EPR study of Gd³⁺ doped lead oxide based glasses

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The electron paramagnetic resonance (EPR) spectra of Gd³⁺ ions in lead germanate and lead phosphate glasses are analyzed as a function of Gd content and host composition in the temperature range between 4.2 and 300 K. The investigated samples were $(40 - x)$PbO·60GeO$_2$· xGd$_2$O$_3$ ($x = 0.25, 0.5, 1, 2, 3, 4$ mol %) and 97.5Pb(PO$_3$)$_2$ · 2.5Gd(PO$_3$)$_3$ glasses, prepared by conventional melting technique. From comparison of spectra on different samples—some of which partially crystallized—no evidence emerges of the existence of distinct types of Gd³⁺ coordination environments. The analysis of the line-broadening by increasing the Gd³⁺ content evidences that the line width of the EPR signal components is proportional to the concentration of rare earth ions, suggesting that clustering effects are negligible, at least up to 4 mol % Gd$_2$O$_3$. © *1999 Kluwer Academic Publishers*

1. Introduction

Rare earth ions (RE) in oxide glasses are currently investigated for their possible applications in luminescent devices. Many studies were devoted to the analysis of the RE coordination structure both through molecular dynamics simulation (and crystal field (CF) theory) [1–3] or by optical measurements (optical absorption and emission and fluorescence line narrowing spectroscopy) [4–6]. A limited number of studies were also performed by analyzing electron paramagnetic resonance (EPR) data. In fact, the possibility of inferring, by EPR spectroscopy, the existence of distinct varieties of environments or clustering effects was discussed in the last decade [7, 8], with particular regard to the spectrum of Gd³⁺ [9–11].

The ground state (GS) of Gd³⁺ (4f⁷, ground state $^8S_{7/2}$) is essentially an S-state. The CF induced by the surrounding ligands does not split an S-state to first order. Nevertheless, although the GS is slightly admixed with higher energy states (the first excited level $^6P_{7/2}$ lies at 31000 cm^{-1} above the GS), relatively large CF splittings are observed [12].

Simplified spin Hamiltonians are usually employed to describe this system [13] containing a Zeeman term as well as CF terms expressed by the Stevens operators. However, only for very simple symmetries can closed formulae for the calculation of RE EPR spectra be derived from the spin Hamiltonian and one can

rarely analyze *ab initio* their complex features. In fact, the EPR signal of Gd³⁺ in disordered hosts (when present at concentration less than 2 mol %) exhibits a complex structure—labelled as the "Ubiquitous" spectrum (U-spectrum) [14–16]—usually consisting of three main features at $g \sim 6$, $g \sim 2.8$ and $g \sim 2$. Numerical procedures and simplifying assumptions had to be chosen for its simulation and interpretation. Brodbeck and Iton [13] showed that all the observed U-spectrum features can be fitted to a single type of Gd³⁺ site with a distribution of the spin-Hamiltonian terms b_2^0 (ranging between 0.04 and 0.06 cm^{-1}) and b_2^2 (ranging between zero and b_2^0). Another recent work by Legein *et al.* [17] followed a similar approach and attributed the U-spectrum to isolated Gd³⁺ ions in a variety of sites with a coordination number generally estimated to be 8 or 9 in tetrahedral network glasses and a distribution of Hamiltonian parameters. Nevertheless, a full agreement with this view is not yet established. Other works in the last years founded their analysis on the assumption that each contribution at $g \sim 6$, $g \sim 2.8$ and $g \sim 2$ to the U-spectrum would arise from distinct coordination symmetries of the Gd³⁺ ion [9–11, 18], despite the fact that Brodbeck and Iton had made evident the inconsistency of this interpretation already present in previous studies [15, 16, 19, 20].

