Characterization of blue-excited yellow phosphor (Y,Ca)$_{6+x/3}$Si$_{11}$(N,O)$_{21}$:Ce by the bond valence sum model

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The new bright yellow phosphor (Y,Ca)$_{6+x/3}$Si$_{11}$(N,O)$_{21}$:Ce (CYSON) providing broad emission excited by blue LED is the product of extensive substitution (about 70% of Y) of Y$^{3+}$ → Ca$^{2+}$ and N$^{3-}$ → O$^{2-}$ in the Y$_6$Si$_{11}$ON$_{20}$:Ce parent host, which exhibits a weak emission excited by near UV-excitation only. Such a considerable difference is caused by particular distribution of substituting ions through the crystal lattice sites. For the first time for the title host, these intricate effects have been thoroughly studied in the present paper. We analyzed distribution of cations and their anion surrounding for each of the three Y sites. In addition, the local charge balance was also considered in detail by calculating the Brown’s bond valence sum (BVS). The results suggest that the number of oxygen ligands is likely to be 0 at the Y$_1$ and Y$_2$ sites, 2−3 at the Ca$_1$ and Ca$_2$ sites, 0−1 at the Y$_3$ site, and 3−4 at the Ca$_3$ site (the subscript enumerates the inequivalent sites in the CYSON lattice). These data indicate that the Ca ions are likely to be coordinated by a greater number of the oxygen ions than the Y ions, which leads to the conclusion that the Y−N bond should be extensively substituted by the Ca−O bond. Therefore, agglomeration of an increased number of the oxygen ions far away from the Ca$^{2+}$ ions is suppressed. It is suggested that as the bond lengths of the cation–anion pairs in CYSON are much larger than the sum, 2.28 Å, of the ionic radii of the Y$^{3+}$ and O$^{2-}$ ions (which yields a smaller BVS and a small local charge balance), the substituted Ca$^{2+}$−O$^{2-}$ pair contributes to the stabilization of electric charge distribution. This is the first detailed study of the structural properties of this new phosphor that allowed to identify most probable coordination around each and every cation site in this complicated structure with many inequivalent crystallographic positions.

1 Introduction

For about a couple of decades, white phosphor-converted light-emitting diodes (LEDs) have been important devices because they provide an efficient conversion of electric energy to visible light. In addition, they are environmentally friendly, since no toxic Hg is used in their production compared to conventional incandescent and fluorescent lamps. One of the main goals on the phosphor markets is the improved luminous efficacy of novel phosphors for various applications. The phosphors excited by the light of 450 nm-peak of efficient blue LED require a much longer wavelength of excitation than the conventional 254 nm wavelength of the excitation light. The nitridosilicates activated by Eu$^{2+}$ or Ce$^{3+}$ (ref. 2–10) ions are likely to have a strong crystal field splitting (CFS) and a low position of the Eu$^{2+}$ or Ce$^{3+}$ 5d states centroid due to coordination by the N$^{3-}$ ions forming highly covalent chemical bonds. This leads to the enhanced nephelauxetic effect, which in turn decreases the energy difference between the ground 4f and the lowest 5d states of the lanthanide ions. In this case, the longest wavelength of excitation, equivalent to the energy difference between the 4f state and the lowest 5d state, increases.

Seto et al. found the new blue-excited yellow phosphor, (Y,Ca)$_{6+x/3}$Si$_{11}$(N,O)$_{21}$:Ce,$^{14}$ (here and thereafter called CYSON) which has two prominent distinguished features. Firstly, extensive substitution (about 70% of Y) of Y$^{3+}$ → Ca$^{2+}$ and N$^{3-}$ → O$^{2-}$ in Y$_6$Si$_{11}$ON$_{20}$:Ce results in (i) much better crystallinity and (ii) brighter emission under a usual condition of synthesizing nitridosilicate phosphor. The prepared Y$_6$Si$_{11}$ON$_{20}$:Ce itself is not a blue-excited phosphor but a near UV-excited phosphor, with much lower crystallinity and weaker emission. The crystal structure of CYSON is shown in Fig. 1. There are three Y$^{3+}$ sites that can be partially substituted by the Ca$^{2+}$ or Ce$^{3+}$ ions and nine sites for the O$^{2-}$, N$^{3-}$ anions, as shown in Fig. 2.
In the present paper we set our goal to investigate whether such extensive and simultaneous substitution provides stable structure from the point of view of the electric charge balance at each cation site. For this purpose, we calculated the Brown's bond valence sum (BVS)\(^\text{12,14}\) for each and every cation site, with and without taking into account effect of the crystal lattice relaxation upon the substitution. The analysis of the obtained results revealed certain peculiar features of coordination of various cations and allowed to understand how such extended cation substitution is realized in the CYSON crystal lattice.

