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Low frequency Raman study of the Boson peak in a Tellurite-tungstate glass over temperature

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ABSTRACT

In this work we present our findings performing low frequency Raman measurements over temperature in a tellurite-tungstate glass sample. The spectra could be fitted by using only two log-Gaussians, which suggests that quasi-elastic light scattering is negligible. The positions of the peaks have the same temperature behavior, being the higher frequency one refereed as Boson Peak in literature. The similar temperature behavior and depolarization ratio indicates that the peaks may have the same origin, being linked to the transversal and longitudinal vibrations of some unit.

1. Introduction

Glasses have been widely exploited by mankind since millennia ago and nowadays those materials are keys for many technologies. The photonics world market for example, which is growing faster than the world economy, employs glasses in lasers, fibers, amplifiers, and many other devices. This have put the interaction between light and matter in evidence in the last few years, aiming to enhance properties, increase efficiency and develop new technologies for many strategic and fundamental fields, such as energy [1] and communication [2,3].

Even though glasses have been so extensively used and studied, some properties remain a puzzle. One of the most interesting example is the observed population of states at Terahertz frequencies found in glasses and any amorphous material [4–6]. This excess of vibrational density of states at such frequencies is known as “Boson Peak” (BP) and it has been observed since the 70s [7] in Raman spectra, however, its origin is still subject of debate in the literature [8–10].

To illustrate the discussion we can look for example for the model of Martin and Brenig [11], by which the BP should consist of both transversal and longitudinal mode acoustic waves, due to a short scale correlation range over mechanical and electrical properties in non-crystalline materials. This could permit phonons of wavelength matching this scale to travel without the usual attenuation of the disordered network. Another important contribution was given by

Malinovsky and Sokolov [12,13], by showing that the form of the BP is independent of the chemical composition and thermal prehistory. By this way, some universal property of disordered materials is expected to describe the BP origin. However, on the recent literature [14] we may found evidences that only transversal phonons (not the longitudinal ones) should be universally linked to the BP.

Looking for evidences of such short scale units in literature, one may found for example the systematic studies about the BP performed by Nemanich [15]. He found in some chalcogenide glasses structural units with a size compatible to the Martin and Brenig model, however, this were not confirmed in all glasses in the study. Buchenau [16] have studied the origin of BP in silica glass by neutron diffraction, and the findings have suggested that such populations of states at BP frequencies are originated by the rotation of SiO₄ tetrahedra. Duval [17] had confirmed the existence of “aggregates” or “microcrystallites” matching the size related to the BP observed in Raman spectra of a silicate glass. Among other evidences of the existence of such units inside the glass, we may point the observation [18] of a new BP by nucleating microcrystallites into the material. Some authors have called this units by “blobs” [4,19,20]. However, a few works have shown that the nature of BP may be more complicated [21–23] that only the “blobs” based model.

In the low energy range of Raman spectra Quasi-elastic light scattering (QES) may also be expected [24–30] at this low energy range. In

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liquids the QES originates from the Doppler shift of the light reflected by one moving particle with speed v relative to the detector, and this phenomena is the basis of a few experimental techniques, such as laser doppler velocimetry. In solids however, the QES origin is still on debate [27] and it seems to be a consensus that this band is centered at 0 cm^{-1} and may extent until $\sim 50 \text{ cm}^{-1}$ [29] in glasses.

Experimental data available in the literature shows us that BP position usually ranges from $\sim 40 \text{ cm}^{-1}$ to $\sim 80 \text{ cm}^{-1}$ [20], depending on composition. The BP Temperature dependence have been investigated in Silica [27], Calcium-aluminosilicate [20], Germania [28], Phosphate [29], Borate [30], Tellurite-Zinc [31] and Tellurite-Oxyhalide [32] glasses, and the results agree that increasing temperature red shifts the peak. This last observation does also agree with the “blobs” idea, once that increasing temperature the material is expanding, which is in favor of longer wavelength phonons, i.e. a shift towards lower frequency. On the other hand, pressure induces a blue shift [4,20,33]. All these experimental findings have driven some work looking for a correlation between fragility and BP [6,34].

One can conclude that the informations available on literature are still not the enough to clarify the question. If we are thinking in more experimental work, one should note that acquire Raman shift data at this range and below can be very difficult. To mention a few points, it is well known that Raman shift intensity may be more or less intense in each sample, in such way that the noise/signal ratio may change our ability to measure ultra low frequencies in some glasses. Once we are usually working in the limit of sensitivity and resolution, just a few cm^{-1} of the laser line, and taking into account that the relative intensity between BP and QES (or even a third band) are different from one sample to another, seldom fit and compare these spectra may be challenging.

By looking to the discussion in the literature, the models still being developed and tested [35–37] or considering that the better understanding of BP could result in the exploration of new phenomena [38] and even in improvements of glass transparency [39], we have performed the low frequency Raman study presented here. The sample investigated is a tellurite-tungstate glass (in %molar $71\text{TeO}_2 - 22.5\text{WO}_3 - 5\text{Na}_2\text{O} - 1.5\text{Nb}_2\text{O}_5$, which we will name here as TWNN). The sample was produced by the melting quenching process under controlled atmosphere as described elsewhere [40], and its optical quality is good enough to enable optical gain [41]. Two peaks instead of the only one usually found in literature were observed at frequencies $< 45 \text{ cm}^{-1}$. By analyzing them, their temperature behavior in the range $30 \text{ }^\circ\text{C}$ to $460 \text{ }^\circ\text{C}$ could be obtained and them discussed.

