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Yellow fluorescence from baghdadite and synthetic $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$

Received: 13 April 2005 / Accepted: 20 August 2005 / Published online: 8 December 2005
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Abstract Baghdadite from Fuka, Okayama Prefecture, Japan shows a bright yellow fluorescence under UV (Hg 253.7 nm) excitation. The photoluminescence (PL) spectrum at 300 K consists of one large band near 580 nm and two small UV bands at 318 and 397 nm. The optical excitation spectrum of the bright yellow fluorescence consists of two bands near 220 and 250 nm. The temperature dependence of the PL intensity exhibits linear thermal quenching. To reveal the origin of the bright yellow fluorescence from baghdadite, powder $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ crystals are synthesized. Synthetic $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ shows luminescence spectra similar to those of baghdadite, and the intensity of the yellow fluorescence is markedly increased by titanium addition. The origin of the bright yellow fluorescence from baghdadite is ascribed to the existence of titanium.

Keywords Baghdadite · Fluorescence · Photoluminescence · $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$

Introduction

Al-Hermezi et al. (1986) found a new calcium zirconium silicate mineral, baghdadite ($\text{Ca}_3\text{ZrSi}_2\text{O}_9$), from the Dupezeh mountain, Qala-Dizeh region, northeastern Iraq. In this type of locality, this mineral occurs as anhedral grains up to 0.25 mm in length in a melilite skarn. Its cathodoluminescence color is dull gray with a

greenish tint. Subsequently, baghdadite from high-grade contact metamorphic rocks at the Oslo Rift, southern Norway was reported by Jamtveit et al. (1997) and that from a garnet-vesuvianite skarn at the Akagane mine, Iwate Prefecture, Japan was reported by Matsubara and Miyawaki (1999). Baghdadite from these localities occurs as crystals up to 0.1 mm in length, and its luminescence color has not been described. Shiraga et al. (2001) reported a fluorescent baghdadite $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ (Bagh 1) up to 0.5 mm in length in gellenite–spurrite skarns from Fuka, Okayama Prefecture, Japan. Recently, one of the present authors (I.K.) has collected a new sample of baghdadite $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ (Bagh 2) up to 1.2 cm in length from Fuka. Its empirical formula is almost the same as those reported by previous investigators, and this baghdadite from Fuka shows a bright yellow fluorescence under UV (Hg 253.7 nm) excitation.

Gittensite $\text{CaZrSi}_2\text{O}_7$ is known as a calcium zirconium (titanium) silicate mineral, in addition to baghdadite. To our knowledge, there exists no literature concerning luminescence properties of gittensite.

On the other hand, luminescence properties of synthetic zirconium (titanium) silicates have been investigated by Blasse and coworkers. (1) Fresnoite-type $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and $\text{Sr}_2\text{TiSi}_2\text{O}_8$ show a green emission at about 530 nm under 250 nm excitation (Blasse 1968, 1979). (2) Pure $\text{BaZrSi}_3\text{O}_9$ shows no emission under 254 nm excitation but shows UV emission at about 285 nm under cathode ray excitation, and Ti^{4+} -activated $\text{BaZrSi}_3\text{O}_9:\text{Ti}^{4+}$ shows a blue-green emission at about 480 nm under 250 nm excitation (Blasse and Brill 1970). (3) Ti^{4+} -activated $\text{SrZrSi}_2\text{O}_7:\text{Ti}^{4+}$ shows UV emission at about 300 nm under 200 nm excitation (Blasse et al. 1993). In these silicates, the Stokes shift depends entirely on the compound.

Plaisier et al. (1995) synthesized $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ (baghdadite without titanium) by firing a mixture of 3CaCO_3 , ZrO_2 and 2SiO_2 , following the method reported by Kordyuk and Gul'ko (1962). X-ray powder diffraction data revealed a monoclinic crystal structure with

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space group $p2_1/c$ and parameters $a=7.3603(1)$, $b=10.1766(3)$, $c=10.4514(3)$ Å and $\beta=90.875(2)^\circ$. Blasse et al. (1995) observed photoluminescence (PL) spectra, optical excitation spectra and the temperature dependence of the PL intensity of synthetic $\text{Ca}_3\text{ZrSi}_2\text{O}_9$, which shows an emission band at about 540 nm under 260 nm excitation.

As described above, the bright yellow fluorescence is one of the characteristics of the baghdadite from Fuka. The objectives of this study are to (1) describe the fluorescence of natural and synthetic $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ in detail and (2) investigate the origin of the bright yellow fluorescence of baghdadite.

