Intrinsic broadband white-light emitting phosphors and a solution-state method for producing them are disclosed. Emitters in accordance with the present invention include layered perovskite-based phosphors that comprise metals and halides and have an emission spectrum that spans the entire visible-light spectrum.
Two-Dimensional Perovskite Phosphor and Method of Formation

Cross Reference to Related Applications


Field of the Invention

[0002] The present invention relates to electronic devices in general, and, more particularly, to solid-state light sources.

Background of the Invention

[0003] Incandescent and fluorescent light sources have been the mainstay of traditional lighting for residential and commercial applications for many decades. Unfortunately, these light sources have inherent energy inefficiencies, which have driven a search for improved light sources as the "green revolution" has progressed.

[0004] Because solid-state lighting (SSL) sources promise improved energy efficiency, they have become attractive alternatives to traditional lighting. The transition to SSL has been projected to reduce global electricity used for lighting by 50% by the year 2025. In addition, unlike most traditional lighting sources, the emission wavelengths from many SSL light sources can be controlled to effect a desired "color temperature."

[0005] Color temperature refers to the color characteristics of light. Light whose hue tends toward yellow (e.g., that emitted by tungsten-based household incandescent lamps) is typically considered "warm," while light having a hue that is more toward blue (e.g., that emitted by conventional fluorescent lamps) is typically considered "cool." The Color Rendering Index (CRI) is a scale, from 1 to 100, that is based on the ability of a light source to accurately render all colors of its spectrum (as compared to a "perfect" black-body light source). The lower a source's CRI rating, the less accurately colors will be reproduced by
that source. Normally, a CRI of at least 90 is considered desirable, and indoor light applications typically require CRI values of at least 80.

[0006] Conventional SSL sources that are based on rare-earth-doped phosphors (e.g., Ce$^{3+}$-activated yellow phosphors, etc.) are excited into emission by absorption of light from blue-wavelength light-emitting diodes (LEDs). These sources generally have poor color rendering properties because they employ phosphors that do not emit across the entire visible light spectrum. Such prior-art phosphors typically lack a red component in their output light; therefore, they produce a white light that appears cold to the eye (i.e., its hue is more "bluish"). CRI indices greater than 90 have been realized in multi-phosphor systems, but these systems generally suffer from poor efficiency due to self-absorption. In addition, the different individual phosphors degrade at a different rates, leading to white light that becomes colored over time. Further, single and mixed phosphors require synthesis at high temperature (typically 1300-1900$^\circ$ C), making their production complex and expensive.

[0007] To circumvent these problems, there has been recent emphasis on research into single-phase broadband white-light emitting phosphors suitable for SSL sources. Two-dimensional, cadmium-sulfide/selenide materials offer some promise and examples of such phosphors are described by W. Ki, et al., in "A Semiconductor Bulk Material That Emits Direct White Light," J. Am. Chem. Soc, Vol. 130, page 8114 (2008). These materials demonstrated that a photoluminescence quantum efficiency (PLQE) of 4-5% could be achieved. The inclusion of cadmium, however, is generally considered undesirable due to its toxicity.

[0008] It has been shown that, by using substitution chemistry, Mn$^{2+}$ doping, and crystal engineering, PLQE can be improved by up to 37%, as reported by M. Roushan, et al., in "Solution-Processable White-Light-Emitting Hybrid Semiconductor Bulk Materials with High Photoluminescence Quantum Efficiency," Chem., Int. Ed., Vol. 51, page 436 (2012). Unfortunately, while these results show progress toward a suitable white-light-emitting phosphor, the reported materials are expensive to synthesize, lack highly defined structure, and include materials that are toxic to humans.

[0009] Other emerging SSL technologies include cadmium-selenide nanocrystal-based sources. Nanostructures characterized by high surface-to-volume ratio (e.g. 1.5-nm quantum dots) have shown white-light emission due to surface states that lead to sub-
band-gap electronic states. Quantum-dot sources based on this technology have shown excellent color-rendering properties. Unfortunately, particle aggregation can quench emission; therefore, a dispersive polymer is typically required to prevent such aggregation. Most polymers, however, tend to degrade rapidly under constant exposure to ultraviolet light, thereby limiting the lifetime of these sources. In addition, as mentioned above, the toxicity of cadmium represents an additional disadvantage in such devices. Further, in order to realize nanocrystals having precise size, complex processing techniques are needed making these sources expensive.

[0010] To date, a viable single-phase, low-cost, long-term-stable, white-light-emitting phosphor has yet to be realized.