## 2 Procedure of calculation

The Brown's equation has a wider area of application than the original Pauling's equation on the bond valence sum so far. According to Brown, the bond valence of cation \(i\) coordinating anion \(j\) can be calculated from the following eqn (1)\(^\text{12,14}\)

\[
V_i = \sum_j \exp\left(\frac{R_{ij} - d_{ij}}{B}\right)
\]  

where \(R_{ij}\) is the bond valence parameter of a cation \(i\) coordinating by an anion \(j\), \(d_{ij}\) is the bond length between the cation \(i\) and anion \(j\), and \(B\) is a constant value (the most reliable value for this parameter is 0.37 Å). The bond valence sum can be obtained for each atomic distance, cation species, and species of anion ligands.

We used the values of all \(d_{ij}, R_{ij}\), and \(B\) from the reference to the CYSON structure,\(^\text{14}\) and Brown's list of the bond balance parameter.\(^\text{13,14}\) The \(R_{ij}\) value depends on the cation and anion species coordinating a particular cation.

CYSON's space group is \(P_{3}1c\) (no. 159) and its typical composition is \(Y_{6+x}Ca_{x}Si_{11}O_{30}+\) (\(x = 1.2, y = 4.5, Ce\) molar ratio = 0.06). Each cation's occupancy in CYSON is shown in Table 1,\(^\text{11}\) whereas the atomic distances (all in Å) in CYSON are shown in Table 2.\(^\text{15}\) It is seen that the \(Y^{3+}, Ca^{2+},\) or \(Ce^{3+}\) ions can occupy all three cationic sites. Taken together with anion substitution, this makes an analysis of the structural properties of this phosphor to be a non-trivial problem.

Table 1 Occupancies of \(Y, Ca,\) and \(Ce\) at each site determined by Rietveld refinement\(^\text{11}\)

| Ln\(_1\) site | Ln\(_2\) site | Ln\(_3\) site |
|-------------|-------------|-------------|
| \(Y\)       | 0.2171      | 0.3318      | 0.1978      |
| \(Ca\)      | 0.7764      | 0.6645      | 0.3036      |
| \(Ce\)      | 0.0066      | 0.0038      | 0.0243      |

Table 2 Atomic distances determined by Rietveld refinement\(^\text{11}\)

| Ln\(_1\) site: \(\text{Ln} - \{\text{O}\}\) | Si\(_2\) site: \(\text{Si} - \{\text{O}\}\) | \(\text{Ce}\) site: \(\text{Ce} - \{\text{O}\}\) |
|----------------|----------------|----------------|
| \(\text{Ln}_{1}\) | 2.553(3)       | 1.693(5)       |
| \(\text{Ln}_{2}\) | 2.536(4)       | 1.695(3)       |
| \(\text{Ln}_{3}\) | 2.420(3)       | 1.798(5)       |
| \(\text{Ln}_{1}\) | 2.453(4)       | 1.781(2)       |
| \(\text{Ln}_{2}\) | 2.519(1)       | 1.665(3)       |
| \(\text{Ln}_{3}\) | 2.500(3)       | 1.757(5)       |
| \(\text{Ln}_{2}\) | 2.537(3)       | 1.816(4)       |
| \(\text{Ln}_{1}\) | 2.477(4)       | 1.754(5)       |
| \(\text{Ln}_{2}\) | 2.471(2)       | 1.722(3)       |
| \(\text{Ln}_{3}\) | 2.520(4)       | 1.823(3)       |
| \(\text{Ln}_{1}\) | 2.288(2)       | 1.690(5)       |
| \(\text{Ln}_{1}\) | 2.592(1)       | 1.684(6)       |
| \(\text{Ln}_{2}\) | 2.592(1)       | 1.916(2)       |
| \(\text{Ln}_{1}\) | 2.592(1)       | 1.663(3)       |
| \(\text{Ln}_{2}\) | 2.531(4)       | 2.218(11)      |
| \(\text{Ln}_{3}\) | 2.531(4)       | 1.797(3)       |
| \(\text{Ln}_{1}\) | 2.531(4)       | 1.648(8)       |
3 Results and discussion

