Visible orange photoluminescence in a barium titanosilicate BaTiSi$_2$O$_7$

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A visible orange photoluminescence (PL) was observed at room temperature from a barium titanosilicate BaTiSi$_2$O$_7$. The diffuse-reflection spectrum revealed the presence of an oxygen defect in the Ti–O polyhedral unit. The broad PL with the peak at 580 nm was observed by ultraviolet (UV) excitation at 321 nm as the PL excitation spectrum maximum, being sufficient for a visual confirmation under UV light. It was suggested that its peculiar PL is related to both the absolutely isolated pyramidal TiO$_6$ unit pair and the oxygen defect in the TiO$_3$ unit in the BaTiSi$_2$O$_7$ phase. © 2006 American Institute of Physics. [DOI: 10.1063/1.2194310]

To date, photoluminescent (PL) materials have been extensively exploited and investigated due to their scientific and practical interests. For example, lanthanide-activated substances, e.g., Eu$^{3+}$:Y$_2$O$_2$S and Eu$^{2+}$:BaMgAl$_{10}$O$_{17}$, are now quite important for applications in cathode ray tubes and plasma display panels. On the other hand, PL studies of the transition from the 2$d$ orbit of Ti$^{4+}$, i.e., O$_2^−$–Ti$^{4+}$ → O$^−$–Ti$^{3+}$, have also been comprehensively carried out. Particularly, the titanium ion has been paid much attention for a long time not only from the standpoint of its ferroelectric property but also in the optic field, e.g., as a tunable solid-state laser, its large optical nonlinearity, and as blue-emitting device material.

According to the studies on the PL of titanates with Ti$^{4+}$, these can be roughly classified into two types, that is, blue and yellow emissions; the former is caused by ultraviolet (UV) excitation but originated from the defect oxygen defects in the titanium-oxygen unit, because the long-wavelength emission, also takes place by UV excitation but originated from the defect titanium center, consisting of a titanium octahedron associated with oxygen defects. In addition, the yellow emission in the titanates is observed only at low temperature. In this study, we have synthesized a barium titanosilicate BaTiSi$_2$O$_7$ and its optical property was then examined. It was found that the BaTiSi$_2$O$_7$ phase showed a clear orange PL with the peak at ~580 nm at room temperature in the BaTiSi$_2$O$_7$ phase by UV excitation, being sufficient for visual confirmation. The manner of the visible orange emission in this study has no precedent.

The BaTiSi$_2$O$_7$ phase examined in this study was synthesized by a conventional solid-state reaction. Commercial powders of reagent grade BaCO$_3$, TiO$_2$, and SiO$_2$ (Kojundo Chemical Laboratory) were thoroughly mixed and ground in an alumina mortar. The mixture with the nominal composition of 1BaO–1TiO$_2$–2SiO$_2$ was placed in a platinum crucible with a lid and calcined at 1000 °C for 24 h in an electric furnace. The batch weight was 10 g. Subsequently, the calcined sample was reground and sintered at 1100 and 1200 °C for 12 h with intermediate mixing in air. Formation of the crystalline phases obtained after the sintering was examined by an x-ray diffraction (XRD) analysis using Cu Kα radiation (RINT-III, Rigaku). The diffuse-reflection spectrum of the crystalline sample (powder state) was measured by a UV-visible spectrometer (V570, JASCO) attached to an integral sphere. The measurement of the photoluminescence excitation (PLE) and PL spectra of the sample was performed using a spectrofluorometer (RD-2200F, SHIMADZU) with a xenon lamp as the excitation source. Confirmation of the visible PL in the sample was carried out using a commercial UV lamp with the wavelength at 316 nm. All of the measurements were done at room temperature.

Figure 1 shows the powder XRD pattern of the crystalline phase synthesized in this study, together with the XRD data of the BaTiSi$_2$O$_7$ (Fig. 1). The powder XRD pattern of the BaTiSi$_2$O$_7$ phase was independently reported by Köppen and Dietzel and Stassen et al. After the final heat treatment at 1200 °C, a white crystalline sintered body was obtained. The XRD pattern of the sintered matter exactly corresponded to that of BaTiSi$_2$O$_7$ reported by Stassen et al. Therefore, the single crystalline phase of BaTiSi$_2$O$_7$ was properly prepared by the synthesizing process used in this study. The diffuse-reflection, PLE, and PL spectra of the BaTiSi$_2$O$_7$ phase synthesized in this study are shown in Fig. 2(a). In the diffuse-reflection spectrum, it was noted that the band edge was quite obscure around 350 nm. This is due to the formation of oxygen defects in the titanium-oxygen unit, because the shoulder near the band edge originated from the oxygen defect in the titanates. In the PLE and PL spectra, an excitation peak at ~321 nm and a broad emission with the peak at ~580 nm were detected. The PL indicated a clear orange color, being easily confirmed by the naked eye, as shown in Fig. 2(b). Thus, we demonstrated the intrinsic orange emission in the BaTiSi$_2$O$_7$ phase at room temperature from both spectroscopic and visual aspects.

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luminescent center of the Ti-polyhedral unit, which is not

In the case of a luminescent center that can be excited by the CT transition, which consists of oxygen and a transition-metal ion with an inert-gas structure, the quenching temperature of the PL increases with increasing wave number of the excitation peak maxima. This effect can be explained by applying the configurational-coordinate model. The relationship between the reported wave number of the excitation peak and the quenching temperature in the titanates is summarized in Fig. 3. It was realized that the presence of the luminescent center of the Ti-polyhedral unit, which is not directly linked to each other (i.e., the isolated TiO$_6$ unit and the pyramidal TiO$_5$ unit that is also isolated or linked with alternating short and long Ti–O bonds), and the higher energy of the maximum excitation for the CT transition should be required for the efficient PL at room temperature. It is obvious that the point of the BaTiSi$_2$O$_7$ phase (double circle in Fig. 3) is deviated from both extrapolations (dashed line). The following two points are quite different from the titanates reported so far: (1) the BaTiSi$_2$O$_7$ phase indicated a clear PL at room temperature by excitation at 321 nm (~31 100 cm$^{-1}$), which is too low to obtain a visible PL at room temperature, and (2) the color of the PL was in the orange region (~580 nm). The color of the PL sufficiently observed at and above room temperature in the titanates is in the wavelength region of 400–500 nm, i.e., a blue color.