**Summary of the Invention**

[0011] The present invention makes possible cost-effective, single-phase, white-light emitting SSL light sources by enabling low-cost, broad band-emission, single-source, white-light phosphors suitable for use with ultraviolet light-emitting diode excitation sources. Phosphors in accordance with the present invention have a two-dimensional perovskite-based crystal structure, have emission spectra that can span the entire visible-light spectrum, and can be formed in a low-cost, solution-state synthesis at room temperature or below. Embodiments of the present invention are particularly well suited for use in solid-state lighting applications, architectural lighting, and alternative-energy applications.

[0012] An illustrative embodiment of the present invention is a phosphor comprising a metal-halide (PbBr$_4$) inorganic structure within an organic-inorganic hybrid material having a two-dimensional hybrid perovskite crystal structure. The phosphor emits light that spans the entire visible-light spectrum. In some embodiments, phosphors include other metal-halides and metal-halide mixtures, such as PbBr$_4$-Cl$_x$, PbCl$_4$, PbI$_4$, and the like.

[0013] A method for forming phosphors in accordance with the present invention is a solution-state-synthesis process that includes forming a liquid solution containing an organic cation (e.g., alkyl ammonium) solution in a hydrohalic acid and an inorganic compound dissolved in the hydrohalic acid, where the inorganic compound includes the desired metal and halide. The desired phosphor crystallizes and precipitates out of the solution, typically while the solution is stirred, and while the solution is kept at or below room temperature. Once formed, the phosphors can be deposited on a desired surface by dissolving them in a
solvent solution, dispensing the phosphor/solvent solution onto the desired surface, and enabling the removal of the solvent (e.g., via evaporation).

[0014] In some embodiments, the broadband emission characteristics of a phosphor are controlled to provide light that ranges from "warm" white light, typically sought for indoor lighting, to "cold" white light that approximates sunlight. In some embodiments, the emission characteristics are controlled by forming the phosphor such that it comprises multiple halides and controlling the ratio of the different halides.

[0015] In some embodiments, phosphors in accordance with the present invention are electroluminescent. Such phosphors are suitable for use in active light sources, such as light-emitting diodes (LEDs).

[0016] In some embodiments, phosphors in accordance with the present invention are doped with strongly luminescent centers to improve their PLQEs.

[0017] In some embodiments, phosphors in accordance with the present invention are included in a solar-cell energy-conversion system. In such embodiments, UV light that cannot be absorbed by the solar cell is incident on the phosphors, which excites the phosphors to emit radiation that is within the absorption spectrum of the solar cell thereby improving the energy-conversion efficiency of the solar cell.

[0018] An embodiment of the present invention is a phosphor having an emission spectrum that includes the visible-light spectrum, the phosphor comprising: a first metal; and a first halide; wherein the first metal and first halide are arranged in a two-dimensional perovskite-based crystal structure.

[0019] Another embodiment of the present invention is a method comprising: mixing a first liquid and a second liquid to form a first solution, the first liquid comprising an organic cation dissolved in a first hydrohalic acid and the second liquid comprising a metal-based reagent dissolved in the hydrohalic acid, wherein the metal-based reagent comprises a first metal and the first hydrohalic acid comprises a first halide; maintaining the temperature of the first solution at or below room temperature; and precipitating a first phosphor from the first solution, wherein the first phosphor is characterized by a two-dimensional perovskite-based crystal structure that includes the first metal and the first halide, and wherein the first phosphor is operative for emitting light having a first emission spectrum that includes the visible-light spectrum.
Brief Description of the Drawings

[0020] FIG. 1 depicts a schematic drawing of a portion of a generalized phosphor structure in accordance with the present invention.

[0021] FIG. 2A depicts operations of a method suitable for forming a phosphor in accordance with the illustrative embodiment of the present invention.

[0022] FIG. 2B depicts operations of a solution-state substitution process for forming a mixed-halide phosphor and controlling the ratio of the halides in the phosphor in accordance with the present invention.

[0023] FIGS. 3A-D depict schematic drawings of the crystal structure of exemplary phosphors in accordance with the present invention.

[0024] FIG. 4 depicts operations of a method for forming phosphor 300.

[0025] FIG. 5 depicts plots of measured absorption and photoluminescence data for phosphors 300, 304, 308, and 310.

[0026] FIGS. 6A and 6B depict plots of photoluminescence intensity as a function of wavelength for single crystals and ball-milled powders of two exemplary phosphors.

[0027] FIGS. 7A-B depict plots of the chromaticity coordinates for phosphors in accordance with the present invention.

[0028] FIG. 8A depicts measured photoluminescence for a mixed-halide phosphor for different halide ratios.