Historically, fluorescence phenomena in minerals, e.g., zincblende, have led to modern developments such as color cathode ray tubes, fluorescent lighting devices, plasma display panels (PDPs) and so on. The results of this study may give a hint for developments of new phosphors.

In this study, we obtain the PL spectra and optical excitation spectra at 300 and 10 K and the temperature dependence of the PL intensity of natural baghdadites from Fuka, and compare the obtained optical spectra with those of the powder $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0, 0.01$ and 0.15) crystals synthesized by Futaba Co., Japan.

Samples

A sample containing baghdadite (Bagh 1) from Fuka was provided by Shiraga et al. (2001). This mineral occurs as grains and prismatic crystals in association with gehlenite, spurrite, tilleyite, perovskite, grandite garnet and vesuvianite. A new sample containing baghdadite (Bagh 2) from Fuka was also used. This mineral occurs as aggregates of prismatic crystals in veins intruded in spurrite and/or tilleyite, in association with euhedral perovskite crystals up to 1 cm in width. After crushing, only the grains of baghdadite emitting fluorescence under UV light were manually selected. The optical and physical properties and chemical composition of Bagh 1 have been reported by Shiraga et al. (2001). The empirical formulae of the baghdadites are as follows: Bagh 1, $(\text{Ca}_{3.03}\text{Na}_{0.01})(\text{Zr}_{0.83}\text{Ti}_{0.15})(\text{Si}_{1.99}\text{Al}_{0.01}\text{Fe}_{0.01})\text{O}_9$ and Bagh 2, $(\text{Ca}_{3.03}\text{Na}_{0.02})(\text{Zr}_{0.83}\text{Ti}_{0.10}\text{Mg}_{0.01}\text{Mn}_{0.01})(\text{Si}_{2.04}\text{Al}_{0.02}\text{Fe}_{0.01})\text{O}_9$. The contents of trace elements in Bagh 1 were determined by inductively coupled plasma-mass spectrometry (ICP-MS).

Powder crystals of synthetic compounds $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0, 0.01$ and 0.15) were prepared by the solid-phase reaction. Mixtures of theoretical amounts of CaCO_3 (purity 99.9%), ZrO_2 (purity 99.99%), TiO_2 (purity 99.999%) and SiO_2 (purity 99.99%) were placed in platinum crucibles and heated for 3 h in air at 1,500°C. X-ray diffraction analysis revealed that the obtained compounds are grown as powder $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ crystals, although they contain small amounts of CaZr_4O_9 and Ca_2SiO_4 .

Experimental

The chemical compositions of Bagh 1 and Bagh 2 were determined using an electron microprobe analyzer (JEOL, JSM-5410LV + JED-2140). In the measurement of contents of trace elements in baghdadite, an ICP-MS analyzer (Seiko SPQ8000H) was used. The sample was dissolved in concentrated HCl before ICP-MS analysis.

Before the measurement of optical spectra, the grains of fluorescent baghdadite were sufficiently powdered using an agate mortar. The powdered sample was packed into a sample holder with a synthetic quartz-glass cover.

The measuring system of PL emission and excitation spectra was almost the same as that used in the previous study (Aierken et al. 2003). In the measurement of PL emission spectra, a 200 W deuterium lamp (Hamamatsu Photonics L1835) and a 500 W xenon short-arc lamp (Ushio UXL-500D) were used as excitation light sources. The excitation wavelengths with a bandwidth of 4 nm were selected using a Ritsu MC-50L grating monochromator. The observation wavelengths with a bandwidth of 1 nm were selected using a Ritsu MC-50 grating monochromator. The PL spectral intensity was converted to an electric signal using a photomultiplier (Hamamatsu Photonics R928). The electric signal was input to a personal computer through a GP-IB cable. The PL spectra were corrected for the spectral sensitivity of the measuring system using a standard tungsten lamp calibrated according to the National Bureau of Standards (NBS), USA.

In the measurement of optical excitation spectra, the same measuring system as that used for the emission spectra was used, except for the excitation bandwidth of 1 nm and the observation bandwidth of 5 nm. As excitation light sources, two types of lamp corresponding to the measurement region were used: a deuterium lamp in the 200–320 nm region and a xenon short-arc lamp in the 280–400 nm region. The ordinate of the excitation spectra was plotted with the excitation efficiency after optical excitation energy correction. The optical excitation energy was measured using a photomultiplier. For a wavelength region below 320 nm, the excitation energy was estimated on the basis of the excitation spectrum of sodium salicylate, which has a nearly constant quantum efficiency in this wavelength region. In the measurement of luminescence properties at low temperatures, the sample temperature was controlled using an Iwatani D310 refrigerator.