In this work we present data which support the one-site attribution of the EPR signal and allow us

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Sample number	Molar composition	Gd^{3+} ion concentration (ions/cm^3)
1	$39.75PbO \cdot 60GeO_2 \cdot 0.25Gd_2O_3$	1.24×10^{20}
2	$39.5PbO \cdot 60GeO_2 \cdot 0.5Gd_2O_3$	2.47×10^{20}
3	$39PbO \cdot 60GeO_2 \cdot 1Gd_2O_3$	4.91×10^{20}
4	$38PbO \cdot 60GeO_2 \cdot 2Gd_2O_3$	9.73×10^{20}
5	$37PbO \cdot 60GeO_2 \cdot 3Gd_2O_3$	1.45×10^{21}
6	$36PbO \cdot 60GeO_2 \cdot 4Gd_2O_3$	1.95×10^{21}
7	$29.75PbO \cdot 70GeO_2 \cdot 0.25Gd_2O_3$	6.21×10^{19}
8	$49.75PbO \cdot 50GeO_2 \cdot 0.25Gd_2O_3$	6.23×10^{19}
9	$97.5Pb(PO_3)_2 \cdot 2.5Gd(PO_3)_3$	1.97×10^{20}

to investigate the effects of increasing Gd^{3+} concentration, to determine whether exchange interactions among RE occur as a result of clustering effects. For this purpose we have performed an analysis, supported by spectral deconvolution methods, on glassy samples with different Gd^{3+} content and different glass composition and also on partially crystallized materials. In particular, we have considered PbO based glasses (lead germanate and lead phosphate) which have attracted attention in the past as hosts for luminescent lanthanide ions, in view of their possible applications as glass lasers [21–23]. The optical properties of these doped glasses, in particular when the impurity is Eu^{3+}, and the effect of the presence of amounts of PbO between 38 and 50 mol % have been discussed [3, 24–26].

2. Experimental

The samples investigated were lead-germanate and lead-phosphate glasses doped with Gd^{3+} (see Table I). One set of samples consisted of a homogeneous series of lead-germanate glasses $(40 - x)PbO \cdot 60GeO_2 \cdot xGd_2O_3$ with different concentration of Gd^{3+} oxide ($x = 0.25, 0.5, 1, 2, 3, 4$ mol % Gd_2O_3). Other samples were prepared with the same Gd^{3+} content but differing glass compositions by changing the ratio between lead and germanium oxides or substituting Ge oxide for P oxide. The samples were prepared by conventional melting in air followed by quenching to room temperature, as described in Refs. [25] and [3] for the germanate and phosphate glasses, respectively. Furthermore, partially crystallized germanate samples were obtained by remelting the glass samples and cooling to room temperature, at a rate of $10\,°C/h$. EPR measurements in X-band (9 GHz) were performed at different temperatures (from 4.2 to 300 K) using a BRUKER spectrometer. Partially crystallized samples were also measured at different sample orientations with respect to the static magnetic field.

3. Results

Representative EPR spectra at room temperature of some of the investigated samples with different Gd^{3+} content are shown in Fig. 1a. The prominent features at $g \sim 6$, $g \sim 2.8$ and $g \sim 2$—characteristic of the U-spectrum—are common to all EPR spectra. In Fig. 1b spectra at different temperatures of one of these samples are reported: the main differences among the spectra are only related to the Boltzmann factor.
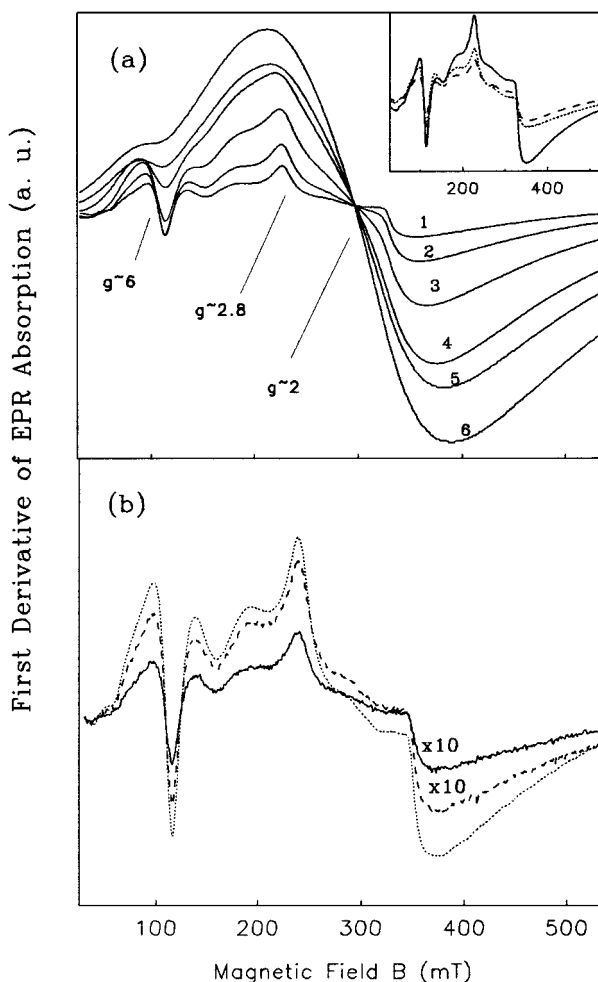