[0029] FIG. 8B depicts the effect of halide substitution on a high-energy shoulder within the photoluminescence spectra of plot 800.

Detailed Description

[0030] The following terms are defined for use in this Specification, including the appended claims:

- **visible-light spectrum** is defined as the wavelengths within the range of approximately 400 nanometers (nm) to approximately 700 nm.
• **Two-dimensional hybrid perovskite crystal structure** is defined as a perovskite crystal structure having alternating layers of organic molecules and inorganic components comprised of corner-sharing metal-halide octahedra.

• **Room temperature** is defined as a temperature within the range of approximately 20 °C to approximately 26 °C.

**Technology Overview**

[0031] The present invention enables stable, single-phase white-light emitting phosphors that can be formed using low-cost, simple solution-state synthesis. The crystal structure of these phosphors is a hybrid perovskite crystal structure that comprises alternating layers of organic and inorganic components. Phosphors in accordance with the present invention are characterized by broadband emission that substantially spans the complete visible-light spectrum, where the emission arises from bulk effects within the crystal structure. As a result, the present invention enables phosphors that are more tunable and that can have longer lifetime than prior-art phosphors.

[0032] In contrast to the present invention, prior-art phosphor materials, such as CdSe quantum dots, are characterized by white-light emission that has been attributed to mid-bandgap states arising from deep traps at surface sites. Unfortunately, such emission has a strong dependence on particle size and is readily quenched by particle aggregation.

[0033] FIG. 1 depicts a schematic drawing of a portion of a generalized phosphor structure in accordance with the present invention. Phosphor 100 includes organic layer 102 and inorganic layers 104, which collectively define a hybrid perovskite crystal structure.

[0034] Organic layer 102 comprises organic molecule 106, which includes organic chains 108. Organic cations suitable for use in embodiments of the present invention include, without limitation, EDBE (2,2'-(ethylenedioxy)bis(ethylammonium)), N-MEDA (N\(^1\)-methylene-l,2-diammonium), N-MPDA (N\(^1\)-methylpropane-l\(^1\)-diammonium), and the like.

[0035] Each of inorganic layers 104 is a crystalline metal-halide layer comprising atoms of metal 110 and atoms of at least one halide (i.e., halide 112). Inorganic layers
can be characterized as flat or corrugated metal-halide sheets that are separated by length \( L \), where \( L \) is based on the length of organic chains 108.

[0036] The metal-halide structures of inorganic layers 104 behave as wide-bandgap semiconductors - similar to the electronic structures of nanostructured halide capping groups. Further, the dielectric mismatch between organic layer 102 and inorganic layers 104 gives rise to strongly bound excitons. The present invention, therefore, enables the electronic properties of quantum-confined systems, such as those discussed above. Such nanostructures, however, have significant size distribution and can require specialized processing techniques. In contrast, phosphor 100 is a bulk crystalline material that is formed in a solution-state, self-assembly reaction, wherein the thickness of inorganic layers 104 is determined by their crystal structure and orientation. As a result, the present invention enables phosphors having little or no size distribution effects between syntheses.

[0037] It is an aspect of the present invention that the crystal orientation and/or structure of inorganic layers 104 is dictated by \( L \). As a result, the choice of organic molecule used in phosphor 100 is typically made based on the desired crystal orientation of the inorganic layers. It should be noted that the emission characteristics of phosphor 100 are affected by its crystal orientation/structure.

[0038] FIG. 2A depicts operations of a method suitable for forming a phosphor in accordance with the illustrative embodiment of the present invention. Method 200 begins with operation 201, wherein a first liquid solution is prepared by dissolving organic molecule 106 in a first portion of a first hydrohalic acid (formed from hydrogen and halide 112) to form an organic cation.

[0039] As operation 202, the temperature of the first liquid solution is maintained at or below room temperature.

[0040] At operation 203, a second liquid solution is prepared by dissolving a first inorganic compound in a second portion of the first hydrohalic acid, where the first inorganic compound comprises metal 110 and halide 112.

[0041] At operation 204, the second solution is added to the first solution to form a third solution.

[0042] At operation 205, phosphor 100 is precipitated out of the third solution. In some embodiments, phosphor 100 is precipitated by cooling the third solution. In some
embodiments, phosphor 100 is precipitated by heating the third solution to an elevated temperature (e.g., 60-100 °C, etc.) at which it is saturated, then cooling the third solution to a temperature at which the phosphor will precipitate, such as a temperature that is at or below room temperature. In some embodiments, phosphor 100 is precipitated by enabling a solvent (e.g., an organic solvent such as acetone, etc.) to diffuse (e.g., through vapor-phase diffusion, etc.) into the third solution.

