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Communications

A New Luminescent Material, $SrZnO_2$:Ba^{2+}, Mn^{2+}

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Schnering and Hoppe reported the crystal structure of $SrZnO_2$.[1] It is in the orthorhombic system in the space group *Pnma*. In $SrZnO_2$, the ZnO_4 tetrahedra share edges with each other and form waved layers. The Sr atoms are located at the cavity between the layers. In the structure, there is one site for the Sr atom, one for the Zn atom, and two for the O atoms. The emission of Mn^{2+} is broad.[2] The emission depends strongly on the host material and varies from green to red. Mn^{2+} is very useful as an activator, not only for commercial phosphor but also for solid-state chemistry. Owing to the high sensitivity to the crystal field, we can obtain information about the environment of Mn^{2+} in a solid by measuring its optical properties.

A new luminescent material, $SrZnO_2$: Ba^{2+}, Mn^{2+}, was synthesized, and its crystal structure and emission properties are reported in the present communication. The material emitted yellow color, and the emission peak shifted to a longer wavelength with the Mn^{2+} concentration. Therefore, the relation between the crystal structure and emission property was discussed. The Rietveld method was used for the refinements, and it was easy to obtain information on the surroundings of the Zn atom site, at which Mn^{2+} was substituted.[3] The information obtained revealed very well the Ba concentration dependence of the emission properties.

$SrZnO_2$:Ba^{2+}, Mn^{2+} were initially prepared by mixing stoichiometric quantities of $BaCO_3$, $SrCO_3$, ZnO, and $MnCO_3$ (Rare Metallic Co Ltd., purity >99.99%). A pressed pellet mixture was fired at 900−1100 °C for 5 h in 5%H_2−Ar gas and quenched. The mixture was then ground. Diffraction data were obtained on a Rigaku RINT 2500V diffractometer system at room temperature. The Rietveld method was performed using RIETAN-2000.[4] Selected bond lengths and angles were calculated using ORFFEPPC.[5] The emission and excitation spectra were obtained by a Hitachi F-4500 spectrophotometer equipped with a Xe lamp. These measurements were done at room temperature.

The emission intensity of $Sr(Zn_{1-x}Mn_x)O_2$ without Ba doping increased up to $x = 0.01$ and then decreased with increasing Mn^{2+} concentration. The emission peaks shifted slightly to a longer wavelength with the Mn^{2+} concentration. Over $x = 0.02$, the amount of MnO and the unknown phase increased gradually with the Mn^{2+} concentration. Because it was not possible to determine the compositions of the unknown phase, it was not possible to perform structural refinement of the samples with the Mn^{2+} concentration over $x = 0.02$. Therefore, the optimum Mn^{2+} concentration was decided at $x = 0.01$.

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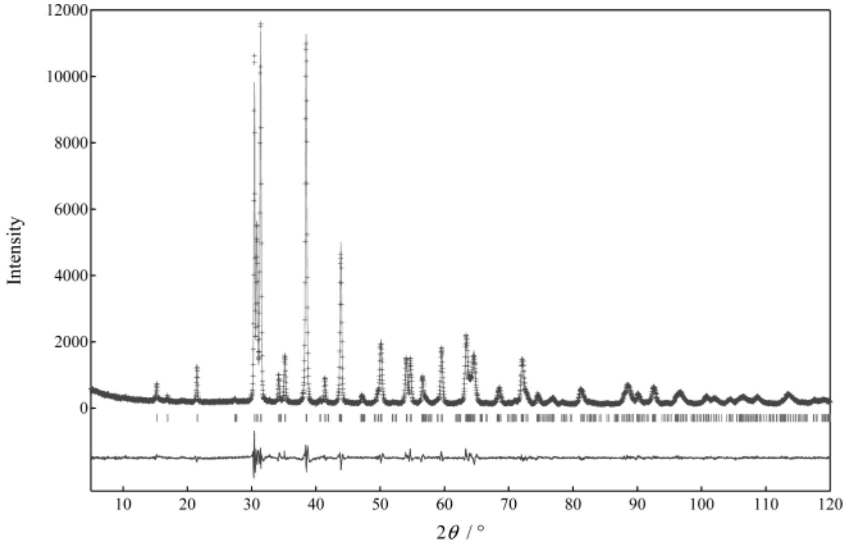

Figure 1. Comparison between the observed and calculated patterns of $(Sr_{0.7}Ba_{0.3})(Zn_{0.99}Mn_{0.01})O_2$. From top to bottom: dotted line, observed intensity; solid line, calculated intensity; vertical short lines, position of reflections; solid line, difference between observed and calculated intensity.

