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LUMINESCENCE AS A PROBE IN PROVENANCE AND TECHNOLOGICAL STUDIES OF EARLY ISLAMIC RAW FURNACE GLASSES

I.K. Sfampa[1], G. S. Polymeris[2,3], N. Zacharias[4], G. Kitis[1], J. Henderson[5]

[1]*Nuclear Physics Laboratory, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece*

[2]*Laboratory of Radiation Applications and Archaeological Dating, Department of Archaeometry and Physicochemical Measurements, 'Athena' - Research and Innovation Center in Information, Communication and Knowledge Technologies, Kimmeria University Campus, GR-67100, Xanthi, Greece*

[3]*Solid State Section, Department of Physics , Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece*

[4]*Laboratory of Archaeometry, Department of History, Archaeology and Cultural Recourses Management, University of Peloponnese, 24100, Kalamata, Greece*

[5]*Department of Archaeology, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

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Corresponding author: isfaba@physics.auth.gr

ABSTRACT

Two different early-Islamic furnace glass fragments from excavations at al-Raqqa, Syria, extensively studied by means of archaeological, typological, isotopic and chemical analyses were used in the present study and for the application of luminescence techniques in the investigation of technology and provenance. The techniques applied were detailed thermoluminescence (TL) and also linearly modulated optically stimulated luminescence (LM-OSL); the latter was the first time it was applied in this way. The sequence protocol applied was very simple, focusing on the variation of sensitivity, sensitization and glow curve shape for both TL and OSL. The results highlight the potential use of luminescence measurements in establishing additional analytical criteria for investigating technological and provenance aspects of archaeological glasses.

KEYWORDS: Thermoluminescence, linearly modulated optically stimulated luminescence, archaeological glass, Raqqa

INTRODUCTION

Luminescence, both in terms of thermoluminescence (TL) - also known as thermally stimulated luminescence (TSL) – and optically stimulated luminescence (OSL), has been well established as an effective as well as a versatile dosimetric technique in various fields such as medical, environmental, personal, space and retrospective dosimetry, (McKeever, 2001; Bøtter Jensen et al., 2003; Yukihara et al., 2006). Examples of the latter fall into two major categories, namely luminescence dating (Liritzis, 2000) and accidental dosimetry (Aitken, 1985; Bailiff, 1994). TL and OSL refer to the luminescence phenomena of light emission from an insulator or semiconductor during heating (TL) or exposure to light (OSL), respectively. The TL signal provides information about traps and recombination sites related to defects of the structure (McKeever, 1985). As already mentioned luminescence techniques are frequently applied in archaeological science for absolute dating studies (Aitken, 1985) or for the characterization of materials of archaeological interest (Liritzis, 1997). Nevertheless, glass has not yet received much attention partly because of its amorphous state; for these types of measurements materials with crystal structures are preferred (e.g. quartz extracted from pottery of sediments).

Several investigations have taken place over the years including on amorphous materials, such as glass, as dosimeters in the radiation field due to the natural radioactivity of both the surrounding environment and cosmic rays. The reliability of luminescence dating mainly depends on the reliability of the absorbed dose evaluation, a consequence of the dosimetric characteristics of the material under study. These characteristics, in their turn, depend strictly on the crystallinity of the material (Sanderson et al., 1983; Müller and Schvoerer, 1993). Archaeological glasses have complex and sometimes inhomogeneous structure because of variable levels of impurities (Lester et al., 2004). They have been melted under unknown and presumably somewhat variable melting conditions and have been exposed to low levels of radiation since burial (Sanderson et al., 1983).

The presence of impurities and defects in an insulating crystal creates discrete energy levels in the energy gap, acting as electron traps (Chen and McKeever, 1997). On the contrary, in highly defective, and especially, amorphous and/or vitreous materials such as archaeological glass, contains amorphous silica plus variable amounts of different oxides (Zallen, 1983) and the presence of impurities leads to a spectral continuum of energy levels, probably leading to enhancement of spontaneous recombination (Blasse and Grabmaier, 1994). Over the last few years, TL/OSL has generally been employed for the characterization of non-crystalline solids, such as artificial sol-gel glasses and obsidian (Vedda et al., 2005; Polymeris et al., 2010; Polymeris et al., 2011). The alkali metals and metal oxides act as electron traps and recombination centers and therefore control the number of the trapped charge carriers that give rise to the TL/OSL signals. This information, which characterizes each particular material, could serve as a means of differentiating from other materials with similar luminescence signals. A limited number of attempts to investigate possible luminescence dating of glass have been made recently (Zacharias et al., 2008; Galli et al., 2011).

