The Bologna Stone: history’s first persistent luminescent material

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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 Sr₃Al₂O₆: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.,...
2. Experimental procedure

The baryte sample from Monte Paderno (Bologna, Italy) was obtained from the Museo di Mineralogia, Università di Padova (Padova, Italy). Pieces of the stone were ground and heated for 7 h at 1200 °C in flowing N₂ + 10 % H₂ to convert the material to BaS. The synthetic non-doped and doped (Pb, Cu, Ag) BaSO₄ were prepared with co-precipitation by mixing aqueous solutions of BaCl₂·2H₂O or Ba(NO₃)₂ and (NH₄)₂SO₄ as well as 0.5 mol% of PbCl₂, CuCl₂ or AgNO₃. The respective BaS materials were obtained by heating the dried sulphates for 7 h at 1200 °C in flowing N₂ + 10 % H₂.

The formation of the Bologna Stone upon heating was studied with simultaneous TG-DTA methods using a TA Instruments SDT 2960 apparatus with a heating rate of 5 °C min⁻¹ in a flowing (100 cm³ min⁻¹) N₂ + 10 % H₂ atmosphere. The crystal structure and purity were investigated with X-ray powder diffraction (XPD) at room temperature using a Huber G670 image-plate Guinier camera (2θ range: 4–100°) with monochromatic copper Kα₁ radiation (λ: 1.5406 Å). The photoluminescence emission and excitation as well as persistent emission spectra of the materials were measured with a Varian Cary Eclipse spectrometer. The photoluminescence excitation source was a 15 W Xe lamp. The persistent luminescence was irradiated with a 4 W UV lamp at 254 nm.

The thermoluminescence (TL) glow curves were measured with an upgraded Risø TL/OSL-DA-12 system using a constant heating rate of 5 °C s⁻¹ in the temperature range from 25 to 400 °C. The global TL emission from UV to 650 nm was monitored. Prior to the TL measurements, the samples were irradiated with a combination of the Philips TL 20W/05 (emission maximum at 360 nm) and TL 20W/03 (420 nm) UV lamps for 30 s. A delay of 3 min between the irradiation and measurement was used.

The elemental contents and the valence of copper were probed with X-ray absorption near-edge structure (XANES) spectroscopy. The measurements were carried out at the beamline E4 in HASYLAB (Hamburger Synchrotronstrahlungslabor) at DESY (Deutsches Elektronen-Synchrotron, Hamburg, Germany) as well as beamline I811 in MAX-lab (Lund, Sweden), both in the fluorescence yield mode.

3. Results and discussion

3.1. Formation of the Bologna Stone and BaS

In order to reconstruct the experiment of Vincenzo Cascariolo in a modern laboratory, the formation of BaS from BaSO₄ was first studied both for the synthetic and natural materials with the simultaneous TG-DTA method in a reducing atmosphere (N₂ + 10 % H₂). For both materials, the breakdown of the sulphate and the accompanying loss of oxygen as H₂O starts at ca. 700 °C resulting in the BaS stoichiometry at 1000 °C (synthetic) or 1200 °C (natural) calculated to correspond to a remaining weight of 73 % (Fig. 1). For the synthetic material, the observed weight loss corresponds exactly to this value, whereas the mineral sample gradually loses ca. 2 % in weight before the decomposition of the sulphate to yield 71 % as the...
remaining mass agreeing well with the calculated value, as well. As expected, due to its probably simpler composition, the synthetic material decomposes in one step and within a rather short temperature interval, while the natural one requires at least two steps and a wider temperature range to be completed. Both DTA curves are rather featureless until the BaS stoichiometry is reached. Then, an endothermal shift is observed followed by an exothermal one probably corresponding to the formation and crystallization of BaS, respectively. Starting from these results, the conditions for baryte annealing were optimized as 7 h at 1200 °C.

3.2. Composition and structure

The baryte sample was received as a strongly textured piece (or a single crystal) as shown by the initial X-ray powder diffraction measurements. After grinding, the composition was determined to be almost pure orthorhombic BaSO₄ (Pnma, No. 62; Hill, 1977) with traces of cubic halite-type BaS (Fm3m, No. 225; Wyckoff, 1963). After the heat treatment, the material was BaS with traces of BaSO₄ (Fig. 2). The sulphate phase was observed also as a trace impurity for the synthetic materials.

Natural baryte has been reported to contain at least the following impurities: Al³⁺, Ti³⁺, Mn²⁺, Mn⁴⁺, Fe²⁺, Fe³⁺, Cu⁺, Cu²⁺, Sr²⁺, Ag⁺, Eu²⁺, Sn⁴⁺, Pb²⁺, Bi³⁺, Bi⁵⁺ and UO₂²⁻ (Gaft & Rudenkova, 1993; Gaft et al., 2001). The present XANES results suggest the presence of copper (Fig. 3). The other regular impurities mentioned above were not detected by XANES, but their presence in trace amounts and thus participation in the persistent luminescence process as well as regular emission cannot be excluded completely.

