Afterglow in synthetic bazirite, $\text{BaZrSi}_3\text{O}_9$

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A blue afterglow was observed in the bazirite-type $\text{BaZrSi}_3\text{O}_9$ synthesized by a solid-state reaction for the first time. The synthetic bazirite phase showed a clear blue long-lasting luminescence at room temperature after the exposure of UV light, in spite of the low in any lanthanide-doping. It was proposed that the afterglow in the $\text{BaZrSi}_3\text{O}_9$ phase was originated from the occupation of $\text{Tl}^{4+}$ as an impurity in the distorted octahedral site.

Key-words: Bazirite, Afterglow, Silicate, Titanium, Impurity

1. Introduction
Investigation and development of long-lasting phosphor have been vigorously performed because of its attractive and extensive application. As well-known phosphors showing afterglow, $^{88}\text{Ra}$-added $\text{Cu}: \text{ZnS}$ and $\text{Eu}^{2+}, \text{Dy}^{3+}: \text{SrAl}_2\text{O}_4$ exist. However, these materials include the radioactive and lanthanide elements. Therefore, it is of particular interest to explore new afterglow material consisting of more conventional and non-toxic substances without any lanthanide-activation. It is also significant for the conservation of lanthanide resources.

It is known that several Ti-included silicate mineral indicates the blue-green photoluminescence (PL) at room temperature, e.g., fresnoite- and benitoite-type phases. Recently, our research group has found and synthesized new titanosilicate phosphors showing the PL at room temperature, e.g., the suzukiite-type $\text{BaTiSi}_2\text{O}_7$ indicating an orange emission, and the fresnoite-type $\text{Ba}_2\text{TiSi}_2\text{O}_8$-nanocrystalized glass indicating a bluish white emission. In this study, we focused on a zirconosilicate mineral, bazirite ($\text{BaZrSi}_3\text{O}_9$), which was newly discovered from Scotland in 1970’s, and was an isostructural of benitoite, $\text{BaTiSi}_3\text{O}_9$. In this paper, we presented the afterglow property in the bazirite-type $\text{BaZrSi}_3\text{O}_9$ synthesized by a solid-state reaction for the first time, and the fundamental origin of the afterglow was discussed.

2. Experimental
2.1 Sample preparation
The bazirite-type $\text{BaZrSi}_3\text{O}_9$ crystalline sample was synthesized by a conventional solid-state reaction. Commercial powders of reagent grade $\text{BaCO}_3$ (99.9%), $\text{ZrO}_2$ (99.9%) and $\text{SiO}_2$ (99.9%) were thoroughly mixed and ground using an alumina mortar (the batch weight was 10 g), and then the mixture was placed in a platinum crucible with a lid or a platinum boat, and calcined at 1000°C for 24 h in an electric furnace under air atmosphere. After the calcining, the mixtures were re-ground and sintered at 1100–1350°C for 2 h with intermediate mixing in air atmosphere until the reaction of mixture was completely finished, and finally, the sintered ceramic (polycrystalline) body was obtained.

2.2 Characterization
Identification and the lattice constants of the sintered matter were examined by a powder X-ray diffraction (XRD) analysis using Cu Kα radiation. Confirmation of PL in the synthesized polycrystalline sample was carried out using an ultraviolet (UV) lamp with a wavelength of 254 nm. The diffuse-reflection spectrum of the crystalline sample was measured in the range of 250–800 nm using a UV-visible spectrometer with an attached integrating sphere. The PL and PL excitation (PLE) spectra, and the afterglow intensity as a function of time, i.e., decay curve, for the synthesized sample was measured by a spectrophotometer with a xenon lamp as an excitation source. In the decay curve measurement, monitoring of the afterglow intensity was started after exposing the sample to the UV light for 30 s. In the optical measurements, the pulverized polycrystalline sample was used. All of experimental measurements were done at room temperature.

3. Results
Figure 1 shows the powder XRD patterns of the crystalline sample synthesized in this study, together with the reported XRD data of $\text{BaZrSi}_3\text{O}_9$. All of the powder XRD peaks were assigned to be the bazirite-type phase by the comparison to the crystallographic data of the bazirite-type $\text{BaZrSi}_3\text{O}_9$ (JCPDS: 29–0214). The bazirite-type $\text{BaZrSi}_3\text{O}_9$ was singly crystallized and then any other impurity phase could not be observed in the XRD pattern. The XRD pattern indicates clear and sharp diffraction peaks, and the ceramic body was white and well-sintered, implying a high sample crystallinity. The XRD pattern of the bazirite-type $\text{BaZrSi}_3\text{O}_9$ in this study had a great analogy to that of benitoite ($\text{BaTiSi}_3\text{O}_9$). The lattice constants of the synthesized bazirite phase were evaluated to be $a=6.773$ Å and $c=10.01$ Å. These values corresponded to those of reported in the JCPDS 29–0214 ($\text{BaZrSi}_3\text{O}_9$). Thus, the bazirite-type $\text{BaZrSi}_3\text{O}_9$, which enables us to the optical measurements, was successfully synthesized.

