A protective material comprising a rare-earth garnet ceramic having general formula



wherein

- 10 a) R^1 is selected from the group consisting of Y, Yb, and combinations thereof, and R^2 is selected from the group consisting of Eu, Gd, Tb, Ho, Tm, Lu, and combinations thereof, R^1 being present in an amount that is more than 90 atomic % of total amount of R^1 and R^2 , and R^2 being present in an amount that is 10 atomic % or less of total amount of R^1 and R^2 , and a is in the range from 3.005 to 3.015, or
- 15 b) R^1 is Yb, or a combination of Y and Yb, and R^2 is selected from the group consisting of Eu, Gd, Tb, Ho, Tm, Lu, and combinations thereof, R^1 is present in an amount that is more than 90 atomic % and less than 100 atomic % of total amount of R^1 and R^2 , and R^2 is present in an amount that is greater than 0 atomic %, and 10 atomic % or less of total amount of R^1 and R^2 , and a is in the range from 3 to 3.015.
- 20
2. The protective material according to claim 1, wherein a is 3 in b).
3. The protective material according to claim 1 or 2, further comprising a sintering agent of at least one of a metal oxide or a metal fluoride selected from the group consisting of SiO_2 , MgO, CaO, MgF_2 , CaF_2 , YF_3 , AlF, and combinations thereof.
- 25
4. The protective material according to claim 3, wherein the sintering agent constitutes less than 1000 ppm of the protective material.
- 30 5. The protective material according to any one of claims 1 to 4, wherein the rare-earth garnet ceramic comprises grains having an average size in the range of 1 μm to 20 μm .

6. The protective material according to any one of claims 1 to 5, wherein the rare-earth garnet ceramic comprises pores having an average size of 100 μm or less, preferably less than 5 μm .
5
7. The protective material according to claim 6, wherein the protective material has a pore volume in the range of 10 ppm to 1000 ppm.
8. The protective material according to any one of claims 1 to 7, wherein the protective
10 material has a three-point bending strength in the range of 150 MPa to 450 MPa.
9. The protective material according to any one of claims 1 to 8, wherein the protective material has an optical transmittance of more than 65 %, as measured on a sample of the protective material having a thickness of 1 cm and using a radiation having a
15 wavelength of 550 nm.
10. The protective material according to any one of claims 1 to 9, wherein the protective material is a ballistic-resistant material.
- 20 11. A ballistic resistant article comprising
 - a) a polymeric support, and
 - b) the protective material according to any one of claims 1 to 10 attached to the polymeric support.
- 25 12. The ballistic resistant article according to claim 11, wherein the protective material is in the form of one or more tiles having a thickness of less than 25 mm.
13. The ballistic resistant article according to claim 12, wherein the one or more tiles have a cross-sectional area in the range of 16 cm^2 to 100 cm^2 and an aspect ratio of 2 or
30 less.

14. The ballistic resistant article according to claim 12 or 13, wherein the one or more tiles has a shape capable of tessellation.
- 5 15. The ballistic resistant article according to any one of claims 11 to 14, in the form of goggles, safety glasses, personal protective equipment, window, screen, windscreen, panel, optical sensor, imager, windows of aircrafts, windows and bridges of ships, windows of building infrastructure, structural member of a military equipment or a vehicle.
- 10 16. Use of the protective material according to any one of claims 1 to 10 in goggles, safety glasses, personal protective equipment, window, screen, windscreen, panel, optical sensor, imager, windows of aircrafts, windows and bridges of ships, windows of building infrastructure, structural member of a military equipment or a vehicle, vehicles as jet fighter canopies, aircraft windows, helicopter canopies or windows;
15 windows, barriers or doors in police or military installations, jails, schools, sport halls, prisons, or hospitals; protective shields for police or military personnel; lenses and windows in optical devices, goggles, safety glasses, windows, screens, eyeglass lenses, camera lenses, microscope lenses, telescope lenses; LED (light-emitting diode) lenses and windows; protective cover for watches and clocks; diffusers, protective
20 and/or decorative covers and bulb materials for artificial lighting, automotive headlights, highway, parking lot lighting.