

Properties of poly(vinyl alcohol)–borax gel doped with neodymium and praseodymium

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Abstract. Neodymium and praseodymium ions, singly and in combination, have been doped into a poly(vinyl alcohol)–borax matrix. X-ray diffraction shows structural correlations from 2 to 6 Å and 15 Å, while small angle neutron scattering indicates that the rare-earth ions do not affect the nanoscale structures of the gels. Differential scanning calorimetry shows the glass transition temperature to increase with concentration of Pr in the gel. Excitation in the ultraviolet region leads to luminescent emission in the visible region. Simultaneous absorption in the visible region then leads to luminescent emission in the near infra-red region. The spectral qualities of the emission bands can be varied by choosing appropriate relative ratios of rare-earth species.

Keywords. PVA; Nd; Pr; UV–visible; SANS; luminescence.

1. Introduction

The luminescent properties of rare-earth salts can be utilized in the fabrication of light emitting gels (LEG), optical fibres, laser materials and optical signal amplifiers (Abdelaziz 2011). The long-term stability and ease of processing permit the use of polymers as host matrices for rare-earth salts. Poly(vinyl alcohol) [PVA], a water soluble polymer, can be modified into physically and chemically cross-linked hydrogels through cross-linking with borax. The cross-linking introduces a negative charge that helps intermolecular hydrogen bonding between the hydroxyl groups on poly(vinyl alcohol) chains thereby causing the gelation (Kanaya *et al* 2005). Earlier studies (Hanafy 2008) in similar gels have revealed that doping with rare-earth salts causes changes in the structural, optical and thermal properties of the host matrix. Some studies have also been reported on poly(vinyl alcohol) thin films doped with a single rare-earth viz. Ho³⁺, Er³⁺, Sm³⁺, Eu³⁺ and Ce³⁺ (Kumar *et al* 1997; Seeta Rama Raju *et al* 2006; Abdel-Kader and Anwer 2007; Abdelaziz 2011). We have not come across studies on PVA matrices with combinations of different rare-earth dopant species. In the present investigation, PVA–borax hydrogels have been doped with Nd³⁺ and Pr³⁺ ions – both singly and in pairs – with the objective of studying the optical and structural consequences using UV–visible, luminescence and FTIR spectroscopy, differential scanning calorimetry, X-ray diffraction and small angle neutron scattering. The effects of rare-earth composition on luminescent and visible absorption spectral characteristics have been examined. The fine tuning

of such spectra may be possible by the appropriate choice of relative rare-earth proportions.

2. Experimental

Neodymium (III) and praseodymium (III) oxides were procured from Thomas Baker. Disodium tetraborate decahydrate (borax) and PVA (molecular weight 1,25,000 g/mol and 86% hydrolyzed) were obtained from SD-Fine Chemicals Limited. All chemicals were used without further purification.

Nitrates of neodymium and praseodymium were formed by dissolving the respective oxides in nitric acid. Borax (25 mg/ml) and PVA (240 mg/ml) were added to each nitrate solution while being continuously stirred for about 15 min. Each gel was allowed to set overnight. The relative weight proportions of Nd₂O₃ and Pr₂O₃ in the gels were respectively 0:0 (the undoped sample), 0:4, 1:3, 2:2, 3:1 and 4:0. Each sample was found to exhibit a homogenous colour, thereby indicating uniform doping throughout the gel.

The undoped gel and the sample doped with praseodymium were rheologically examined using an Anton Paar MCR 301 stress-controlled rheometer with cone and plate assembly having cone diameter of 5 cm and cone angle 1°. UV–visible measurements were performed on all samples, using a Shimadzu UV-2401 PC spectrometer in absorption mode in the wavelength range of 190–900 nm. Luminescence emission spectra were obtained with a Shimadzu RF 5301 PC spectrofluorophotometer on excitation with 220 nm and at several of the visible absorption peak wavelengths. Fourier–transform infra-red spectral measurements were performed on the gels with a Shimadzu FTIR 8900 spectrometer in the wavenumber range of 350–4000 cm⁻¹. Thermal investigations were conducted

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on each gel using a Shimadzu DSC-60 differential scanning calorimeter in the temperature range of 20–120 °C. X-ray diffraction measurements were performed using a Rigaku Ultima IV diffractometer in the 2θ range 3–80° with a step of 0.02°/min. Small angle neutron scattering (SANS) measurements were carried out at room temperature, on the undoped gel and on the gels doped with only neodymium or praseodymium (though, as chloride salts) using the SANS instrument (Aswal and Goyal 2000) at Dhruva Reactor, BARC, Trombay in the Q (wave vector) range of 0.017–0.35 Å⁻¹. Data accumulation times for the SANS measurements varied from 8 to 16 h.