Figure 1 (a) Room temperature EPR spectra at X band of Gd^{3+} in lead-germanate glasses with different Gd_2O_3 contents (labels as in Table I). Inset: Comparison among spectra of samples with comparable Gd_2O_3 content and different glass composition (samples 7, 8 and 9 of Table I in full line, dashed line and dotted line, respectively). (b) Spectra of sample 1 at 100 K (full line), 50 K (dashed line) and 4.2 K (dotted line).

To obtain more detailed indications on the Gd^{3+} sites, we have performed EPR measurements on partially crystallized samples. Their EPR spectra exhibit an angular dependence, as evidenced, for example, in Fig. 2a where EPR spectra at two different orientations with respect to the static magnetic field are shown. The whole angular scan is shown in the inset in Fig. 2a. By grinding the samples, we have checked the effects of the angular average (Fig. 2b): the general behavior of the spectrum resembles those of glassy samples, even though it shows the presence of more resolved structures, preferably placed at $g > 2$.

No attempt was made by us to reproduce the features of the spectrum by *ab initio* calculation of the transitions within the 7/2 multiplet of Gd^{3+} ion since this procedure is strongly affected by the controversial choice of the Hamiltonian parameters [13, 16]. Instead, simple deconvolutions of the spectra have been carried out to have a tool for the analysis of amplitudes and widths of the spectrum structures as a function of the Gd^{3+} content. Taking into account the results from partially crystallized samples, and from the analysis of the more structured EPR spectrum (observed in the sample with smaller Gd^{3+} concentration) we have evaluated
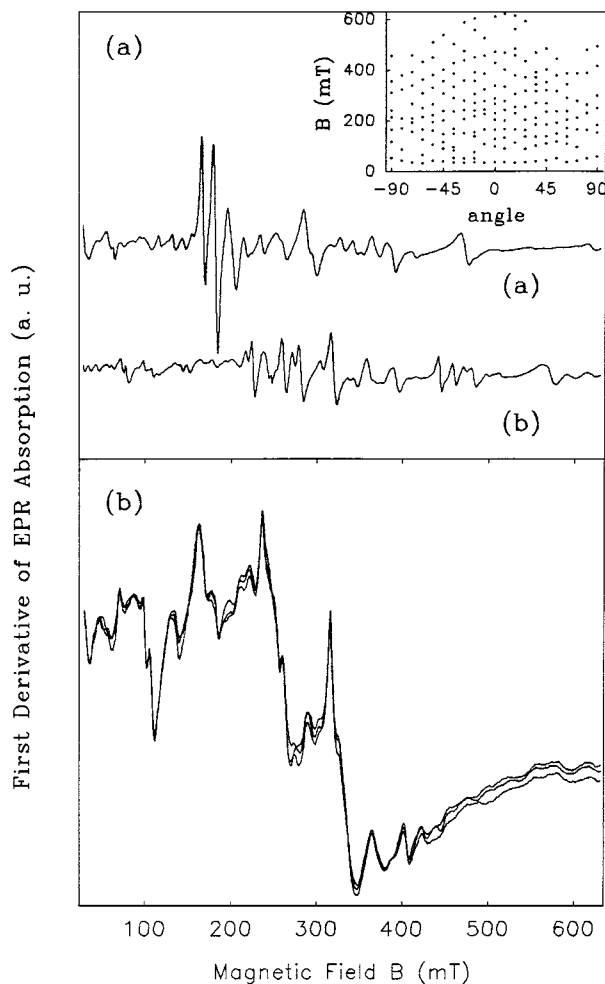
Figure 2 (a) Room temperature EPR spectra at X band of a partially crystallized sample (obtained from sample 9), at two different orientations (curves (a) and (b) differ by 99°). Resonance field positions observed in a 180° angular scan are plotted in the inset. (b) EPR spectra of the same sample after grinding, at three different orientations in the static magnetic field.

the minimum number of gaussian components needed to account for the experimental spectral shape, together with their central positions. Good fits of the samples with differing Gd^{3+} contents have been obtained by choosing the same centers and relative intensities of the components and by changing only their line width (Fig. 3).

