Relationship between laser-induced gratings and vibrational properties of Eu-doped glasses

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Four-wave-mixing techniques have been shown previously to produce permanent refractive index gratings in Eu-doped glasses by resonant excitation of the Eu³⁺ ions. A variety of glass hosts were studied and it was found that permanent holographic gratings could be established in some of these but not in others. We report here an extension of our previous work which includes investigations of new materials, attempts to form gratings with different excitation wavelengths, and a comparison of the Raman and resonant Raman spectra of glasses which do and do not exhibit permanent holographic gratings. It was found that direct excitation into the ⁵D₀ level did not produce permanent gratings. It was also found that glasses which do exhibit permanent gratings have high-frequency vibrational modes which couple strongly to the Eu³⁺ ions. These results help to verify the model proposed previously to explain the origin of the holographic grating in terms of structural changes caused by thermal effects arising from radiationless relaxation through high-frequency local modes.

I. INTRODUCTION

We reported recently the observation of four-wavemixing (FWM) signals in Eu^{3+} -doped glasses produced through resonant excitation of the Eu^{3+} ions in the 5D_2 level.¹ The observed signals had two components: a transient component associated with a Eu^{3+} population grating, and a permanent component associated with a holographic grating. The physical processes responsible for this latter component have not been established. The purpose of this paper is to report the results of further research in this area which provides additional information relevant to our understanding of the mechanism of producing this type of laser-induced grating.

The type of holographic grating of interest here is established with a buildup time of about 15 min with the write beams in resonance with the absorption transition to the ${}^{5}D_{2}$ level of Eu³⁺. The grating can be erased optically only if the erase beam is in resonance with the ${}^{5}D_{2}$ absorption transition. The grating is stable at room temperature, but thermal erasure occurs with an increasing rate as temperature is raised above room temperature. Seven different types of oxide and fluoride glasses were studied previously, and under the same experimental conditions holographic gratings were observed in only three of these. An empiricial model was suggested to explain the origin of these gratings based on having a local glass structure at the site of the Eu³ ions which allows each electronic state to be described by a double-minimum potential curve. It is assumed in this model that the refractive index of the material is different, depending on which potential minimum is occupied by the Eu^{3+} ions. It is further assumed that the heat generated through radiationless relaxation of the excited Eu³⁺ ions can cause the local structure to change so that the ions move from one potential minimum to the other.

The model described above is consistent with the results reported previously, but further work is required to better understand the physical processes involved. The work reported here extends our previous investigations by looking at different types of glass hosts, different types of rareearth ions, and different excitation wavelengths. In addition, the Raman and resonant Raman spectra were compared for example glasses that do and do not exhibit holographic gratings.

II. EXPERIMENTAL RESULTS

The initial set of glasses investigated¹ included three that exhibited permanent holographic gratings (europium pentaphosphate, lithium phosphate, and sodium silicate) and four glasses that did not produce holographic gratings (lithium silicate, lithium borate, lithium germanate, and zirconium fluoride). In addition to these, we have now investigated several other heavy-metal fluoride glasses, various other germanate and borate oxide glasses, and $La_x Eu_{1-x}(PO_3)_3$ with x between 0.8 and 0.99. Holographic gratings were observed only in the last of these. This sample exhibited similar grating properties to the europium pentaphosphate sample but had a higher diffraction efficiency.

Several additional experiments were performed on the europium pentaphosphate (EuP₅O₁₄) sample which exhibited strong holographic gratings. For example, the effects of changing the polarization direction of the probe beam compared to the polarization directions of the write beams were investigated. No dependence of scattering efficiency on the probe-beam polarization direction was observed. Also, a phosphate glass sample (52.3 P₂O₅, 30.0 Li₂O, 10.0 CaO, 4.7 Al₂O₃, 3.0 Eu₂O₃ in mol %) was investigated which contained approximately the same concentration of europium as the lithium phosphate glass studied earlier but which had a mixture Eu³⁺ and Eu²⁺ valence states. No holographic grating was observed in this sample.

Attempts were made to observe permanent gratings in samples having different rare-earth ions in similar types

of glass hosts, such as NdP₅O₁₄ glass. Under excitation conditions which should produce the same amount of heat through radiationless processes as in the EuP₅O₁₄ glass, no grating formation was observed. Instead, strong thermal lensing effects were seen. In fact, it was found for several different types of trivalent rare-earth ions that thermal lensing was observed instead of the development of holographic gratings. Apparently the onset of thermal lensing inhibits the formation of holographic gratings. The relationship between these two types of processes is now being studied.

