**The Bologna Stone: history’s first persistent luminescent material**

MIKA LASTUSAARI1,2,* TANELI LAAMANEN1,3, MARJA MALKAMÄKI1,3, KARI O. ESKOLA4, ALEKSEI KOTLOV5, STEFAN CARLSON6, EDMUND WELTER5, HERMI F. BRITO7, MARCO BETTINELLI8, HÖGNE JUNGNER4 and JORMA HÖLSÄ1,2,7

1 Department of Chemistry, University of Turku, Turku, Finland
2 Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland
*Corresponding author, e-mail: miklas@utu.fi
3 Graduate School of Materials Research (GSMR), Turku, Finland
4 Dating Laboratory, University of Helsinki, Helsinki, Finland
5 Deutsches Elektronen-Synchrotron, A Research Centre of the Helmholtz Association, Hamburg, Germany
6 MAX-Lab, Lund University, Lund, Sweden
7 Instituto de Química, Universidade de São Paulo, São Paulo-SP, Brazil
8 Dipartimento di Biotecnologie, Università di Verona, Verona, Italy

**Abstract:** In 1603, the Italian shoemaker Vincenzo Cascariolo found that a stone (baryte) from the outskirts of Bologna emitted light in the dark without any external excitation source. However, the calcination of the baryte was needed prior to this observation. The stone later named as the Bologna Stone was among the first luminescent materials and the first documented material to show persistent luminescence. The mechanism behind the persistent emission in this material has remained a mystery ever since. In this work, the Bologna Stone (BaS) was prepared from the natural baryte (Bologna, Italy) used by Cascariolo. Its properties, e.g. impurities (dopants) and their valences, luminescence, persistent luminescence and trap structure, were compared to those of the pure BaS materials doped with different (transition) metals (Cu, Ag, Pb) known to yield strong luminescence. The work was carried out by using different methods (XANES, TL, VUV-UV-vis luminescence, TGA-DTA, XPD). A plausible mechanism for the persistent luminescence from the Bologna Stone with Cu⁺ as the emitting species was constructed based on the results obtained. The puzzle of the Bologna Stone can thus be considered as resolved after some 400 years of studies.

**Key-words:** Persistent luminescence, Bologna Stone, baryte, copper, barium sulphide, XANES, thermoluminescence, thermogravimetry, differential thermal analysis, X-ray powder diffraction.

1. **Introduction**

The year 1603 marked the beginning of modern luminescent materials. Then, an Italian shoemaker named Vincenzo Cascariolo synthesized the famous Bologna Stone by calcining a particular mineral from Monte Paderno close to Bologna, Italy. This new material, later tentatively identified as BaS prepared from BaSO₄ (baryte), was described as being able to attract the “golden light of the Sun”, i.e. to emit light without heat if illuminated prior by either sunlight or flames (Newton Harvey, 1957). Today, this phenomenon is known as persistent luminescence, which is a special case of thermoluminescence (Chen & McKeever, 1997) at room temperature. The Bologna Stone was among the first luminescent materials and the first scientifically documented material to show persistent luminescence (Licetus, 1640). The phenomenon itself had been known for over 1000 years from natural materials, documented in e.g. ancient Chinese paintings that would glow in the dark due to the special pearl shells included in the paints (Newton Harvey, 1957).

From the early years after Cascariolo’s discovery, the reasons behind the persistent luminescence aroused interest in the scientific community. Even the great Galileo joined the general discussion on the stone, though he never wrote anything on the subject. It took almost 400 years for the discussion to heat up again, i.e. with the introduction of the modern materials Sr₂Al₂O₄:Eu²⁺,Dy³⁺ (Matsuzawa et al., 1996) and Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ (Lin et al., 2001). These materials are capable of more than 24 h of persistent luminescence. For these aluminates and disilicates the emitter (Eu²⁺) and the storage of excitation energy for persistent luminescence to trap sites is agreed upon, whilst the nature and/or origin of the traps is still contested. The detailed mechanism(s) of persistent luminescence remain(s) partly unresolved (Aitasalo et al.,...