Fig. 3(a)–(c) show all the values of the calculated charge imbalance at the Ln1, Ln2, and Ln3 sites, respectively. The smallest value of charge imbalance is obtained in the case of all nitrogen ligands, if the Y3+ ions occupy the Ln1, Ln2, and Ln3 sites, whereas when the Ca2+ ions occupy the same sites, the smallest value is obtained in the case of 3 oxygen and 3 nitrogen ligands for the Ln1 and Ln2 sites, and in the case of 4 oxygen and 3 nitrogen ligands for the Ln3 site. To understand the conditions that minimize the charge imbalance all the sets of the O\(^2\) and N\(^3\) ligands providing the smallest three values of charge imbalance are shown in Table 5. The minimal values of charge imbalance are relatively high, 0.2514, 0.1120, and 0.0014 for the Y1, Y2, and Y3 sites, while the same values are much smaller, 0.0037, 0.0049, and 0.0014 for the Ca1, Ca2, and Ca3 sites.

We may take another consideration that the atomic distance between the ionic radius of the anion and cation’s valence (charge imbalance) calculated in case no. 9 (one of all 64 cases of N/O coordination) is

\[
R_{ij} = \frac{1}{2} \left( \frac{r_{A} + r_{B}}{C_{0}} \right)
\]

As an example, Table 3 shows just a few anion arrangements out of all 64 cases of the nitrogen or oxygen coordination around the Y\(^{3+}\) or Ca\(^{2+}\) cations at the Ln1 site. Table 4 shows the typical results of the BVS calculations for the case no. 9 from Table 3 (one of all 64 cases), including the difference between the BVS and cation’s valence, which is called the value of charge imbalance here. All other cases can be calculated in a similar way and are not shown here for the sake of brevity. We present all the calculated results in the next section in the form of diagrams.

### Table 3

| Cation–(anion) site no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | ... | 61 | 62 | 63 | 64 |
|------------------------|---|---|---|---|---|---|---|---|---|------|---|---|---|---|
| Y–(O/N)\(_{1}\) | N | O | N | N | N | N | O | O | O | ... | O | O | N | O |
| Y–(O/N)\(_{2}\) | N | N | O | N | N | N | O | N | O | ... | O | N | O | O |
| Y–(O/N)\(_{3}\) | N | N | N | O | N | N | N | O | N | ... | O | O | O | O |
| Y–(O/N)\(_{4}\) | N | N | N | N | O | N | N | O | N | ... | O | O | O | O |
| Ca–(O/N)\(_{1}\) | N | O | N | N | N | N | O | O | N | ... | O | O | N | O |
| Ca–(O/N)\(_{2}\) | N | N | O | N | N | N | O | N | O | ... | O | O | O | O |
| Ca–(O/N)\(_{3}\) | N | N | N | O | N | N | O | N | N | ... | O | O | O | O |
| Ca–(O/N)\(_{4}\) | N | N | N | N | O | N | N | N | N | ... | O | O | O | O |
| Number of oxygen in 6 ligands | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | ... | 5 | 5 | 5 | 6 |

