The role of opacifiers in the luminescence of mosaic glass: Characterization of the optical properties of cassiterite (SnO$_2$)

A. Galli [a,b,*], M. Martini [a,c], E. Sibilia [a,c], F. Fumagalli [a]

[a] Dipartimento di Scienza dei Materiali, Università degli Studi di Milano, via R. Cozzi 53, 20125 Milano, Italy
[b] CNR-Istituto di Fotonica e Nanostrutture, Italy
[c] INFN, Sezione di Milano Bicocca, Piazza della Scienza 1, I-20126 Milano, Italy

A B S T R A C T

Thermoluminescence (TL) and radioluminescence (RL) have been exploited to study the optical properties of a few glass *tesserae* of the baroque mosaics of the vault of San Pietro cathedral in Rome. Recent results gave evidence that the dosimetric properties of mosaic glass depend on the presence of microcrystals in the glass network. For the samples analyzed in the present study, taking into account their chemical composition and presence and type of crystalline inclusions, it was observed that those opacified with tin-based additives (in particular, cassiterite, tin dioxide) showed higher luminescence sensitivity, being therefore more suitable for dating applications. The correlation between the presence of cassiterite and the possibility of successfully evaluating the equivalent dose has been investigated.

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1. Introduction

Thermoluminescence, TL, is a technique fruitfully applied in the study of defects in materials and in the dosimetry field, and also exploited for ceramics dating. The idea is based on the possible use of the natural crystals present in the clay, and consequently in shards, acting as dosimeters of the radiation field due to natural radioactivity of both ceramics and surrounding environment and cosmic rays.

The reliability of luminescence dating mainly stands on the reliability of the absorbed dose evaluation, a consequence of the dosimetric characteristics of the material under study. These characteristics, on their turn, strictly depend on the crystallinity of the material.

In an insulating crystal, the presence of impurities and defects creates discrete energy levels in the energy gap, acting as traps, where electrons accumulate (Chen and McKeever, 1997). On the other hand, in an amorphous material the presence of impurities leads to a continuum of energy, the probability of spontaneous recombination being therefore enhanced (Blasse and Grabmaier, 1994). Archaeological glass, which is based on amorphous silica

plus variable amounts of different oxides, belongs to this second category of materials (Zallen, 1983). The possibility of luminescence dating of glass has been previously investigated (Sanderson et al., 1983; Müller and Schvoerer, 1993), but up to now without fully satisfactory results even if recent encouraging results on Greek glass beads have been reported (Zacharias et al., 2008).

Glass mosaics, assembled with small pieces (tesserae) of glass variously colored, are semi-transparent or opaque. To give impressive results when placed on a wall or a floor, mosaic tesserae had to be more colored and less transparent than normal glasses. Crystals used to be added to the fused glassy phase as fine powder containing suitable components. Glass coloration is obtained combining to the glassy matrix base metal oxides with coloring and opacifying properties. Type and extent of coloration depend on the oxidation state of the oxide ions. Opacifiers are added to modify the chromatic effect, as frequently observed in mosaic glasses. In antiquity, the opacity of glass could be obtained with different techniques. Typically the addition of specific elements in fused glass, leading to the separation of white microcrystals (de-vitrification or secondary crystallisation) was a common practice. In pre-Roman and Roman periods calcium antimoniate was the main opacifier employed and it was still in use in the late first millennium. Tin oxide was instead more used in later times.

Since a few years ago, we have been involved in studies on the luminescence properties of glass mosaics (Galli et al., 2003, 2010), and we demonstrated that their relatively good TL emission is due

* Corresponding author. Dipartimento di Scienza dei Materiali, Università degli Studi di Milano, via R. Cozzi 53, 20125 Milano, Italy.
E-mail addresses: anna.galli@mater.unimib.it, anna.galli@unimib.it (A. Galli).

to the crystallinity degree of the silica base and/or to the presence of crystals dispersed in it. The good luminescent sensitivity of an archaeological material is a necessary condition for its dating, but not a sufficient one. The signal stability over time and the linear growth with irradiation dose have to be verified, in order to obtain reliable evaluation of the absorbed dose, as illustrated later on.

The data that we will be discussing in the following have been chosen as representative among those obtained from a few glass mosaic tessera coming from the vault of the dome of San Pietro in Rome, newly decorated since 1576 AD by remaking in form of mosaic all the paintings of the basilica by exactly copying the original frescoes. This gave a rebirth to the local glass technology, with the development of new recipes.

The glass was mainly opacified with tin-based additives (lead stannate and tin oxide). The formation of phases before the $SiO_2-PbO-SnO_2$ mixture melting allows the SnO_2 particles to react to form $PbSnO_3$. At temperatures between 650 °C and 750 °C, the mixture melts completely, SnO_2 precipitates, and new crystals appear. This crystallization is activated immediately after the fusion and during either heating or cooling until the temperature is sufficiently low or the tin supply is exhausted. This mechanism creates a good distribution of small SnO_2 crystals in the fuse (Molera et al., 1999). Actually the presence of this kind of crystals in the mosaic tesserae under study (Arletti et al., 2011) allowed us to characterize the properties of a cassiterite natural mineral. Cassiterite is the mineral form of tin dioxide, that crystallizes with the rutile structure, wherein the tin atoms are six fold coordinated and the oxygen atoms three fold coordinated.