Results

The contents of trace elements in Bagh 1 determined by ICP-MS are shown in Table 1. The contents of major elements in the host crystal are not shown.

Figure 1a and b shows the PL emission spectra (EM) of Bagh 1 and Bagh 2 under 254 nm excitation at 300

Table 1 Contents ($\mu\text{g/g}$) of trace elements in the baghdadite (Bagh 1) from Fuka

Element	Content ($\mu\text{g/g}$)	Element	Content ($\mu\text{g/g}$)	Element	Content ($\mu\text{g/g}$)	Element	Content ($\mu\text{g/g}$)
Mg	435	Ga	675	La	33	Dy	15
Sc	29	Ge	27	Ce	75	Ho	5
Cr	440	Sr	86	Pr	24	Er	13
Mn	77	Y	132	Nd	58	Tm	2
Co	11	Nb	115	Sm	11	Yb	15
Ni	41	Mo	19	Eu	1	Lu	2
Cu	13	Ag	1,900	Gd	3	Hf	1,450
Zn	42	Ba	15	Tb	5	U	22

and 10 K, respectively. The PL spectra consist of one large yellow band and two small UV bands. The maximum of the yellow band at 300 K is observed at 580 nm in Bagh 1 and 565 nm in Bagh 2. The profile of the yellow band slightly depends on the temperature. The small UV bands have two maxima at 318 and 397 nm at 300 K. The excitation spectra (EX) of Bagh 1 and Bagh 2 were obtained by monitoring the yellow fluorescence at 590 nm at the temperatures of 300 and 10 K. The excitation spectra consist of two bands near 220 and 250 nm.

Figure 2 shows the temperature dependence of the PL intensity of Bagh 1 obtained by monitoring the yellow fluorescence at 585 nm under 254 nm excitation. The PL intensity is almost constant at temperatures between 10 and 80 K. As the temperature increases, the PL intensity almost linearly decreases at temperatures from 115 to 300 K. The PL intensity at 300 K is quenched to approximately 1/6 of that at low temperatures.

The small UV bands in Fig. 1a are separately observed as the UV1 band at 333 nm under 225 nm excitation and the UV2 band at 392 nm under 335 nm

excitation at 10 K. Figure 3 shows the UV1 band (EM) of Bagh 1 under 225 nm excitation at 10 K. A vibronic structure appears on this band at low temperatures. The excitation spectrum (EX) obtained by monitoring the UV fluorescence at 339 nm consists of three bands at 202, 225 and 278 nm.

Figure 4 shows the UV2 band (EM) of Bagh 1 under 335 nm excitation at 10 K. A vibronic structure appears on this band at low temperatures. The excitation spectrum (EX) was obtained by monitoring the UV fluorescence at 392 nm. The vibronic structure also appears on the excitation band at low temperatures.

Figure 5 shows the PL spectra (EM) and excitation spectra (EX) of synthetic $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0, 0.01$, and 0.15) at 300 K. The optical spectra of Bagh 2 in Fig. 1a are also shown for comparison. All the PL spectra (EM) were obtained under 254 nm excitation and all the excitation spectra were obtained by monitoring the fluorescence at 550 nm. The height of each band reflects the relative efficiency of the fluorescence. $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ without titanium ($x=0$) shows an emission band at 567 nm and two excitation bands near