### Table 4

| Species of anion ligand (the above: case number) | \(\text{O}_2\) | \(\text{N}_3\) | \(\text{Ca}^{2+}\) | \(\text{Y}^{3+}\) | \(\text{BV}\) | \(\text{R}_{ij}\) (Å) | \(\text{Y}^{3+}\) | \(\text{Ca}^{2+}\) | \(\text{BV}\) |
|----------------------------------|--------|--------|----------|----------|---------------|----------------|----------|----------|---------------|
| \(\text{Y}–\text{O}_1\) | 2.019  | 2.553  | 0.236    | \(\text{Ca}–\text{O}_1\) | 1.967  | 2.553  | 0.223    | \(\text{Y}–\text{O}_2\) | 2.17   | 2.356  | 0.604    | \(\text{Ca}–\text{O}_2\) | 2.14   | 2.356  | 0.514    |
| \(\text{Y}–\text{O}_3\) | 2.019  | 2.42   | 0.338    | \(\text{Ca}–\text{O}_3\) | 2.17   | 2.453  | 0.465    | \(\text{Y}–\text{O}_4\) | 2.17   | 2.519  | 0.389    | \(\text{Ca}–\text{O}_4\) | 2.14   | 2.519  | 0.331    |
| \(\text{Y}–\text{O}_5\) | 2.17   | 2.519  | 0.389    | \(\text{Ca}–\text{O}_5\) | 2.14   | 2.547  | 0.396    | \(\text{Y}–\text{N}_6\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_6\) | 2.14   | 2.5    | 0.349    |
| \(\text{Y}–\text{N}_7\) | 2.17   | 2.453  | 0.465    | \(\text{Ca}–\text{N}_7\) | 2.14   | 2.453  | 0.396    | \(\text{Y}–\text{N}_8\) | 2.17   | 2.42   | 0.410    | \(\text{Ca}–\text{N}_8\) | 2.14   | 2.42   | 0.349    |
| \(\text{Y}–\text{N}_9\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_9\) | 2.14   | 2.5    | 0.349    | \(\text{Y}–\text{N}_10\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_{10}\) | 2.14   | 2.5    | 0.349    |
| \(\text{Y}–\text{N}_11\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_{11}\) | 2.14   | 2.5    | 0.349    | \(\text{Y}–\text{N}_12\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_{12}\) | 2.14   | 2.5    | 0.349    |
| \(\text{Y}–\text{N}_13\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_{13}\) | 2.14   | 2.5    | 0.349    | \(\text{Y}–\text{N}_14\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_{14}\) | 2.14   | 2.5    | 0.349    |
| \(\text{Y}–\text{N}_15\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_{15}\) | 2.14   | 2.5    | 0.349    | \(\text{Y}–\text{N}_16\) | 2.17   | 2.5    | 0.410    | \(\text{Ca}–\text{N}_{16}\) | 2.14   | 2.5    | 0.349    |

possible configurations of nitrogen and/or oxygen ligands coordinating the Ln1, Ln2, and Ln3 sites, respectively.
The sets of $Y^{3+}$/Ca$^{2+}$–O$^{2-}$/N$^{3-}$ ligands providing the smallest values of charge imbalance are shown in Table 6. The smallest value of charge imbalance significantly decreases from 0.2688 to 0.0779 (Y$_3$ site), from 0.3016 to 0.1131 (Y$_2$ site), and from 0.1120 to 0.0247 (Y$_1$ site) when the two $Y^{3+}$-anion and Ca$^{2+}$-anion distances at the same site are modified taking into account differences of the ionic radii in the corresponding pairs. The coordination number of oxygen yielding the smallest value of charge imbalance is slightly changed from 3 to 2 (Ca$_1$ and Ca$_2$ sites), from 4 to 3 (Ca$_3$ site), from 0 to 1 (Y$_3$ site).

On total consideration including both cases of the same distance (Table 2) and the different distances, the number of the oxygen ligands seems to be 0–1 at the Y$_3$ sites and 2–4 at the Ca$_3$ sites, which suggests that the Ca ions are likely to be coordinated by more oxygen ions than the Y ions. The result coincides with the rough but essential Pauling's second rule where O$^{2-}$ should be substituted for the N$^{3-}$ site near the Ca$^{2+}$ ions rather than near Y$^{3+}$ ions because it can minimize the local volume where the sum of electric charge, $-1$, caused by the Y$^{3+} \rightarrow$ Ca$^{2+}$ substitution, is localized. The ratio O/(O + N) is likely to be 0% at Y$_3$, 33–50% at Ca$_2$ at the Ln$_1$ and Ln$_3$ sites, 0–14% at Y$_1$, 43–57% at Ca$_2$ at the Ln$_3$ site. Then, on the consideration of occupancies of (Y + tiny amount of Ce) and Ca in Table 1, the average ratio O/(O + N) is likely to be 26–39% at Ln$_1$ site, 22–33% at Ln$_3$ site, and 25–39% at Ln$_3$ site respectively. Total ratio of O/(O + N) in CYSON is $\{1–1.2 + 4.5\}/21 = 21\%$, which is roughly at the same level with the above ratios in all three Ln sites.