3. Results and discussion

3.1 Rheology

In a preliminary experiment, the dynamic rheological data were determined, for the undoped sample, for stress values in the range of 6–6000 Pa at a fixed frequency of 1 Hz. The results of the measurement shown in figure 1, revealed the linearity of G' and G'' up to a stress value of approximately 1000 Pa. A stress value of 10 Pa, which lay in the visco-elastic regime, was chosen for the performance of the succeeding experiments.

Frequency sweep measurements were performed for both the samples. As shown in figure 2, neither sample exhibits a cross-over of the storage and loss moduli curves for the entire frequency range from 0.1 to 100 rad/s. For each sample, the storage modulus is consistently higher than the loss modulus, with both moduli being parallel to each other (on a log scale) – confirming the gel-like character of the samples (Almdal *et al* 1993; Kavanagh and Ross-Murphy 1998). Due to the similar type of dopant ions used in the other samples, the rheological data are expected to demonstrate similar trends.

The plot of complex viscosity (η) against frequency shown in figure 3, supports the above findings. The complex viscosity of both the samples are seen to decrease with frequency, pointing to the destruction of the gel-like nature with shear. Also, doping reduces the complex viscosity.

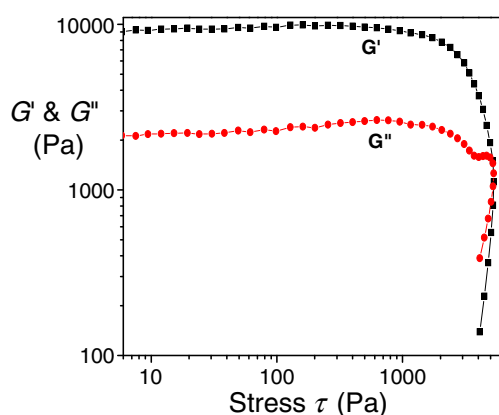


Figure 1. Typical amplitude sweep measurement of the gels.

3.2 UV-visible absorption spectroscopy

Figure 4 shows the UV-visible absorption spectrum obtained from the gel containing only neodymium as dopant. The positions of the peaks are found to be at the known wavelengths (Long and Han 2006). Figure 5 shows spectra from the gels with varying Nd:Pr ratios. The undoped sample shows a weak band at 280 nm due to the carbonyl groups associated with ethylene unsaturation which indicates the presence of conjugated polyene double bonds (Adiyodi *et al* 2009). This weak band reduces in intensity as the relative concentration of Pr³⁺ increases in the gels.

When Nd³⁺ and Pr³⁺ ions are both present as dopants, the spectra exhibit the characteristic peaks corresponding to 4*f* transitions of both the individual rare-earth ions (Long and Han 2006; Rai and Rai 2006). Tables 1 and 2 compare the absorption levels exhibited by these gels with the reported values.

The spectra are found to be in a linear superposition of the absorption spectra obtained of each rare-earth type, appropriately weighted by their relative weights as shown in figure 6. The relative intensity of the peaks depends directly on the concentration of the particular rare-earth absorber in the gel.

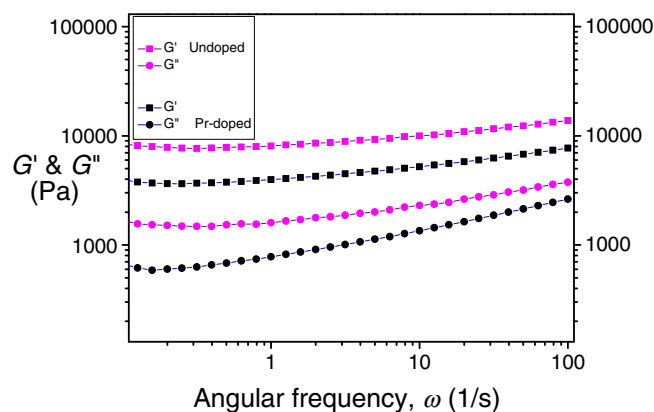


Figure 2. Storage and loss moduli at various frequencies.

