Positron annihilation in transparent ceramics

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Abstract: Transparent ceramics are emerging as excellent candidates for many photonic applications including laser, scintillation and illumination. However achieving perfect transparency is essential in these applications and requires high technology processing and complete understanding for the ceramic microstructure and its effect on the optical properties. Positron annihilation spectroscopy (PAS) is the perfect tool to study porosity and defects. It has been applied to investigate many ceramic structures; and transparent ceramics field may be greatly advanced by applying PAS. In this work positron lifetime (PLT) measurements were carried out in parallel with optical studies on yttrium aluminum garnet transparent ceramics in order to gain an understanding for their structure at the atomic level and its effect on the transparency and light scattering. The study confirmed that PAS can provide useful information on their microstructure and guide the technology of manufacturing and advancing transparent ceramics.

1. Introduction

Transparent ceramics are optical materials formed by consolidation of nanocrystalline precursors into a fully dense solid [1]. They feature good mechanical strength, high melting points and good transmission in the IR spectrum. They have some advantages over single crystals as they can be molded and shaped as needed for any particular application. Moreover, manufacturing transparent ceramics does not require the same amount of time or complex facilities that single crystals require [2]. Cubic crystal structure is the best choice for transparent ceramics to minimize light scattering and lanthanide aluminum garnets-in particular- were shown to be promising transparent ceramics for laser and scintillation applications [1]. These potential applications require perfect transparency and minimum light scattering. However the presence of grains and grain boundaries tend to increase light scattering. Therefore it is critical to study the microstructure of transparent ceramics and reveal their grain sizes and distributions. The focus of this work is to study the transparency and microstructure of undoped Y₃Al₅O₁₂, yttrium aluminum garnet (YAG) and Ce doped YAG transparent ceramics. This will be done by combining positron lifetime (PLT) spectroscopy with optical transmission measurements. Positron annihilation spectroscopy is a powerful tool for investigating defects and open volumes in solids and polymers. It has been successfully applied to...
study the microstructure of a number of ceramics [3-13], as large fraction of positrons often annihilate at the grain boundaries providing information about their size and character.

The basics of PLT spectroscopy of defects and microstructures can be explained as follows [14, 15]. When positron enters a medium, it thermalizes in about 10 ps, then diffuses until it annihilates with an electron emitting two 511 keV photons. In homogeneous defect-free matter, all positrons annihilate in the bulk with characteristic bulk lifetime $\tau_B$. In the presence of defects or open volumes, the positron may become trapped in open-volume defects (monovacancies, larger vacancy clusters, grain boundaries or open volumes). This is because the positron is repelled by the positively charged ion cores. Hence, defects with missing atoms or a reduced density of ions provide an attractive potential for positrons. Positron trapping at defects lead to longer lifetime. The positron lifetime is the difference between time of creation of the positron (usually marked using a time-coincident gamma-ray in case of radioactive source or using the beginning of a pulse in case of pulsed positron beam) and the time of annihilation, marked by detection of one of the 511 keV annihilation radiations. This gives the lifetime of a single positron, and one typically accumulates a spectrum of lifetimes over a period of hours. The annihilation rate $\lambda$, reciprocal to the mean positron lifetime $\tau$, is given by [15]:

$$\lambda = \frac{1}{\tau} = \pi r_0 c^3 \int \left| \psi(r) \right|^2 n(r) \gamma \, dr$$  

in which $r_0$ is the classical electron radius, $c$ is the speed of light, $r$ is the position vector, $\left| \psi(r) \right|^2$ is the positron probability density, $n(r)$ is the electron density and $\gamma$ is an enhancement factor representing an increase in the local electron density due to the attractive coulomb interaction between the positron and nearby electrons. Since the positron lifetime is a function of the electron density at the annihilation site, lifetime measurements can discriminate among the different lattice locations at which the positron annihilates, and consequently gives information about defects and open volumes. In a defect-free material, positrons form Bloch states and annihilate as free particles with a well-defined “bulk” annihilation rate. This leads to a single exponential decay [15] in the lifetime spectrum with a characteristic “bulk” lifetime. Positrons annihilating in different defects will have different characteristic lifetimes $\tau_i$. A general lifetime spectrum $N(t)$ will be a sum of components corresponding to each annihilation site:

