Mechanisms of laser induced modification of lead and barium vanadate glasses

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We report on our investigations on the mechanisms for structural and morphological change in lead and barium vanadate glasses modified by 785 nm laser irradiation. The fundamental process is thermal in nature, leading to phase decomposition, phase changes, and mass transport in the center of the irradiated region, as well as the formation of lead- or barium-rich debris zones. Crystallization is also a consequence of the exposure to the laser light. We further report on preirradiation experiments in which low-power exposure above a determined energy threshold results in structural changes that bridge the gap between the amorphous state and the ultimate crystalline arrangement. Finally, we discuss the application of the laser irradiation in the making of vanadate microspheres.

I. INTRODUCTION

Recently we reported on laser-induced modification of lead vanadate and alkali borate glasses using laser irradiation. These alterations occurred at relatively low powers, ranging from 15 to 200 mW, and they resulted in a variety of changes: crystallization (at powers greater than 38 mW for the lead vanadates), accompanied by ejecta and debris deposition; refractive index variation (at powers less than 38 mW). Several questions remain outstanding: the exact structural rearrangements, the effects of lower and higher levels of power in the laser irradiation, and the effect of a first irradiation on subsequent laser light exposures. In this paper we discuss a possible mechanism for the structural changes, and also report on our analysis of the morphology of the irradiated areas, mainly for glasses at the metavanadate composition.

The structure of lead metavanadate crystals is quite relevant to this work. Previous work has established that there are three phases, of which only one is stable. The stable phase (I) is an orthorhombic structure, with distorted edge-sharing vanadium octahedra. The two metastable phases include a monoclinic variant, phase (II), with double chains of edge-sharing square pyramids, and an orthorhombic modification, phase (III), made of zigzag chains of corner-sharing tetrahedra.

In the case of barium metavanadate crystals, the structure has been determined to be orthorhombic, consisting of chains of vertex-shared tetrahedra joined by interstitial Ba atoms. It is analogous to the stable lead metavanadate phase (I) as well as the orthorhombic metastable modification (III). We note that the orthorhombic structures of lead and barium metavanadates are quite similar to the network present in the glass, also composed of zigzag chains of tetrahedra.

II. EXPERIMENTAL PROCEDURES

A. Glassmaking procedure and thermal characterization

Glasses were prepared according to the stoichiometries

\[ x\text{PbO} + (1 - x)\text{V}_2\text{O}_5 \rightarrow x\text{PbO} \cdot (1 - x)\text{V}_2\text{O}_5, \]

\[ x\text{BaCO}_3 + (1 - x)\text{V}_2\text{O}_5 \rightarrow x\text{BaO} \cdot (1 - x)\text{V}_2\text{O}_5 + x\text{CO}_2. \]

The starting materials for the glasses were lead (II) oxide (Aldrich, 99.9%), barium carbonate (Aldrich, 99+%), and vanadium (V) oxide (Aldrich, 99.6%). Lead vanadate glasses with stoichiometries ranging from \( x=0.1 \) to \( x=0.6 \) were prepared, while the barium vanadates ranged from \( x=0.1 \) to 0.66. The powders were thoroughly mixed in a platinum crucible and heated to 900–1000 °C in an electric muffle furnace, depending on the composition. After 10 min the melt was removed from the furnace, let cool, and a weight measurement taken to ensure composition. All weight losses were within the expected range (<0.1 g from calculated). The sample was then placed back in the furnace for a further 10 min at the same initial temperature and subsequently cooled to the glassy state by splat quenching between two stainless steel plates. The cooling rate was approximately 10 000 °C/s. Sample thickness was 1.5±0.3 mm.

Glass transition \( (T_g) \) and crystallization temperatures \( (T_c) \) were measured with a Perkin-Elmer DSC-7. Thermal scans were performed at 40 °C/min and the onset definition of the \( T_g \) and \( T_c \) was used. The estimate for experimental error in calculating the specific heat \( C_p \) is ±5 °C. To determine the specific heat, we subtracted the baseline heat flow curve from that of the sample and encapsulating pan. The value of the difference \( \Delta T \) at a point in the stable range 60–90 °C was taken to calculate the specific heat \( C_p \) near room temperature. By running a few references such as indium and gold, we estimated the specific heat error to be on the order of ±2%.

