Photoinduced refractive-index changes in several Eu^{3+}-, Pr^{3+}-, and Er^{3+}-doped oxide glasses

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We have observed permanent and transient refractive-index grating formation following excitation of the $^5D_2$ state of Eu^{3+} in a silicate, a metaphosphate and a pentaphosphate glass at 300 K, using four-wave mixing (FWM). These refractive-index changes recently have been ascribed to a high-energy phonon-mediated structure rearrangement involving two-level systems. In order to test this model, these measurements were extended to several Er^{3+}- and Pr^{3+}-doped glasses, which both have transitions that create similar energy phonons. The $^4I_{11/2}$ state of an Er^{3+}-doped silicate and a metaphosphate glass was resonantly excited at 980 nm. No permanent gratings were observed in these Er^{3+} glasses. A single, resonant-pump-beam experiment showed only transient thermal lensing in the Er^{3+}-silicate glass. This is consistent with the FWM results of this glass. Similarly no permanent refractive-index gratings were observed following excitation of the $^3P_0$ state in Pr^{3+}-doped sodium silicate, metaphosphate, and lanthanum and aluminum borate glasses. The Er^{3+} and Pr^{3+} results are inconsistent with the two-level-system model and its analysis of the difference in polarizability between the two potential wells as applied to the Eu^{3+} glasses.

I. INTRODUCTION

Photoinduced permanent changes in inorganic, insulating glasses are of current interest because they contribute towards our understanding of the structure of disordered solids, and for their technological importance. Exposure of germanosilicate glass optical waveguides to blue or green light results in the formation of refractive-index gratings that are stable at room temperature.[1] These glasses also show second harmonic frequency generation and both effects are ascribed to the interaction of light with Ge-related defects.[2] Permanent refractive-index changes have also been observed (at 300 K) upon resonant excitation of particular $4f-4f$ transitions in Tb^{3+} (Ref. 3), Eu^{3+}-, and Pr^{3+}-doped multicomponent oxide glasses,[4–8] as well as in Ce^{3+}-doped SiO_2.[9] These photoinduced permanent refractive-index gratings are different from resonantly induced permanent birefringence observed in Nd^{3+}-doped glasses.[10] Whereas in the Ce^{3+} case photoionization and subsequent formation of color centers is responsible for the index change, in the Eu^{3+}- and Pr^{3+}-doped systems a light-induced reordering of the ligand atoms around the rare-earth ion has been proposed to be responsible for the permanent refractive index change. It has been suggested[6] that this modification of the local structure is mediated by several high-energy (hot) phonons, which are created during the nonradiative relaxation of the excited state. A double-minimum potential well model was invoked (two-level systems), in which these phonons induce transitions between the two wells which have different polarizabilities α.[4] The effect of changing network modifiers and the writing temperature on the permanent refractive-index change in a variety of Eu^{3+}-doped glasses was explained in terms of this two-level-system model.[5,6] However, several puzzling issues remain about these permanent gratings in rare-earth (RE) doped glass. (1) Are these permanent changes limited to only certain RE's? (2) Why do only (partially) nonradiative transitions of these ions, which create high-energy phonons (≈ 1000 cm^{-1}), result in index changes in some glasses? (3) As is well known, glasses are characterized by a wide distribution in barrier heights in these two-level systems;[11] therefore permanent index changes would be expected for a variety of nonradiative gaps between neighboring Stark manifolds, regardless of the magnitude of that gap. (4) What determines the dynamics of the growth and erasure of the permanent refractive-index changes? (5) What is the nature of the crossover behavior[4,5] of the writing temperature dependence of the scattering efficiency, as observed in several Eu^{3+}- and Pr^{3+}-doped glasses? (6) Are these gratings perhaps not related to phonon-induced structural changes at all, but instead are due to some multistep electronic process?

