A New Luminescent Material, $Sr_3Al_{10}SiO_{20}$:Tb^{3+}

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There has been considerable interest in the development of advanced luminescent materials for applications such as large flat panel displays, for example, PDPs (plasma display panels) and FEDs (field emission displays). The properties of these materials arise from complex interactions among the host structure, activators, and defects and interfaces, all of which are strongly dependent on composition.[1,2] To create efficient luminescent materials, it is necessary to suppress nonradiative processes in which the energy of the excited state is used to excite the vibrations of the host lattice, that is, to heat the host lattice. Point defects in the crystal structure also contribute to this nonradiative process. A discrepancy in the pure composition and/or the charge compensation induces point defects in the structure.

An efficient luminescent center for green emission, a Tb^{3+} ion, is activated in many materials. As a host of luminescent material, a bulk sample of single-phase $Sr_3Al_{10}SiO_{20}$ was prepared. The crystal structure of single-phase $Sr_3Al_{10}SiO_{20}$ was determined from the powder X-ray diffraction (XRD) data, revealing one-dimensional pillars of edge-sharing AlO_6 octahedra and six-membered rings of corner-sharing $(Al,Si)O_4$.[3] The structure is unique and has not previously been observed among luminescent aluminum-based oxides.[4−6] The composition $Sr_3Al_{10}SiO_{20}$ is in the monoclinic system in a space group of $C2/m$. The Tb^{3+} ion possesses an excessive positive charge relative to that of the Sr^{2+} ion and thus requires charge compensation. Therefore, charge compensation is required when the Sr^{2+} ion is replaced by the Tb^{3+} ion in this material. Replacement of Si^{4+} with Al^{3+} ions can maintain the charge compensation of the material. There are four different sites, that is, 8*j*, 8*j*, 4*h*, and 2*a*, for the Al^{3+} ions in the structure.[7] The Si^{4+} and Al^{3+} ions occupy two 8j sites in common. The occupancy of the Al^{3+} and Si^{4+} ions at 8j sites is 0.875 and 0.125, respectively. Therefore, substitution of Si^{4+} with Al^{3+} ions ap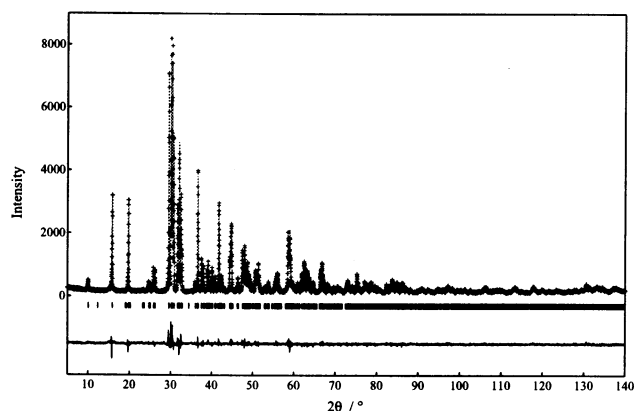pears to be an easy means of maintaining charge compensation. Using the method considered here, we prepared and characterized a new luminescent material, $Sr_3Al_{10}SiO_{20}$:Tb^{3+}. The relative emission intensity of this material is higher than that of other Tb^{3+}-doped strontium aluminum silicates, for example, $Sr_2Al_2SiO_7$ and $SrAl_2Si_2O_8$, and is also higher than that of the strontium aluminate $SrAl_{12}O_{19}$ under UV excitation.

Figure 1. Comparison between the observed and calculated patterns of $(Sr_{0.95}Tb_{0.05})_3Al_{10.15}Si_{0.85}O_{20}$. From upper to lower: dotted line, observed intensity; solid line, calculated intensity; vertical short lines, position of reflections; solid line, difference between observed and calculated intensity.

To systematically study this luminescent material, a series of bulk powder samples of composition $(Sr_{1−x}Tb_x)_3$-$Al_{10+3x}Si_{1−3x}O_{20}$, with x ranging from 0 to 0.1, were synthesized by conventional solid-state synthesis. $SrCO_3$, Al_2O_3, SiO_2, and Tb_4O_7 (>99.99% purity) were mixed in the molar ratio given by the formula. The mixture was calcined for 2−10 h at 1500−1700 °C in a reducing atmosphere with one intermediate. Other Tb^{3+}-doped strontium aluminum silicates, $Sr_2Al_2SiO_7$ and $SrAl_2Si_2O_8$, and the strontium aluminate $SrAl_{12}O_{19}$ were calcined under the same conditions. All samples were checked by XRD. The profile refinement, using the Rietveld method, was performed using RIETAN-2000.[8] Selected bond lengths and angles were calculated by ORFFE.[9] The photoluminescent (PL) excitation and emission spectra of $(Sr_{1−3x}Tb_x)_3Al_{10+3x}Si_{1−x}O_{20}$ were taken using a Hitachi F-4500 spectrophotometer in the reflection mode.