The data that will be discussed in the following have been obtained from the tessera richest in cassiterite and from a sample of natural cassiterite mineral.

Studies on luminescence emission of natural cassiterite are few. To the best of our knowledge only De Murcia et al. (1978) and Hall and Ribbe (1971) studied the luminescence of cassiterite crystals. Further analysis of thermoluminescence (TL) and radio-luminescence (RL) emissions could therefore add new information focused on the use of cassiterite as natural dosimeters in mosaic samples. TL is based on the emission of light from a solid sample (insulator or semiconductor) when the sample is heated after being irradiated by X-rays, or ionizing radiation in general. During heating, the TL signal is recorded as a function of temperature (and also wavelength, in the case of spectral measurements). The luminescent intensity and shape and position of the TL peaks are functions of both radiation absorbed dose and heating rate. TL provides information about traps and recombination sites related defects of the structure (McKeever, 1985).

RL is a radiation induced luminescence stimulated by X-rays, but differently to TL, the emission is measured contemporarily to the absorption of the X-rays. The RL emission is a result of radiative recombination of electron–holes excited by primary X-ray photons and secondary electrons. RL is a dynamic or *prompt* emission derived from several centers, either intrinsic or defect – related and supplies information on the efficiency of recombination centers rather than on shallow traps (Mckeever, 1985).

2. Experimental

Following a previous study (Galli et al., 2011) in a group of thirty tesserae of the baroque mosaics of the vault of San Pietro cathedral in Rome, the one richest in crystalline phases was selected (Lab. code: SP1). It is yellow colored; X-ray diffraction identified the crystalline phases of cassiterite (SnO_2) and, to a lesser extent, lead stannate ($PbSnO_3$) (Arletti et al., 2011).

For comparison, a sample of natural cassiterite mineral has also been investigated.

Under red laboratory light the sample was gently powdered, after eliminating about 1 mm of the external exposed side. The powder (2–8 micron) was distributed onto aluminum discs 10 mm diameter and fixed with Dow Corning 805 resin. 30–40 aliquots could be prepared.

The radioluminescence RL measurements were carried out at room temperature (RT) using a home-made apparatus featuring, as detection system, a charge coupled device (CCD) (Jobin-Yvon Spectrum One 3000) coupled to a spectrograph operating in the 200–1100 nm range (Jobin-Yvon Triax 180). The data were corrected for the spectral response of the detection system. RL excitation was obtained by X-rays irradiation through a Be window, using a Philips 2274 X-ray tube with Tungsten target operated at 20 kV. During each measurement the sample was given a dose of 30 ± 5 Gy. RL spectra were deconvoluted into gaussian components using the least squares method with the Levenberg–Marquardt algorithm (Origin 8.0).

To study the wavelengths of TL emission, a high-sensitivity home-made apparatus was used, featuring a two-stage micro-channel plate (MCP) with a 1024-photodiode array. The spectra, recorded at 1 °C/s, were corrected for the wavelength response (Martini et al., 1996).

TL was measured using a home-made system based on photon counting technique, (heating-rate 1–15 °C/s from 50 to 480 °C), detecting the signal with a bialkali EMI 9635QB photomultiplier (maximum quantum efficiency: 350–400 nm), with an optional BG12 filter (5 mm thick), currently used for TL dating. BG12 transmits in the 320–500 nm region, with maximum transmittance (45%) at 400 nm.

Irradiations were made with a $^{90}Sr-^{90}Y$ beta source delivering 4.34 Gy min^{-1} ($\pm 2\%$) to the sample position.

The activation energies of the TL traps were measured by the *initial rise technique* together with the *partial cleaning method* (Martini and Meinardi, 1997). The samples were irradiated (20 Gy), heated to a temperature T_{STOP}, cooled and heated again to a temperature of 480 °C to record the glow curve. The cycle was repeated enhancing the value of T_{STOP} by 30 °C from 70 to 290 °C.

Absorbed doses were evaluated with TL, using the single aliquot regeneration method (SAR, Murray and Wintle, 2003). The main sequence of steps of the SAR protocol adopted in this study is given in Table 1.

Even if the lowest test dose achievable with good precision by the irradiation system (0.7 Gy corresponding to 10 s irradiation) was given, its contribution to the total absorbed dose was not negligible, considering that the values of absorbed dose to be measured are of the same order of magnitude [for 400–500 years old samples a very few Gy are expected]. The dose contribution of the *test dose* was therefore taken into account in calculations. It was possible to study the relation between the sensitivity corrected regenerated signal versus dose.

Table 1
Details on the single aliquot reconstruction protocols used for TL dose evaluation.

STEP	
1	Measure TL (H.R. = 15 °C/s, temperature range 50 °C–450 °C) (N_0)
2	Irradiation with test dose Dt (Dt = 0.7 Gy)
3	Preheat for 60 s at 200 °C
4	Measure TL (H.R. = 15 °C/s, temperature range 50 °C–450 °C) (T_0)
5	Irradiation with regeneration dose D[a]
6	Preheat for 60 s at 200 °C
7	Measure TL (H.R. = 15 °C/s, temperature range 50 °C–450 °C) (L_x)
8	Irradiation with Test Dose Dt (Dt = 0.7 Gy)
9	Preheat for 60 s at 200 °C
10	Measure TL (H.R. = 15 °C/s, temperature range 50 °C–450 °C) (T_x)
11	Repeat steps 5–10

[a] D = 1, 4, 6 Gy.