Combinatorial Fluorescence Lifetime Measuring System for Developing Er-Doped Transparent Glass Ceramics

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Abstract

Fluorescence lifetime of Er^{3+} was measured for F-doped tellurite glasses with parallel heat treatment under a temperature gradient atmosphere in order to find the annealing condition to make transparent glass ceramics in which Er^{3+} ions are located in the precipitated crystals. The preparation and annealing of the samples were performed in a vertical temperature gradient furnace, where molten glass was sucked into a pre-heated Pyrex glass tube. The annealing temperature range is between 350°C and 800°C. After the annealing treatment, time-resolved fluorescence emission of Er^{3+} (1.55um; excitation light source is 977nm) were measured sequentially along the tube. The lifetime of the emission was about 2.6 msec for as-prepared glass. We have found that the lifetime increased to 5.2 msec when the glass was annealed at 470°C for 5 min and 550°C for 5 min successively, although its transparency was lost. This increase implies that the Er^{3+} ions are embedded in fluorine-rich phase to bring about reduced non-radiative emission. We are now continuing to find the condition to get transparent glass ceramics.

Key words: tellurite glass, erbium, fluorescence lifetime

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1 Introduction

Transparent glass ceramics, especially nano-crystallite-dispersed glass materials play an important role in optical and/or photonics devices because they combine merits of glass and crystal materials[1]. One of the promising works was done by Wang and Ohwaki[2]. They made a aluminosilica oxyfluoride glass sample in which Er^{3+}-doped PbF_2 nano-crystallites are precipitated. After the heat treatment for precipitation, the sample showed 100 times larger green upconversion fluorescence of Er^{3+}. This is due to a significant decrease of non-radiative decay of Er^{3+}, that is, reduced vibration energy of surrounding ligands; oxygen to fluorine.

In order to determine the recipe of such kind of materials, the following parameters should be optimized. (1) glass composition in which Er^{3+} ions are incorporated in precipitated non-oxide phase, (2) the first annealing temperature and time for nucleation, and (3) the second annealing temperature and time for crystal growth. Therefore, development of new transparent glass ceramics needs considerable experiments and/or empirical sense, and only few recipes have been found until now[1]. Such investigations would be accelerated efficiently if combinatorial methodology is applied.

Recently, the authors have developed a combinatorial evaluation system for thermal stability of glass materials with low-softening temperature[3,4]. In this system, about-40-cm-long glass sample can be prepared quickly and successively annealed

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under a temperature gradient of from 350°C to 800°C(see Fig. 1(a)). Thus, this system is appropriate for surveying annealing conditions.

In this study, Er^{3+}-doped tellurium oxyfluride glasses are annealed and the lifetime of Er^{3+} fluorescence of 1.5μm is evaluated by a newly constructed equipment. Tellurite glass system is chosen because of the following reasons. (1) Its melting temperature is so low ($\sim$ 800°C) that our combinatorial system can treat with the melt. (2) Tellurite glass is known to show attractive properties such as non-linear optical effect[5], acousto-optics effect[6] and ultra-wideband Raman amplification in fiber form[7]. (3) The authors have succeeded to make a new optical coupling structure where a pair of optical fibers are spliced via tellurite glass melt recently[8], which is expected to realize new optical devices.

2 Experimental

The glass composition in this study is 75TeO_2-22MgO-2YF_3-1ErF_3(in mol%), which is chosen because of the following reasons. (1) TeO_2-MgO system gives a large glass forming region[9]. (2) ionic radii of Y and Er are nearly the same. (3) TeO_2-$YO_{3/2}$ system gives no glass forming region[9]. A mixture of reagent grade power material of each components are melted at about 800°C in a Pt crucible placed at the bottom of the vertical temperature gradient furnace shown in Fig. 1(a). A Pyrex glass capillary (75cm $\times$ 8mm OD $\times$ 1.5mm ID) was inserted into the furnace from the top so as to be heated under a temperature gradient of $800 \sim 350$°C in 50cm-span. The temperature profile inside the capillary along its length had been determined in advance by inserting a thermo-couple into a empty capillary.