Table 2 and Fig. 1 shows that there are six four-fold coordinated sites for the Si$^{4+}$ ions (Si$_1$, Si$_2$, Si$_3$, Si$_4a$, Si$_4b$, Si$_5$). We also calculated the BVS and the values of charge imbalance for these Si sites, which are shown in Table 7. The minimum value of charge imbalance is obtained for the Si–O (N, N, N) composition in almost every Si site in CYSON. It means that the ratio O/(O + N) at Si sites, ~25%, providing the minimum instability

**Table 5** The sets of O$^{2-}$ and N$^{3-}$ ligands providing the smallest values of charge imbalance

| Y$_3$–[N$_1$, N$_2$, N$_3$, N$_4$, O$_5$, O$_6$, O$_9$] | 0.2688 |
| Y$_2$–[O$_1$, N$_2$, N$_3$, N$_4$, N$_5$, N$_6$, O$_9$] | 0.3016 |
| Y$_1$–[N$_1$, N$_2$, N$_3$, O$_4$, O$_5$, O$_9$] | 0.1120 |
| Ca$_1$–[O$_1$, O$_2$, N$_3$, N$_4$, N$_5$, O$_9$] | 0.2191 |
| Ca$_2$–[O$_1$, O$_2$, N$_3$, N$_4$, N$_5$, O$_9$] | 0.2191 |
| Ca$_3$–[N$_2$, N$_3$, O$_4$, O$_5$, O$_6$, O$_9$] | 0.0014 |
| Ca$_4$–[N$_2$, N$_3$, O$_4$, O$_5$, O$_6$, O$_9$] | 0.0182 |
| Ca$_5$–[N$_2$, O$_3$, N$_4$, O$_5$, O$_6$, O$_9$] | 0.0182 |

The sets of Y$^{3+}$–Ca$^{2+}$–O$^{2-}$–N$^{3-}$ and N$^{3-}$–Ca$^{2+}$–O$^{2-}$–O$^{2-}$ are obtained from a relation $\Delta R = 0.5 \times 0.10$ Å because the corresponding Shannon radii are 0.90 Å (Y$^{3+}$, coordination number (CN):6), 1.00 Å (Ca$^{2+}$, CN:6), 0.96 Å (Y$^{3+}$, CN:7), and 1.06 Å (Ca$^{2+}$, CN:7). We take the distance in the Y$^{3+}$-anion pair as $(-0.025$ Å + the distance of Ln$_2$-anion in Table 2) and the distance in the Ca$^{2+}$-anion pair as $(0.025$ Å + the distance of Ln$_2$-anion in Table 2), where the 0.05 Å value (half of the difference in distance between Y$^{3+}$-anion and Ca$^{2+}$-anion) can be obtained from a relation $[0.025$ Å $- (-0.025$ Å)]. The BVS and the value of charge imbalance are calculated from these values of reasonably re-estimated in such way cation–anion distances. Fig. 4(a)–(c) show all the values of charge imbalance at the Ln$_1$, Ln$_2$, and Ln$_3$ sites originated from the modified bond distance, respectively. The sets of the O$^{2-}$ and N$^{3-}$ ligands providing the smallest three values of charge imbalance are shown in Table 6. The smallest value of charge imbalance significantly decreases from 0.2688 to 0.0779 (Y$_3$ site), from 0.3016 to 0.1131 (Y$_2$ site), and from 0.1120 to 0.0247 (Y$_1$ site) when the two Y$^{3+}$-anion and Ca$^{2+}$-anion distances at the same site are modified taking into account differences of the ionic radii in the corresponding pairs. The coordination number of oxygen yielding the smallest value of charge imbalance is slightly changed from 3 to 2 (Ca$_1$ and Ca$_2$ sites), from 4 to 3 (Ca$_3$ site), from 0 to 1 (Y$_3$ site).