For all of the glasses which exhibit holographic gratings, all of the fluorescence emission occurs from the ${}^{5}D_{0}$ level regardless of the pumping conditions. Although this is also true for many of the glasses in which holographic gratings could not be produced, some of these glasses such as Eu-doped BZLT (27 ZnF₂, 19 BaF₂, 26 LuF₃, 27 ThF₄, 1 EuF₃ in mol %) showed a significant amount of fluorescence emission from the higher-lying ${}^{5}D_{J}$ levels. In this case there are fewer phonons emitted during relaxation in the excited state. To further establish the importance of radiationless relaxation in the excited state, an attempt was made to produce holographic gratings by exciting directly into the ${}^{5}D_{0}$ level instead of the ${}^{5}D_{2}$ level as was done previously. An argon-laser-pumped ring dye laser with R6G was used for these experiments. The laser power was set to achieve the same density of excited Eu³⁺ ions as obtained in the previous experiment in which gratings were formed. Several samples were investigated, including the europium pentaphosphate sample which exhibits strong holographic gratings for ${}^{5}D_{2}$ excitation. No gratings were observed in any of the samples for ${}^{5}D_{0}$ excitation. This confirms the importance of having radiationless relaxation in the excited state to establish this type of grating. These nonradiative processes for rare-earth ions in glasses are known to take place through multiphonon emission involving several high-energy phonons.²

To further understand the vibrational modes involved in the writing of holographic gratings of this type, we compared the Raman spectra and resonant Raman spectra for glasses which exhibited gratings with those of glasses in which no gratings could be produced. Typical results are shown in Figs. 1 and 2. An argon laser was used as the source and an Instruments S. A. Ramanor U-1000 with computer-controlled data acquisition was used to record the spectra. The 514.5-nm argon-laser line gives the normal Raman spectra shown by dashed lines in Figs. 1 and 2, while the 472.7-nm laser line is close to the ${}^{7}F_{0}$ - ${}^{5}D_{2}$ Eu³⁺ transition and therefore produces resonant Raman scattering. The solid lines in the figures show the latter type of spectra.

The disordered structure of glasses causes the network vibrations to have a short coherence length compared to the optical wavelength. This causes a breakdown of the wave-vector selection rule which is present for crystalline Raman spectra and results in Raman spectra for glasses





FIG. 1. Raman spectra (dashed lines) and resonant Raman spectra (solid lines) of (a) europium pentaphosphate glass, and (b) Eu^{3+} -doped lithium phosphate glass. (See text for exact glass compositions.)

FIG. 2. Raman spectra (dashed lines) and resonant Raman spectra (solid lines) of (a) Eu^{3+} -doped sodium silicate glass, and (b) Eu^{3+} -doped lithium silicate glass. (See text for exact glass compositions.)

$$I(\omega_0,\omega) = (\hbar v E_0^2 / 2\pi c^3) \{ (\omega_0 + \omega)^4 [n(\omega) + 1] / \omega \} \\ \times \sum_b C_b(\omega_0,\omega) \rho_b(\omega) ,$$

where b refers to the different bands, E_0 and ω_o are the incident electric field and frequency, respectively, ω is the frequency of the Raman shift, $\rho_b(\omega)$ is the vibrational density of states for band b, $n(\omega) = [\exp(\hbar\omega/k_BT) - 1]^{-1}$ is the population factor, and $C_b(\omega_0, \omega) = |\sum_l P^l u_l^b(\omega)|^2$ is the coupling constant for the b band. Here P^l is the electronic polarizability and u_l is the normal displacement coordinate where l refers to the 3N Cartesian coordinates of the atoms. When ω_0 is close to an electronic transition frequency of Eu^{3+} , the coupling coefficient is dominated by contributions of $P^l u_l^b$ associated with vibrational modes localized around the Eu^{3+} ions.

The Raman spectra for the europium pentaphosphate (EP) and lithium phosphate (LP) (52.3 P₂O₅, 30.0 Li₂O, 10.0 CaO, 4.7 Al₂O₃, 3.0 Eu₂O₃ in mol %) samples shown in Fig. 1 both show a high-frequency band near 1200 cm^{-1} which is enhanced in the resonant Raman spectra. This indicates that the vibrational mode of this frequency is strongly coupled to the Eu^{3+} ions. Figure 2 shows similar spectra obtained on sodium silicate (NS) (15.0 Na₂O, 5.0 BaO, 5.0 ZrO, 72.0 SiO₂, 3.0 Eu₂O₃ in mol %) and lithium silicate (LS) (27.5 Li₂O, 10.0 CaO, 2.5 Al₂O₃, 57.0 SiO₂, 3.0 Eu₂O₃ in mol %) glass. The resonant Raman spectrum of the NS glass shows a strong enhancement of a band near 1050 cm^{-1} . This same band appears in the spectra of the LS sample, but no significant enhancement occurs under resonant excitation conditions. Such high-frequency bands do not appear in the Raman spectra of borate and fluorite glasses.⁵⁻