The inserted capillary was held in the furnace for 10 min in order to reach thermally

equilibrium state. Then, the glass melt was sucked into the capillary by a vacuum pump, which was connected to the top of the capillary, to make a sample library. The melt stopped rising within 1 second because its temperature decreases and its viscosity increases during the run of about 300mm. Then the library was moved to an appropriate positions in the furnace to be annealed at different temperature in parallel. After the annealing treatment, the capillary is pulled out completely. Three samples which are annealed differently were prepared(see Fig. 1(b)); (0) no annealing, (1) annealed for 5min, and (2) another successive annealing at a different position for 5min.

The sample library is mounted in a fluorescence lifetime measuring equipment shown in Fig. 2. Its light source is a CW Ti:Sapphire laser of 977nm (Spectra-Physics, 3900) pumped by LD-pumped YAG laser (SpectraPhysics, Millenia Vs). Its detector is a multi-channel spectrometer (Soma Optics, S-2700) which can store time-resolved spectra in every millisecond. These three are optically connected through multi-mode optical fibers. For fluorescence lifetime measurement, the CW light is chopped by a mechanical shutter and fluorescence decay curve for 1.5μm band of Er^{3+} ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) is stored. This measurement is performed sequentially along the sample library in every 1mm. The whole system is controlled by a real-time operating system (ART-Linux) on a personal computer.

3 Results

Figure 3 shows the annealing condition of the sample libraries, that is, every 1mm segment in the libraries is plotted as a function of annealing temperatures, the 1st annealing temperature, T_1 and the 2nd, T_2. For example, the annealing conditions for the segment A_2 in the Sample (2) and A_1 in the Sample (1) are $(T_1, T_2) =$

$(470, 550)$ and $T_1 = 470$, respectively. Sample (0) is also plotted for reference. A_0 and A_1 are located at the same position in the library. Consequently, the relation among these segments is represented as follows.

$$\begin{array}{ccccc} (\mathrm{melt}) & \xrightarrow[T_1 = 470 \text{ for 5min}]{\text{1st anneal}} & & \xrightarrow[T_2 = 550 \text{ for 5min}]{\text{2nd anneal}} & \\ \downarrow & & \downarrow & & \downarrow \\ \mathrm{A}_0 & & \mathrm{A}_1 & & \mathrm{A}_2 \end{array} \tag{1}$$

As the heat treatment proceeded, crystallization occurred and the portion of transparent segments in the library decreased. Appearance of each segment is judged by eye and plotted in Fig. 3 by the following way. Completely transparent segment is plotted as ◯, white segment as ·, the rest, i.e. not white but not completely transparent, as •. For convenience, the third one is called as "opaque" from here. The appearance of the segments in Sample (0) varies along the length because their initial temperatures in quenching are different each other.

Fluorescence spectra of Er^{3+} for the segment of A_0, A_1 and A_2 (see Fig. 3) is shown in the left part of Fig. 4. The shapes of the spectra for A_0 and A_1 are almost the same, while that for A_2 is different from the others. Fluorescence lifetime of each segment is calculated from the stored decay curves of 1.533nm fluorescence on the assumption that the curve is expressed by a single exponential(see the right part of Fig. 4). Again the lifetime of A_0 and A_1 are nearly the same, while that of A_2 is two times larger than the others. Figure 5 shows the calculated lifetime plotted along the library or as a function of the 1st annealing temperature, T_1. An increase of lifetime is observed after the 2nd heat treatment. For the the segments in Sample (2) at around $T_1 = 470$ (A_2 in Fig. 3), not only lifetime but also the shape of their fluorescence spectra was also changed(see Fig. 4).

4 Discussion

Although the lifetime does not vary after the 1st heat treatment (compare Sample (0) and (1) in Fig. 3), an increase is observed after the 2nd one. So let us examine the segments shown in Eq. (1) and the following(see Fig. 3).

$$\begin{array}{c}(\mathrm{melt}) \\ \downarrow \\ \mathrm{B}_0\end{array} \xrightarrow[T_1 = 550 \ \text{for 5min}]{\text{1st anneal}} \begin{array}{c}\downarrow \\ \mathrm{B}_1\end{array} \tag{2}$$

Among these segments, only A_2 shows the largest lifetime value of about 5.2 msec. The rest shows nearly the same value of about 2.6 msec. Thus, the increase in lifetime occurred in the 2nd heat treatment of $T_2 = 550$. On the contrary, the 1st annealing of $T_1 = 550$ did not bring about any increase in B_1. Thus, the cause of this increase is considered to be due to a phenomena during the 1st annealing of $T_1 = 470$.