As far as the broadening of the EPR spectrum by increasing Gd^{3+} content is concerned, the deconvolutions of the spectra of Fig. 1 suggest a linear increase of the line width of the components with the Gd^{3+} concentration (see Fig. 4 for the component at $g \sim 6$).

4. Discussion

The results obtained on partially crystallized samples, showing the anisotropy of the Gd^{3+} spectra (Fig. 2), suggest that the local symmetry at Gd^{3+} sites is lower than cubic. Comparison of spectra of glassy samples and partially crystallized samples before and after grinding shows that the structures of the glass spectrum arise from the angular average of several anisotropic components. In particular no isolated isotropic component is observed at $g \sim 6$ (as proposed by some authors
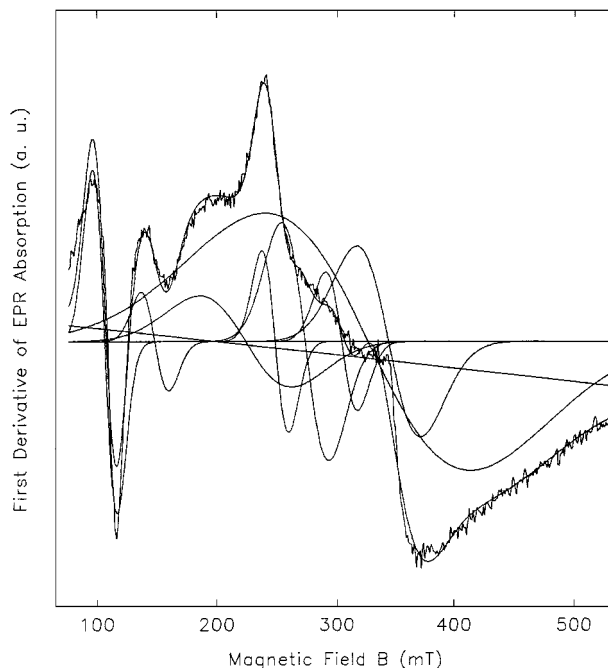

Figure 3 Deconvolution of the 300 K EPR spectrum of sample 1 (dotted line) obtained with several gaussian components (full lines). A straight line accounts for the baseline drift.
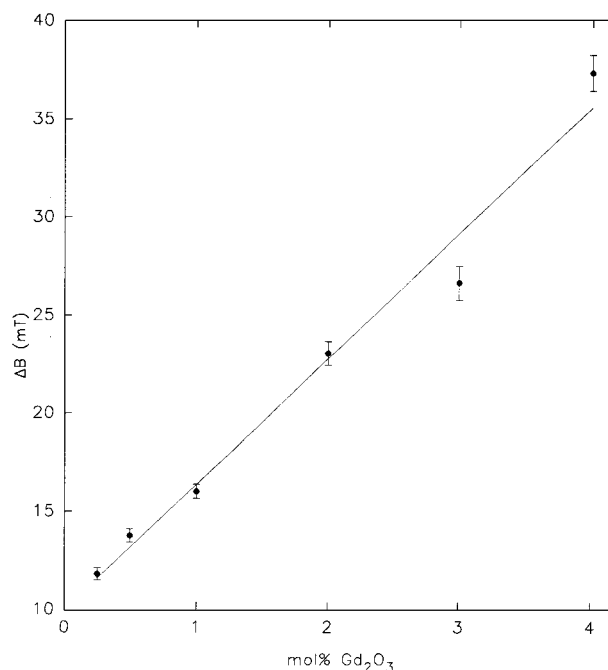

Figure 4 Dependence on the Gd^{3+} concentration of the line width of the $g \sim 6$ feature, as derived from the Gaussian deconvolution (see text).

[10, 11]), but several components are in that spectral range. Therefore all the structures of the spectrum are signal envelopes not identifiable with particular transitions of Gd^{3+} ions.