III. DISCUSSION AND CONCLUSIONS

The results described above show that the formation of holographic gratings of the type of interest here requires a glass host having high-frequency local modes of vibration and further requires these modes to be strongly coupled to the Eu^{3+} ions. This enhances the radiationless relaxation processes compared to the radiative processes occurring after excitation of the Eu^{3+} ions, and these produce the local heating necessary for causing the structural modification of the host.

So far the best hosts for establishing these permanent gratings have been found to be phosphate glasses. The fundamental skeletal structure of phosphate glasses can be represented by practically infinite chains of interlinked PO₄ tetrahedra with two of the oxygens shared with neighboring tetrahedra. The vibrational band observed around 1200 cm⁻¹ is attributed to stretching vibrations of PO₂ lateral groups^{9,10} which involves the two unshared oxygens of the tetrahedra. The resonant enhancement of

this band shows that the Eu^{3+} ions are bonded to the PO_2 lateral groups and not to the chains. Thus the Eu^{3+} enter the glass structure as network modifiers. Because of the motional freedom of the lateral group oxygen ions, it is not unreasonable to expect different possible equilibrium positions for these groups, leading to different local environments for dopant ions such as Eu^{3+} .

On the other hand, silicate glasses have fundamental structures which are generally better described as a continuously randomly packed network with SiO_4 tetrahedra as the basic unit.¹¹ The introduction of alkali-metal ions partly breaks down this type of structure. These glasses exhibit a vibrational band near 1100 cm⁻¹ that is attributed to the bond-stretching vibration of the Si-O nonbridging group.^{12,13} In our samples, the resonantly enhanced band between 1000-1100 cm⁻¹ can be seen as the superposition of three different bands with frequencies 940, 1020, and 1100 cm⁻¹. This last band corresponds to the stretching vibration of the Si-O nonbridging group. These vibrational bands are weaker in the LS sample due to the weaker activation of this vibrational mode by the Li^+ ion as compared with the Na⁺ ions.¹² The Raman spectra suggest that part of the Eu³⁺ ions are bonded with the nonbridging oxygen ions in the NS sample, entering the glass structure as network modifiers along with the Na⁺ ions. As in the pentaphosphate glasses, it is not unreasonable to expect different possible equilibrium positions for the nonbridging oxygens, leading to different Eu³⁺ environments.

The types of suggested structural modifications discussed above are not applicable to borate glasses where the structure is more rigid and can be formed by various cyclic units depending on the alkali-metal or alkaline-earthmetal content of the material.⁵⁻⁷ The major vibrational band of borate glasses is around 805 cm^{-1} and is associated with the breathing mode of the boroxol rings forming the basic structural unit of the glass.^{5–7} The other vibra-tional bands are at lower frequencies. The structure of the ZrF₄-based glasses can be described by chains of ZrF₆ octahedra sharing two oxygens with each of two other octahedra.⁸ This is somewhat similar to the phosphate glass structure except that the octahedron are more rigid and exhibit a lower degree of disorder, making it more difficult to consider local structural modifications. The major vibrational bands of these glasses appear around 500-600 cm⁻¹ and are associated with stretching vibrations of the Zr—F nonbridging bonds of the ZrF₆ octahedron forming the basic structural unit of the glass.⁸

The results described here are consistent with the model proposed previously for the formation of holographic gratings through resonant excitation of Eu^{3+} ions in glasses. The criteria for forming gratings of this type include having a glass structure which allows different local configurations for the Eu^{3+} ions through different possible equilibrium positions of the surrounding oxygen ions. The mechanism for switching between different types of equilibrium positions requires structures with high-frequency local vibrational modes such as those associated with structural defects (lateral or nonbridging groups) and further requires that the Eu^{3+} ions are strongly coupled to these vibrational modes. It also appears that these modes

should be uncoupled with the rest of the vibrational modes of the structure so that the generation of local heating through radiationless relaxation of the Eu^{3+} ions leads to structural changes instead of becoming thermalized and causing thermal lensing. There are still many questions to be answered concerning the details of grating formation and erasure on the atomic scale.

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