[0043] The solution-state assembly of phosphor 100 is directed by the choice of the organic cation included in the solution - specifically, the length of organic chains 108 and hydrogen-bonding interactions between the organic molecule and the inorganic sheets. For example, in some embodiments, a short-length organic cation is used to dictate assembly of (110) perovskite crystals. In other embodiments, a longer-length organic cation is used to dictate assembly of (001) perovskite crystals.

[0044] In some embodiments, the shape (e.g., peak wavelength, center wavelength, etc.) of the emission spectrum of phosphor 100 is controlled by controlling the ratio of the first halide with a second halide included in inorganic layers 102.

[0045] FIG. 2B depicts operations of a solution-state substitution process for forming a mixed-halide phosphor and controlling the ratio of the halides in the phosphor in accordance with the present invention. Method 206 begins with operation 207, wherein a fourth solution is prepared, the fourth solution comprising a specific ratio of the first hydrohalic acid and a second hydrohalic acid that is based on a second halide.

[0046] At operation 208, the crystalline material of phosphor 100, which was obtained in operation 205, is dissolved in the fourth solution to form a fifth solution.

[0047] At operation 209, a cold organic solvent is added to the fifth solution.

[0048] At operation 210, a mixed-halide phosphor is precipitated from the fifth solution. The inorganic layers of the precipitated mixed-halide phosphor includes the first and second halides in a specific ratio that is based on the ratio of the first and second hydrohalic acids in the third solution.

[0049] It should be noted that, instead of adding a cold solvent to the fifth solution, the mixed-halide phosphor can be precipitated from the fifth solution by using another known prior-art technique or any of the techniques described above and with respect to operation 205.
It should also be noted that phosphors in accordance with the present invention can be deposited on a desired surface using techniques analogous to prior-art solution-state methods used to deposit organic phosphors. As a result, the present invention enables applications wherein inexpensive, large-area coatings of broadband-emitting phosphors are desirable.

Turning now to specific embodiments, FIGS. 3A-D depict schematic drawings of the crystal structure of exemplary phosphors in accordance with the present invention. Phosphors 300, 304, and 308 are examples of phosphors that emit light whose spectrum spans the entire white-light spectrum (i.e., phosphors 300, 304, and 308 are white-light emitting phosphors). Phosphor 310 is an example of a phosphor that emits light that does not span the entire white-light spectrum but, instead, emits predominantly green light (i.e., phosphor 310 is a green-light emitting phosphor); however, phosphor 310 can be formed using solution-state synthesis in accordance with the present invention.

Phosphor 300 is a layered perovskite crystal of (EDBE)[PbBr$_4$]. Phosphor 300 includes atoms of lead, bromine, oxygen, nitrogen, carbon, and hydrogen (not shown for clarity), which are arranged in corrugated lead-halide sheets that collectively define a hybrid perovskite crystal structure.

In phosphor 300 inorganic layers 104 have a (110) crystal structure having a generally octahedral metal coordination environment (as shown in inset 302). Hydrogen bonds between terminal ammonium groups and oxygen atoms in adjacent organic molecules enforce a paired configuration for EDBE cations in the phosphor, thereby stabilizing the (110) structure of inorganic layers 104.

Phosphor 304 is a layered perovskite crystal of (EDBE)[PbCl$_4$]. Phosphor 304 includes atoms of lead, chlorine, oxygen, nitrogen, carbon, and hydrogen (not shown for clarity).

In phosphor 304, inorganic layers 104 have a (100) crystal structure with a pronounced distortion from an octahedral geometry around the metal atoms (as shown in inset 306).

As discussed above and with respect to FIG. 1, organic molecules other than EDBE can be used without departing from the scope of the present invention. Phosphor
308 is an example of a phosphor in accordance with the present invention wherein organic molecule 106 is N-MEDA (N^methylethane-l^-diammonium), rather than EDBE.

[0057] Phosphor 308 has a (110) crystal structure due, in part, to the short length of organic chains 108 in N-MEDA. The short polymer chain length inhibits the formation of (001) perovskite structure, as it would likely bring adjacent inorganic layers 104 too close together. As a dication, N-MEDA also cannot occupy the A'-site of a three-dimensional perovskite. Due to the corrugated nature of the (110) sheets (i.e., inorganic layers 104), the primary ammonium group of N-MEDA can form hydrogen bonds with halides from two adjacent inorganic sheets, likely stabilizing the (110) structure.

[0058] Phosphor 310 is a layered perovskite crystal of (EDBE)[Pbl_4]. Phosphor 310 includes atoms of lead, iodine, oxygen, nitrogen, carbon, and hydrogen (not shown for clarity).

