



Luminescence properties of BaZrO₃ perovskites under synchrotron radiation.

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Abstract

Luminescence emitted by a pure BaZrO₃ at low temperatures under exposure to UV or x-ray radiation has been known for a long time and is generally ascribed to the decay of intrinsic self-trapped excitons. In this talk, for the first time the luminescence properties of BaZrO₃ were studied under vacuum ultraviolet (VUV) and ultraviolet (UV) synchrotron radiation (3.6 – 25 eV) emitted from DORIS III storage ring at SUPERLUMI station [2], HASYLAB DESY, Hamburg, in the wide temperature range of 10–293 K. The use of synchrotron radiation provides ideal conditions for the multiplication of electronic excitations, when each absorbed photon produces two or more electronic excitations. To study this effect, we have measured the appropriate excitation spectra of the so-called green emission (~500 nm). In particular, a prominent threshold for excitation multiplication at ca. 14 eV (as high as ~4 Eg) was discovered.

Introduction and experiment

Photoluminescence measurements were carried out using pulsed synchrotron radiation at the SUPERLUMI station HASYLAB (DESY, Hamburg). The excitation spectra were recorded with a spectral resolution of 0.3 nm, whereas the spectral resolution of the analyzing monochromator is 11 nm. Luminescence spectra were recorded with a photomultiplier (Hamamatsu R6358P) and liquid nitrogen cooled CCD detector from Princeton Instruments. Sample – single crystal BaZrO₃ from CrystTec (100)K, 10X10X1, one surface side was polished.

The photoluminescence (PL) properties of BZO are still puzzling and controversial. The greenish luminescence (GL) having a maximum at 2.2–2.4 eV of photon energy (wavelength ~ 500 nm) that is emitted by pure STO at low temperature under exposure to UV or x-ray radiation has been known since a long time [1–3] and is generally ascribed to the decay of intrinsic self-trapped excitons (STEs). [4–7]. A STE can be roughly depicted as a tightly bound state of a hole and a Ti³⁺ polaron [8]. However, this purely intrinsic scenario has been recently called into question by Mochizuki *et al.*, [9–10] who argued for a crucial role of defects and possibly of surfaces in this greenish emission. Very recently, another PL emission taking place in the blue luminescence (BL), with its maximum at 2.8–2.9 eV (~ 430 nm), was reported for STO at RT. This BL emission, potentially useful for optoelectronic applications, is well visible both in intrinsic samples at sufficiently high excitation intensities [9; 11] and in suitably *n*-doped samples, in the latter case at much lower excitation intensities [11, 12].

At low temperatures, the BL is accompanied by a spectrally narrow near-UV luminescence (UVL) located at 3.2 eV (~390 nm), i.e., at band edge [9; 11, 12]. Moreover, in some cases, the BL may also be accompanied by a long green "tail" covering a spectrum similar to the GL discussed above but still visible at room temperature. [9; 13] It is not clear what determines the appearance of this high-temperature greenish component, but the surface state of oxidation seems to play an important role [9] This GL is clearly visible at high excitation intensities. [14, 15].

In this poster we report luminescence properties of BaZrO₃ using synchrotron radiation. As it is well known, BaZrO₃ experimentally determined indirect band gap energy Eg= 3.25 eV, whereas the direct band gap energy is 3.75 eV [16, 17], and thus use of synchrotron radiation provides ideal conditions for the multiplication of electronic excitations, when each absorbed photon produces two or more electronic excitations. To study this effect, we have measured the appropriate excitation spectra of the so-called green emission (~500 nm). In particular, a prominent threshold for excitation multiplication at ca. 14 eV (as high as ~4 Eg) was discovered.

Luminescence spectra

In the case of excitation of the BZO polished surface side, only single STE emission at 2.5 eV is observed. It is almost quenched at T> 40 K.

The shape of the spectrum does not depend on excitation energy

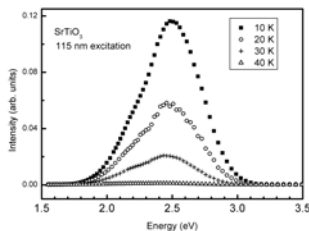


Fig.1

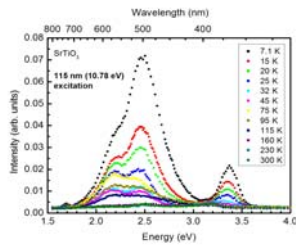


Fig.2

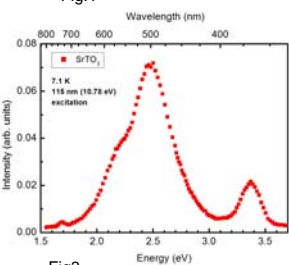


Fig.3

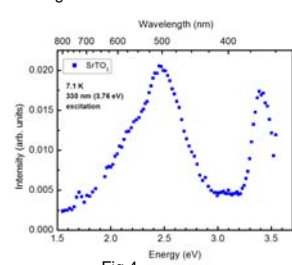


Fig.4

In the case of the excitation of the opposite side of the sample the emission spectra show more complicated behavior