In this paper we address only the first of these questions and report on the comparison of permanent refractive-index changes in several Eu^{3+}- and Pr^{3+}-doped silicate and phosphate glasses with similar Er^{3+}-doped glasses at 300 K. In contrast to the excitation of the Eu^{3+} ions ($^7F_0 \rightarrow {}^5D_2$ at 466 nm) and the Pr^{3+} ions ($^3H_4 \rightarrow {}^3P_0$ at 488 nm), the Er^{3+} ions are resonantly excited in the near-ir into the $^4I_{11/2}$ state at 980 nm. This level decays nonradiatively with a gap of approximately 3500 cm^{-1}, which is comparable to the $^5D_2$-$^5D_0$, $^3P_0$-$^1D_2$ gaps in Eu^{3+} and Pr^{3+}, respectively (see Fig. 1 for relevant energy levels of these three RE's). It should be mentioned that excitation of Er^{3+} ions at 514 nm ($^4I_{15/2} \rightarrow {}^2H_{11/2}$) in a silicate glass did not create a permanent or transient refractive-index change, which was ascribed to the small gap (several hundred cm^{-1}) between the latter level and the metastable $^4S_{3/2}$ state below this level.[5] Measuring any refractive-index changes in the near-ir allows for testing the hot-phonon model against some other, e.g., electronic effect, such as charge transfer

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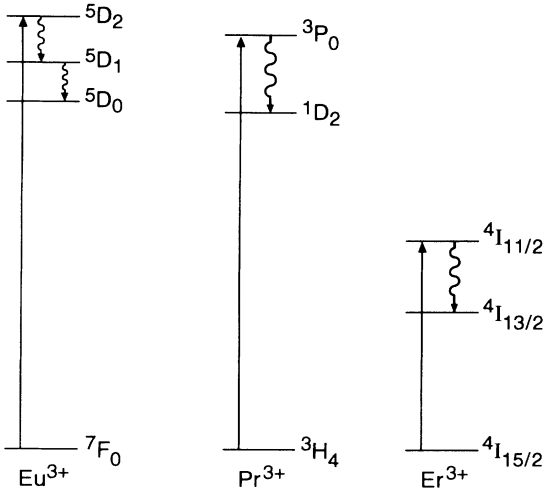

FIG. 1. Simplified energy-level diagram of Eu^{3+}, Pr^{3+}, and Er^{3+}. Solid arrows indicate grating write wavelengths at 466, 488, and 980 nm, respectively. Wiggly arrows indicate nonradiative transitions.

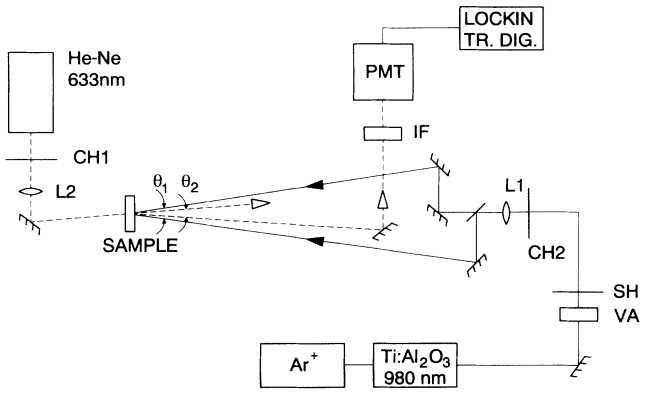

FIG. 2. Four-wave-mixing setup. The shown configuration is for an Er^{3+} sample; for the Eu^{3+} and Pr^{3+} samples the argon (Ar^+) laser is used for the write beams. VA: variable attenuator; SH: shutter; CH(1,2): choppers; L(1,2): lenses; IF: 633-nm band-pass interference filter; PMT: photomultiplier tube; and Tr. Dig: transient digitizer.

and color-center creation following excitation in the blue spectral region, which Tb^{3+}, Eu^{3+}, and Pr^{3+} have in common. The possibility of such processes occurring in Er^{3+} upon excitation into the $^4I_{11/2}$ level is significantly reduced because of very little excited-state absorption from this manifold into higher bands in Er-doped glasses.[12]