Reference crystals were grown from the glasses by devitrification. The 50PbO•50V2O5 glass was held at 420 °C for 10 000 °C/s.
for 48 h, and the subsequent crystal was checked with x-ray diffractometry (Bruker Discover D8, Cu K$_\alpha$ wavelength). We then used the crystals as references in our Raman measurements. We were unable to make pure crystals of the metastable phases using faster plate cooling on the melt.

B. Laser irradiation procedure

The Raman system used for the laser irradiation (and analysis) was a JASCO NRS-3100 microRaman spectrophotometer. A Torsana Starbright 785 nm SLM diode laser was used to irradiate the sample at various power settings (16, 41, 84, and 160 mW) for durations ranging from 5–20 s. Spectra were then acquired at 1.7 mW at various sites in the resulting affected area; this power level was not enough to cause surface alterations. The laser beam spot size was circular with approximately 1 $\mu$m radius.

C. Atomic force microscopy

Representative irradiated areas were also imaged using a Veeco Multimode Scanning Probe Microscope. The tapping atomic force mode was used, with a scanner mapping out $25 \times 25$ $\mu$m$^2$ areas with a maximum z-range of 5.1 $\mu$m. The tips used were phosphorus-doped Si, with a resonance frequency in the range of 280 kHz. Other than the standard plane-fitting algorithm, no other filters were applied.

D. Scanning electron microscopy and EDX

Pristine and irradiated areas were studied using a TESCAN Vega II Scanning Electron microscope running at 10–20 keV. Secondary-and backscattered electron detector configuration were both used. The elemental analysis was carried out using an attached Oxford EDX system. Two dimensional mapping of the elemental concentrations was also carried out with the Oxford software.

To check the concentration results we carried out 15 spot measurements of the pristine (unirradiated) region, and the average (mean) values were $50.4 \pm 2.9$ wt % Pb, $25.6 \pm 1.8$ wt % V, and $24 \pm 1.2$ wt % O. These results are to be compared to the expected values from the stoichiometry, 51.15 wt % Pb, 25.15 wt % V, and 23.7 wt % O. The elemental concentrations appear close to what is expected, but it is not known whether any variations are due to true compositional changes upon melting, or instrumental error. The comparisons we will be making are relative, and thus this is not a significant concern. Based on the standard deviations of the measurements and the instrumental error, we estimate the error in the chemical analysis for each element to be $\pm 3\%$.

III. RESULTS AND DISCUSSION

We began by looking at the changes in the chemical composition induced by the laser irradiation at sufficiently high powers ($>84$ mW). Figure 1(a) shows the electron micrograph of the surface morphology of one such modified spot on a 50PbO•50V$_2$O$_5$ sample, while Fig. 1(b) illustrates a cross section of a similar spot measured from atomic force microscopy. We note the appearance of three concentric regions: a center depression, a crystalline ridge, and a debris zone. The depression is lower than the original glass surface, while the ridge is higher. The debris zone (marked by the half-arc) is at the same level as the original glass, but some ejecta has landed on this surface.

A. Modification mechanism

The appearance of the modified spot, as well as the cracks that often accompany it, point to a thermal mechanism for the modification. The details of the change in the glass structure are clarified with further examination of the compositional changes.

EDX analysis of the center depression indicates a drastic decrease in the concentration of lead. The 50PbO•50V$_2$O$_5$ sample ought to have 51.15 stoichiometric weight percent lead, but the EDX (averaged over the center of 15 irradiation spots) indicates that only 18 wt % is present, as shown in Table I. The surrounding crystalline ridge, on the other hand, remains at the original stoichiometry, and the debris zone appears enriched in lead. Indeed, the debris zone can attain concentrations as high as 75 wt % Pb, but more typically in the range of 60–70 wt % Pb. The depth of the affected region can be estimated from Fig. 2, a cross section of an irradiated...
The figure shows both the excavated center of the spot, and a hemispherical modified region approximately 60 µm in depth.

The EDX data is confirmed by the use of Raman spectroscopy. Figure 3 shows a comparison of the 1:1 lead vanadate crystal (PbO·V₂O₅) with the spectrum from the crystalline ridge, and a similar comparison between the 2:1 crystal (2PbO·V₂O₅) and the debris zone.