As for the appearance of the segments, the annealing of 550°C made A_2 white but B_1 remain transparent. The white color must be due to the precipitated crystals containing TeO_2, for it is the main component of this glass. Thus, it is natural to consider that the heat treatment at 470 °C on this glass composition caused nucleation and the further annealing at 550 °C promoted crystal growth on the generated nuclei.

Therefore, the change in lifetime can be explained in the viewpoint of coordination environment around Er^{3+}. In the as-prepared segments, Sample (0), it is reasonable to assume that Er^{3+} ions are coordinated mainly by oxygen anions. The situation is not changed after the 1st heat treatment because both the lifetime and the shape of fluorescence spectra are not changed. After the 2nd annealing at around 550°C, Er^{3+} ions are not incorporated by the precipitated oxide crystals and stay in

fluorine-rich residual phase.

When Er^{3+} ions in the residual phase are coordinated by fluorine anions, electrons in the excited state of Er^{3+} stays longer, in other words, the non-radiative decay rate is smaller compared with that in oxide matrix, because the vibration energy of surrounding fluorine is smaller than that of oxygen. The change in spectral shape shown in Fig. 4 also support the change in coordination around Er^{3+}.

Among the samples in this study, the segments showing increased lifetime simultaneously lost their transparency. This combinatorial evaluation system is, however, proved to be a powerful tool to develop transparent glass ceramics because only three samples, with one preparation process and one measurement per each, can provide rich information described above. We are now continuing to find the condition to prepare transparent glass ceramics.

5 Conclusion

Combinatorial evaluation system for Er^{3+}-doped glass materials is developed. It includes a parallel annealing furnace for sample preparation and a sequential measurement equipment for fluorescence lifetime. Er^{3+}-doped tellurium magnesium oxyfluoride glass samples are prepared and annealed at various temperatures. Then, the lifetime of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ fluorescence ($\sim$1.5μm) is evaluated. The lifetime showed a twofold increase when the glass is annealed at 470°C for 5min and successively at 550°C for 5min. This is considered to be due to a change in cordination around Er^{3+} ions, that is, oxygen ligands are replaced by fluorine anions during the growth of oxide crystals in the 2nd heat treatment. This system is useful to survey conditions for making transparent glass ceramics.

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Figure Captions

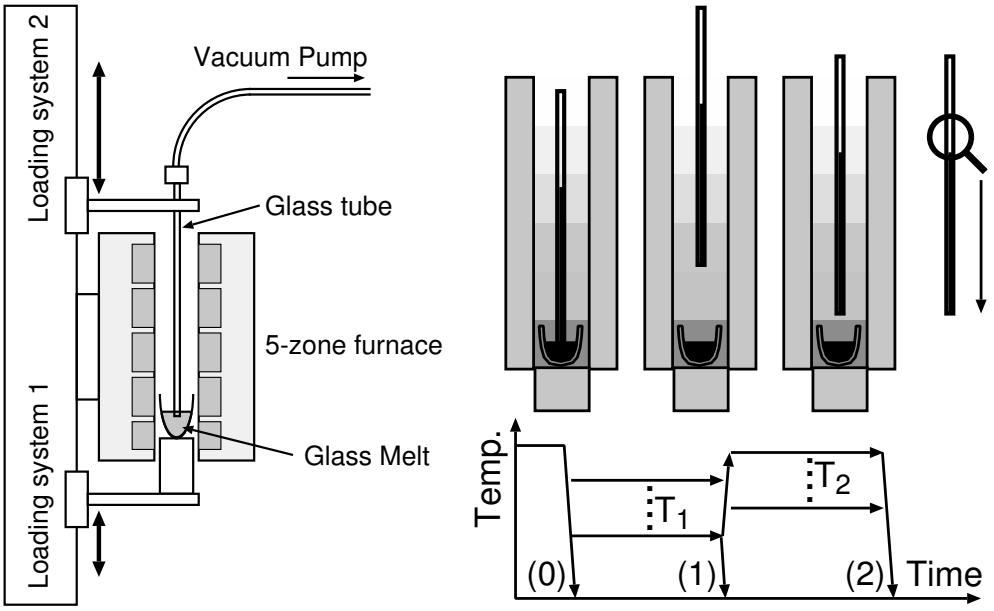
Fig. 1 (a: left) The structure of vertical temperature gradient furnace used in this study and (b: right) an illustration showing 2-step annealing procedure(see text).