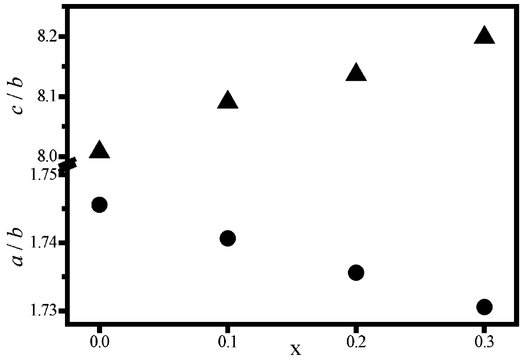

Figure 2. Concentration dependence of the ratios of the length of the parameters, *a*/*b* (*a*-axis length/*b*-axis length) and *c*/*b* (*c*-axis length/*b*-axis length).

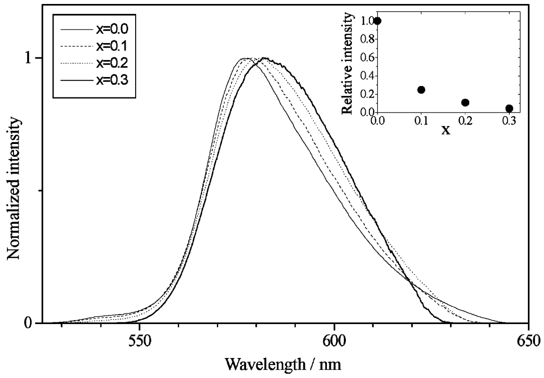

Figure 3. Mn^{2+} concentration dependence of the emission spectra (λ_{exc} = 281−283 nm) of $(Sr_{1-x}Ba_x)Zn_{0.99}Mn_{0.01}O_2$.

Figure 1 shows the Rietveld refinement of $(Sr_{0.7}Ba_{0.3})(Zn_{0.99}Mn_{0.01})O_2$. The factors of the refinement were R_{wp} = 0.0838, R_p = 0.0630, R_I = 0.0209, R_F = 0.0123, and s = 1.65. The sample had a single-phase crystal structure with the following cell parameters: a = 5.868(3) Å, b = 3.391(2) Å, and c = 11.589(5) Å (the numbers in parentheses are the errors in the last digits). $BaZnO_2$ is in the hexagonal system in space group $P3_121$, and its crystal structure is different from that of $SrZnO_2$.[6] In X-ray diffraction, patterns of $(Sr_{1-x}Ba_x)Zn_{0.99}Mn_{0.01}O_2$ and the reflection peaks of $BaCO_3$ and ZnO appeared over x = 0.4. Therefore, this fact led to the conclusion that the Ba solid solubility limit in $Sr(Zn_{0.99}Mn_{0.01})O_2$ was between x = 0.3 and x = 0.4. The Rietveld refinement was done to samples with x = 0.0, 0.1, 0.2, and 0.3. An attempt to dope Ca was unsuccessful.

The cell parameters and the unit cell volume increased with the Ba^{2+} concentration, but the unit cells did not expand equally in all directions of the axis. The ratios of the length of the parameters, *a*/*b* (*a*-axis length/*b*-axis length) and *c*/*b* (*c*-axis length/*b*-axis length) were calculated. Figure 2 shows the result. *a*/*b* decreased with the Ba concentration, but *c*/*b* increased. The unit cell expanded especially in the *c*-axis direction. The ZnO_4 tetrahedra form a layer on the *ab* plain. Therefore, the Zn atom and surrounding O atoms cannot widely move in the *a*- and *b*-axis directions. The layers are not connected to each other in the *c*-axis direction. They were separated by a longer distance by a larger atom Ba than Sr.[7] This is the reason the unit cell expanded especially in the *c*-axis direction.

Figures 3 and 4 show the Mn^{2+} concentration dependence of the emission and excitation spectra of $(Sr_{1-x}Ba_x)Zn_{0.99}Mn_{0.01}O_2$, respectively. The peak of emission shifted to a longer wavelength, from 578 to 582 nm, with the Ba concentration. As shown in the inset, the emission intensity decreased with the Ba concentration. The excitation spectra of $(Sr_{1-x}Ba_x)Zn_{0.99}Mn_{0.01}O_2$ were very broad, from around 200 to 450 nm, and consisted of five or six peaks. In the case of (Zn, Mg)S:Mn^{2+}, the crystal system of this solid solution was hexagonal, and the cell constants *a* and *c* increased with an Mg concentration up to x = 0.32.[8] In addition, the emission peak shifted