We believe that the laser heating causes a decomposition of the metavanadate glass into two phases. It is known⁷ that at 310 °C the glass transforms according to

\[
\begin{align*}
a \cdot 50\text{PbO} \cdot 50\text{V}_2\text{O}_5 & \xrightarrow{310^\circ\text{C}} c \cdot \text{PbV}_2\text{O}_5(\text{III}) \\
+ c \cdot 2\text{PbO} \cdot \text{V}_2\text{O}_5 & \\
+ a \cdot \text{V}_2\text{O}_5,
\end{align*}
\]

where “c” indicates a crystalline phase and “a” an amorphous one.

The metastable (III) crystalline phase further transforms⁷ into the stable (I) phase at temperatures greater than 390 °C. Hence the center depression undergoes a decomposition into a lead-rich crystal and a lead-poor amorphous liquid. The laser heating causes the lead-rich phase to boil off as ejecta, which land closer or farther from the center depending on the exact laser power. Its relative position is also affected by the

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<th>Irradiated lead</th>
<th>Irradiated oxygen</th>
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FIG. 2. Scanning electron micrograph of a modified spot in a 50PbO·50V₂O₅ sample after a cross-sectional fracture. Note the missing mass from the center region.

FIG. 3. (Color online) Comparison of Raman spectra between crystalline 2PbO·V₂O₅ and the debris region (upper pair), and between the crystallized ridge and the PbO·V₂O₅ crystal (lower pair).
overall size of the affected spot, which also depends on the laser power. The remaining material in the depression surface is amorphous and poor in lead content.

The ridge surrounding the center depression does not attain temperature high enough to cause ablation. Rather, the transformation is from an amorphous metavanadate phase to a crystalline one. We are not able to identify this phase as the stable one \( \text{H}_2 \text{O}_{849} \text{I} \text{H}_2 \text{O}_{850} \), or as one of the two metastable ones because of the small size of the region.

The ablation debris that landed in the outer periphery took the form of small \( \text{H}_2 \text{O}_{849} \text{approximately 1} \text{H}_9262 \text{m} \text{H}_2 \text{O}_{850} \), lead-rich particles that carpeted an arc of the region surrounding the ridge, and they brought lead enrichment to the region. The hypothesis that it was the debris causing the enrichment was checked using an atomic force microscope (AFM). In Fig. 4 we show a modified spot with debris after it has been scanned by the tip from the AFM with settings designed to cause the tip to press down quite firmly on the surface. As a consequence, some of the debris has been removed by the sweeping action of the tip. EDX mapping spectra [Fig. 4(b)] of those “scrubbed” regions show decreased lead concentrations (for spectra 3, 4, 5, and 6 the lead concentrations are 28.60 wt %, 32.23 wt %, 30.62 wt %, and 41.06 wt %, respectively). Not many of the ejected particles were detached by the AFM, pointing to the debris being molten before it landed, thus leading to a strong attachment to the surface. EDX analysis of the debris (of 15 different irradiation spots), as previously mentioned, yields excess lead contents of 58 ± 5 wt %. We did not establish whether vanadium or vanadium oxide is also ejected, perhaps in forms that are not so easily detected or that land much farther out.

The effect of sample composition on crystallization is not dramatic. All of the samples, whether lead- or barium-modified, could attain some crystallization by laser irradiation. Up until the metavanadate composition the ease of crystallization increased. Table II shows that the specific heat of the glasses decreased with increasing modifier content. This decrease leads to greater increases in the temperature of the irradiated area for the deposited energy. The optical absorption is not a factor as it remains extremely high for all compositions. The metavanadate composition also crystallizes easily, but this may well be because it matches a crystal composition for both the lead and the barium vanadates. In general, most vanadate glasses have low thermal stabilities \( \text{T}_g \text{H}_2 \text{O}_{849} \text{Tx} ,389 \text{H}_2 \text{O}_{850} \text{for two hours. As the figure shows, the series of spots made in the preirradiation region are significantly} \)

<table>
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<tr>
<th>Composition</th>
<th>( C_p ) (J kg(^{-1}) K(^{-1})) ±2%</th>
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<td>10PbO.90V(_2)O(_5)</td>
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<tr>
<td>20PbO.80V(_2)O(_5)</td>
<td>639</td>
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<td>30PbO.70V(_2)O(_5)</td>
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<td>60BaO.40V(_2)O(_5)</td>
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</table>

B. Effect of preirradiation

A barium metavanadate sample illustrates the alteration that occurs under a first-stage low power irradiation. The preirradiation results in no visible changes in the glass, with the exception that the extreme edges of the laser light swath do tend to crystallize. In Fig. 5 we show, in an optical micrograph, the differences in the modified spots that were created in both a pristine glassy region as well as a region that had been preirradiated. Also shown in the figure is a third series of modified spots made in a region that had been annealed at the sample’s crystallization temperature, \( T_x,389 \text{\degree C} \) for two hours. As the figure shows, the series of spots made in the preirradiation region are significantly

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larger than those made in the pristine region, a difference that holds for all power levels. Furthermore, the annealed region behaves quite similarly to the pristine region, with little to no impact on the size of the series of modified spots.