With respect to (1), the titanates with the isolated TiO$_6$ octahedral and the pyramidal TiO$_5$ unit more and less show the PL around room temperature, as seen in Fig. 3. It is also expected that the BaTiSi$_2$O$_7$ phase consists of the isolated Ti-polyhedral unit. Unfortunately, the detailed crystal structure of the BaTiSi$_2$O$_7$ is still unknown. However, it is pointed out that this phase crystallizes in a monoclinic system and would have the structural similarity to suzukiite (BaVSi$_2$O$_7$, tetragonal), because the ionic radius of Ti$^{4+}$ with five coordinations (0.51 Å) is almost the same as that of V$^{4+}$ (0.55 Å). Figure 4 shows the crystal structure of suzukiite. This mineral is composed of the Si$_4$O$_8$ ring and the absolutely isolated pyramidal VO$_5$ unit pair, i.e., the bases of the two pyramids mirror symmetrically met each other. The compounds with the pyramidal TiO$_5$ unit, CsTiP$_2$O$_6$, and Ba$_2$TiSi$_2$O$_6$ possess isotopic structures of the vanadium counterparts, which also contain the pyramidal VO$_5$ unit. Furthermore, the XRD pattern of the BaVSi$_2$O$_7$ phase (Liu and Greendan, in Fig. 1 and Takeuchi and Joswig, ) has a significant analogy to the simplified pattern of the BaTiSi$_2$O$_7$ phase. Consequently, it was verified that the BaTiSi$_2$O$_7$ phase possesses a slightly distorted but basically the same structure as suzukiite. Therefore, it is considered that the BaTiSi$_2$O$_7$ phase meets one of the necessary condi-

FIG. 1. Powder XRD patterns for the crystalline phases obtained by sintering the composition of 1BaO–1TiO$_2$–2SiO$_2$. The diffraction data of BaTiSi$_2$O$_7$ (below) and BaVSi$_2$O$_7$ (above) are also included.

FIG. 2. (a) Diffuse-reflection (dashed line), PL, and PLE spectra (solid line) of the BaTiSi$_2$O$_7$ phase synthesized in this study and (b) the BaTiSi$_2$O$_7$ crystalline phase under natural light (left) and exposed to a UV light at the peak wavelength of 316 nm (right). The sample showed a clear PL at room temperature. The chromaticity coordinates of the PL are $x=0.472$ and $y=0.418$, corresponding to the orange color in the CIE chromaticity diagram.

FIG. 3. Wave number of excitation peak vs the quenching temperature of the titanates reported so far. These data were cited from Refs. 5, 10, and 12–14. The quenching temperature of the PL is defined as the point of intersection of the abscissa and a straight line drawn through the points at which the PL intensity has fallen to 80% and 20% of the maximum value when the PL intensity is plotted as a function of temperature (Ref. 9). In this letter, the expression in the literature, “efficient luminescence at room temperature,” was regarded as that the 300 K for the sake of convenience.

FIG. 4. The crystal structure of suzukiite. This mineral is composed of the Si$_4$O$_8$ ring and the absolutely isolated pyramidal VO$_5$ unit pair, i.e., the bases of the two pyramids mirror symmetrically met each other. The compounds with the pyramidal TiO$_5$ unit, CsTiP$_2$O$_6$, and Ba$_2$TiSi$_2$O$_6$ possess isotopic structures of the vanadium counterparts, which also contain the pyramidal VO$_5$ unit. Furthermore, the XRD pattern of the BaVSi$_2$O$_7$ phase (Liu and Greendan, in Fig. 1 and Takeuchi and Joswig, ) has a significant analogy to the simplified pattern of the BaTiSi$_2$O$_7$ phase. Consequently, it was verified that the BaTiSi$_2$O$_7$ phase possesses a slightly distorted but basically the same structure as suzukiite. Therefore, it is considered that the BaTiSi$_2$O$_7$ phase meets one of the necessary condi-
clear. However, we can deduce that both the existence of the peculiar pyramidal TiO_5 unit pair and the oxygen defect in its TiO_6 unit pair are responsible for it, because the former and the latter play a key role in the efficient PL at room temperature and the emission in the longer-wavelength region, respectively. Further investigations will be done in order to elucidate the mechanism of the orange PL.

In summary, we reported the visible orange emission at room temperature of a barium titanosilicate BaTiSi_2O_7. The diffuse-reflection spectrum indicated the existence of a defect titanate center in the BaTiSi_2O_7 phase. The broad emission band with the peak at ∼580 nm was observed at the UV excitation of 321 nm (the peak of the PLE spectrum). A clear orange emission was also sufficiently confirmed by visual observation during the exposure to UV light. Although the explicit interpretation of the origin of orange PL in the BaTiSi_2O_7 phase has not been given in this study, it is possible ascribed to the cooperative effect of the oxygen defect and the peculiar pyramidal TiO_5 unit pair of the luminescent center of the BaTiSi_2O_7 phase.

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**FIG. 4. Crystal structure of suzukiite (BaVSi_2O_7).** Sphere and dark (blue in online) and blight (red) polyhedra correspond to barium ion and SiO_4 tetrahedron and pyramidal VO_5 units, respectively.