

Positron lifetime study of the devitrification process in a cordierite glass

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The devitrification of the 13.3% MgO–32.0% Al₂O₃–52.7% SiO₂–2.0% BaO ceramic–glass via isochronal heating up to a stable crystalline structure has been studied by the positron annihilation technique. The lifetime spectra showed two components. This devitrification results as a two-stage process. The long-lifetime τ_2 , attributed to the pick-off annihilation of *ortho*-Ps states, decreased on crystallization, but it was insensitive to the hexagonal–orthorhombic transformation of the crystalline cordierite. On the contrary, the effective lifetime of positrons annihilating in states that are not Ps, increased. This increase has been attributed to the Al/Si order process inherent to the hexagonal–orthorhombic transformation. Moreover, the Ps fraction in the crystalline phases was higher than in the glassy phase. However the free volume model might qualitatively explain the relationship observed between I_2 and τ_2 .

1. Introduction

It is well established that energetic positrons implanted in a material are rapidly thermalized by collisions with ions and electrons. After thermalization, the positron fate is usually to decay into two photons by annihilation with an electron. Then, the positron lifetime which will depend on the local electron density, is typically 100 to 400 psec. In isolating materials such as glass–ceramics and molecular substances, thermalized positrons have some probability of capturing an electron and of forming a bound state like positronium atom. Positrons in these states have two ways of decaying depending on whether they are in a *para*-Ps state (antiparallel spins), or in an *ortho*-Ps state (parallel spins). The *para*-Ps state decays into two photons with a lifetime of 0.125 nsec, while *ortho*-Ps decays via three photons with a lifetime much longer than the *para*-Ps lifetime, by about 10³ times. Nevertheless in any material, there exists a high probability that the positrons in *ortho*-Ps states will interact with a surrounding anti-parallel spin electron, annihilating via a two photon decay with a lifetime of about 1 nsec. This process is

called “pick-off”. This pick-off annihilation will occur when the positron wave function in the *ortho*-Ps state overlaps with that of the surrounding electrons. So, the different components which are found in the positron lifetime spectra may be attributed to the possible annihilation modes in the material, at least in principle.

Positron annihilation experiments have been performed in several glass systems as: Na₂O–B₂O₃ [1–3], CaO–P₂O₅ [2, 4], LiO₂–SiO₂ [5–7] and other complex silicate glasses [8]. The positron lifetime of these glasses showed either two or three resolvable components. The long-lifetime component, generally about 1 nsec, is attributed to *ortho*-Ps decay via a pick-off process, while the short-lifetime component is attributed to the *para*-Ps self-annihilation and the annihilation of free positrons. This component may be disturbed by some intermediate-lifetime components coming from the annihilation of bound positrons in states other than the *ortho*-Ps states, so that the lifetime of this component might range between 0.2 to 0.4 nsec. This may be specially noticeable when a resolvable

intermediate-lifetime component is not found in the lifetime spectra. The origin of the intermediate component is not clear, as it will depend on the particular annihilation mechanisms in the different glasses, and moreover, it might not exist. So there is a considerable disagreement regarding the origin of this.

The positron annihilation technique has been found sensible to the structural changes produced during the devitrification process in some nitrate glasses [9], and specially in silicate glasses [5, 6, 8]. The long-lifetime and its intensity were found to decrease with the crystallinity degree of these glasses. The results have been partially explained by the free-volume model proposed by Brandt and Spirn [10], and Thosar *et al* [11] for molecular materials. A complete explanation of the results leads to suggest the interaction of free positrons and/or *ortho*-Ps with structural defects, the formation of bound positron-anion states [8], and even a probable *ortho-para* transition via a spin-conversion induced by transition metal impurities [2, 4].

At present, the new applications of the glass-ceramics have resulted in an increasing interest by the study of the devitrification process in these materials. The devitrification process in cordierite glasses is particularly interesting since crystalline cordierite bodies with complicated shapes may be produced by the devitrification of cordierite glass bodies previously sintered. Due to the low thermal expansion and high corrosion resistance of the crystalline cordierite, these bodies have many technological applications such as holders of automotive catalytic converters and heat exchangers for gas turbines and furnaces, besides production of high-strength glass fibres.