II. EXPERIMENTAL DETAILS

Nondegenerate four-wave mixing (FWM) was used to measure refractive index changes Δn in several Eu^{3+}-, Pr^{3+}-, and Er^{3+}-doped glasses, as shown in Fig. 2. The Eu^{3+} ions were excited into the low-energy side of the $^5D_2$ manifold with two write beams at 466 nm from an Ar^+ laser, whereas the Pr^{3+} ions were excited at 488 nm in the low-energy wing of the $^3P_0$ state. In the case of the Er-doped samples the two write beams were generated with an Ar^+-ion laser pumped $Ti:Al_2O_3$ (TiS) laser at 980 nm (Fig. 2). In all three cases the two write beams were focused weakly (spot-size diameter ≈ 0.05 cm for the two Ar^+ lines and ≤ 0.1 cm for the TiS laser) and at a small angle θ_1 ($< 2.5°$) onto the sample. Typical total write power in these experiments is ≤ 500 mW. The path-length difference between the two write beams was less than the coherence length of both the Ar^+ (in the Eu and Pr cases) and the TiS laser (in the Er case), resulting in a standing wave inside the sample. Small-angle Bragg scattering of a focused 10-mW He-Ne laser at 633 nm was used to read any refractive-index gratings. The advantage of using a nondegenerate read beam (i.e., $\lambda_r \neq \lambda_w$) is that it allows a better discrimination of the diffracted signal against strong write-beam scattering due to striae in the glass. These are particularly pronounced in the phosphate glasses. The scattered signal beam was diffracted by an angle θ_2 from the read beam and detected with a photomultiplier tube (PMT) after going through an interference filter. The grating period Λ_g is given by $\Lambda_g = \lambda_p / [2 \sin(\theta_1/2)]$. Using the Bragg condition and the former expression, the relationship between the angles θ_1 and θ_2 is given by

$$\sin\left[\frac{\theta_2}{2}\right] = \frac{\lambda_r}{\lambda_p} \sin\left[\frac{\theta_1}{2}\right], \quad (1)$$

in which θ_1 and θ_2 are the angles outside the sample and λ_p and λ_r are the vacuum wavelengths of the pump and read beams, respectively. The read beam was chopped during the (long-time) grating writing and decay measurements and the signal was analyzed with standard phase-sensitive detection. For the measurement of transient refractive-index gratings the write beams were mechanically chopped by focusing (and recollimating) the beam from the Ar^+, respectively TiS, laser onto the chopper wheel, resulting in a turn-off time (10%-90%) of ≈ 20 μsec. The resulting time dependence of the signal (the read beam is continuous in this case) was analyzed with a transient digitizer and signal averager. The Eu^{3+}-, Pr^{3+}-, and Er^{3+}-doped samples investigated in this study are listed in Table I. Two parallel surfaces were polished

TABLE I. Eu^{3+}-, Pr^{3+}-, and Er^{3+}-doped glass compositions.

Sample	Composition (mol %)
Pr:Na-Si-O	$1.5Pr_2O_3$-$24.6Na_2O$-$73.9SiO_2$
Pr:B-Al-O	$25Pr_2O_3$-$25Al_2O_3$-$50B_2O_3$
Pr:La-B-O	$25Pr_2O_3$-$25La_2O_3$-$50B_2O_3$
Pr:P-O	$25Pr_2O_3$-$75P_2O_5$
Eu:Na-Si-O	$1.5Eu_2O_3$-$24.6Na_2O$-$73.9SiO_2$
Eu:La-P-O	$12.5Eu_2O_3$-$12.5La_2O_3$-$75P_2O_5$
Eu:P-O	$16.7Eu_2O_3$-$83.5P_2O_5$
Er(2 mol %):Na-Si-O	$2Er_2O_3$-$24.5Na_2O$-$73.5SiO_2$
Er(5 mol %):Na-Si-O	$5Er_2O_3$-$23.8Na_2O$-$71.2SiO_2$
Er:La-P-O	$10Er_2O_3$-$15La_2O_3$-$75P_2O_5$

on the samples and they were mounted on a horizontal platform, which was rotated and tip-tilted to ensure the retroreflection of one write beam off the entrance surface on the other write beam. This causes the grating pattern to be written perpendicular to the sample entrance/exit surfaces.[13]

Another method to measure transient and permanent refractive-index changes is the use of lensing, induced by a single pump beam.[14] Such a setup was constructed for the Er-doped samples in order to compare the Δn obtained with this technique with the FWM results. A single beam at 980 nm and a He-Ne probe beam at 630 nm are focused to approximately 80-μm-diam (calculated values) overlapping spots. Lensing was measured by monitoring any change in the intensity of the central part of the transmitted probe beam (behind a 50-μm-diam pinhole) in the far field as the pump beam was chopped. The transmitted probe signal was again detected with a PMT and analyzed with a transient digitizer.