The changes of the spectrum with Gd^{3+} content are successfully reproduced by keeping fixed relative intensities and central positions of the deconvolution components. We have also noted a similar dependence changing the composition of the host glass (inset of Fig. 1a). This similarity agrees with that proposed by Brodbeck and Iton in the case of the smaller concentration range [13] based on the similarity of the relative
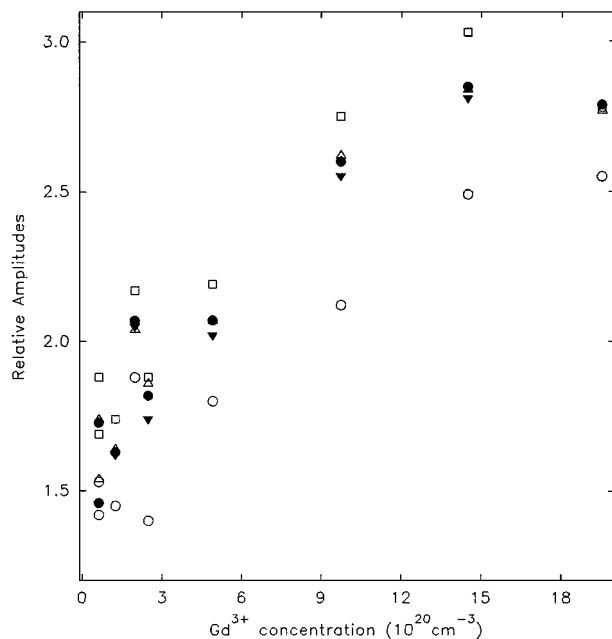
Figure 5 Peak-to-peak EPR amplitudes of the structures at $g \sim 6$ and at $g \sim 2.8$, for all the samples, at 4.2 K (hollow circles), at 50 K (filled circles), at 100 K (hollow triangles up), at 130 K (filled triangles down) and at 300 K (hollow squares).

amplitudes of the U-spectrum features. We remark in this regard that an analysis of the experimental spectrum, based on the apparent amplitudes of the features at $g \sim 2$, $g \sim 2.8$ and $g \sim 6$, gives different results as shown in Fig. 5, where a trend is observed by increasing Gd^{3+} content owing to the complex effects of the broadening of the components on the intensity. In fact, no relevant change of the relative amplitudes should be detected by varying the Gd^{3+} concentration if the observed structures arise from envelopes of transitions of Gd^{3+} in equivalent sites. Instead, changes of relative amplitudes are generally expected for components due to Gd^{3+} in sites with differing magnitudes of the b_n^i coefficients, since it is unlikely that different sites may be present with the same ratio in different compositions or by changing the Gd^{3+} content. These constraints rule out attributions of the $g \sim 2$, $g \sim 2.8$ and $g \sim 6$ structures to distinct Gd^{3+} environments.

The analysis of the broadening of the spectra by increasing Gd^{3+} content suggests that the line width of the spectral components is proportional to the concentration of rare earth ions. No detectable effect due to clustering of Gd^{3+} ions is observed with increasing Gd content: in fact Gd^{3+} clustering effects should give deviations from linearity in the broadening of the spectrum and no evidence for this dependence is observed in Fig. 4 within the experimental errors. This fact, jointly with the evidence that the line shape is not modified, proves that Gd^{3+} ions are well diluted in the investigated glass hosts, at least up to 4 mol % of Gd_2O_3 concentration.

Magnetic susceptibility measurements, carried out on the same samples as a function of the temperature [27], indeed confirm this fact, as no exchange interactions are observed with increasing Gd^{3+} content, but only a nearly constant contribution from antiferromagnetic interactions probably due to Gd^{3+} dimers.

5. Conclusions

From EPR measurements on several lead-germanate and lead-phosphate glassy or partially crystallized samples, containing different concentrations of Gd_2O_3, we inferred the presence of only one type of site for Gd^{3+}, with symmetry lower than cubic. The one-kind-of-site interpretation is confirmed by comparing Gd^{3+} spectra in different hosts, but similar Gd^{3+} contents. Therefore we agree with the interpretation given by Brodbeck and Iton [13], and recently by others [17], which assign the general features of the U-spectrum to transitions within the multiplet of energy levels of Gd^{3+} ions in only one kind of site.

Moreover, from the linear relationship between concentration and line width, without any detectable modification of the line shape of the components, we can conclude that concentration-dependent clustering effect induced by increasing Gd^{3+} content in the investigated glasses at least up to 4 mol % of Gd_2O_3 concentration is not present. This information is valuable for the understanding of the cross relaxation and energy transfer processes contributing to the relaxation of the excited states of RE ions in the glasses under investigation.