Glass coloration relies on a variety of factors (Henderson 2013), two of which are the control of the furnace atmosphere and the addition of colorant and opacifying raw materials (Galli et al., 2003; Galli et al., 2010). The colour that finally appears in different types of glass depends on the oxidation state of the oxide ions (often transition metals). Examples are different manganese ions that gives different purple coloration (Mn^{3+}, Mn^{4+}), but can also act as a decolourizer (Mn^{2+}), negating the colouring effect of iron ions. Other examples of colorant ions that are found in archaeological glasses are copper (Cu^{2+}) which was mainly used to produce turquoise blue, cobalt for dark blue (Co^{2+}) and purple (Co^{3+}) (Galli et al., 2003), and iron for dark green, light green and pale blue (Fe^{2+} or Fe^{3+}). Finally, examples of opacifiers are calcium antimonate and tin oxide, forming crystals dispersed in the base glass (Henderson, 2013; Galli et al., 2003). The research by Galli et al., (2003) demonstrates that relatively good TL emission is due to the degree of crystallinity in the silicate matrix glass and/or to the presence of crystals dispersed in it (Galli et al., 2012).

The results of these studies demonstrate that a classification of luminescence signals of ancient glassy materials using non-destructive TL/OSL examination can be achieved; data related to the signal type, sensitivity and radiation dose response (Zacharias et al., 2008).

In the present work two different types of archaeological glass from excavations of 9th century al-Raqqa, Syria were used and studied. The archaeological evidence of glass production suggests that the 2 km long industrial complex at al-Raqqa was associated with an urban landscape consisting of two Islamic cities (al-Raqqa and al-Rafika) and a series of palace complexes. The glass fused and worked there was presumably for local as well as for regional consumption. Al-Raqqa currently appears to have produced the earliest well-dated production on record in the Middle East of an Islamic high-magnesia glass based on an alkaline plant ash flux and quartz (Henderson et al., 2004).

The main aim of the present investigation is to try to discriminate between two types of archaeological glass by applying only luminescence techniques. Both TL and OSL measurements were applied to the samples in order to investigate their luminescence properties.

MATERIALS AND METHODS

Two fragments of raw transparent furnace glasses found at al-Raqqa, Syria, were selected. Al-Raqqa 40 is a translucent purple color and is a rare example of raw glass imported to the production site of al-Raqqa. Al-Raqqa 35, a translucent green sample, was actually fused from raw materials at al-Raqqa. The chemical composition and physical properties of the glasses suggested that al-Raqqa 35 (plant ash type 1 hereafter) and al-Raqqa 40 (plant ash type 2 hereafter) are compositionally quite distinct, (e.g. type 2 has lower MgO : K_2O ratio) (Henderson et al., 2004). Moreover, Thermal Ionization Mass Spectrometry measurements have shown that $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios yield a very distinctly different provenance for the two types of glasses (Henderson et al., 2009).

Each type of glass consisted of a batch of three pieces, resulting in a total number of six pieces, namely 1A, 1B, 1C, 2A, 2B and 2C. All pieces had a rectangular shape with less than 2 mm^2 area. Each one was independently crushed and grains with sizes of between 80 and 140 microns were selected from each individual piece. The measurements were performed independently on the grains of each one of the six sub-samples. The aim of this approach was to check homogeneity and reproducibility between the pieces from the same batch, as well as to discriminate between these two types of plant ash.

TL measurements were applied to all sub-samples, while some preliminary blue LM-OSL measurements were also performed. In all cases a beta test dose of 75 Gy was provided by a $^{90}Sr/^{90}Y$ source. All TL measurements were performed in a nitrogen atmosphere with a constant heating rate of 2°C s^{-1} in order to avoid significant temperature lag, up to a maximum temperature of 500°C. Mass reproducibility for all samples was kept within ±5%. OSL measurements were performed using a Risø TL/OSL-DA-15 reader, equipped with a $^{90}Sr/^{90}Y$ beta source delivering 0.07 Gy s^{-1}, calibrated on grains sized between 80-140 μm. The reader was fitted with a 9635QA photomultiplier tube. The detection optics consisted of a 7.5 mm Hoya U-340 (λ_p ~ 340 nm, FWHM 80 nm) filter, transmitting in the 280–380 nm regions, with maximum transmittance (57%) at 330 nm. An array of blue light emitting diodes (LEDs, 470±30 nm), was used for stimulation. The ramping rate was 0.04 $mWcm^{-2}s^{-1}$, reaching the maximum stimulation power at 1000 s. Measurements were taken at the temperature of 125°C.The main properties that were studied were the glow curve shape, the sensitivity and the sensitization following repeated cycles of irradiation-measurement. Last but not least, preliminary LM-OSL measurements were performed in order to study their shape sensitivity.

RESULTS

First of all, it should be stated that the shape of the zero dose glow curves, is identical for all six sub-samples.