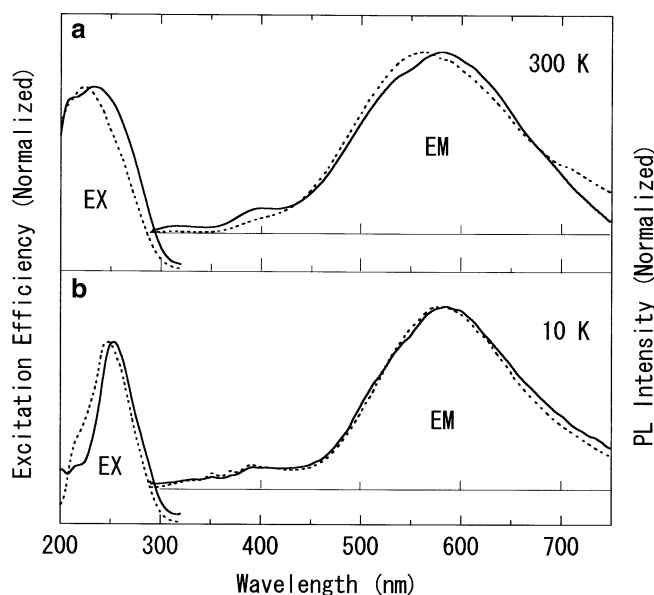


Fig. 1 PL emission spectra (EM) and excitation spectra (EX) of the baghdadites, Bagh 1 (solid lines) and Bagh 2 (dotted lines) from Fuka at 300 K (a) and 10 K (b). EM was obtained under 254 nm excitation and EX by monitoring yellow fluorescence at 590 nm

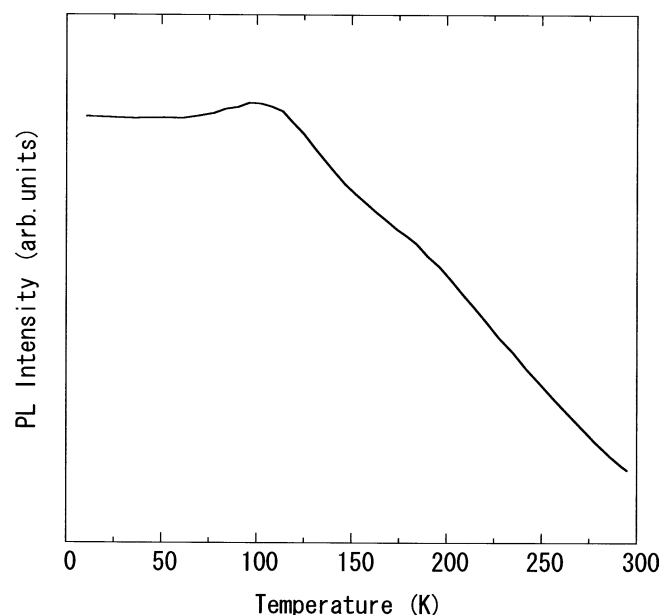


Fig. 2 Temperature dependence of PL intensity of the baghdadite (Bagh 1) from Fuka by monitoring yellow fluorescence at 585 nm under 254 nm excitation

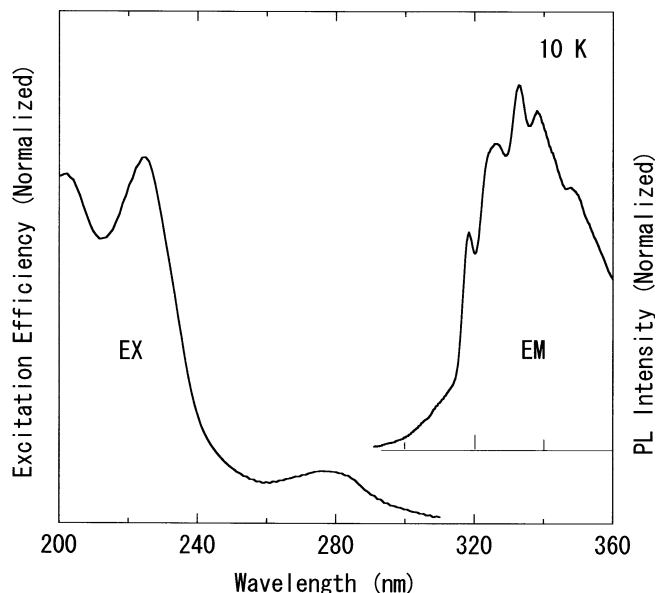


Fig. 3 PL emission spectrum (EM) and excitation spectrum (EX) of the baghdadite (Bagh 1) from Fuka at 10 K. EM was obtained under 225 nm excitation and EX by monitoring UV1 fluorescence at 339 nm

210 and 250 nm. The corresponding bands of synthetic $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ at 4.2 K were reported by Blasse et al. (1995): an emission band at 540 nm and an excitation band at 260 nm. The emission bands of $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0.01$ and 0.15) are observed at 580 nm ($x=0.01$) and 579 nm ($x=0.15$), and their excitation spectra consist of two bands near 210 and 250 nm. The optical spectra of $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0.01$ and 0.15) are almost the same as those of Bagh 2 (dotted lines), but the intensity of the