[0059] Like phosphor 300, the inorganic layers 104 in phosphor 310 have a (110) crystal structure having a generally octahedral metal coordination environment (as shown in inset 312). As described above, hydrogen bonds between terminal ammonium groups and oxygen atoms in adjacent organic molecules stabilize the crystal structure of inorganic layers 104 by enforcing a paired configuration for EDBE cations in the phosphor.

[0060] FIG. 4 depicts operations of a method for forming phosphor 300. Method 400 is a specific example of method 200, and begins with operation 401, wherein a first solution comprising lead(II)bromide (i.e., PbBr2) dissolved in hydrobromic acid is prepared. An exemplary first solution is a 4-mL solution of PbBr2 (1.00 g, 2.72 mmol) in 9-M HBr.

[0061] At operation 402, a second solution comprising EDBE dissolved in hydrobromic acid is prepared. An exemplary second solution is a 5-mL solution of EDBE (1.00 mL, 6.85 mmol) in 9-M HBr.

[0062] At operation 403, the second solution is stirred and its temperature is maintained at or below room temperature (e.g., -70 °C).

[0063] At operation 404, the first solution is added to the second solution to form a third solution.

[0064] After 10 minutes, at operation 405, phosphor 300 is precipitated out of the third solution, filtered using a glass frit, and washed with cold diethyl ether (5 x 5 mL).
One skilled in the art will recognize that the specific operations of method 400 are merely exemplary and that alternative operations suitable for forming phosphor 300 can be employed without departing from the scope of the present invention. Further, method 400 exemplifies operations suitable for forming other phosphors in accordance with the present invention (e.g., phosphors 304, 308, and 310, etc.) with appropriate substitution of halides. Still further, it will be clear that the concentrations and mixtures provided are merely examples of suitable concentrations and solution compositions.

FIG. 5 depicts plots of measured absorption and photoluminescence data for phosphors 300, 304, 308, and 310. Plots 500, 502, 504, and 506 depict data for phosphors 300, 304, 308, and 310, respectively.

The absorption spectra of phosphors 300, 304, 308, and 310 are similar to those of other two-dimensional lead-halide perovskites. The dielectric mismatch between organic and inorganic layers leads to strongly bound excitons, reflected in the sharp excitonic absorption bands at 351, 371, 395, and 470 nm for phosphors 304, 300, 308, and 310, respectively.

Upon excitation with light at 365-nm, phosphor 300 emits light whose emission spectrum spans the entire visible wavelength, with a maximum at 573 nm and a full width at half maximum (FWHM) of 215 nm (0.80 eV). It also exhibits a higher-energy shoulder at 410 nm.

In similar fashion, when excited with light having a wavelength of 310 nm, phosphor 304 also emits light whose emission spectrum spans the entire visible wavelength, with a maximum at 538 nm and an FWHM of 208 nm (0.95 eV). The emission spectrum of phosphor 304 also features a less intense but well-defined shoulder at 358 nm.

When excited with light at 410 nm, phosphor 308 emits light whose emission spectrum spans the entire visible wavelength, with a maximum at 558 nm and a full width at half maximum (FWHM) of 165 nm.

As briefly mentioned above, phosphors 300, 304, and 308 can be characterized as "white-light emitters," since they emit light whose spectra spans the entire white-light spectrum. The light emitted by phosphor 310, on the other hand, does not quite span the entire white-light spectrum and is generally concentrated in the 470 nm to 600 nm wavelength range. As a result, phosphor 310 can be generally characterized as a
"green-light emitter." One skilled in the art will recognize, after reading this Specification, that, while a green-light emitter has limited utility as compared to a white-light emitter, the ability to form a green-light emitter using low-cost solution-state synthesis in accordance with the present invention still affords embodiments of the present invention based on phosphor 310 advantages over the prior art.

[0072] As can be seen from plot 506, phosphor 310 displays a sharper green emission spectrum centered at 515 nm in response to excitation at 400 nm, with a FWHM of 70 nm (0.32 eV). It should be noted that the emission spectrum of phosphor 310 does not quite span the entire visible-light spectrum, covering wavelengths within the range of approximately 450 nm to approximately 700 nm.

[0073] It should be noted that the very large Stokes shifts exhibited by phosphors 300, 304, 308, and 310 advantageously lead to low self-absorption in these materials.