The PL, PLE, and diffuse-reflection spectra in the synthesized bazirite-type $\text{BaZrSi}_3\text{O}_9$ are shown in Fig. 2. The excitation band around 254 nm (Exc. in Fig. 2), and the broad emission band in the visible blue region (Em.) with a peak around 460 nm were detected. Although the addition of $\text{Tl}^{4+}$
The PL property of the synthesized BaZrSi3O9 phase is similar to that of the Ti4+−doped phase.9 In addition, an absorption band was observed in the diffuse-reflection spectrum (Diff.) in the region of 250–300 nm.

Figure 3 shows (a) the afterglow intensity as a function of the passage of time, i.e., decay curve, after the excitation of UV light with the wavelength of 254 nm in the BaZrSi3O9 phase, together with the perovskite-type BaZrO3 (discussed later), and (b) the photo of BaZrSi3O9 sintered body and a wristwatch with the afterglow function after the UV irradiation. From the Fig. 3, we can realize that the BaZrSi3O9 phase indicated an obvious afterglow, being sufficient for a visual confirmation for a few ten seconds. Generally, in the long-lasting material, the afterglow property is described by the following equation; \[ I = I_0 t^{-n} \]
where \( I \) is the afterglow intensity, and \( I_0 \) and \( t \) are the initial intensity and time.1 The value of \( n \) is inherent in the phosphor, and the smaller the \( n \) becomes, the slower the decay of afterglow delay, e.g., the \( n \) values of Eu2+, Dy3+:SrAl2O4 and Cu:ZnS are reported to be 1.1 and 1.3.1 For the BaZrSi3O9 phase in this study, the \( n \) was evaluated to be 0.64.

Although some zirconate compounds showing the PL had been considered to be a self-activated phosphor, subsequently it was found that the origin of PL was due to the presence of Ti4+ in the zirconia (ZrO2) as an impurity. According to Sarver, baddeleyite-type ZrO2 indicates the PL and afterglow in green color region, and the ZrO2 regent, from which the Ti4+ is chemically eliminated throughout, did not indicate the PL.10 Therefore, it is necessary to check the existence of Ti4+ in the ZrO2 regent. By an inductively coupled plasma mass spectrometer, the analytical results of \( \sim 3.0 \times 10^3 \) mg/g and \( \sim 7.2 \times 10^5 \) mg/g were obtained for the Ti and Zr elements, respectively, meaning that about 0.2% (2000 ppm) of Ti element was present in the ZrO2 regent used in this study. Although the result contradicts the value estimated from the purity of ZrO2 regent (99.9%), this is probably due to the so-called matrix effect. Thus, the order of 1000
ppm of Ti element was detected in the ZrO$_2$ regent, indicating that the synthesized BaZrSi$_3$O$_9$ phase involved a trace of Ti$^{4+}$.

4. Discussion

Since the bazirite-type BaZrSi$_3$O$_9$ were singly crystallized, it could be considered that the afterglow property confirmed in this study is not due to the residual (non-reacted) ZrO$_2$ regent, but is a characteristic of the bazirite-type phase. In order to check it, examination of afterglow properties for other zirconate compound, which was made from the same ZrO$_2$ regent used in this study, was performed. In here, perovskite-type cubic BaZrO$_3$ was chosen as a counterpart of the bazirite-type BaZr$_2$SiO$_6$ because the BaZrO$_3$ phase also consists of octahedral TiO$_6$ unit. The BaZrO$_3$ phase could be prepared from the stoichiometric mixture of regents (BaCO$_3$:ZrO$_2$ = 1:1) by sintering at 1400°C for 6 h in air. In the Fig. 3, although the n of perovskite-type BaZrO$_3$ (0.14) is apparently smaller than that of bazirite-type BaZr$_2$SiO$_6$ (0.64), the BaZrO$_3$ phase hardly showed the PL and afterglow. Thus, it was verified that the afterglow in the synthesized BaZr$_2$SiO$_6$ phase is an intrinsic property.