Fig. 2 The fluorescence lifetime measuring equipment used in this study(see text).

Fig. 3 Annealing condition of the sample libraries and appearance of the annealed glass segments inside. (0) with no annealing treatment for reference. (1) with 1st annealing for 5min only. (2) with two successive heat treatments, each for 5min. Thick line plotted by ◯: completely transparent segment, thin line by · : white, and medium line by ●: opaque(see text). A_n and B_n indicate specific glass segments. These notations are also used in Fig. 4 and Fig. 5.

Fig. 4 (Left) Fluorescence spectra of Er^{3+} and (right) decay curves of 1533nm fluorescence for the glass segments of A_0, A_1 and A_2(see Fig. 3). For the decay curve, triangle points are not used for lifetime calculation.

Fig. 5 Lifetime of 1.533nm fluorescence of Er^{3+} plotted along the library or as a function of the 1st annealing temperature, T_1.



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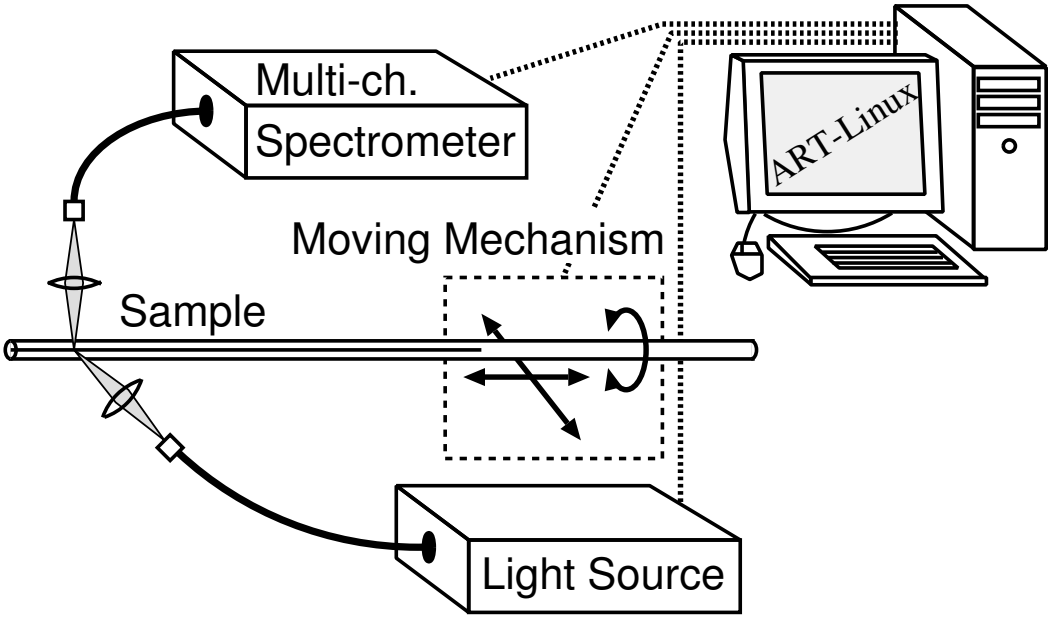