III. FWM RESULTS

A. Eu^{3+}-doped silicate and phosphate glasses

Upon excitation at 466 nm, permanent Δn_p's were observed at 300 K only in the Eu:Na-Si-O and Eu:La-P-O samples. Off-resonance excitation at 472 nm did not yield any grating formation. An example of the growth of the diffracted read-beam intensity (and hence Δn) in the Eu:Na-Si-O sample with a total write power of 160 mW on the sample is shown in Fig. 3. The nature of the oscillations in the rise of the diffracted read beam is not clear, since they appeared to depend on the location of the grating in the sample. A possibility is a slow thermal drift in the various optics. The maximum (saturated) grating scattering efficiency in Eu:Na-Si-O was measured to be $\approx 5\times10^{-5}$. This corresponds to a $\Delta n_p \approx 3\times10^{-7}$, assuming a grating length of approximately 0.5 cm.[15] After reaching a steady state, the induced Δn was bleached by exposing the same region in the sample to a single beam at 466 nm, as can be seen in Figs. 3 and 4; the arrow in the former indicates the blocking of one of the write beams. The photoinduced bleaching rate was observed to be inversely proportional to the bleach power. A similar bleaching efficiency was observed by exposure to (off-resonance) 458-nm radiation, as can be seen in Fig. 4.

When the write beams were blocked, the scattered intensity dropped exponentially to approximately 75% of the steady-state value with a $1/e$ time of 2.6 msec. This time constant is approximately the fluorescence lifetime of the metastable $^5D_0$ level in this glass.[8] This can be understood from the following relationship between the scattered probe intensity I_s (and hence the scattering efficiency) and the total Δn, which is the sum of the transient Δn_t and permanent Δn_p:[15]

$$I_s \simeq |\Delta n|^2 = |\Delta n_t + \Delta n_p|^2 = |\Delta n_t|^2 e^{-2t/\tau} + 2|\Delta n_t\, \Delta n_p| e^{-t/\tau} + |\Delta n_p|^2 \quad (2)$$

with τ the (electronic) lifetime of the metastable state. The time dependence of the observed transient grating is clearly given by the second term in Eq. (2) as a result of the interference of the transient Δn_t and permanent Δn_p. The last term describes the permanent grating component. After this initial rapid decay the grating efficiency was observed to decrease (Fig. 5) to approx. 50% in 48 h under constant illumination with the 10-mW probe beam at 300 K. The Eu:La-P-O sample also showed permanent grating formation with a similar rise time (approximately 1h) as the Eu:Na-Si-O sample. Its maximum diffraction efficiency was ≈ 10 times smaller than that of the latter, even though the nominal Eu^{3+} concentration is 1.3×10^{21} cm^{-3} vs 3.7×10^{20} cm^{-3} in the Eu:Na-Si-O sample.

The Eu:P-O sample only showed a transient grating, which decayed exponentially with a lifetime between 1.2 and 1.6 msec. This decay time was observed to be inversely proportional to the total writing power (maximum total write power was approximately 175 mW on

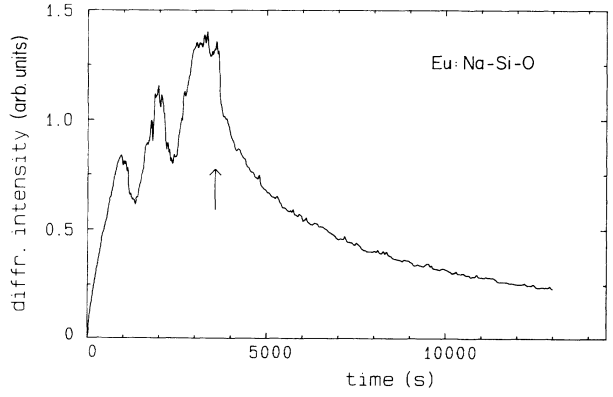

FIG. 3. Rise and bleaching of the diffracted read-beam intensity in a 1.5 mol %Eu_2O_3–24.6 mol %Na_2O–73.9 mol %SiO_2 glass (Eu:Na-Si-O) with 466-nm excitation. The arrow indicates the blocking of one of the two write beams.