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp \left( -\frac{t}{\tau_i} \right)$$  

in which $k+1$ is the number of time components in the spectrum relating to $k$ defects and for positron annihilation in the bulk; $\tau$ and $I$ are the lifetime and intensity of the $i$th component in the spectrum. The spectrum is fitted with Eq. (2) after convoluting the sum with the time-resolution function of the spectrometer. The fitted lifetimes give information about defect/open volume sizes and characteristics and the intensities determine their concentrations [14,15].

In porous materials with large open volumes, the positron may first form a positronium with an electron, then annihilate based on the relative spin orientation between the electron and positron. The positron lifetimes in vacuum for para-positronium (singlet state) and ortho-positronium (triplet state) are 125 ps and 142 ns respectively. In matter, the pick-off annihilation process [15] takes place leading to few nanoseconds lifetimes.

2. Experimental details

Transparent ceramics of undoped YAG and Ce doped YAG samples were obtained from Baikowski/Konoshima Inc. They are round samples of 1 cm diameter and 1 mm thickness with very good polished surfaces. Figure 1 shows an image for the undoped and Ce doped YAG samples with their names written underneath to demonstrate their good transparency.
Positron lifetime spectra were measured using a conventional fast-fast time coincidence spectrometer with two BaF$_2$ detectors in a collinear geometry and with time resolution of ~200 ps [16]. $^{22}$Na with about 20 μCi activity was used as a positron source; it was made by depositing NaCl on a 0.8 microns kapton foil. The source was sandwiched between two identical samples. Na-22 emits a photon with the energy of 1.274 MeV in coincidence with each positron. This photon can be used to provide a start signal for PLT measurements. One of the two 511 keV annihilation photons is used to provide the stop signal. Each PLT spectrum contained at least 1.3x10$^6$ counts and multiple runs were made for better statistics. The spectra were analyzed using PATFIT’88 software [16]. A detailed description of the resolution function required for spectrum analysis in PATFIT’88 used three Gaussian functions. The lifetime spectrum was then analyzed as a sum of exponential decay components with the Gaussians functions describing the spectrometer timing resolution. Decay components due to annihilation in NaCl ($\approx 430$ ps) and kapton foil ($\approx 382$ ps) were subtracted from each spectrum. These values have been previously determined for the setup using annealed defect free aluminum single crystals.

Optical transmission measurements were conducted from 190-1100 nm using a Perkin Elmer UV-VIS-NIR Spectrometer [17]. For comparison, measurements were also made on undoped and Ce doped YAG single crystals of the same size and thickness.

3. Results and discussion

All PLT spectra were well fitted to two lifetime components $\tau_1$ and $\tau_2$ and their intensities $I_1$ and $I_2$. $\tau_1$ is reduced from the bulk lifetime by an amount that depends on the trapping rate of defects, while $\tau_2$ represents the defect lifetime. Obtained lifetimes and intensities are summarized in tables 1 and 2. Variances of the fit are also included in the tables. Undoped YAG samples were measured only two times; while measurements on Ce doped YAG were repeated five times to confirm the large value of $\tau_2$. Bulk and average lifetimes were calculated using equations (3) and (4).

$$\tau_b = \left( \frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1}$$

$$\tau_{avg} = \sum_i I_i \cdot \tau_i$$

Table 1 and 2 shows that the defect lifetime $\tau_2$ for Ce doped YAG is about 560 ps, much larger than $\tau_2$ for the undoped material (342 ps). The ratio $\tau_2/\tau_b$ can was also estimated. It can give some indication about the nature of open volume defects. It is 1.9 for the undoped ceramic and 3.5 for Ce:YAG ceramic revealing much larger open volume defects in Ce:YAG samples. The reason for that could be the large size of Ce ion, as it exists in Ce$^{3+}$ (its size is 1.1 Å) compared to 0.93 Å for Y$^{3+}$ [18]. This probably
leads to the formation of vacancy clusters next to the Ce ion, a phenomena we have noticed earlier in Ce doped YAG single crystals [18, 19]. The large defect lifetime in Ce:YAG ceramics also indicates the presence of micro voids and large grain boundaries in the structure. This is an indication that the porosity of Ce:YAG ceramics is higher compared to undoped YAG ceramics, which is consistent with the optical transmission data described below. In case of CeYAG, sintering process probably did not eliminate all the pores at the grain boundaries.