In the case of the glass of plant ash type-1, all three parts provided similar results. A typical example of glow curve resulting from part 1A following repeated cycles of irradiation-measurements is presented in Figure 1. We note that, the "110°C" TL glow peak is the only prominent peak. There are strong indications suggesting the presence of at least two more peaks below 200°C; however the peak signals are poorly resolved from the background.

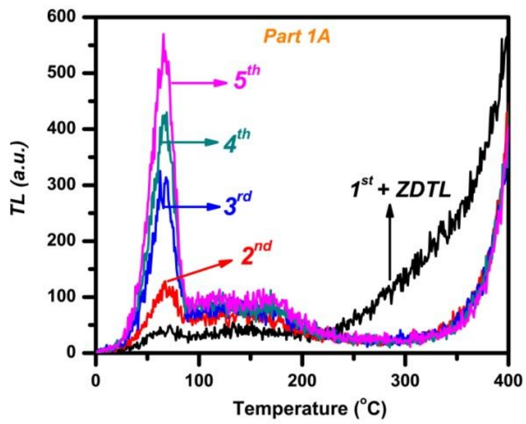

Figure 1: TL glow curves for the glass part 1A after repeated cycles of irradiation-measurement. The first irradiation takes place on the sample that already contains its Zero Dose TL signal.

Despite the fact that TL signals can be detected in archaeological glass fragments, their amorphous state distorts the trapping-detrapping mechanisms used for TL dating applications. Thus it has to be stressed that the ZDTL (Zero Dose TL) signal is a residual thermoluminescence signal probably linked to the production technology use to make the glass rather than as a signal to be used for dating applications. The transparency of glass fragments which, under some conditions can allow for sun-bleaching effects to occur could potentially be an additional issue to take into account if an attempt is being made to use residual signals for dating purposes.

Furthermore, repeated cycles of irradiation and measurement resulted only in sensitization in the case of the "110°C" TL glow peak. The sensitization pattern for the "110°C" TL glow peak for all three sub-samples of plant ash type-1 is presented in Figure 2. Unfortunately, there is only a qualitative similarity between these three sensitization patterns. In general, besides the quantitative differences in the sensitization patterns of these three sub-samples, all other TL properties suggest a coherent homogeneity for them.

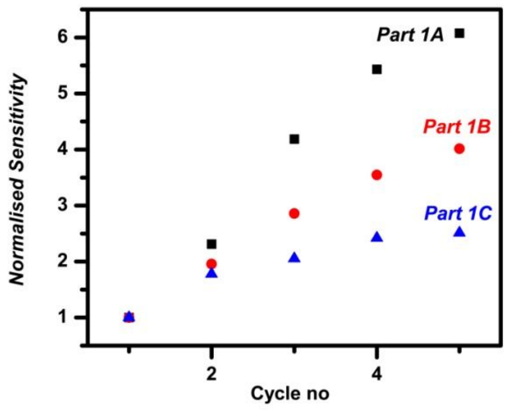

Figure 2: Sensitization patterns for the case of the "110 °C" TL glow peak of all parts of type 1 glass.

Finally, the sub-samples of plant ash type-1 exhibit a behaviour which is very similar to that of un-heated quartz samples, due to the fact that the "110 °C" TL glow peak is the most intense and dominant in the entire glow curve.

That sample has a chemical composition of 65.45 wt% SiO_2, 9.72 wt% CaO and 14.18 wt% Na_2O with Al_2O_3 at 1.30 wt% (Henderson et al., 2004, Table 1). All forms of quartz contain aluminum, substituting for silicon in the lattice. The monovalent charge compensators, including Na^+, are always present as interstitials ions.

In as-grown state the monovalent alkali ions act as charge compensators for Al^{3+} ions, but irradiation at room temperature drifts the alkali ions to the luminescence centers (Koul, 2008). This mechanism in quartz is the main cause of sensitization, but it also looks as though it works in the case of type-1 plant ash glass from al-Raqqa.

In contrast, Figure 3 presents glow curves following repeated cycles of irradiation-measurement resulting for sub-samples 2A and 2B. Three different prominent peaks can be easily discriminated below 200°C. Moreover, after the first cycle of irradiation-measurement, another prominent peak is also visible.

These four different TL peaks were found in all three sub-samples of plant ash type-2 glass. Like the first sample, this suggests that the three sub-samples share the same level of homogeneity. However, both sensitivity as well as sensitization of each peak differs from one sub-sample to the other.