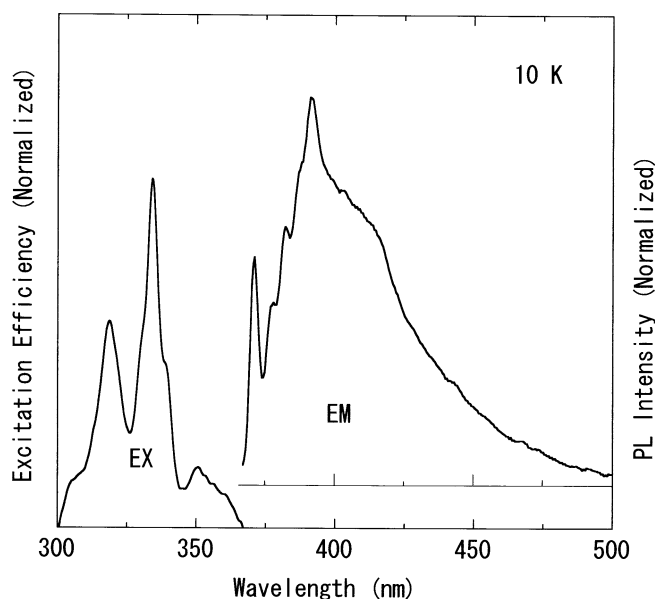


Fig. 4 PL emission spectrum (EM) and excitation spectrum (EX) of the baghdadite (Bagh 1) from Fuka at 10 K. EM was obtained under 335 nm excitation and EX by monitoring UV2 fluorescence at 392 nm

yellow fluorescence is markedly increased by titanium addition. The fluorescence efficiency of $x=0.01$ exceeds about two times that of Bagh 2. The fluorescence efficiency of $x=0.15$, which is lower than that of $x=0.01$, may be caused by concentration quenching. In other words, this indicates that the fluorescence efficiency of synthetic $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ with an optimum x exceeds that with $x=0.01$.

Manganese-activated zinc silicate $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ is known as a standard phosphor, which shows a bright green luminescence under cathode ray or short-wavelength Hg line (253.7 nm) excitation. The optical excitation spectrum of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ in a short-wavelength region (Koike et al. 1979) is similar to that of baghdadite. To estimate the fluorescence efficiency of baghdadite, the present authors also obtained the PL emission spectrum of standard $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor. The height of the PL emission band of $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0.01$) is approximately 1/40 that of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ under 253.7 nm excitation.

Discussion

In the localized Mn^{2+} center of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, the Stokes shift is only about 1.4 k cm^{-1} (Palumbo and Brown 1970) and the full width at half maximum (FWHM) of the emission band is 1.5 k cm^{-1} (about 40 nm). On the other hand, a very large Stokes shift of 22.3 k cm^{-1} and a very large FWHM of 5.60 k cm^{-1} (about 180 nm) of the yellow emission band are characteristics of the luminescence of baghdadite. These support the following discussion on charge transfer transition.

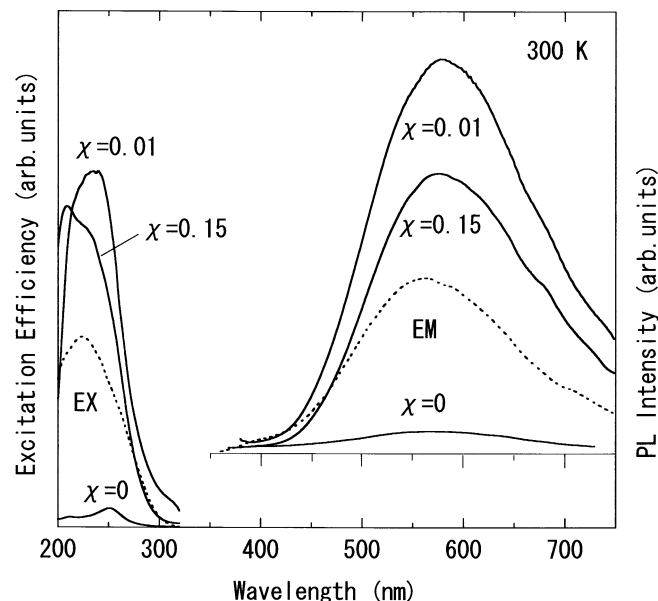


Fig. 5 PL emission spectra (EM) and excitation spectra (EX) of synthetic $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0, 0.01$ and 0.15) at 300 K. The optical spectra of the baghdadite (Bagh 2) in Fig. 1a are shown by dotted lines for comparison. EM was obtained under 254 nm excitation and EX by monitoring fluorescence at 550 nm