Figure 6 shows that the preirradiation does indeed alter the structure of the glass $50\text{BaO} \cdot 50\text{V}_2\text{O}_5$. The Raman spectrum shows growth in the band at 860 cm$^{-1}$, typically assigned$^{8,9}$ to V–O–V “bridge” vibrations, accompanied by a decrease in the 950 cm$^{-1}$ band, usually associated with V–O stretching modes. This can be interpreted as a modification of the amorphous network into a more ordered, crystal-like arrangement. It is most likely that the glass begins to rearrange into longer chains (leading to the increase in V–O–V bridges), enhancing its similarity to the orthorhombic BaV phase. Once this is accomplished, the glass is more analogous to the crystalline structure, and a second irradiation at higher power results in a faster and more widespread change to a full crystal region. Other low power measurements with EDX (not reported) indicate that there are no chemical composition changes in the irradiated areas.

In Fig. 7 the Raman spectra compare the pristine $50\text{BaO} \cdot 50\text{V}_2\text{O}_5$ glass (a), the center of the preirradiated region (b), and the extreme edge of the preirradiated region (c). The center of the irradiation swath shows the changes we previously discussed. The edge, on the other hand, crystallized readily. As the swath’s edge is quite close to the physical edge of the glass sample, we believe that this may have aided the crystallization through the presence of defects near the fractured side.
the same levels.

This is true regardless of the power level used in the preirradiation—as long as the net energy deposited attains per unit area, which assumes 100% absorption. When the energy deposited reaches a value of $1 \pm 0.05 \, \mu J/\mu m^2$, the size of subsequent irradiation spots increase in diameter when compared to the same exposure on a pristine glass. This is true regardless of the power level used in the preirradiation—as long as the net energy deposited attains the same levels.

C. Spheroidization

One application of vanadate glasses that arises from their ease of thermal modification is the ability to make microspheres. In Fig. 9 we show a variety of microspheres and other shapes made by relatively low power laser irradiation. The spheroidization process is very rapid, and can be carried out by sweeping the laser beam across a fairly wide swath. Any small glass particles within the swath are spheroidized, though the laser light passes result in only partial spheres, ovoids, or other deformed shapes for larger grains.

The glass fragments that were prepared to be turned into spheres were sieved using a 20 μm sieve. This opens the possibility of achieving nanosize spheres by simply generating a milled powder that contains smaller precursor grains.

IV. CONCLUSIONS

Our study of the mechanism leading to the modification of lead and barium vanadate glasses using 785 nm laser irradiation has yielded several results:

(a) At the metavanadate composition, the center of the irradiation area attains high temperatures and the material therein is heated to the point where phases separate. The lead-rich phase (likely chervetite, $\text{Pb}_2\text{V}_2\text{O}_7$) is then ejected from the center region.

(b) The mass transport resulting from the irradiation takes the form of hot ejecta that land in an arc surrounding the irradiation region. As the debris is high in lead content, this causes a local enrichment of the debris zone.

(c) The concentric zone that surrounds the center spot appears to crystallize into the stoichiometrically-expected metavanadate crystal, $\text{Pb}_2\text{V}_2\text{O}_7$ (I). This is the thermodynamically stable phase.

(d) Low power preirradiation of the glass resulted in a greater impact by later laser light exposures. The effect of secondary irradiation was the formation of larger and more significant modified spots, building on the changes induced by the low-power primary irradiation. Raman spectra indicated a modification of the glass network, interpreted as a rearrangement into longer chains which turns the glass into a structure more similar to the orthorhombic $\text{BaV}$ phase. This phenomenon had a clear threshold as a function of the deposited energy per unit area, approximately $1 \, \mu J/\mu m^2$.

(e) Evidence for the high temperatures attained by the vanadate glasses also come in the form of our ability to spheroidize small glass fragment by laser irradiation. It also points to an application in which small spheres of radii $<10 \, \mu m$ can be manufactured by applying a wide-swath laser beam.

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