| Ce:YAG | $\tau_1$ (ps) | $\tau_2$ (ps) | $I_1$ | $I_2$ | $\tau_B$ (ps) | $\tau_2/\tau_B$ | $\tau_{avg}$ (ps) | Fit | Var |
|--------|---------------|---------------|-------|-------|---------------|-----------------|------------------|-----|-----|
| Run 1  | 154.9 (0.2)   | 664.8 (11.2)  | 97.99% (0.058) | 2.01% (0.058) | 157.3         | 4.22632        | 165.1           |     |     |
| Run 2  | 154 (0.2)     | 612.7 (6.4)   | 97.45% (0.048) | 2.55% (0.048) | 157           | 3.90255        | 165.7           |     |     |
| Run 3  | 153.1 (0.8)   | 466.1 (9.5)   | 91.53% (0.377) | 8.47% (0.377) | 162.3         | 2.87184        | 179.6           |     |     |
| Run 4  | 155.3 (0.4)   | 532.4 (8)     | 94% (0.18)     | 6% (0.18)     | 162.2         | 3.28237        | 177.9           |     |     |
| Run 5  | 157.9 (0.3)   | 522.3 (5.3)   | 93.16% (0.14)  | 06.84% (0.14) | 165.8         | 3.15018        | 182.8           |     |     |
| Averages | 155         | 559.7         | 94.83% (0.14)  | 5.17% (0.14)  | 160.9         | 3.48665        | 174.2           |     |     |

Table 2. PLT data for two runs on YAG transparent ceramics. $\tau_1$ represents the reduced PLT in bulk material with respective annihilation fraction $I_1$, $\tau_2$ represents the positron lifetime of defects with annihilation fraction $I_2$, $\tau_B$ is the calculated bulk lifetime and $\tau_{avg}$ is the average lifetime.

| YAG   | $\tau_1$ (ps) | $\tau_2$ (ps) | $I_1$ | $I_2$ | $\tau_B$ (ps) | $\tau_2/\tau_B$ | $\tau_{avg}$ (ps) | Fit | Var |
|-------|---------------|---------------|-------|-------|---------------|-----------------|------------------|-----|-----|
| Run 1 | 141.8 (0.7)   | 267.6 (1.2)   | 61.99% (0.63) | 38.01% (0.63) | 172.7         | 1.54951        | 189.6           |     |     |
| Run 2 | 172.9 (0.9)   | 417.7 (40.9)  | 96.01% (0.72) | 3.91% (0.72)  | 177.4         | 2.35457        | 180.6           |     |     |
| Averages | 157.4    | 342.7         | 79%   | 20.76%| 175.1        | 1.95204        | 185.1           |     |     |

Optical transmission spectra of undoped and Ce doped YAG transparent ceramics are shown in Figure 2. More than 80% transmission in the region from 200 to 1100 nm can be seen in the spectra. The dips in CeYAG spectra are due to 5d to 4f transitions in Ce$^{3+}$. The graph also displays the optical transmission spectra for similar single crystals for comparison. It is interesting to observe that YAG ceramics has higher transparency than single crystals. However this is not the case for CeYAG samples. This is also in agreement with PLT data which revealed larger open volume defects and micro voids in CeYAG structure that are expected to increase light scattering.
4. Conclusions
PLT measurements indicated the absence of large voids and nanopores in undoped and Ce doped YAG transparent ceramics. This explains the reason behind their good transparency (more than 80% transparency in the visible region). However measurements also revealed small open volume defects in the structure, which are much larger for Ce doped samples. Positron annihilation spectroscopy is shown to be a good tool to investigate the microstructures of transparent ceramics and provide a feedback to guide ceramics technology.

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