On total consideration including both cases of the same distance (Table 2) and the different distances, the number of the oxygen ligands seems to be 0–1 at the Y$_3$ sites and 2–4 at the Ca$_3$ sites, which suggests that the Ca ions are likely to be coordinated by more oxygen ions than the Y ions. The result coincides with the rough but essential Pauling’s second rule where O$^{2-}$ should be substituted for the N$^{3-}$ site near the Ca$^{2+}$ ions rather than near Y$^{3+}$ ions because it can minimize the local volume where the sum of electric charge, $-1$, caused by the Y$^{3+}$ → Ca$^{2+}$ substitution, is localized. The ratio O/(O + N) is likely to be 0% at Y$_3$, 33–50% at Ca$_2$ at the Ln$_1$ and Ln$_3$ sites, 0–14% at Y$_1$, 43–57% at Ca$_2$ at the Ln$_3$ site. Then, on the consideration of occupancies of (Y + tiny amount of Ce) and Ca in Table 1, the average ratio O/(O + N) is likely to be 26–39% at Ln$_1$ site, 22–33% at Ln$_3$ site, and 25–39% at Ln$_3$ site respectively. Total ratio of O/(O + N) in CYSON is $\{1–1.2 + 4.5\}/21 = 21\%$, which is roughly at the same level with the above ratios in all three Ln sites.

Table 2 and Fig. 1 shows that there are six four-fold coordinated sites for the Si$^{4+}$ ions (Si$_1$, Si$_2$, Si$_3$, Si$_4a$, Si$_4b$, Si$_5$). We also calculated the BVS and the values of charge imbalance for these Si sites, which are shown in Table 7. The minimum value of charge imbalance is obtained for the Si–O (N, N, N) composition in almost every Si site in CYSON. It means that the ratio O/(O + N) at Si sites, ~25%, providing the minimum instability

**Table 5** The sets of O$^{2-}$ and N$^{3-}$ ligands providing the smallest values of charge imbalance

| Sets of Y$^{3+}$–Ca$^{2+}$–O$^{2-}$–N$^{3-}$ | Values of charge imbalance |
|------------------------------------------|---------------------------|
| Y$_3$–[N$_1$, N$_2$, N$_3$, N$_4$, O$_5$, O$_6$, O$_9$] | 0.2688 |
| Y$_2$–[O$_1$, N$_2$, N$_3$, N$_4$, N$_5$, N$_6$, O$_9$] | 0.3016 |
| Y$_1$–[N$_1$, N$_2$, N$_3$, O$_4$, O$_5$, O$_9$] | 0.1120 |
| Ca$_1$–[O$_1$, O$_2$, N$_3$, N$_4$, N$_5$, O$_9$] | 0.2191 |
| Ca$_2$–[O$_1$, O$_2$, N$_3$, N$_4$, N$_5$, O$_9$] | 0.2191 |
| Ca$_3$–[N$_2$, N$_3$, O$_4$, O$_5$, O$_6$, O$_9$] | 0.0014 |
| Ca$_4$–[N$_2$, N$_3$, O$_4$, O$_5$, O$_6$, O$_9$] | 0.0182 |
| Ca$_5$–[N$_2$, O$_3$, N$_4$, O$_5$, O$_6$, O$_9$] | 0.0182 |
value, is almost at the same level as total ratio \( O/(O + N) \) of CYSON, 21%, again. From the above consistent results, it is considered that one of the reason for successful extensive substitution of \( Y^3+/Ca^{2+} \) is an existence of the structure with the bond lengths much greater than the sum, 2.28 Å, of radii of \( Y^{3+} \) \( (CN:6) \) and \( O^{2-} \) ions yielding a smaller BVS, which leads to an increased oxygen coordination and the stabilization of charge distribution near the \( Ca^{2+} \) ions.