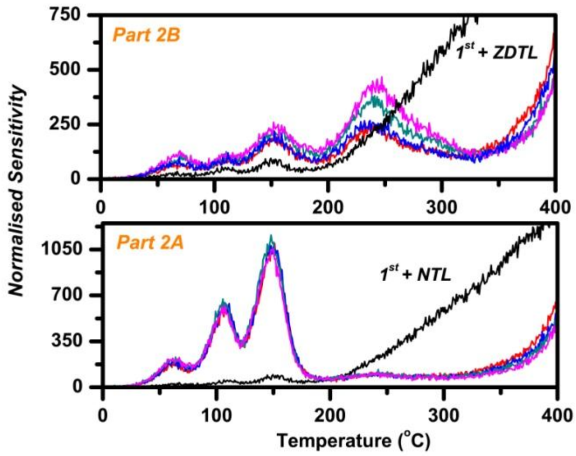

Figure 3: TL glow curves after repeated cycles of irradiation-measurement cycles for the parts 2A and 2B. The first irradiation takes place on the sample that already contains its Zero Dose TL signal.

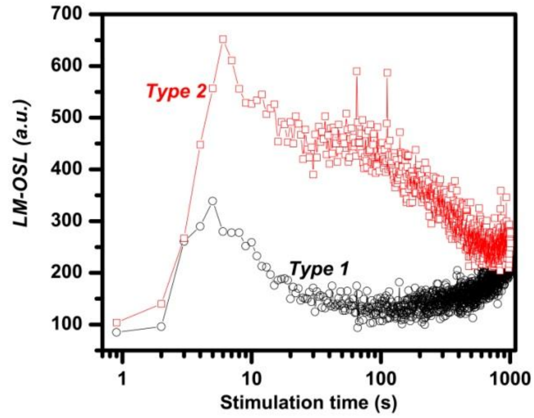

Figure 4: LM-OSL curves for both of two glass types. Measurement for T=125 °C.

Another prevalent feature for all three sub-samples of the second glass type is the strong sensitization that is induced in all glow peaks following the first heating. Also, the relatively low sensitization observed to the "110 °C" TL glow peak after the second heating, is something that we should definitely take into account.

It has to be mentioned that, in general, the glass type 2 does not present a quartz-like behaviour. The main reason arises from the fact that the "110 °C" TL glow peak is a less sensitive and dominant peak in the glow curve.

Preliminary LM-OSL measurements are presented in Figure 4. Both measurements were taken at 125 °C. As this figure reveals, there is a well-defined fast OSL component for both type-1 and type-2 glass samples; however, the intensity strongly differs for these two measurements. Moreover, in the case of plant ash type-2 there is also a substantial OSL arising from the medium and slow components. These differences could be attributed to the different TL intensities of all sub-samples of type-1 and the sub-sample 2B of glass type-2. Kitis et al. (2010) have noted that the blue bleaching in quartz is continuous across the entire glow-curve and that it does not influence only a certain part.

Therefore, in the case of type 2B, blue light stimulates traps with larger sensitivities resulting in both quantitative and qualitative differences. It should be mentioned that this is the first time that discrimination is partly achieved by using OSL.

Differences occur on the basis that these two glass types have different chemical compositions, and each component oxide may either help or deter the efficiency of luminescence centers. For example, type-1 contains more SiO_2 than type-2, and that may be the reason why it appears quartz like behaviour. On the other hand, type-2 contains more Al_2O_3, and the third peak on its glow curve may derive from it.

Moreover research using porosity and AFM measurements shows that sub-micron quartz crystals are sometimes present in translucent plant ash glass from al-Raqqa (Lester et al., 2004). These results may also explain the quartz like behaviour of type-1 sample.

The TL examination has been found to be in accordance with recently published observations on glass beads (Zacharias et al., 2008) while the first use of LM-OSL has provided additional spectroscopic data. TL signals from similar materials in the future may provide technological and provenance information about historical and archaeological glass materials.

CONCLUSIONS

In the present study the application of luminescence in the effective discrimination between two different translucent early Islamic raw furnaces glass fragments from al-Raqqa, Syria, has been investigated. These glass samples were fabricated in different locations and have been studied extensively by means of isotopic and chemical analyses.

Results so far suggest that the TL signal could provide a useful diagnostic tool in discriminating between the different provenances and manufacturing technologies in the case of archaeological glass fragments. The sequence protocol applied was very simple, focusing on the variation of sensitivity, sensitization and glow curve shape for both TL and OSL. The shape of both TL and OSL curves was shown to be a very sensitive indicator of different manufacturing conditions. Special emphasis should be given to the fact that there is a lack of homogeneity in several TL features for the three sub-samples of glass type-2 as indicated by variations in the sensitivity and sensitivity patterns. This lack of homogeneity, possibly due to poor mixing of the glass batch, may be a drawback for a luminescence study of the specific glass type; however it stands as an additional criterion for discriminating between these two glass types. Further work is required in order to study more luminescent properties, of more samples in order to generate a generalized experimental protocol.

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