In the cubic halite structure Ba occupies the 4a (0, 0, 0) site and S the 4b (½, ½, ½) one with a = 6.3875 Å and Z = 4 (Wyckoff, 1963). Barium is octahedrally coordinated to six sulphurs with a distance of 3.19 Å. With respect to space available, this large Ba²⁺ site (rCN₆: 1.35 Å; Shannon, 1976) can easily accommodate the impurity (dopant) cations typical of the possible dopants. The size mismatch exceeding the 15 % empirically required for complete solid solubility, better known as the Vegard’s law (Vegard, 1921), should not be a limiting factor due to the low concentrations (below 1 mol%) typical of the possible dopants. The charge mismatch, on the other hand, must be compensated by the creation of Ba or S vacancies, V_Ba or V_S, according to the Kroger-Vink notation (Kröger & Vink, 1958), when M³⁺ or M⁺ respectively, substitute for Ba²⁺. Interstitial ions may also be possible, however.

The dielectric measurements on synthetic BaS:Cu (Rao & Rao, 1984) have shown the presence of non-negligible concentrations of charged point defects in this material as well as the formation of neutral defect clusters. These clusters, known to be required for efficient persistent luminescence (Aitasalo et al., 2006; Carlson et al., 2009), can be easily formed between two adjacent dopants in the BaS structure, e.g. as M⁺_Ba-V_Ba-M⁺_Ba or M⁺_Ba-V_S²⁻-M⁺_Ba for M⁺ and M⁺, respectively. The vacancies, interstitials and the local structural distortions due to size mismatch create defect energy levels within the energy gap of the BaS host. These levels, together with those of the impurity ions, may serve as energy storage traps for persistent luminescence.

3.3. Luminescence and luminescent centre

The natural baryte sample showed bluish white emission with bands centred at 395 and 760 nm. However, upon heating to produce the sulphide, the emission changes to orange, peaking at 610 nm (Fig. 4). The more or less widespread misunderstanding that the baryte is the Bologna Stone is thus definitely shown to be incorrect. In order to identify the luminescent centre in the Bologna Stone...
Stone, the spectra of the synthetic BaS materials doped with known efficient emitters (Cu\(^{2+}\), Ag\(^{+}\), Pb\(^{2+}\)) were also measured. Although CaS and SrS emit in the red with Eu\(^{3+}\) doping, BaS:Eu\(^{2+}\) has been reported to give emission at 572 nm (Smet et al., 2004). Thus, europium can be ruled out as a possible emitter in the Bologna Stone, even if its emission in baryte (at 375 nm; Gaft et al., 2008) is close to that observed in this work. Mn\(^{2+}\) is also a known red emitter, but in BaS the emission wavelengths have been reported as 545 and 640 nm (Ihanus et al., 2004), not matching with the present results. BaS:Bi\(^{3+}\) has been reported to show emission either at 575 (Singh et al., 2010) or 608 nm (Kim et al., 1999), but the typical emission of BaSO\(_4\):Bi\(^{3+}\) (421, 500 and 625 nm; Gaft et al., 2001) was not observed for the Monte Paderno baryte thus excluding Bi\(^{3+}\) as a possible emitter in the Bologna Stone. With Cu doping, however, emission similar to that of the natural material is obtained (\(\lambda_{\text{max}}\): 613 nm), whilst Ag\(^{+}\) gives emission at 575 nm. Pb\(^{2+}\) shows no emission at all around 600 nm.

The XANES data suggests that copper is monovalent both in the baryte and the Bologna stone, since the CuK absorption edge for both materials falls between those of the metallic copper and CuO (Fig. 3). The present luminescence results for the natural baryte agree also rather well with the emission bands at 410 and 740 nm reported previously for synthetic BaSO\(_4\):Cu\(^{+}\) (Gaft et al., 2001). Thus, the main emitting species was confirmed to be Cu\(^{+}\). Subsequently, the existence of Cu\(_{\text{Ga}}\)-V\(_{\text{Cu,S \& \,Cu}}\) defect aggregates with the sulphide vacancies as possible electron traps is expected for the Bologna Stone.