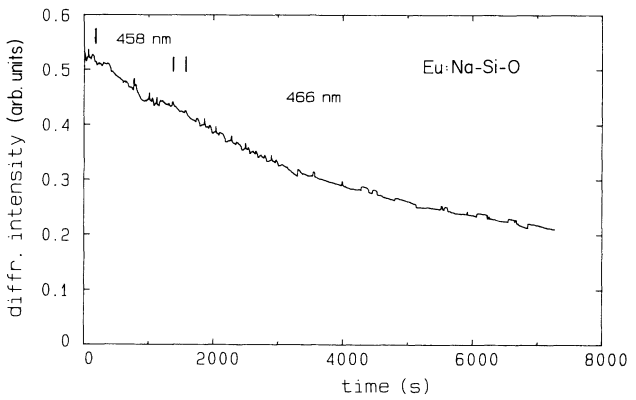

FIG. 4. Resonant (466-nm) and nonresonant (458 nm) bleaching of the diffracted read-beam intensity off a permanent refractive-index grating in the sample shown in Fig. 2 (Eu:Na-Si-O) at 300 K. During the first 180 sec both write beams (466 nm) are on; between $t=180$ and 1400 sec the grating is exposed to a single beam at 458 nm and for $t > 1600$ sec to a single beam at 466 nm.

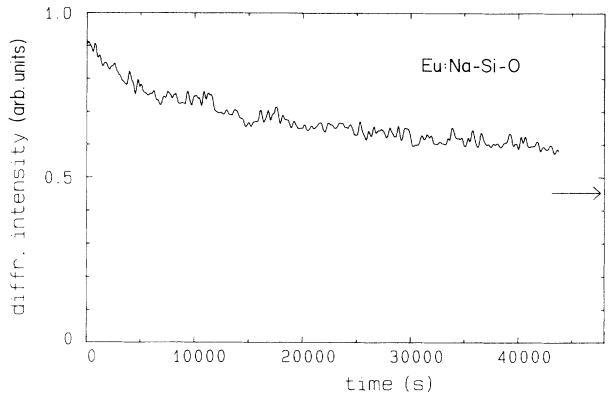

FIG. 5. Decay of the diffracted read-beam intensity off the permanent refractive index grating in the Eu:Na-Si-O sample (see Fig. 1) at 300 K: at $t=0$ both write beams are blocked. During the decay the grating is continuously exposed to the read beam (10 mW at 633 nm). The arrow indicates the intensity after 48 h.

the sample). The diffracted signal intensity was measured as a function of the total writing power from the laser. Fig. 6 clearly shows a linear relationship between these two variables.

B. Pr^{3+}-doped silicate, metaphosphate, and borate glasses

The main reason for studying grating formation in several Pr^{3+}-doped glasses is the large gap between the $^3P_0$ and the $^1D_2$ manifold ($\approx 3800\ cm^{-1}$), which is similar to the $^5D_2$-$^5D_0$ gap in Eu^{3+} ($\approx 2400\ cm^{-1}$ for $^5D_2$-$^5D_1$ and $\approx 1800\ cm^{-1}$ for $^5D_1$-$^5D_0$) and the convenient overlap of the $^3P_0$ state with the 488-nm Ar^+ line. This results in the creation of only a few high-energy phonons (the maximum phonon energies are $\approx 1000\ cm^{-1}$ for silicates, 1100 cm^{-1} for phosphates, and 1300 cm^{-1} for borate glasses[16]) following excitation into the $^3P_0$ state, which is a requirement of the phonon model.[5,6] Since both the $^3P_0$ and the $^1D_2$ states luminesce, the phonon yield per absorbed write photon will be less than in the Eu or Er case, which are both excited in purely nonradiative states. The Pr^{3+}-doped lanthanum and aluminum borate samples (Pr:La-B-O and Pr:B-Al-O) did not show a transient nor a permanent grating upon exposure to 350 and 500 mW (total write power) on the sample, respectively. Similarly the metaphosphate sample (Pr:P-O) showed no grating formation with 450-mW (on sample) illumination. However, speckle of the transmitted read beam was observed to move, for a few seconds, after blocking and unblocking the write beams. This clearly indicates some thermal lensing of the read beam by the (weakly focused) write beams at this power level. The silicate sample (Pr:Na-Si-O) also showed no grating formation up to ≈ 400 mW total write power on the sample, at which intensity the sample was physically damaged. This cracking was observed with the same spot size and approximately similar absorbance (≈ 0.9) at 488 nm as for the metaphosphate and both borate samples.