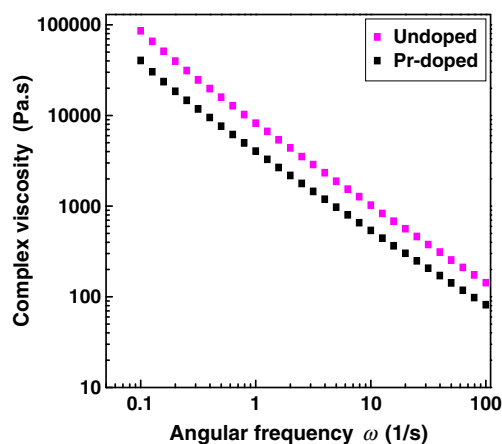


Figure 3. Comparison of complex viscosity of the gels at various frequencies.

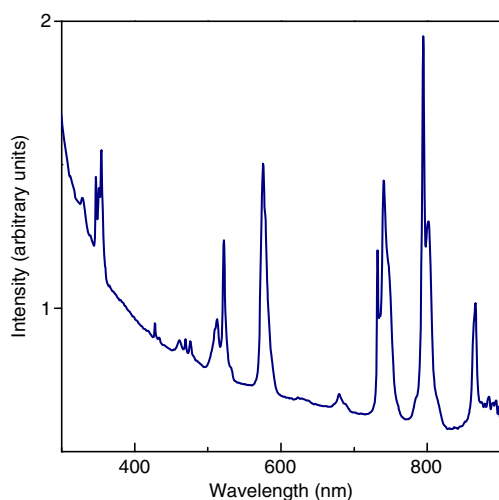


Figure 4. UV-visible absorption spectrum from PVA:Nd gel.

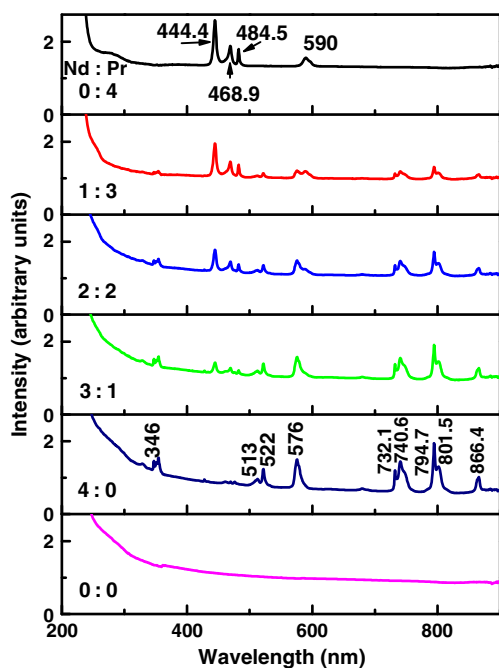


Figure 5. Absorption spectra from the PVA gels with varying Nd:Pr ratio.

Table 1. Absorption levels of praseodymium-doped PVA gel compared with the reported $4f$ transition levels of Pr^{3+} (Long and Han 2006).

Transition	Observed (nm)	Reported (nm)
$^3H_4 \rightarrow ^3P_2$	444.4	441.6
$^3H_4 \rightarrow ^3P_1$	468.9	467.1
$^3H_4 \rightarrow ^3P_0$	484.5	481.6
$^3H_4 \rightarrow ^1D_2$	590	587.1

Table 2. Absorption levels of neodymium-doped PVA gel compared with the reported $4f$ transition levels of Nd^{3+} (Rai and Rai 2006).

Transition	Observed (nm)	Reported (nm)
$^4I_{9/2} \rightarrow ^4D_{1/2}$	354	352.7
$^4I_{9/2} \rightarrow ^2G_{9/2}$	513	518.7
$^4I_{9/2} \rightarrow ^4G_{7/2}$	522	530
$^4I_{9/2} \rightarrow ^4G_{5/2}$	576	588.9
$^4I_{9/2} \rightarrow ^4S_{3/2}$	740.6	747.9
$^4I_{9/2} \rightarrow ^4F_{5/2}$	794.7	794
$^4I_{9/2} \rightarrow ^2H_{9/2}$	801.5	802.3
$^4I_{9/2} \rightarrow ^4F_{3/2}$	866.4	865