[0074] As discussed above, in contrast to prior-art phosphors, the white-light emission of phosphors in accordance with the present invention arises due to bulk effects in their crystal structure. This is illustrated by exemplary mechanistic studies of phosphor 300, which indicate that its white-light emission likely includes contributions from both distorted excited states due to strong electron-phonon coupling in a deformable lattice as well as inhomogeneous broadening resulting from a distribution of trap states. One skilled in the art will recognize, after reading this Specification, that strong coupling of excited electrons/holes to lattice deformations can lead to a broad emission with a pronounced Stokes shift (as evinced by plot 500 in FIG. 5A) due to stabilized, distorted electronic states. It was found that, consistent with electron-lattice coupling, the broad emission of phosphor 300 becomes more intense and narrower with increasing temperature. Accordingly, the PLQE of phosphor 300 was found to increase with decreasing temperature from 9% at 300 K to reach 85(1)% at 105 K.

[0075] Further, one skilled in the art would recognize that white-light emission due to surface defects would be particle-size dependent. The emission characteristics of phosphors in accordance with the present invention, however, are substantially size-independent.

[0076] FIGS. 6A and 6B depict plots of photoluminescence intensity as a function of wavelength for single crystals and ball-milled powders of two exemplary phosphors. Plots
600 and 602 depict the photoluminescence for samples of phosphors 300 and 304, respectively. Single crystals of phosphor 300 have a particle size of 1x0.4x0.1 cm, while single crystals of phosphor 304 have a particle size of 1x0.5x0.1 cm. The ball-milled powders of each phosphor have a particle size of ca. 1 micron.

[0077] It be seen from each of plots 600 and 602 that the emission spectra for the two different sizes of particulates of the two phosphors are virtually identical, indicating that their emissions are not due to defects at the crystal surface but are, instead, due to bulk effects.

[0078] FIGS. 7A-B depict plots of the chromaticity coordinates for phosphors in accordance with the present invention.

[0079] Plot 700 indicates the chromaticity coordinates for phosphors 300, 304, and 310 as compared to bright sunlight. The emission from phosphor 300 has CIE chromaticity coordinates of (0.39, 0.42), with a larger contribution from the red region of the spectrum compared to pure white light, which has chromaticity coordinates of (0.33, 0.33). This gives the emission from phosphor 300 a correlated color temperature (CCT) of 3990 K, which corresponds to ‘warm’ white light that is ideal for indoor illumination. The broad emission also leads to a high color-rendering index (CRI) of 84. By way of comparison, the emission from phosphor 304 has CIE coordinates of (0.33, 0.39), which corresponds to a CCT of 5509 that affords ‘cold’ white light, and a CRI of 81.

[0080] Plot 702 indicates the chromaticity coordinates for phosphor 308 as compared to bright sunlight, as well as a conventional incandescent light source - namely, a tungsten filament. Like phosphor 300 (also based on a lead-bromine halide crystal), phosphor 308 has significant emission intensity in the red region of the visible spectrum. As a consequence, its emission lies to the yellow side of pure white light with a CIE of (0.36, 0.41) and a CCT of 4669 K. As a result, both of phosphors 300 and 308 emit “warm” white light.

[0081] As discussed above, it is an aspect of the present invention that shape of the emission spectrum of a metal-halide phosphor can be tuned via halide substitution in a solution-state reaction. Plot 702 also indicates the chromaticity coordinates for exemplary tuned phosphor 704, which is a mixed-halide phosphor that includes both bromine and chlorine atoms and has the formula (N-MEDA)[PbBr2.sCl2].
[0082] Phosphor 704 is formed in a manner analogous to method 206 described above and with respect to FIGS. 1 and 2.

[0083] In a first exemplary method, 0.01 grams of crystalline phosphor 308 is dissolved in 0.4 mL of a solution having a 5:3 mol ratio of HBr and HCl. This solution is then sonicated for several minutes to ensure complete dissolution of the solid phosphor material. Approximately 4 mL of cold acetone (e.g., 0 °C) is then added to the first solution. This second solution is then sonicated again for several minutes, after which a crystalline precipitate of phosphor 704 is realized. Typically, the precipitate is then filtered, washed with an organic solvent (e.g., acetone), and dried in reduced pressure atmosphere.

[0084] It should be noted that the choice of organic molecule 106 within the phosphor does not significantly affect the ability to perform halide substitution in the manner described herein. For example, in a second exemplary method, 0.05 grams of crystalline phosphor 300 is dissolved in a 1 mL aqueous solution having a ratio of 9-M HBr:12-M HCl. This solution is then sonicated for several minutes to ensure complete dissolution of the solid phosphor 300. As in the first exemplary method, approximately 4 mL of cold acetone (e.g., 0 °C) is then added to the first solution and the second solution is then sonicated for several minutes to realize a crystalline precipitate of a second phosphor having a desired ratio of bromine and chlorine.