It is notable that the new type of calculation by use of Brown's BVS in this work shed light on the phenomenon, the substitution of \( O^{2-} \) for the \( N^{3-} \) site coordinating \( Ca^{2+} \) ions rather than \( Y^{3+} \) ions, because the phenomenon is consistent with the principle of ceramics that cations and anions are arranged so that local region forming electric charge as a sum might be minimized.

Table 6 The sets of \( O^{2-} \) and \( N^{3-} \) ligands providing the smallest three values of charge imbalance

| Sets of \( Y^{3+}/Ca^{2+}/O^{2-}/N^{3-} \) | Values of charge imbalance |
|-----------------------------------------------|-----------------------------|
| \( Y_1\)–[N_1, N_2, N_3, N_4, N_5, N_8] | 0.0779 |
| \( Y_1\)–[O_1, N_2, N_3, N_4, N_5, N_8] | 0.2051 |
| \( Y_1\)–[N_1, O_2, O_3, N_4, N_5, N_8] | 0.2174 |
| \( Ca_1\)–[N_1, O_2, O_3, N_4, O_5, O_8] | 0.0042 |
| \( Ca_1\)–[N_1, O_2, O_3, N_4, O_5, O_8] | 0.0098 |
| \( Ca_1\)–[O_1, N_2, N_3, N_4, O_5, O_8] | 0.0174 |
| \( Y_2\)–[N_1, N_2, N_3, N_4, N_5, N_8] | 0.0113 |
| \( Y_2\)–[O_1, N_2, N_3, N_4, N_5, N_8] | 0.2322 |
| \( Y_2\)–[N_1, O_2, N_3, N_4, N_5, N_8] | 0.2466 |
| \( Ca_2\)–[O_1, N_2, N_3, N_4, O_5, O_8] | 0.0153 |
| \( Ca_2\)–[O_1, N_2, N_3, N_4, O_5, O_8] | 0.0262 |
| \( Ca_2\)–[N_1, O_2, N_3, N_4, O_5, O_8] | 0.0281 |
| \( Y_3\)–[N_1, N_2, O_3, N_4, N_5, N_8] | 0.0247 |
| \( Y_3\)–[O_1, N_2, N_3, N_4, N_5, N_8] | 0.0247 |
| \( Y_3\)–[O_1, O_2, N_3, N_4, O_5, O_8] | 0.0247 |
| \( Ca_3\)–[N_1, N_2, O_3, N_4, O_5, O_8] | 0.0076 |
| \( Ca_3\)–[O_1, N_2, N_3, N_4, O_5, O_8] | 0.0076 |
| \( Ca_3\)–[O_1, N_2, N_3, N_4, O_5, O_8] | 0.0076 |

Table 7 A set of anion ligands providing the minimum value of charge imbalance at each \( Si^{4+} \) site

| A set of \( Si^{4+} \) and \( O/N \) ligands | Value of charge imbalance |
|---------------------------------------------|-----------------------------|
| \( Si_1\)–[O_1, N_3, N_4, N_5] | 0.0331 |
| \( Si_2\)–[O_2, N_3, N_4, N_5] | 0.0914 |
| \( Si_3\)–[O_1, N_3, N_4, N_5] | 0.0036 |
| \( Si_{4a}\)–[O_3, N_3, N_3, N_3] | 0.0418 |
| \( Si_{4b}\)–[O_3, N_3, N_3, N_3] | 0.1536 |
| \( Si_5\)–[O_2, N_3, N_3, N_3] | 0.1287 |