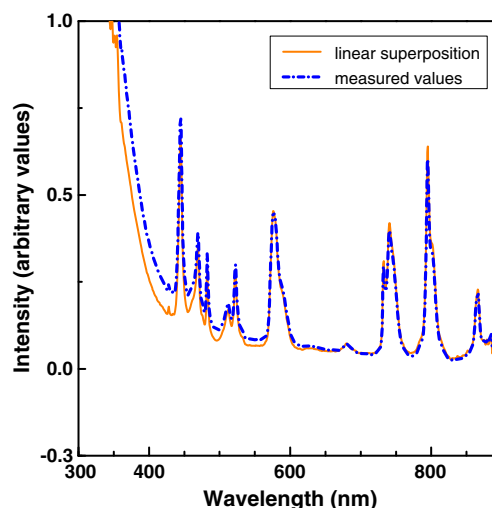


Figure 6. A comparison of the linear superposition of PVA gel spectra containing single rare-earths (samples 0:4, 4:0) with the measured spectrum from the gel having both rare-earths (sample 2:2).

The presence of one type of rare-earth ion does not affect the wavelengths of transitions emanating from the other type of rare-earth ions which are simultaneously present in the matrix. These observations are in excellent qualitative agreement with calculations of transition frequencies reported by Judd (1962). However, for the gels having both rare-earth types, Pr absorption lines were slightly more intense than for the gel containing only Pr as dopant. Thus, the presence of Nd slightly enhanced the absorptions due to Pr. Thus, although the local structure of the rare-earth ions and the vibrational properties of the host matrix of these ions do not substantially affect transition frequencies, transition probabilities between absorption levels were slightly affected.

3.3 Photoluminescent spectroscopy

Figures 7–11 exhibit the results of the photoluminescent spectroscopic studies conducted on the gels. Figure 7 shows spectra obtained when the gels were excited with the ultraviolet wavelength of 220 nm. It is observed that each

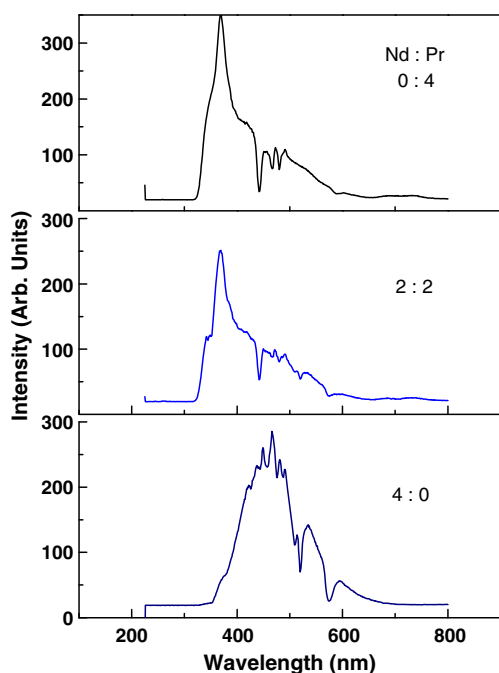


Figure 7. Photoluminescent spectra from the gels when the excitation wavelength is 220 nm.

spectrum has absorption minima due to the appropriate rare-earth ion(s) superimposed on the emission bands. Lifetime measurements (Mendiratta 2009) of these emission bands vary between 1.094 and 1.225 μs .

A linear superposition of emission spectra from the single ion appropriately weighted and scaled is compared, in figure 8, with the measured emission spectrum of the gel containing equal quantities of the rare-earth species. Agreement of the two curves is good apart from the height of the maximum in comparison with the rest of the spectrum. It appears that the intensity of emission from praseodymium is enhanced when neodymium is present as also found in UV-visible data.

The gel samples were also subjected to all excitation wavelengths pertaining to the visible absorption peaks of neodymium and praseodymium. The exercise resulted in emissions for only some of the wavelengths, which are shown in figures 9 and 10, respectively.

Figure 11 shows the result of a similar effort applied to the gel containing both rare-earth species. As expected, emissions from the ions existing singly in the gels are also present when both rare-earth ion types are present.