Blasse et al. (1995) observed a yellow emission band with a maximum at 540 nm for synthetic $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ under 255 nm excitation. The profiles of the PL spectrum and excitation spectrum of $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0$) in Fig. 5 are similar to those reported by Blasse et al. (1995), except that the peak wavelength (567 nm) of the emission band in Fig. 5 ($x=0$) is slightly larger than that (540 nm) reported by them. In the Zn_2O_{10} group of $\text{Ca}_3\text{ZrSi}_2\text{O}_9$, one [O(9)] of the oxygen atoms is surrounded by three calcium atoms and one zirconium atom. The atomic distance (1.989 Å) of Zr–O(9) is smaller than the other Zr–O distances (2.106–2.224 Å) (Plaisier et al. 1995; Blasse et al. 1995). Blasse et al. (1995) attributed the excitation transition of $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ to the charge transfer transition between Zr and the neighboring O(9).

Blasse and coworkers have reported the Ti^{4+} fluorescence of synthetic silicates (Blasse 1968, 1979; Blasse and Bril 1970; Blasse et al. 1993). The Ti^{4+} fluorescence efficiency of $\text{SrZrSi}_2\text{O}_7:\text{Ti}^{4+}$ is low (Blasse et al. 1993), while that of synthetic fresnoite $\text{Ba}_2\text{TiSi}_2\text{O}_8$ is high (Blasse 1968, 1979). $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ is thought to belong to the latter case. The temperature dependence of the PL intensity of the yellow fluorescence in Bagh 1 (Fig. 2) is similar to that of the green fluorescence in synthetic $\text{Sr}_2\text{TiSi}_2\text{O}_8$ with a fresnoite structure (Blasse 1968). As the ionic radius of Ti^{4+} (0.605 Å) is smaller than that of Zr^{4+} (0.72 Å) (Shannon 1976) that is substituted by Ti^{4+} , the smallest Ti–O distance in baghdadite is expected to be smaller than the corresponding Zr–O distance (1.989 Å) in $\text{Ca}_3\text{ZrSi}_2\text{O}_9$. Therefore, it is appropriate to attribute the bright yellow fluorescence of baghdadite to the charge transfer transition between the titanium ion and one of the neighboring oxygen ions in a TiO_6 octahedron. Indeed the intensity of the bright yellow fluorescence of synthetic $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ is markedly increased by titanium addition (Fig. 5).

The fluorescence efficiency of synthetic $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ ($x=0.01$) exceeds about two times that of natural baghdadite (Fig. 5), but the height of the PL emission band is approximately 1/40 that of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$. However, the fluorescence efficiency of synthetic $\text{Ca}_3(\text{Zr}_{1-x}\text{Ti}_x)\text{Si}_2\text{O}_9$ depends on the conditions used for synthesis, such as x , heating temperature, heating duration and so on, and is expected to be markedly improved under optimum conditions.

The origin of the two UV bands may be the presence of trace elements in baghdadite. Contents of trace elements in baghdadite are shown in Table 1. Rare-earth ions often form luminescence centers in minerals. However, their contents in baghdadite are very low. Other candidates for impurity centers are Cr (440 µg/g), Mn (77 µg/g), Ga (675 µg/g), Ag (1,900 µg/g) and U (22 µg/g). On the two UV bands, vibronic structures appear at low temperatures. A typical vibronic structure is observed on the optical spectra of $\text{MgO}:\text{Bi}^{3+}$ and $\text{CaO}:\text{Bi}^{3+}$ (Hughes and Pells 1975; Asano and Yamashita 1981). When the ionic radii of the luminescent

impurities are larger than those of the host elements substituted by the impurities, the thermal vibration of the impurity ions in the crystal lattice is restricted, and only the vibronic structure with a local vibration mode appears on the optical spectra at low temperatures. This gives us a hint of the origin of the two UV bands; however, further study on the synthesis of $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9:\text{Me}$ activated by a known metal ion, Me, for example, is required.

Acknowledgements The authors thank Mr. Takuya Hamada and Mr. Yoshitaka Satoh of Futaba Corporation, Japan for synthesizing the $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ compounds. The analysis of the contents of trace elements in baghdadite was carried out at the Satellite Venture Business Laboratory (SVBL) in Okayama University. The authors are also grateful to members of SVBL for performing the ICP-MS analysis. They also wish to thank Dr. Masanori Kurosawa, University of Tsukuba, for helpful suggestions regarding this paper.

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