

The Bologna Stone: History's First Persistent Luminescent Material

Mika Lastusaari^{1,2}, Marco Bettinelli³, Kari O. Eskola⁴, Jorma Hölsä^{1,2,5}, Högne Jungner⁴, Aleksei Kotlov⁶, Taneli Laamanen^{1,7}, Marja Malkamäki^{1,7}, Edmund Welter⁶

¹University of Turku, Department of Chemistry, Turku, Finland

²Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland

³Università di Verona, Dipartimento Scientifico e Tecnologico, Verona, Italy

⁴University of Helsinki, Dating Laboratory, Helsinki, Finland

⁵Universidade de São Paulo, Instituto de Química, São Paulo-SP, Brazil

⁶Deutsches Elektronen-Synchrotron, a Research Centre of the Helmholtz Association, Hamburg, Germany

⁷Graduate School of Materials Research (GSMR), Turku, Finland

In 1603, an Italian shoemaker, Vincenzo Cascariolo, found that a stone from the outskirts of Bologna emitted light in the dark without any external excitation source though calcination was needed. The stone, Baryte (BaSO₄) mineral reduced to sulphide, was among the first luminescent materials and the first documented material to show persistent luminescence [1].

The persistent luminescence is thermoluminescence exhibited at room temperature and, at present, has many both sophisticated and everyday applications (self-lit exit signs, watches, sensors, *etc.*). The best modern materials, *e.g.* Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ and SrAl₂O₄:Eu²⁺, Dy³⁺, can emit in excess of 24 h in the dark [2]. For these disilicates and aluminates, the emitter (Eu²⁺) and the storage of excitation energy for persistent luminescence to trap sites, but not the nature and/or origin of the traps, is agreed upon. The detailed mechanism(s) of persistent luminescence are thus pretty much as unresolved today as 400 years ago [3].

In this work, the Bologna stone was prepared from the natural Baryte (Bologna, Italy; from Museo di Mineralogia, Università di Padova, Italy). Its properties (*e.g.* impurities (dopants) and their valences, luminescence, persistent luminescence, trap structure) were compared to those of the pure BaS materials doped with different (transition) metals (Cu, Ag, Pb) known to yield strong luminescence. Derived from a mineral, the Bologna Stone may, however, contain numerous other impurities (dopants), which makes the simulation of all the properties of the natural product very challenging. The work was carried out by using different methods (XRF, XANES, EXAFS, TL, VUV-UV-vis luminescence, TGA-DTA, XPD). The goal was to unveil the mechanism behind the persistent luminescence of the Bologna Stone.

The Baryte showed short purple afterglow at 395 nm. Heating for 7 h at 1200 °C in N₂ + 10 % H₂ converted the sulphate to BaS with much longer orange persistent emission at 620 nm. The emitting species was identified as Cu⁺ suggesting close similarity to ZnS:Cu⁺ [4], the persistent luminescence phosphor used prior to the advent of the Eu²⁺ doped aluminates in the mid-1990s. The TL data yielded trap depths from 0.84 to 0.90 eV being in the range typical of the best persistent luminescence materials [5]. A plausible mechanism for the persistent luminescence from the Bologna Stone was constructed based on the results obtained.

References:

1. Newton Harvey, E., Amer. Phil. Soc., Philadelphia, USA, 1957, Chapter VIII.
2. Aitasalo, T., Hölsä, J., Jungner, H., Lastusaari, M., and Niittykoski, J., J. Phys. Chem. B 110 (2006) 4589.
3. Hölsä, J., Electrochem. Soc. Interface 18(4) (2009) 42.
4. Clabau, F., Rocquefelte, X., Le Mercier, T., Deniard, P., Jobic, S., and Whangbo, M.-H., Chem. Mater. 18 (2006) 3212.
5. Brito, H.F., Hassinen, J., Hölsä, J., Jungner, H., Laamanen, T., Lastusaari, M., Malkamäki, M., Niittykoski, J., Novák, P., and Rodrigues, L.C.V., J. Therm. Anal. Calorim. (2011), online: March 3, 2011.