Although the devitrification in cordierite glasses has been extensively studied using many different techniques, such as X-ray diffraction, differential thermal analysis, infrared spectroscopy, dilatometry, electron microscopy etc. [12–16] (see [17, 18] for review), so far it does not seem that the positron annihilation technique has been applied to study this subject in cordierite glasses. However, Hsu and Vance [19] have used this technique to study natural cordierites under dehydration.

In this work, we have studied the positron lifetime spectra from a cordierite type glass

which was devitrificated by successive isochronal heating. The results show two well-defined stages for the lifetime components of this glass when the heatings are prolonged until a stable crystalline phase is reached.

2. Experimental details

In these experiments flat flakes of cordierite glass from Ferro Corporation, Independence, Ohio, were used. The frit composition was 13.3 wt % MgO, 32.0 wt % Al₂O₃, 52.7 wt % SiO₂ and 2.0 wt % BaO. Two pairs of these flakes 0.8 mm thick, and with smooth surfaces were isochronally heated for 1 h over the range 650 to 1700 K in vacuum ($\sim 10^{-2}$ Pa). The heating and cooling rates were approximately 20 K min⁻¹. As-received, and after each heating, the positron lifetime spectra of the samples were recorded at room temperature using a conventional fast-slow coincidence system with a time resolution (FWHM) of 305 psec for the ⁶⁰Co prompt curve measured with ²²Na energy windows. The positron source (7×10^5 Bq), used in the common sandwich geometry, was prepared by evaporating an aqueous ²²NaCl solution onto a 0.7 mg cm⁻² nickel foil.

X-ray diffraction measurements were carried out on the as-received samples, and after heating the samples at various temperatures of the run. These measurements were taken in a Siemens Kristalloflex 810 using the CuK α_1 radiation. The purpose of these measurements was to get rough information about the structural stage of the samples.

3. Results and discussion

The spectra, having 6×10^5 counts under the peak, were analysed using a modified version of the program Positronfit extended [20]. We tried to fit the spectra with two and three lifetime components including two corrections, one for annihilation in the nickel foil and another for annihilation in the source itself. A three-component fit of the spectra was tried, but it resulted in unacceptable standard deviations and a considerable dispersion in the lifetime and intensity values. It even failed due to the convergence lack in some cases. The two-component fit yielded a good variance and the results were adequate for the experiment discussion. These are shown in Figs. 1 and 2.

Two stages in the lifetime components, τ_1 and

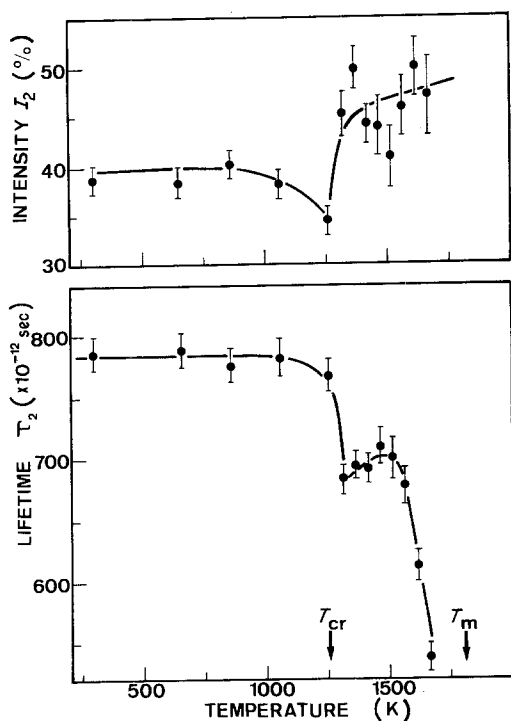


Figure 1 Lifetime τ_2 and intensity I_2 of the long component against heating temperature. T_{cr} and T_m represent the crystallization and melting temperature respectively.