2. Methods

The measurements were performed in a Raman spectrophotometer (Horiba Jobin Yvon HR 800) under excitation power of 37 mW at 514.5 nm (Argon Laser). A $\times 50$ microscope objective lens were used. The sample was heated at steps of $50 \text{ }^\circ\text{C}$, and a shorter step of $10 \text{ }^\circ\text{C}$ between $330 \text{ }^\circ\text{C}$ and $400 \text{ }^\circ\text{C}$ to have a better insight around the glass transition. The measurements were performed 15 min after the system had reached each sample, to avoid inaccurate temperature data. If by one hand this helped to be confident about the sample's temperature, by another some crystallization were observed, as we can see in Fig. 1.

As we have interpreted that this crystallization have induced Raman peaks $\sim 60 \text{ cm}^{-1}$, to deconvolute and compare properly the ultra low frequency peaks observed we have used only the data in the range $3\text{--}53 \text{ cm}^{-1}$, which were ~ 100 data points. We justify that this peak $\sim 60 \text{ cm}^{-1}$ was not present in the beginning of the experiment neither for some of the highest temperatures, once the glass have melted. However, we decided to keep the same range for all spectra to guarantee the same fitting procedure for all curves.

The theory of Malinovsky, Novikov and Sokolov [13] predicts at least two log-normal components [12] in the low frequency range of the Raman spectra. By this way all data are presented in log-scale, in which

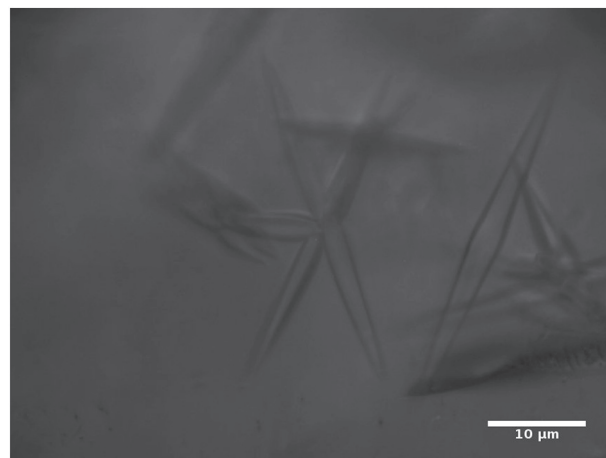


Fig. 1. Example of crystal observed growing during the Raman experiments.

as we are going to show two Gaussians could fit pretty well the data.

The peak centered at 0 cm^{-1} , usually is attributed to QES and fitted by a Lorentzian [30] or power law [31] function. Here we have just kept the data for $\omega < 3 \text{ cm}^{-1}$ out of the fitting process, and the results justify by itself the empirical analysis performed.

3. Results and discussion

Fig. 2 shows the low frequency Raman spectra for room temperature, before glass transition ($T = 300 \text{ }^\circ\text{C}$) and for the highest temperature reached in our experiments ($T = 460 \text{ }^\circ\text{C}$). As one can see, the characteristic shape of BP can be clearly seen at $\sim 40 \text{ cm}^{-1}$, which is the same position where it is found in other Tellurite glasses [31,32,42,43]. However, the shape of the curves around $3\text{--}12 \text{ cm}^{-1}$ are for the best of our knowledge particularly different from the data for other materials.

To explain our analysis, in Fig. 3 we show the fitting result for the spectrum at $420 \text{ }^\circ\text{C}$. As one can see, the data can be interpreted as the sum of two peaks centered at $\sim 6 \text{ cm}^{-1}$ and $\sim 30 \text{ cm}^{-1}$, respectively. We found remarkably that these two peaks could fit the data in such way, giving for all spectra a coefficient of determination $R^2 > 0.999$. This may indicate that the intensity ratio QES/BP is negligible in our sample at this range. Fig. 4 shows the position of both peaks as function of temperature, as well the width of them which are plotted in the inset.

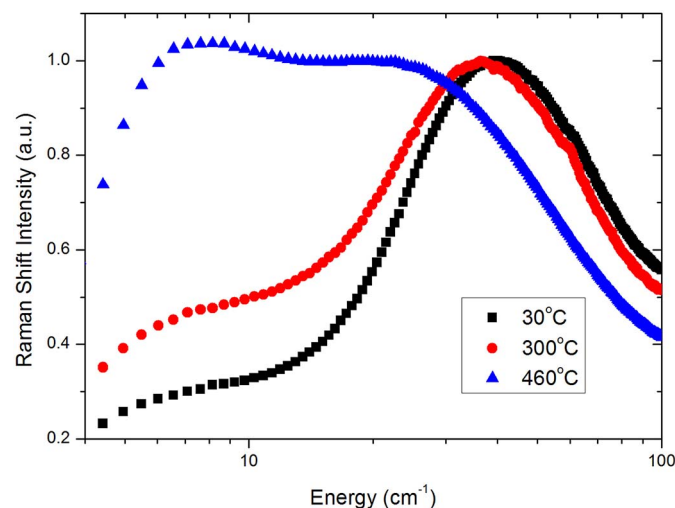


Fig. 2. Low frequency Raman spectra. Once that at 60 cm^{-1} the crystallization produces a new peak during heating, in all spectra just the range $3\text{--}53 \text{ cm}^{-1}$ was selected to be fitted.

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