The PL, PLE and diffuse-reflection spectra in the synthesized BaZr$_2$SiO$_6$ phase have a great similarity to those of benitoite (BaTiSi$_3$O$_9$). Referring to the luminescent mechanism of BaTiSi$_3$O$_9$, in the diffuse-reflection spectra, the large absorption around 250–300 nm is ascribed to the charge-transfer (CT) transition from the 2p orbit of the surrounding oxygen ion to the empty outer 3d orbit of Ti$^{4+}$ in the titanium-oxygen octahedral unit, i.e., O$^2-$ → Ti$^{4+}$ → O$^-$ → Ti$^{3+}$. The excitation and emission bands in the spectra correspond to the CT transition of O$^2-$ → Ti$^{4+}$ and the transition of Ti$^{3+}$$-$$\rightarrow$A$_1$, which was excited by the CT transition, respectively. Since the BaZr$_2$Si$_3$O$_9$ phase synthesized in this study includes the Ti$^{3+}$ as an impurity, it is obvious that the emission properties (i.e., the PL and afterglow phenomena) are closely related to the presence of Ti$^{3+}$ in the BaZr$_2$Si$_3$O$_9$ phase.

In titanate compounds, the coordination state of Ti$^{4+}$ strongly affects the PL property, meaning the efficient luminescent center. On the contrary, the perovskite-type phases, in which the octahedral TiO$_6$ units are three-dimensionally interlinked, show the PL and afterglow phenomena i.e., the PL and afterglow phenomena are sufficient for a visual confirmation after the exposure of UV light, in spite of the free from any lanthanide-doping. Although the explicit interpretation of afterglow in the bazirite-type BaZr$_2$Si$_3$O$_9$ has not been given in this study, it was strongly suggested that the afterglow phenomenon was caused by the presence of Ti$^{4+}$ as an impurity and the occupation in the distorted octahedral ZrO$_6$ site of the luminescent center.

In baddeleyite, the low-temperature phase of ZrO$_2$, has a distorted fluorite structure (monoclinic system), and the Zr$^{4+}$ takes seven-fold coordination. In addition, afterglow in the Ti$^{4+}$-doped yttrium oxyorthosilicate, Y$_2$O$_5$S, without any lanthanide-doping is recently demonstrated as well as the baddeleyite-type ZrO$_2$. Furthermore, the Y$^{3+}$ site, which is replaceable by Ti$^{4+}$, takes also seven-fold coordination in the Y$_2$O$_5$S (i.e., three short and one long Y-O bond, and three Y-S bond). We note that the cation site, in which the doped-Ti$^{4+}$ should occupy, in these compounds is a low symmetry. In the case of the bazirite, the octahedral ZrO$_6$ unit is trigonally distorted (not regular polyhedron) unlike to the perovskite-type BaZr$_2$O$_6$ phase with the regular ZrO$_6$ octahedron. According to the crystal structure of bazirite, the angle of O-Zr-O bond lies in the range of ~85°–92° (the Zr-O distances are equivalent). Thus, it is strongly suggested that the afterglow material with the Ti$^{4+}$ as a luminescent center appears in such conditions as i) the doped-Ti$^{4+}$ occupies at the distorted (i.e., low-symmetry) site of luminescent center, and ii) the low concentration (doping-level) of Ti$^{4+}$ is dissolved in the crystalline phase because the baddeleyite mineral (BaTiSi$_3$O$_9$) never indicated the afterglow. This prediction would be informative to explore the Ti-involved new afterglow material. According to it, wadeite, K$_2$ZrSi$_3$O$_9$, is a promising candidate for the afterglow host crystal because the wadeite consists of the isolated and distorted octahedral ZrO$_6$ unit (but not isostructural of bazirite), i.e., the O-Zr-O angle and Zr-O distance lie in the range of ~87–92° and ~0.205–0.210 nm, respectively.

Although the afterglow mechanism for the BaZr$_2$Si$_3$O$_9$ phase is not still clear, we deduce that the afterglow in the BaZr$_2$Si$_3$O$_9$ phase is originated from both the presence of Ti$^{4+}$, and the recombination of hole and electron, which is excited through the CT transition by the UV absorption, and captured by a trap, similar to the case of Ti$^{4+}$: ZrO$_2$. Further investigations will be done in order to elucidate the mechanism of the afterglow.

5. Summary

We synthesized the BaZr$_2$Si$_3$O$_9$ phase with bazirite-type structure and investigated its afterglow property. The BaZr$_2$Si$_3$O$_9$ phase was synthesized by means of a solid-state reaction. The crystalline phase indicated a clear blue photoluminescence and afterglow at room temperature, being sufficient for a visual confirmation after the exposure of UV light, in spite of the free from any lanthanide-doping. Although the explicit interpretation of afterglow in the bazirite-type BaZr$_2$Si$_3$O$_9$ has not been given in this study, it was strongly suggested that the afterglow phenomenon was caused by the presence of Ti$^{4+}$ as an impurity and the occupation in the distorted octahedral ZrO$_6$ site of the luminescent center.

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References

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