τ_2 are shown. The first stage in τ_2 starts at about 1250 K, and coincides with a minimum in its intensity. The τ_2 value decreases about 12% and above approximately 1550 K, it starts to decrease again. Over the range 1300 to 1500 K, no changes are seen in τ_2 , but I_2 increases abruptly at about 1300 K. On the other hand, the first stage in τ_1 appears to start above 1400 K, increasing up to 17%. The second stage in τ_1 coincides with that observed in τ_2 .

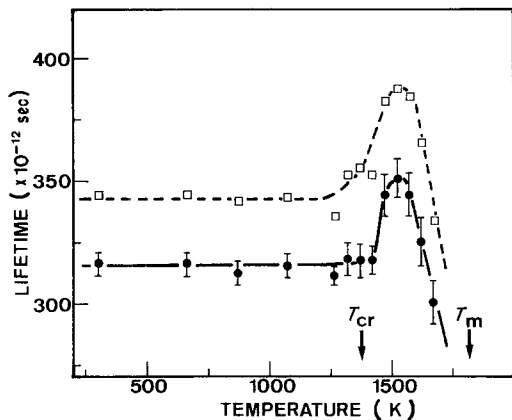


Figure 2 Lifetime of the (\square) short component τ_1 and (\bullet) estimated lifetime τ_{e+} against heating temperature.

In principle, we attributed the long-lifetime component, τ_2 , to the pick-off annihilation of the *ortho*-Ps which are formed in the free-volume of the glass according to the generally accepted view for these materials. After heating at 1375 K, the X-ray diffraction indicated that the samples were crystallized. So that, the first stage in τ_2 and the drop in I_2 are attributed to the setting up of the crystallization. The behaviour of these parameters on the crystallization coincides with that observed by James *et al.* [6] in $\text{LiO}_2-2\text{SiO}_3$. Although the behaviour on crystallization observed generally in I_2 is to decrease in every glass studied so far, it is reported that τ_2 increases in $\text{LiO}_2-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses [8] and in nitrate glasses [9]. The free-volume model can account for the decrease of the pick-off intensity since it predicts a drop in this when the free-volume is reduced on crystallization. After heating at 1320 K, the abrupt raise in I_2 and the simultaneous drop in τ_2 suggest that there are changes in the regions where the pick-off annihilation takes place. This would mean that these regions reduce their volume on crystallization and in this way the overlap between the bound positron and the surrounding electron wave functions increases. As it is well known, this produces an increase in the annihilation rate and therefore the decrease in τ_2 . To explain the increase in I_2 , we suggest that when the crystalline structure is complete, the number of open volume regions in the material where the *ortho*-Ps formation is possible according to the Ore Gap Concept [21], increases. This argument is supported by the structural characteristics of the crystalline cordierite. It is known that the more frequent crystalline phases of the cordierite silicates have a dominant structure consisting of six-membered hexagonal rings of linked (Si, Al) O_4 tetrahedra stacked above each other to form a column of rings enclosing a large empty channel parallel to the *c*-axis [22]. Positrons might be bounded like *ortho*-Ps in this channel.

We should mention the fact that the short-lifetime τ_1 goes up to approximately 11% over the range 1400 to 1500 K while τ_2 and I_2 remain constant. In principle, this component may be attributed to the mix of unresolved components. One of them being that which corresponds to the *para*-Ps self annihilation. So, τ_1 would be the weighted-mean of the *para*-Ps lifetime and of the lifetimes of positrons annihilating in free states

and/or in other possible states different from the Ps states. As the ratio of *para*-Ps to *ortho*-Ps states is assumed 1 to 3, a rise in the pick-off intensity results in an increase of the weight of the *para*-Ps lifetime in the τ_1 value. Therefore, it seems probable that the first stage in τ_1 , noted above 1425 K, has been delayed because of this effect. Assuming that τ_2 is only due to pick-off annihilation and that all remaining positron annihilations appear unresolved as the short-lifetime component, one could say

$$\tau_1 = I_p \tau_p + (1 - I_p) \tau_{e+} \quad (1)$$

where I_p is the intensity of the component due to *para*-Ps self-annihilation, the lifetime of which τ_p , is assumed to be 125 psec, and τ_{e+} is the effective lifetime of positrons annihilating in states different from the Ps states.