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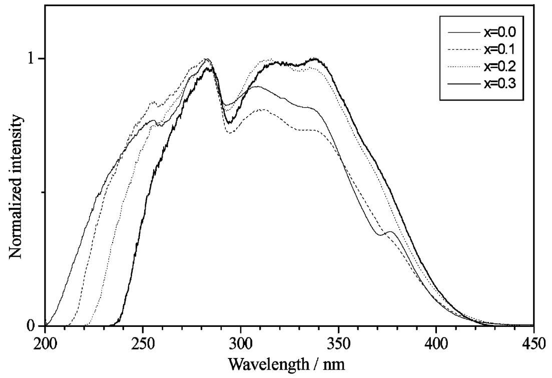

Figure 4. Mn^{2+} concentration dependence of the excitation spectra (λ_{em} is wavelength with maximum emission intensity) of $(Sr_{1-x}Ba_x)Zn_{0.99}Mn_{0.01}O_2$.

from 585 nm at $x = 0.0$ to 552 nm at $x = 0.32$. The Mn^{2+} emission originated in the $d - d$, ${}^4T_1$ (${}^6S$) − ${}^6A_1$ (${}^4G$), transition.[2] The transition was strongly influenced by the crystal field. ${}^6A_1$ is the ground level. ${}^4T_1$ is the lowest excitation level at which the energy deceased with the increase of the crystal field. The authors concluded the following: that the increase of cell constants led to the reduction of the crystal field, and then the weakened crystal field originated the blue shift. In the case of $(Sr_{1-x}Ba_x)Zn_{0.99}Mn_{0.01}O_2$, however, the relation between the Mn^{2+} concentration dependence of the emission peak and that of the cell parameters was inconsistent with that of (Zn, Mg)S:Mn^{2+}. Though the lattice constants increased, the emission peak shifted to a longer wavelength, that is, red-shifted. Therefore, the environment of the Zn site was precisely studied.

Figure 5 shows the differences in the Zn−O distances between the Ba-doped and undoped samples of $(Sr_{1-x}Ba_x)Zn_{0.99}Mn_{0.01}O_2$. The distances were calculated from the results of RIETAN-2000 using ORFFEPPC. The differences in the Zn−O distances between the Ba-doped and undoped samples, that is, Δ(Zn−O) = (Zn−O distance of $(Sr_{1-x}Ba_x)(Zn_{0.99}Mn_{0.01})O_2$) − (Zn−O distance of $Sr(Zn_{0.99}Mn_{0.01})O_2$). Zn−O$1^{iii}$ and Zn−O2^{ii} barely increased with the Ba^{2+} concentration. However, Zn−O1 drastically decreased with the Ba^{2+} concentration. These results show that the ZnO tetrahedra do not shrink linearly. The shrinking leads to a stronger crystal field, and then the energy level of ${}^4T_1$ (${}^6S$) decreased. This is the mechanism of the red-shifting of emission. The Sr atom connected with seven O atoms. The averages of the Sr−O distances increased with the Ba concentration. As mentioned above, the unit cell expanded, especially in the *c*-axis direction, but the Zn atom and surrounding O atoms changed their positions slightly to the *a*- and *c*-axis direction, while keeping the tetrahedra and layers.

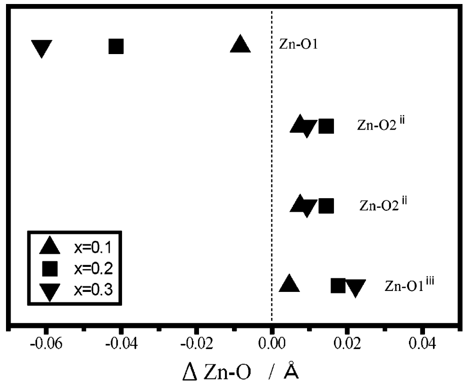

Figure 5. Differences in the Zn−O distances between the Ba-doped and undoped samples of $(Sr_{1-x}Ba_x)Zn_{0.99}Mn_{0.01}O_2$. Symmetry code: (i) $^1/_2 - x$, $^3/_4$, $z + {}^1/_2$; (ii) $-x$, $^3/_4$, $-z$; (iii) $x + {}^1/_2$, $^1/_4$, $^1/_2 - z$.[9]

It was not possible to explain the red-shifting of emission in $SrZnO_2$: Ba^{2+}, Mn^{2+} by the changes of the cell constants, but instead by the changes of the Zn−O distances. This proves that the refinements of the crystal structure are very useful for understanding the phenomena of materials.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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