Figure 1 shows the comparison between the observed and calculated patterns as well as the difference curve of the Rietveld refinement of $(Sr_{0.95}Tb_{0.05})_3Al_{10.15}Si_{0.85}O_{20}$. The factors of the refinement are $R_p = 0.0567$, $R_{wp} = 0.0749$, and $R_{exp} = 0.0561$. The sample has the single-phase crystal structure of $(Sr_{0.95}Tb_{0.05})_3Al_{10.15}Si_{0.85}O_{20}$ with the following cell parameters: $a = 15.1181(5)$ Å, $b = 11.1866(3)$ Å, $c = 4.9022(2)$ Å, and $\beta = 108.131(2)°$ (the numbers in parentheses are the errors in the last digits). There are two crystallographically independent Sr atoms in the $Sr_3Al_{10}SiO_{20}$ structure, with different

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(1) Blasse, G.; Grabmaier, B. C. *Luminscent Materials*; Springer-Verlag: Berlin, 1994.
(2) Wang, J.; Yoo, Y.; Gao, C.; Takeuchi, I.; Sun, X.; Chang, H.; Xiang, X.-D.; Schults, G. *Science* **1998**, *279*, 1712.
(3) Kubota, S.; Yamane, H.; Shimada, M. *Acta Crystallogr.* **2001**, *E57*, 60.
(4) Kimata, M. *Z. Kristallogr.* **1984**, *167*, 103.
(5) Chiari, G.; Calleri, M.; Bruno, E.; Ribbe, P. H. *Am. Mineral.* **1975**, *60*, 111.
(6) Park, J.-G.; Cormack, A. N. *J. Solid State Chem.* **1996**, *121*, 278.
(7) Arnold, H. *International Tables for Crystallography*; Hahn, T., Ed.; Kluwer Academic: Dordrecht, 1996; Vol. A.

(8) Izumi, F.; Ikeda, T. *Mater. Sci. Forum* **2000**, *198*, 321.
(9) Busing, W. R. Martin, K. O.; Levy, H. A. *ORFFE Fortran Crystallographic Function and Error Program*; Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1964.
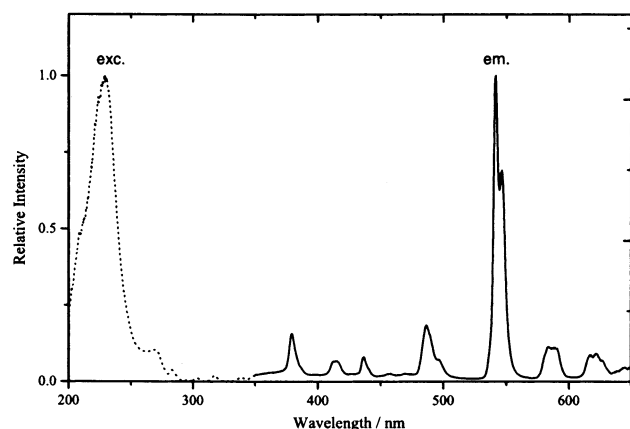
Figure 2. Photoluminescencent excitation and emission spectra of a powder sample of $(Sr_{0.93}Tb_{0.07})_3Al_{10.21}Si_{0.79}O_{20}$.

Figure 3. Concentration dependence of the emission intensity of $(Sr_{1-x}Tb_x)_3Al_{10+3x}Si_{1-3x}O_{20}$ $(0.0 \leq x \leq 0.1)$. The area of peaks of emission from the $^5D_3$ level (triangle), $^5D_4$ level (square), and total area (circle).

coordination environments, that is, ten-coordinated for Sr(1) and eight-coordinated for Sr(2).