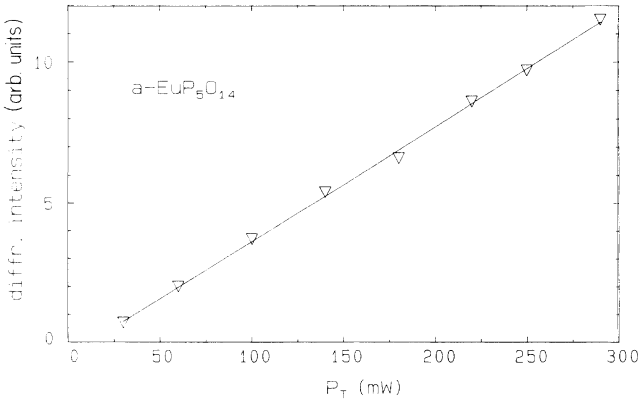

FIG. 6. Dependence of diffracted read-beam intensity of refractive-index grating in a EuP_5O_{14} glass at 300 K as a function of total laser output power at 466 nm. Approximately 60% of this power hits the sample.

C. Er^{3+}-doped silicate and metaphosphate glasses

Both the Er(2 mol %):Na-Si-O and Er(5 mol %):Na-Si-O glasses, as well as the Er:La-P-O samples, showed no transient or permanent grating formation after exposure (on sample) to approximately 350 mW for 45 min. All FWM results are summarized in Table II. As mentioned earlier, another method for detecting light-induced permanent refractive index changes is lensing of a probe beam. This technique was applied to the Er(5 mol %):Na-Si-O sample; with 200 mW applied to the sample only transient lensing was observed, as is shown in Figs. 7 and 8. The former shows the short-time transient lensing behavior when the pump beam was chopped at 10 Hz: as the pump turned on the intensity at the center of the transmitted probe beam decreased and stabilized in approximately 20 msec. After the pump beam was blocked the transmitted probe intensity recovered completely. This time response and the spot size of the pump beam are consistent with a thermal lensing effect, caused by the nonradiative decay of the excited $^4I_{11/2}$

TABLE II. FWM results at 300 K.

Sample	Δn_t	Δn_p
Pr:Na-Si-O	no	no
Pr:La-B-O	no	no
Pr:B-Al-O	no	no
Pr:P-O	no	no
Eu:Na-Si-O	yes	yes ($\tau_{1/e}=2.6$ msec)
Eu:La-P-O	yes	yes
Eu:P-O	yes ($\tau_{1/e}=1.2$–1.6 msec)	no
Er(2 mol %):Na-Si-O	no	no
Er(5 mol %):Na-Si-O	no[a]	no
Er:La-P-O	no	no

[a] This sample shows Δn_t in the thermal lensing experiment.

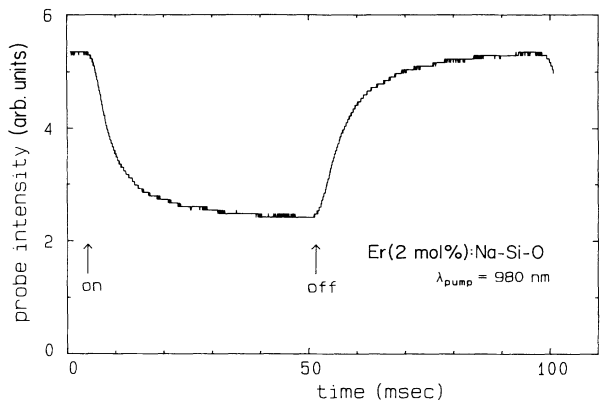

FIG. 7. Transmitted probe intensity genreated by resonantly pumped (980 nm) thermal lensing in a 2 mol %Er_2O_3–24.5 mol %Na_2O–73.5 mol %SiO_2 glass at 300 K. The two arrows indicate the blocking and unblocking of the single pump beam, respectively.

state to the $^4I_{13/2}$ manifold. Figure 8 shows the same behavior, but now over a longer time scale. The pump beam was turned on for approximately 15 min, after which it is blocked. As can be seen the transmitted probe intensity completely recovers again and there is no evidence of any permanent lens formation (i.e., no permanent Δn_p was generated). This long exposure duration was chosen, since permanent index modifications typically occur on that time scale (see the above results for Eu^{3+}).