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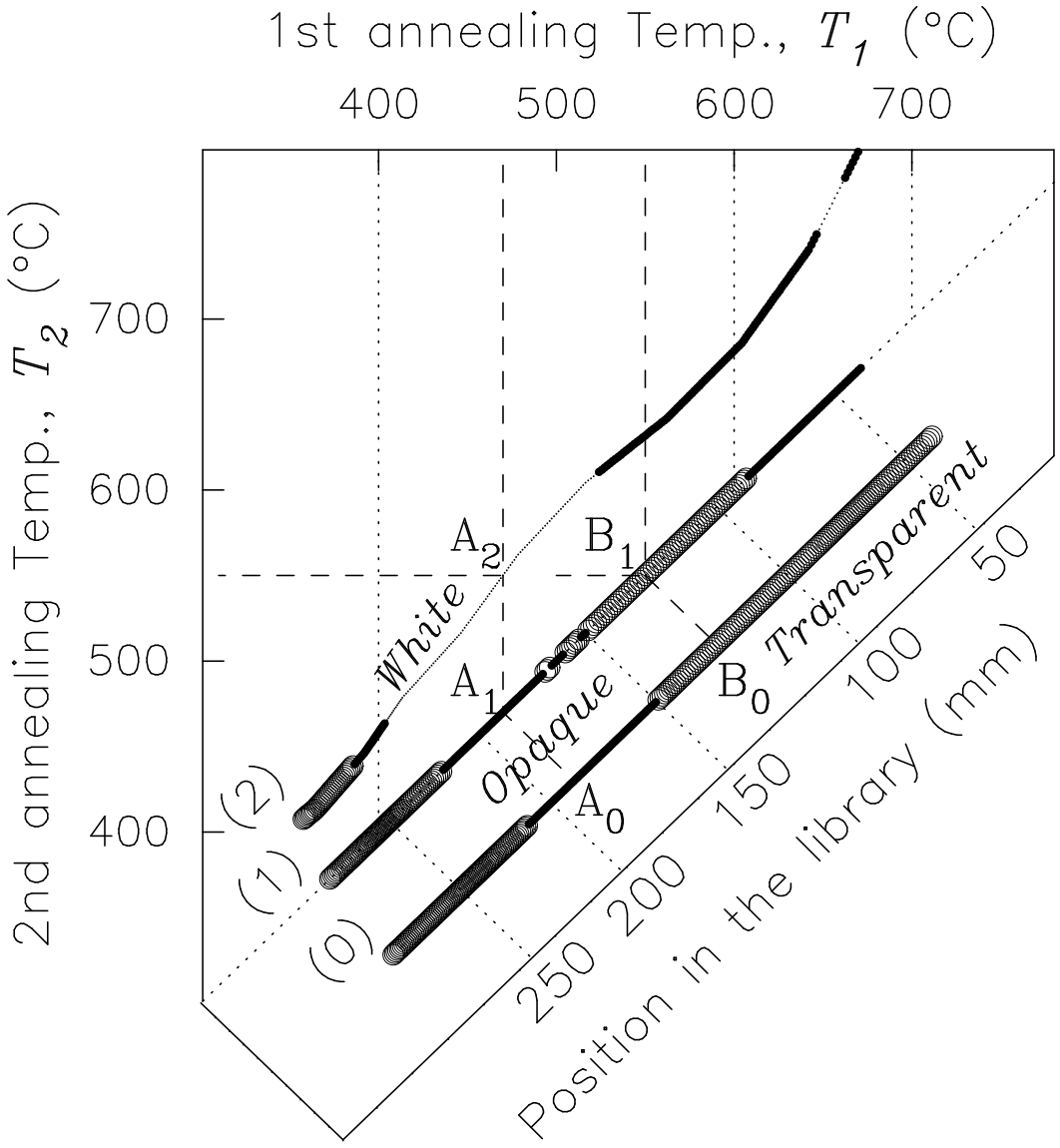

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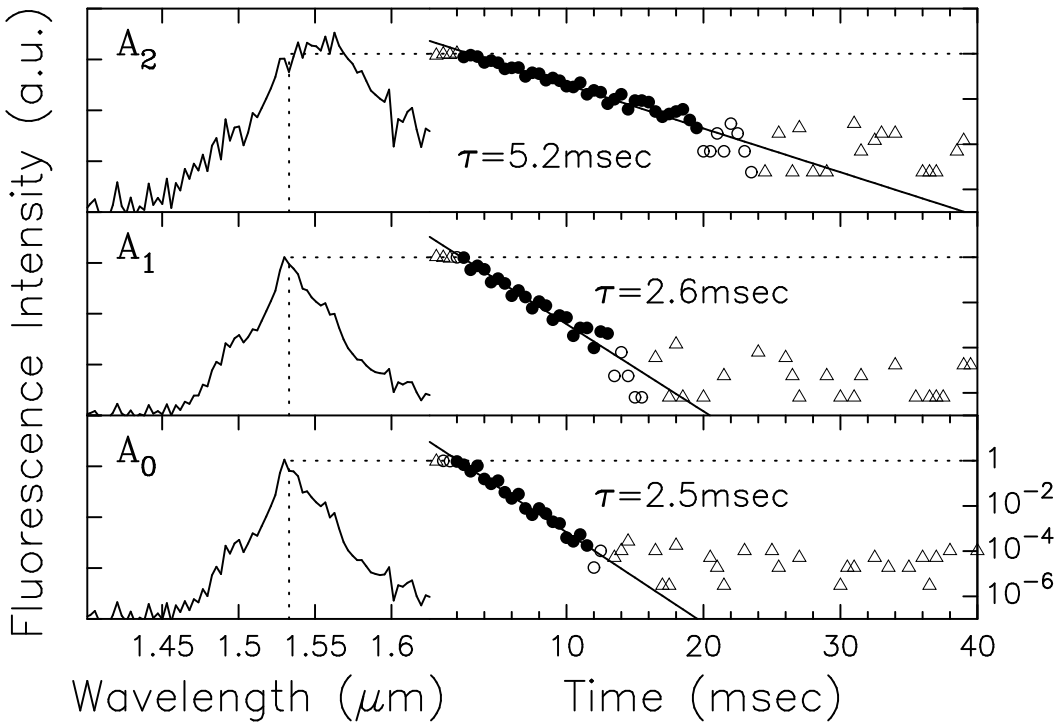