Within this framework, taking into account the statistical relationship between the *para*-Ps and the *ortho*-Ps states, we have

$$I_2 = \frac{3}{4} F_{Ps} \quad (2)$$

and

$$I_p = \frac{1}{4} F_{Ps} = \frac{1}{3} I_2 \quad (3)$$

where I_2 is the intensity due to *ortho*-Ps annihilations, and F_{Ps} is the positron fraction in Ps states. From Equations 1 and 3 one obtains

$$\tau_{e+} = \frac{3\tau_1 - I_2\tau_p}{3 - I_2} \quad (4)$$

The τ_{e+} values from Equation 4 are given with τ_1 in Fig. 2. Now it may be noted that the increase of the Ps states in the samples coincides with the rise of the effective positron lifetime τ_{e+} . Its value is about 340 psec in the glassy samples, starting to increase after heating at 1320 K up to reaching a maximum value of about 390 psec in the crystallized samples. The estimated Ps fraction is 52% in glassy samples and increases up to a value of about 61% after heating at 1320 K. Above this temperature it remained practically constant. This means that the structural changes above 1320 K and those producing the simultaneous descent in τ_1 and τ_2 do not perceptibly disturb the Ps formation in the samples.

The X-ray diffraction patterns support the idea that the initiation of the crystallization coincides with the cup in I_2 and the start of the

τ_2 drop. At this temperature, 1250 K, it is known that a first crystalline phase appears during the isothermal devitrification of similar cordierite glasses. This crystalline phase, named μ -cordierite, has been identified as a stuffed high-quartz phase with cordierite composition [12, 17]. This does not have the characteristic empty channels of the other crystalline cordierite phases where positrons could become Ps as stated above. This would explain the decrease in the Ps fraction after heating at 1250 K. According to Langer and Schreyer [12], sustained heating at or above 1250 K destroys this phase via a reconstructive transformation which results in a new crystalline phase named high-cordierite. This has a hexagonal structure characterized by the random distribution of the Al and Si ions in the centres of oxygen tetrahedra framing the typical hexagonal rings in the cordierite structures. It is important to point out that the μ -phase is only produced when the cordierite glass is slowly devitrified, that is, if the devitrification is carried out over the range 1100 to 1250 K [17]. This probably prevents the μ -phase subsisting after heating at 1320 K, just where τ_{e+} and I_2 start to increase. On the other hand, heatings at higher temperatures, approximately in the range 1550 to 1600 K, induce the hexagonal high-cordierite \leftrightarrow orthorhombic low-cordierite transformation via an Al/Si order process [12, 22].

The X-ray diffraction measurements did not allow for clear identification of the structures present since the aim was to only get qualitative information about the structural state of the samples, and therefore they were not powder X-ray measurements. However, some noticeable differences were seen in the X-ray diagrams. After heating at 1525 K some peaks present in the X-ray diffraction pattern after heating at 1375 K disappeared, but new diffraction peaks did not appear. Three of the disappeared peaks might be attributed to the hexagonal structure, but the others which disappeared could not be identified. Only a few of the remaining peaks after heating at 1525 K could be indexed as belonging to an orthorhombic structure. This leads us to believe that there is a possible phase separation after crystallization, at least partially, in addition to a simultaneous presence of the hexagonal and orthorhombic phases after heating at 1375 K. Therefore, the increase in τ_{e+} may

be attributed to the hexagonal–orthorhombic transformation. Since this transformation is via an Al/Si order process in the hexagonal rings of (Al, Si)O₄ tetrahedra, we suggest that this may be the origin of the increase in τ_{e+} above 1320 K. In natural cordierites, Hsu and Vance [19] attributed the intermediate-lifetime increase to an Al/Si order.