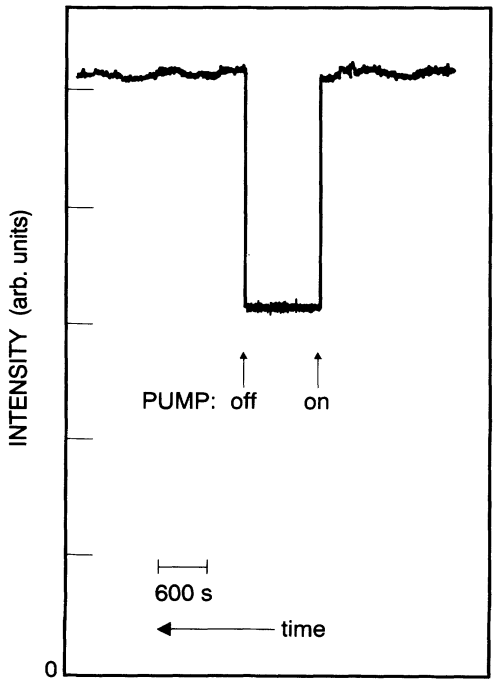

FIG. 8. Same as Fig. 7, but now the blocking time of the pump beam is approximately 15 min. Note that the transmitted probe intensity recovers completely after the pump has been blocked.

IV. DISCUSSION

The observation of transient and permanent changes in the refractive index Δn_p in the Eu^{3+}-doped silicate and metaphosphate glasses at 300 K qualitatively agrees with the results from other studies.[6–8] Several important differences were found, however. The rise time of the permanent Δn_p in the Eu:Na-Si-O and Eu:La-P-O samples are on similar time scales ($\approx$1 h), in contrast to the rise time of the grating efficiency in a Eu^{3+}-doped multicomponent soda-silicate glass, which was reported to be much shorter than in the phosphate glasses.[8] Because the latter silicate glass contained multiple network modifiers, a quantitative comparison is very difficult, especially in terms of a two-level-system model in which only one modifier ion changes position.[4] The Eu:Na-Si-O yielded a higher scattering efficiency than the Eu:La-P-O sample with a lower Eu concentration; this is the opposite behavior of that observed by Durville *et al.*,[8] who observed a larger permanent efficiency for a fully concentrated sample (Eu:P-O) than for a diluted sample comparable to our Eu:Na-Si-O sample. The permanent grating in the Eu:Na-Si-O sample could be bleached by illumination with one beam at 466 nm, as well as with (nonresonant) 458-nm light. The latter presumably still excites the Eu^{3+} ion through a phonon-assisted transition, as evidenced by the observed luminescence—albeit weaker than that when pumped at 466 nm—from the $^5D_0$ state.

An interesting observation is the absence of a permanent change in the refractive index in the Eu:P-O sample: for this stoichiometric (and hence nominally identical) composition both transient and permanent grating formation were reported previously.[8] The 1.2–1.6 msec decay time we observed in our sample is consistent with the absence of a permanent Δn_p, as expressed by the first term in Eq. (2), since the lifetime τ (of the metastable $^5D_0$ state) in this host was reported to be approximately 2.7 msec. Since $\Delta n_t \simeq I_w$ (the write-beam intensity),[15] the observed linear dependence of the scattering efficiency on the total write power (Fig. 6) is rather remarkable. It should be mentioned here that a similar linear dependence of the transient scattering efficiency was measured by Durville *et al.* in their Eu:P-O sample.[8] In the latter case the transient grating was observed to decay with a 2.67-msec lifetime; this corresponds to the second term in Eq. (2). However, since that term contains the product $|\Delta n_t\, \Delta n_p|$, a similar quadratic write-power dependence would be expected there as well. Although the reason for the observed linear dependence of the transient grating efficiency is not clear, it may be related to the inverse proportionality between the decay time and total write power, indicating some sort of cooperative effect (e.g., stepwise up-conversion) between two Eu^{3+} ions.

As mentioned earlier, the absence of a permanent grating in our Eu:P-O sample was rather surprising. This indicates that the two-level model is incomplete in explaining grating formation in these Eu^{3+}-doped glasses. This model contains two important items: (1) the high-energy phonon-induced redistribution of a ligand between two local configurations, and (2) a difference in polarizability $\Delta\alpha_p$, and hence Δn_p, between those two configurations

arising from mixing of $5d$ and ng resonances into the $4f-4f$ transition moments.[4,17] Assuming the contribution from the $4f^n$-$15d$ state to be dominant, this change $\Delta\alpha_p$ was shown to be

$$\Delta\alpha_p \simeq |\langle 4f|r|5d\rangle|^2 \left[\frac{1}{(\nu_0^{5d}-\nu_{ex})^2-\nu^2} - \frac{1}{(\nu_0^{5d})^2-\nu^2} \right] \quad (3)$$