- Two additional bands are recorded (Fig.2 and 3)
- Emission spectrum depends on the excitation energy (Fig.3 and 4)
- High-temperature greenish component is clearly seen (Fig.2)

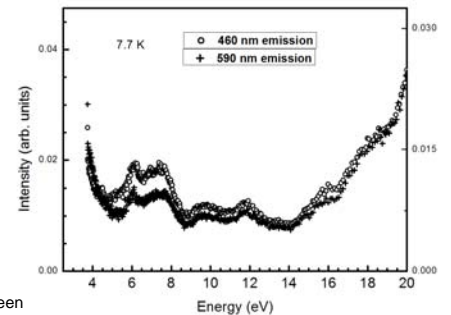
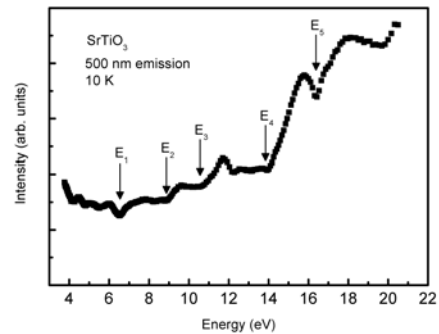
Excitation spectra

The use of synchrotron radiation has made it possible to investigate the effect of the multiplication of electronic excitation (MEE). In many alkali halides and oxides, a photon with an energy exceeding the value of the threshold energy $E_{th} \sim (3 - 4) E_g$ creates a hot electron and a hot hole whose energies are sufficient for the formation of a secondary electron-hole pair [18]

The excitation spectrum of 2.5 eV emission consist of several interesting features, at which the emission intensity increases:

$E_1 = 6.5$ eV (~2 Eg), $E_2 = 8.8$ eV, $E_3 = 10.5$ eV (~3 Eg), $E_4 = 14.0$ eV (~4 Eg), $E_5 = 16.5$ eV (~5 Eg),

In the energy region above ~14 eV the rise of the intensity in the excitation spectra is seen, which is caused probably by the beginning of MEE process.



Similar excitation spectra have been found Green emissions in the case of unpolished BZO surface.

References

- [1] L. Grabner, *Phys. Rev.* **177**, 1315 (1969).
- [2] T. Feng, *Phys. Rev. B* **25**, 627 (1982).
- [3] M. Aguilar and F. Agullo-Lopez, *J. Appl. Phys.* **53**, 9009 (1982).
- [4] R. Leonelli and J. L. Brebner, *Phys. Rev. B* **33**, 8649 (1986).
- [5] T. Hasegawa *et al.*, *J. Lumin.* **87–89**, 1217 (2000).
- [6] M. Deguchi *et al.*, *Phys. Rev. B* **78**, 073103 (2008).
- [7] Y. Qiu *et al.*, *Phys. Lett. A* **372**, 2920 (2008).
- [8] R. Eglitis *et al.*, *Eur. Phys. J. B*, **27**(2002) 483
- [9] S. Mochizuki *et al.*, *J. Phys.: Condens. Matter* **17**, 923 (2005).
- [10] S. Mochizuki *et al.*, *Physica B* **376–377**, 816 (2006)
- [11] D. Kan *et al.*, *Nature Mater.* **4**, 816 (2005).
- [12] D. Kan *et al.*, *Appl. Phys. Lett.* **88**, 191916 (2006).
- [13] Z.-h. Li *et al.*, *Nanotechnology* **18**, 165703 (2007).
- [14] A. Rubano *et al.*, *Phys. Rev. B* **76**, 125115 (2007).
- [15] A. Rubano *et al.*, *Appl. Phys. Lett.* **92**, 021102 (2008)
- [16] M. Cardona, *Phys. Rev.* **140** (1965) A651.
- [17] K. Van Benthem *et al.*, *J. Appl. Phys.* **90** (2001) 6156.
- [18] Ch.Lushchik *et al.*, *J.Phys.Condens.Matter* **6**(1994) 11177