The Cu\(^{+}\) ion has the 3d\(^{10}\) electron configuration, and thus its emission transitions may be difficult to assign. Usually, the emission is interpreted to be due to the 3d\(^{9}\)4s\(^{1}\) \(\rightarrow\) 3d\(^{10}\) transitions, and this approach is also adopted here. The photoluminescence excitation spectra (not shown here) indicated the valence to conduction band excitation for the Bologna Stone and the synthetic BaS:M materials at 337 nm corresponding to 3.68 eV as the band gap energy, \(E_g\). This value is in good agreement with the 3.9 eV reported from optical absorption measurements (Zollweg, 1958). A band peaking at 440 nm (2.82 eV) was observed only for the Bologna Stone and BaS:Cu. This was identified to be due to the 3d\(^{10}\) \(\rightarrow\) 3d\(^{9}\)4s\(^{1}\) transition of Cu\(^{+}\). The Stokes shift of 0.79 eV between the excitation and the emission at 610 nm (2.03 eV) can be explained by the strong relaxation in the 3d\(^{9}\)4s\(^{1}\) excited state. The location of the ground level of the Cu\(^{+}\) ion in the host band gap can be obtained from the S\(^{2-}\)–Cu\(^{2+}\) charge transfer energy. In the present case, this was not observed from the excitation spectra. However, this energy has been reported to be ca.1.3 eV for ZnS and CdS (Heitz et al., 1992) suggesting that a similar value should be true for BaS, as well.

### 3.4. Persistent luminescence

A short bluish persistent luminescence (less than 1 min) was observed for the baryte sample. This wrong colour and too short an emission confirm further that the baryte is not the original Bologna Stone. For the reduced material, on the other hand, the persistent luminescence was orange peaking at 610 nm (Fig. 4) indicating the correct origin of Bologna Stone. The same emission wavelength for both the persistent emission and the regular photoluminescence confirms that the Cu\(^{+}\) ion is responsible for both. With UV irradiation for 15 min, the emission persisted in excess of 30 min. This is already rather good an achievement for a red/orange persistent phosphor because of the insensitivity of the human eye in red. Moreover, there is no doubt that the persistence could be enhanced by optimizing the heat treatment as well as by adding co-dopants in a way similar to e.g. Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\) (R: rare earth) (e.g., Brito et al., 2011). Unfortunately, however, the poor chemical stability of BaS in ambient and wet conditions prevents the use of this material for practical applications without a protective coating that would inevitably weaken the performance of the material.

### 3.5. Traps

As discussed above (see Sections 3.2. and 3.3.), the presence of the Cu\(^{+}\) ion as the luminescence centre located in the Ba\(^{2+}\) site (Cu\(_{\text{Ga}}\)) demands charge compensation by sulphide vacancies (V\(_{\text{S}}\)). Brito et al. (2011) reported, based on combined DFT calculations and thermoluminescence measurements, that the main energy trapping species in the Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\) materials are oxygen (i.e., anion) vacancies located close to the conduction band. For the Bologna Stone, it can thus be assumed that the energy storage properties are due to electron trapping by sulphide vacancies close to the conduction band.

The thermoluminescence glow curve of the Bologna Stone shows a rather wide band with moderate intensity between 50 and 150 °C with a weak shoulder at 175 °C.
3.6. Persistent luminescence mechanism

Based on the results discussed above, the mechanism can be described as follows: during the charging stage, the irradiation of the Bologna Stone results in the photoexcitation of Cu$^+$ via the $3d^{10} \rightarrow 3d^94s^1$ transitions. The excited electrons are first captured by the conduction band and then by sulphide vacancies acting as traps close to the conduction band. In the discharging stage, the trapped electrons are released gradually by the thermal energy available at room temperature and migrated to the copper centre through the conduction band. Finally, persistent emission results from the $3d^94s^1 \rightarrow 3d^{10}$ transitions. As an alternative to the recombination of the electron with the hole at or close to Cu$^+$, the retrapping of the electron can occur. This would prolong even further the duration of persistent luminescence from the Bologna Stone.

4. Conclusions

The Bologna Stone was successfully synthesized from the Monte Paderno baryte by reduction. The persistent luminescence was orange and the emitter was identified as Cu$^+$ based on comparison to the properties of synthetic Ba:S:M materials. The emission lasted ca. 30 min, which is rather good for an orange/red emitting material. The persistent luminescence intensity was only moderate due to the low concentration of the Cu$^+$ ions (below 0.1 mol%), even if the trap structure was observed to be almost ideal for persistent luminescence. The short duration is deduced to result from the low density of high-temperature traps responsible for the energy storage.

A plausible mechanism for the persistent luminescence in the Bologna Stone was constructed for the first time since the discovery of the material some 400 years ago. Although the details need still to be identified with e.g. EPR measurements, the mystery of the Bologna Stone can now be considered finally solved. The effect of the other than Cu$^+$ impurities, so inevitable for minerals, on the persistent luminescence should be studied, too.

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