4 Conclusions

The unique extensive substitution (about 70% of \( Y^3+ \) to \( Ca^{2+} \) and \( N^{3-} \) to \( O^{2-} \) in the blue-excited yellow phosphor \( (Y, Ca)_{8/12}Si_{11}(N, O)_{21}:Ce \) was investigated by calculating the Brown's bond valence sums at each three \( Y/Ca/Ce \) cation sites, including all inequivalent positions. Due to the partial occupancy of the cation and anion sites in the “parent” CYSON structure, the coordination of anions at each cationic site was not known up to now. The obtained results for the first time allow to determine the number of anions of different kinds at each site. In particular, the number of the oxygen ligands is likely to be 0 at \( Y_1 \) and \( Y_2 \) sites and 2–3 at \( Ca_1 \) and \( Ca_2 \) sites, 0–1 at \( Y_3 \) site, and 3–4 at \( Ca_3 \) site. It indicates that the oxygen ions prefer to form coordination around the \( Ca^{2+} \) ions rather than around the \( Y^{3+} \) ions, which leads to a further conclusion that the \( Y–N \) bond should be extensively substituted by the \( Ca–O \) bond instead of agglomeration of the oxygen ions far apart from the \( Ca^{2+} \) ions. On the basis of the performed analysis, it became possible to find a chemically-based strong explanation for the successful extensive substitution of the \( Y–N \) pairs by the \( Ca–O \) pairs. It can be realized on account of formation of a stable...
structure having the bond lengths much greater than the simple sum (equal to 2.28 Å) of the ionic radii of the six-fold coordinated $\text{Y}^{3+}$ and $\text{O}^{2-}$ ions. Such substitution yields smaller BVS values and is accompanied by increased oxygen coordination and the stabilization of charge distribution near the $\text{Ca}^{2+}$ ions. The performed analysis can be efficiently applied to other crystals with partial cation/anion occupancy or solid solutions; it helps to understand the local coordination around various sites in crystal lattice. The method acquires a special importance for the doped phosphor materials, since in this case the nearest coordination of an impurity ion determines the crystal field strength, point symmetry and, as such, the overall pattern of the crystal field splitting of impurity ions energy levels, and, finally, spectroscopic properties of such doped material.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 S. Nakamura and G. Fasol, *The blue laser diode: GaN Based Light Emitters and Lasers*, Springer, Berlin, 1997.

2 K. Uheda, N. Hirosaki, H. Yamamoto, H. Yamane, Y. Yamamoto, W. Inami and K. Tsuda, *The 206th Annual Meeting of the Electrochemical Society (Abstract No. 2073)*, Honolulu, Oct 3 2004.

3 N. Kijima, T. Seto and N. Hirosaki, *ECS Trans.*, 2009, 25, 247–252.

4 H. A. Hoppe, H. Lutz, P. Morys, W. Schnick and A. Seilmeier, *J. Phys. Chem. Solids*, 2000, 61, 2001–2006.

5 C. Hecht, F. Stadler, P. J. Schmidt, J. S. Gunne, V. Baumann and W. Schnick, *Chem. Mater.*, 2009, 21, 1595–1601.

6 Y. Q. Li, A. C. A. Delising, G. de With and H. T. Hintzen, *Chem. Mater.*, 2005, 17, 3242–3248.

7 R.-J. Xie, M. Mitomo, K. Uheda, F.-F. Xu and Y. Akimune, *J. Am. Ceram. Soc.*, 2002, 85, 1229–1234.

8 N. Hirosaki, R.-J. Xie, K. Kimoto, T. Sekiguchi, Y. Yamamoto, T. Suehiro and M. Mitomo, *Appl. Phys. Lett.*, 2005, 86, 211905.

9 Y. Liu, X. Zhang, Z. Hao, X. Wang and J. Zhang, *J. Mater. Chem.*, 2011, 21, 6354–6358.

10 Y. Liu, J. Zhang, C. Zhang, J. Xu, G. Liu, J. Jiang and H. Jiang, *Adv. Opt. Mater.*, 2015, 3, 1096–1101.

11 T. Seto and T. Izawa, *ECS J. Solid State Sci. Technol.*, 2015, 4, R83–R88.

12 I. D. Brown, *Structure and Bonding in Crystals*, Academic Press, New York, 1981, vol. 2, pp. 1–30.

13 I. D. Brown and D. Altermatt, *Acta Crystallogr.*, 1985, 41, 244–247.

14 N. E. Brese and M. O’Keeffe, *Acta Crystallogr.*, 1991, 47, 192–197.

15 P. Dorenbos, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, 62, 15640–15649.

16 P. E. D. Morgan, *J. Mater. Sci.*, 1986, 21, 4305–4309.