with ν_0^{5d} the average energy of the $4f^{n-1}5d$ state ($n=6$ for Eu^{3+}), ν the read-beam energy, and ν_{ex} the energy difference between the two local configurations.[4,17] The radial integral $\langle 4f|r|5d\rangle$ is approximated by the free-ion value. Equation (3) can be used to obtain the difference of the ground state of Eu^{3+} (or any other RE ion) in the two structural configurations: when applied to the case of Pr^{3+} and Er^{3+}, with the corresponding values for the $5d$ band energy and free-ion radial integrals,[18] similar $\Delta\alpha_p$'s are obtained for these RE's as for Eu^{3+}. This, of course, conflicts with our observed absence of a permanent Δn_p in the Pr^{3+}- and Er^{3+}-doped systems. Based on the above $\Delta\alpha_p$ analysis, therefore, the absence of permanent grating formation in the latter two systems, and of course in the Eu:P-O glass as well, cannot be explained.

In fact, applying the two-level formalism, as developed for a variety of low-temperature properties,[11] to this room-temperature (and above) grating formation problem appears questionable. A rather remarkable characteristic of disordered solids is that many properties, such as the thermal conductivity,[19] are strikingly similar in magnitude and temperature dependence for various inorganic and organic glasses. In our RE-doped systems we definitely did not observe such "universal" behavior in permanent grating formation. Although this does not constitute proof that thermally activated local structure changes do not play a role in these gratings, it certainly opens the possibility of other effects, such as a charge-transfer process to nearby trapping sites following a multistep excitation or multi-ion interaction. It is interesting to note in this context that other valencies of Tb^{3+}, Pr^{3+}, and Eu^{3+} occur in solids: the first two exist also in the $4+$ state and a latter also has the $2+$ valency.

V. CONCLUSIONS

We have observed transient (population) and permanent refractive-index changes (gratings) upon resonant excitation of the $^5D_2$ manifold in a Eu^{3+}-doped silicate and lanthanum metaphosphate glass at 300 K using four-wave mixing. A maximum scattering efficiency of 5×10^{-5} was obtained for the silicate sample, with a half-life of approximately 48 h at 300 K. Similarly, a Eu^{3+}-doped pentaphosphate glass sample showed only a transient grating, the decay of which was consistent with a regular electronic (population) grating. The results qualitatively agree with earlier observations by others, which were explained by a hot-phonon (local mode) induced structure rearrangement around the Eu^{3+} site between the two potential wells of a two-level system. In order to test the validity of applying this two-level-system (tunneling system) model to this permanent grating formation in glasses and exclude possible multiphoton electronic effects playing a role, we have extended these measurements to the near-ir spectral region, where the $^4I_{11/2}$ state of Er^{3+} doped in a silicate and a lanthanum metaphosphate glass was resonantly excited (980 nm). No permanent refractive-index gratings were observed at 300 K in these Er^{3+}-doped systems. A single pump/probe lensing experiment in the Er-silicate sample showed only transient thermal lensing, which is consistent with the FWM result. Permanent gratings have also been reported in a Pr^{3+}-doped silicate glass following resonant excitation (488 nm) into the $^3P_0$ state, which has also a large energy gap below it. In our investigation we have searched for permanent grating formation in a Pr^{3+}-doped soda silicate, a lanthanum borate, an aluminum borate, and a metaphosphate glass. No permanent Δn_p was observed in any of these glasses.

The permanent change in the refractive index has been explained by a difference in the polarizability $\Delta\alpha_p$ between the two potential wells.[4] Applying such an analysis to the cases of the Pr^{3+} and Er^{3+}, we expect similar values for $\Delta\alpha_p$ for these two RE's, which disagrees with our observed absence of permanent Δn_p formation. This suggests that this description of the periodic modulation of the refractive index in terms of the standard tunneling-system model is incomplete for predicting results on other trivalent RE-doped glasses, such as Pr^{3+} and Er^{3+}. Aside from the specific details on these light-induced permanent refractive-index changes, it appears from these experiments that either the local structure has been rearranged or that another process, such as an irreversible charge redistribution between the RE and its ligands, has taken place, resulting in a modulation of the refractive index. In both cases different fluorescence properties of the RE ions in the exposed regions versus the unexposed regions would be expected. An intriguing question is whether that would lead to permanent spectral hole burning at 300 K in these active glasses.

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