[0085] By controlling the ratio of the hydrohalic acids, the ratio of the two halide atoms in the crystal structure can be controlled. For example, dissolving phosphor 300 in solutions having ratios of HBr:HCl of 1:0, 1:1, 2:3, 3:5, and 1:4 results in mixed-halide phosphors having the formula (EDBE)[PbBr_{4-x}Cl_x], where x=0, 0.24, 0.41, 1.56, and 1.84, respectively.

[0086] FIG. 8A depicts measured photoluminescence for a mixed-halide phosphor for different halide ratios. Plot 800 includes photoluminescence data for a phosphor having the formula (EDBE)[PbBr_{4-x}Cl_x], where x=0, 0.24, 0.41, 1.56, and 1.84, as indicated.

[0087] It can be seen from plot 800 that, while the intensity of the mixed-halide phosphor decreases with increasing chlorine content, the center wavelength and FWHM of the emission spectrum remains substantially unchanged.

[0088] FIG. 8B depicts the effect of halide substitution on a high-energy shoulder within the photoluminescence spectra of plot 800.
[0089] Plot 802 shows that there is a marked blueshift with increasing chloride content in the mixed-halide phosphor. This spectral content enables control over the CIE coordinates of the phosphor. This control is exhibited in plot 702 described above, which shows CIE coordinates for phosphors 308 and 704, which have CIE coordinates of (0.36, 0.41) and (0.31, 0.36), respectively. It should be noted that, simply via halide substitution, the CIE coordinates of phosphor 704 are moved significantly closer to the desirable CIE coordinates of pure white light (0.33, 0.33).

[0090] It is to be understood that the disclosure teaches just one example of the illustrative embodiment and that many variations of the invention can easily be devised by those skilled in the art after reading this disclosure and that the scope of the present invention is to be determined by the following claims.
What is claimed is:

1. A phosphor having an emission spectrum that includes the visible-light spectrum, the phosphor comprising:
   a first metal; and
   a first halide;
wherein the first metal and the first halide are arranged in a two-dimensional perovskite-based crystal structure.

2. The phosphor of claim 1, wherein the first metal comprises metal that is selected from the group consisting of lead, bismuth, tin, and germanium.

3. The phosphor of claim 1, wherein the first halide comprises a halide that is selected from the group consisting of fluorine, chlorine, bromine, and iodine.

4. The phosphor of claim 1 further comprising an organic molecule, wherein the organic molecule is characterized by chain length and functional groups, and wherein the crystal structure of the two-dimensional perovskite crystal is directed by the organic molecule.

5. The phosphor of claim 1, further comprising a second halide, wherein the first metal, the first halide, and second halide are arranged in the two-dimensional perovskite-based crystal structure, and wherein the shape of the emission spectrum is based on the ratio of the first halide and the second halide.

6. The phosphor of claim 1, wherein the perovskite-based crystal structure is a hybrid perovskite crystal structure.

7. The phosphor of claim 1, wherein the perovskite-based crystal structure is corrugated.

8. The phosphor of claim 1, wherein the emission spectrum is based on a bulk effect within the perovskite-based crystal structure.

9. The phosphor of claim 1, wherein the perovskite-based crystal structure comprises (110) inorganic sheets.
10. A method comprising:

mixing a first liquid and a second liquid to form a first solution, the first liquid comprising an organic molecule dissolved in a first hydrohalic acid and the second liquid comprising first inorganic compound dissolved in the hydrohalic acid, wherein the first inorganic compound includes a first metal and a first halide, and wherein the first hydrohalic acid comprises the first halide; and

enabling the precipitation of a first phosphor from the first solution, wherein the first phosphor is characterized by a two-dimensional perovskite-based crystal structure that includes the first metal and the first halide, and wherein the first phosphor is operative for emitting light having a first emission spectrum that includes the visible-light spectrum.

11. The method of claim 10 further comprising:

dissolving the first phosphor in a second solution including the first hydrohalic acid and a second hydrohalic acid that comprises a second halide;

adding a third liquid to the second solution to form a third solution, the third liquid containing an organic solvent, wherein the third liquid is added while at a temperature below room temperature; and

precipitating a second phosphor from the third solution, wherein the second phosphor is characterized by a two-dimensional perovskite-based crystal structure that includes the first metal, the first halide, and the second halide, and wherein the second phosphor is operative for emitting light having a second emission spectrum that includes the visible-light spectrum, and further wherein the shape of the second emission spectrum is based on the ratio of the first halide and second halide in the second phosphor.
12. The method of claim 10 further comprising enabling the precipitation of the first phosphor by an operation selected from the group consisting of:
   maintaining the temperature of the first solution at or below room temperature;
   diffusing an organic solvent into the first solution; and
   sub-operations including:
      (i) forming the first solution such that it is a saturated solution at a first temperature that is greater than room temperature; and
      (ii) cooling the first solution to a second temperature that is less than the first temperature.