Moreover, no changes would be expected in τ_2 and I_2 during the hexagonal–orthorhombic transformation, if this component is actually due to the pick-off annihilation in the empty channels of the structure due to both phases keeping the same empty channel structure.

Infrared absorption studies in the same cordierite glass, carried out in our laboratory and published elsewhere [23], support the above suggestion on the increase of τ_2 . After heating at 1575 K, the characteristic splitting of the absorption bands produced by the stretching modes of the AlO₄ and SiO₄ tetrahedra was observed. This splitting has been attributed by Langer and Schreyer [12] to a short-range order process of the Al and Si cations which results in a domain structure during the first stage of the hexagonal–orthorhombic transformation. Nevertheless, this does not happen if the heating temperature is below approximately 1400 K, according to the infrared absorption experiment [12, 16, 23]. Therefore, the above considerations lead us to believe that the increase in τ_{e+} may be due to this domain structure, since this might imply the change of local atom density in the material in such a way that the effective annihilation rate decreases.

To explain the drop in τ_{e+} above 1550 K, we could say that this is due to the long-range order process taking place in the second stage of the hexagonal–orthorhombic transition, which destroys the domain structure, according to the model proposed by Langer and Schreyer [12] based on infrared absorption and powder X-ray measurements. However, this would not explain the simultaneous decrease in τ_2 , since the channels should have more or less the same empty volume in both phases. Probably, the explanation is in the formation of new phases above 1550 K, unknown low-cordierite phases such as Schreyer and Schairer [24] have claimed.

Finally, the plot of I_2 against τ_2 in Fig. 3 reveals a relationship between both, which could be qualitatively explained by the free-volume

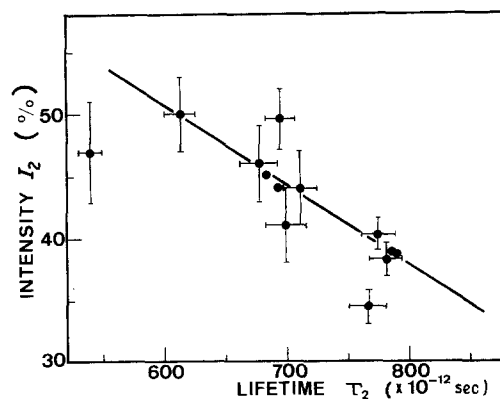


Figure 3 Intensity of the long-lifetime component I_2 against its lifetime τ_2 . The error flags are omitted for several points.

model proposed by Thosar *et al.* [11]. Two points are noticeably at a distance from the generally observed tendency. These are the points corresponding to 1250 K, the start of crystallization, and the last temperature point. This may be considered as further evidence for the presence of anomalous cordierite phases at the start of the crystallization process and at temperatures near the melting point, these are likely to have structural characteristics different from those corresponding to the typical hexagonal and orthorhombic phases.

4. Conclusions

1. The results have shown that the devitrification of the cordierite glass via the isochronal heating up to a stable crystalline structure, is a two-stage process.

2. Two components have been found in the positron lifetime spectra. The long-lifetime component has been attributed to the pick-off annihilation of the *ortho*-Ps states. The results suggest that the value of τ_2 is insensitive to the polymorphic transitions of the crystalline cordierite below 1550 K. An increase of Ps states in the samples is observed upon crystallization.

3. The value of the effective positron lifetime of positrons annihilating in states that are not Ps was estimated from τ_1 and I_2 . This lifetime was sensitive to the short-range order process involving the cations of the (Al, Si)O₄ tetrahedra during the hexagonal–orthorhombic transition in the range 1300 to 1600 K. The τ_1 and τ_2 drop above 1550 K may be attributed either to the formation of unknown low-cordierite phases or to the phase separation.

4. A correlation has been found between the intensity and the lifetime of the pick-off component. This may be explained by the free-volume model, at least qualitatively.

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