References
1. G. CORMIER, J. A. CAPOBIANCO and C. A. MORRISON, *J. Chem. Soc. Faraday Trans.* **90** (1994) 755.
2. G. CORMIER, J. A. CAPOBIANCO, A. MONTEIL and C. A. MORRISON, *Phys. Rev. B* **48** (1993) 16290.
3. J. A. CAPOBIANCO, P. P. PROULX, M. BETTINELLI and F. NEGRISOLO, *ibid.* **42** (1990) 5936.
4. C. BRECHER and L. A. RISEBERG, *ibid.* **13** (1976) 81.
5. J. L. SKINNER and W. E. MOERNER, *J. Phys. Chem.* **100** (1996) 13251.
6. T. OKUNO, K. TANAKA, K. KOYAMA, M. NAMIKI and T. SUEMOTO, *J. Lumin.* **58** (1994) 184.
7. D. W. MOON, J. M. AITKEN, R. K. MACCRONE and G. S. CIELOSZYK, *Phys. Chem. Glasses* **16** (1975) 91.
8. S. K. MENDIRATTA and E. G. DE SOUSA, *J. Mater. Sci. Lett.* **7** (1988) 733.
9. S. K. MENDIRATTA, L. C. COSTA and E. G. DE SOUSA, *ibid.* **9** (1990) 301.
10. E. CULEA and I. MILEA, *J. Non-Cryst. Solids* **189** (1995) 246.
11. E. CULEA, A. POP and I. COSMA, *J. Magn. Magn. Mater.* **157/158** (1996) 163.
12. J. SYTSMA, K. M. MURDOCH, N. M. EDELSTEIN, L. A. BOATNER and M. M. ABRAHAM, *Phys. Rev. B* **52** (1995) 12668.
13. C. M. BRODBECK and L. E. ITON, *J. Chem. Phys.* **83** (1985) 4285.
14. L. E. ITON and J. TURKEVICH, *J. Phys. Chem.* **81** (1977) 435.
15. R. C. NICKLIN, J. K. JOHNSTONE, R. G. BARNES and D. R. WILDER, *J. Chem. Phys.* **59** (1973) 1652.
16. L. CUGUNOV and J. KLIAVA, *J. Phys. C* **15** (1982) L933.
17. C. LEGEIN, J. Y. BUZARÉ, G. SILLY and C. JACOBONI, *J. Phys.: Condens. Matter* **8** (1996) 4339.
18. I. ARDELEAN, E. BURZO, D. MITULESCU-UNGUR and S. SIMON, *J. Non-Cryst. Solids* **146** (1992) 256.
19. I. V. CHEPELEVA and V. N. LAZUKIN, *Dokl. Akad. Nauk SSSR* **226** (1976) 311.

20. H. J. A. KOOPMANS, M. M. A. PERIK, B. NIEUWENHUIJSE and P. J. GELLINGS, *Phys. Status Solidi B* **120** (1983) 745.
21. J. WANG, J. R. LINCOLN, W. S. BROCKLESBY, R. S. DEOL, C. J. MACKECHNIE, A. PEARSON, A. C. TROPPER, D. C. HANNA and D. N. PAYNE, *J. Appl. Phys.* **73** (1993) 8066.
22. D. P. SHEPHERD, D. J. B. BRINCK, J. WANG, A. C. TROPPER, D. C. HANNA, G. KAKARANTZAS and P. D. TOWNSEND, *Optics Letters* **19** (1994) 954.
23. M. J. WEBER, L. A. BOATNER and B. C. SALES, *J. Non-Cryst. Solids* **74** (1985) 167.
24. G. INGLETTO, M. BETTINELLI, L. DI SIPIO, F. NEGRISOLO and C. ASCHIERI, *Inorg. Chim. Acta* **188** (1991) 201.
25. M. WACHTLER, A. SPEGHINI, S. PIGORINI, R. ROLLI and M. BETTINELLI, *J. Non-Cryst. Solids* **217** (1997) 111.
26. M. WACHTLER, A. SPEGHINI, K. GATTERER, H. P. FRITZER, D. AJÒ and M. BETTINELLI, *J. Amer. Ceram. Soc.* **81** (1998) 2045.
27. K. GATTERER, personal communication.