13. The method of claim 10 further comprising:
   providing the first hydrohalic acid such that the first halide is selected from the group consisting of fluorine, chlorine, bromine, and iodine; and
   providing the first inorganic compound such that the first metal is selected from the group consisting of lead, bismuth, tin, and germanium.

14. The method of claim 10 further comprising providing the organic molecule, wherein the organic molecule is characterized by chain length and functional groups, and where the crystal structure of the first phosphor is directed by the organic molecule.

15. The method of claim 14 wherein the organic molecule, the first metal and the first halide collectively define a layered hybrid perovskite crystal structure in the first phosphor.
<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>201</td>
<td>Dissolve organic polymer 106 in a first portion of a first hydrochloric acid</td>
</tr>
<tr>
<td>202</td>
<td>Maintain the temperature of the first solution at or below room temperature</td>
</tr>
<tr>
<td>203</td>
<td>Dissolve an inorganic compound of metal 110 and halide 112 in a second portion of the first hydrochloric acid to form a second solution</td>
</tr>
<tr>
<td>204</td>
<td>Add the second solution to the first solution</td>
</tr>
<tr>
<td>205</td>
<td>Precipitate crystalline phosphor 100</td>
</tr>
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<td>206</td>
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<tr>
<td>207</td>
<td>Prepare a fourth solution comprising a desired ratio of the first hydrochloric acid and a second hydrochloric acid that is based on a second halide</td>
</tr>
<tr>
<td>208</td>
<td>Dissolve phosphor 100 in the fourth solution</td>
</tr>
<tr>
<td>209</td>
<td>Add cold organic solvent to the fourth solution to form a fifth solution</td>
</tr>
<tr>
<td>210</td>
<td>Precipitate a second phosphor having a desired ratio of the first halide and second halide</td>
</tr>
</tbody>
</table>
Prepare a first solution of PbBr₂ dissolved in hydrobromic acid

Prepare a second solution of EDBE dissolved in hydrobromic acid

Maintain the temperature of the second solution at or below room temperature

Add the first solution to the second solution to form a third solution

Precipitate crystalline phosphor 300 from the third solution
A. CLASSIFICATION OF SUBJECT MATTER

C09K II/66(2006.01), C09K II/08(2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K 11/66; B32B 7/02; C09K 11/06; C07D 333/02; C07D 413/00; C09K 11/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KEIPO internal) & Keywords: perovskite, hybrid, metal-halide, 2-dimensional, phosphor, crystal, visible-light, emission, bulk effect, large stoke shift

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
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<tbody>
<tr>
<td>X</td>
<td>Li, Y. Y. et al. 'Novel &lt;110&gt;-or indexed organo c- inorganic perovskite compound stabilized by N-(3-Aminopropyl)imidazole with improved optical property i.e.' Chemistry of Materials. 2006, Vol. 18, No. 15, pages 3463-3469. See abstract; pages 3464-3466; scheme 1; and figures 1, 2 and 3.</td>
<td>1-4, 6-10, 12-15</td>
</tr>
<tr>
<td>A</td>
<td>US 6429318 B1 (MITZI, DAVID BRIAN) 06 August 2002 See abstract; columns 3-8; and figures la-3.</td>
<td>5, 11</td>
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<tr>
<td>A</td>
<td>US 61590536 A (CHONDROUDIS, Konstantinos et al.) 21 November 2000 See abstract; columns 2-4; and figures 1, 3 and 5.</td>
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</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

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

Date of the actual completion of the international search
17 February 2015 (17.02.2015)

Date of mailing of the international search report
17 February 2015 (17.02.2015)

Name and mailing address of the ISA/KR
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Authorized officer
LEE, Jeong A
Telephone No. +82-42-481-8740
**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US2014/061946

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<tr>
<td>A</td>
<td>BAIKIE, Tom et al. 'Synthesis and crystal chemistry of the hybrid perovskite (CH3NH3)PbI3 for solid-state sensitised solar cell applications' Journal of Materials Chemistry A. 12 March 2013 (Epub.), Vol. 1, No. 18, pages 5628-5641. See abstract; and pages 5628-5631.</td>
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<td>Patent document cited in search report</td>
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