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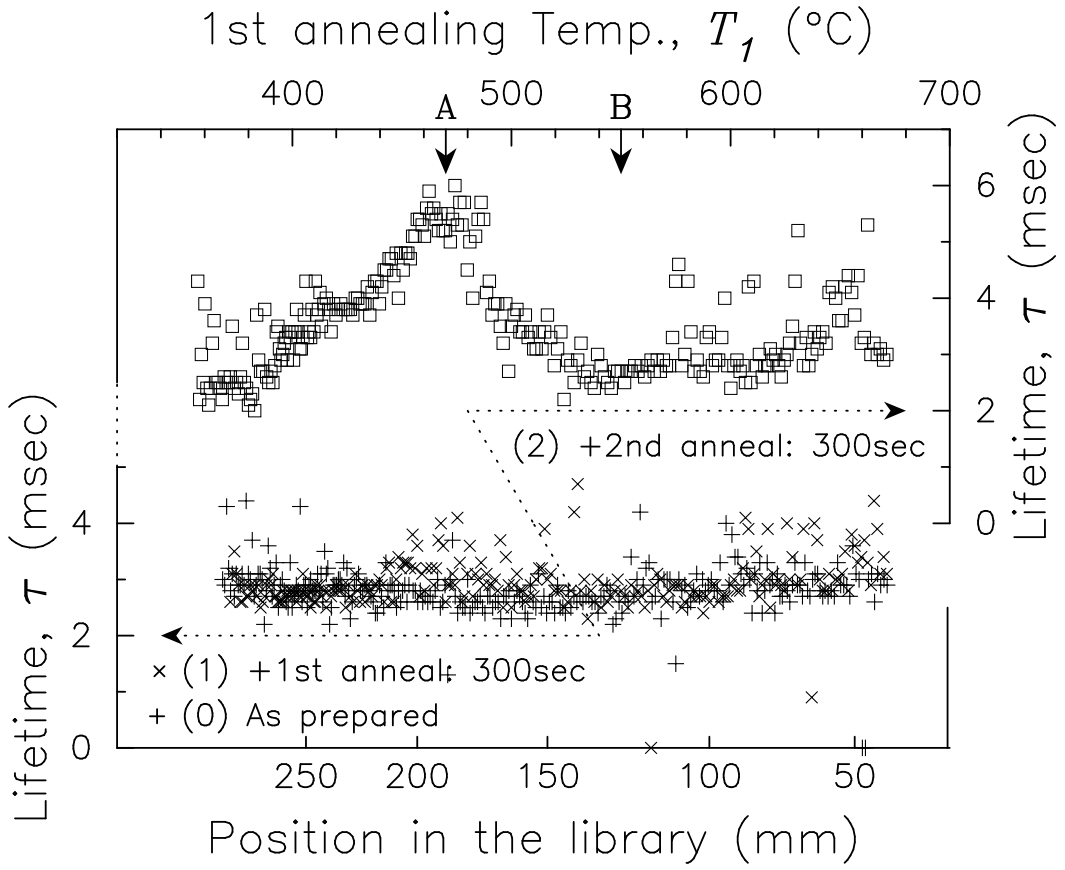

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