The refinement revealed that the Tb^{3+} ions were located only at the Sr(1) sites, whereas the possibility that the Tb^{3+} ion located at the Sr(2) site or at both sites was rejected by the negative occupancy parameters of the Tb^{3+} ions at the Sr(2) site. A comparison of the crystal structure of $(Sr_{0.95}Tb_{0.05})_3Al_{10.15}Si_{0.85}O_{20}$ with that of $Sr_3Al_{10}SiO_{20}$ revealed that the volume of the unit cell of $(Sr_{0.95}Tb_{0.05})_3Al_{10.15}Si_{0.85}O_{20}$ was smaller than that of $Sr_3Al_{10}SiO_{20}$. The results are explained by the difference in the ionic radius between Sr^{2+} (1.25 Å for eight-coordination) and Tb^{3+} (1.04 Å for eight-coordination).[10] The average distances of Sr1–O decreased more than that of Sr2–O with increasing Tb^{3+} concentration. This result is coincident with the fact that the Tb^{3+} ion exists only at the Sr1 site.

The excitation and emission spectra of $(Sr_{0.93}Tb_{0.07})_3Al_{10.21}Si_{0.79}O_{20}$ (Figure 2) display maxima at 228.4 and 541.4 nm, respectively. The emission peaks are assigned to the transition from $^5D_{J=3,4}$ to $^5F_{J=3,4,5,6}$ of the Tb^{3+} ion.[11]

The PL intensity is shown in Figure 3 as a function of x. The emission intensity of $^5D_{J=3} - {}^5F_{J=3,4,5,6}$ around 375 and 475 nm decreased with increases in the Tb^{3+} concentration, whereas the emission intensity of $^5D_{J=4} - {}^5F_{J=3,4,5,6}$ around 475 and 640 nm increased. This

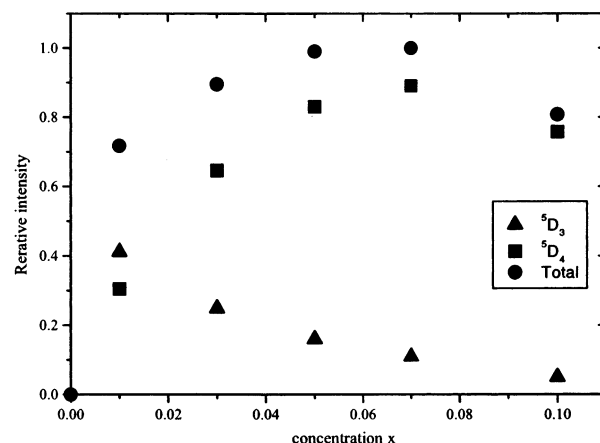finding is explained by the following cross-relaxations between Tb^{3+} ions: $Tb^{3+}(^5D_3) + Tb^{3+}(^7F_6) \rightarrow Tb^{3+}(^5D_4) + Tb^{3+}(^7F_0)$.[12]

The Tb^{3+}-doped strontium aluminum silicates, $Sr_2Al_2SiO_7$ and $SrAl_2Si_2O_8$, and the strontium aluminate $SrAl_{12}O_{19}$ were synthesized under the described conditions (the Tb^{3+} concentration of each sample was 7 mol % of the Sr^{2+} ion), and their emission intensities were compared with that of $(Sr_{0.93}Tb_{0.07})_3Al_{10.21}Si_{0.79}O_{20}$. AlO_4 and SiO_4 tetrahedra form five-membered rings, sharing corners in $Sr_2Al_2SiO_7$,[4] whereas AlO_4 and SiO_4 tetrahedra form the six-membered rings in the $SrAl_2Si_2O_8$ structure.[5] The $SrAl_{12}O_{19}$ belongs to the magnetoplumbite structure, which is identical to that of BAM $(BaMgAl_{10}O_{17})$.[6] In this compound, AlO_6 forms walls that connect at each edge, and these walls are connected via AlO_4 and AlO_6. Under UV excitation, the relative emission intensity of $Sr_2Al_2SiO_7$, $Sr_2Al_2SiO_7$, and $SrAl_{12}O_{19}$ were 63, 6, and 20%, respectively, of $(Sr_{0.93}Tb_{0.07})_3Al_{10.21}Si_{0.79}O_{20}$.

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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(10) Shannon, R. D.; Preivitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.

(11) Dieke, G. H. In *Spectra and Energy Levels of Rare Earth Ions in Crystals*; Crosswhite, H. M., Crosswhite, H., Eds.; Interscience: New York, 1968; p 253.

(12) Blasse, G.; Bril, A. *Philips Res. Rep.* **1967**, *22*, 481.