3.4 Fourier transform infra-red spectroscopy

FTIR spectra from the gel samples are shown in figure 12. For the undoped gel, the broad band from 3200 to 3600 cm^{-1} may be assigned to the hydroxyl groups of PVA that have formed complexes with the borate ions as well as those which are involved in intermolecular hydrogen bonding (Manna and Patil 2009). The feature at 1639 cm^{-1} points to the

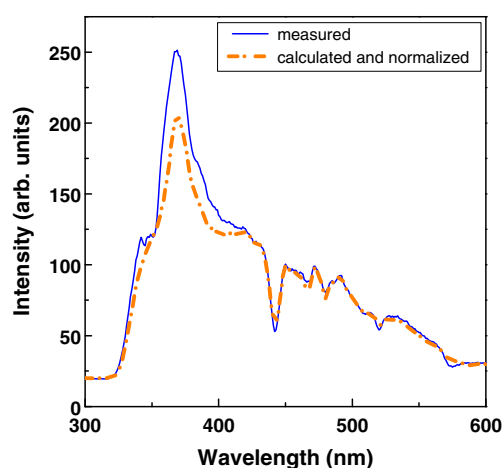


Figure 8. A comparison of the linear superposition of luminescent spectra containing single rare-earths (samples 0:4, 4:0) with the measured spectrum from the gel having both rare-earths (sample 2:2).

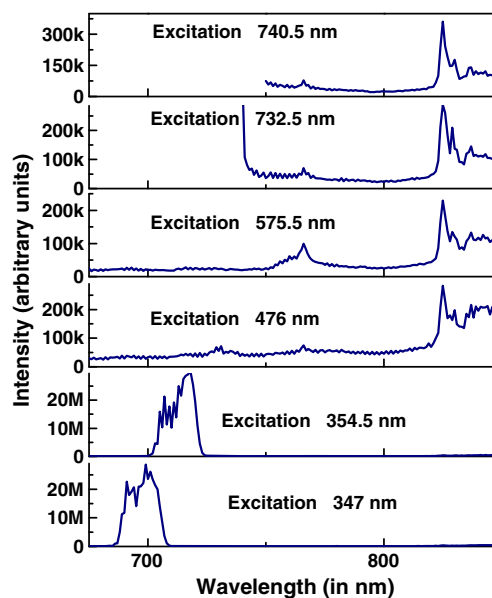


Figure 9. Photoluminescent spectra from the gel containing only Nd^{3+} ions when excited at various wavelengths.

presence of nitro groups while those at 1382 and 1096 cm^{-1} may be assigned to C–O bonds. Transmission peaks are seen at 2359 and 2337 cm^{-1} in the un-doped gel and the ones having neodymium and praseodymium in the relative proportions of 4:0 and 3:1. Only one such peak is visible for the gel with the doping proportion of 1:3. These small features re-appear – though as absorptions – at 2360 and 2537 cm^{-1} in the gel with only praseodymium. The features at 831, 921 and 1096 cm^{-1} are absent in the spectra from the doped gels indicating that the presence of the dopant(s) may be causing the suppression of C–O bending vibrations. The details given here relate to the PVA vibrational spectrum. It is clear, therefore, that the presence of dopants does not appreciably affect the PVA host's vibrational spectrum in the measured

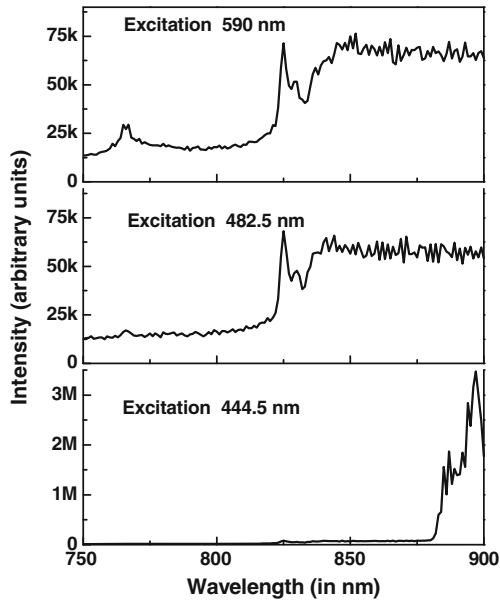


Figure 10. Photoluminescent spectra from the gel containing only Pr^{3+} ions when excited at various wavelengths.

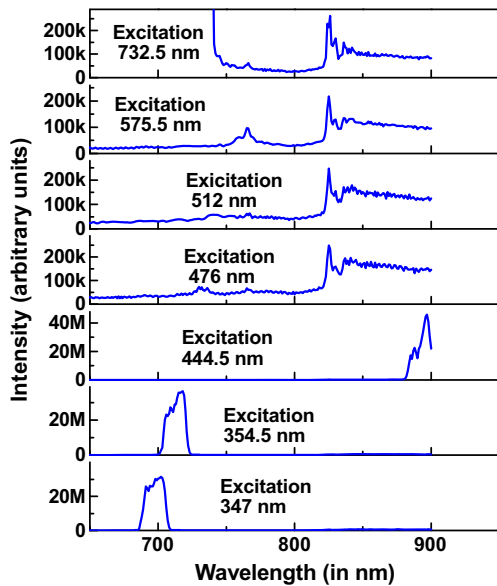


Figure 11. Photoluminescent spectra from the gel containing Nd^{3+} and Pr^{3+} ions in equal proportion, when excited at various wavelengths.

region. Hence, the rare-earth ions are not bonded to PVA chains but rather attach themselves to the crystallite or junction regions in the gel. Their vibrational energies lie below the minimum measured wavenumber of these data.

3.5 Differential scanning calorimetry

Figure 13 shows thermograms obtained from DSC measurements. The gels having both rare-earth types show an

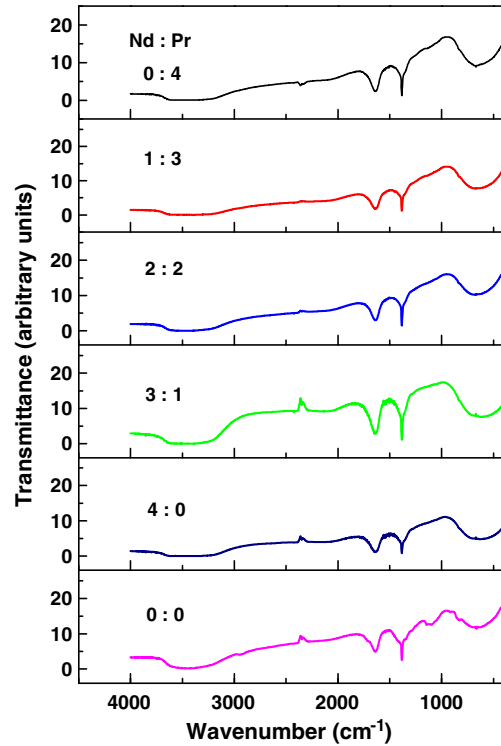


Figure 12. FTIR spectra from the doped and undoped PVA gels.

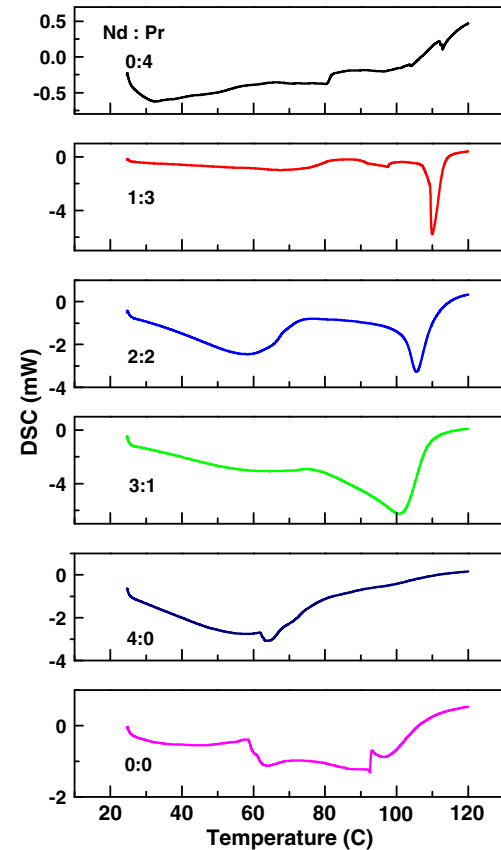


Figure 13. DSC thermograms of PVA gels with varying Nd:Pr ratio.

endothermic feature at about 95 °C which may be linked to their dissociation. In these gels, there is also a broad endothermic feature at about 60 °C which is likely to be their glass transition temperature. This is supported by the observation that the gels became liquid-like at temperatures slightly above this value.

3.6 X-ray diffraction

XRD investigations were conducted in order to understand the above changes. The resulting diffraction pattern is shown in figure 14. The XRD pattern of the undoped gel exhibits a broad diffuse maximum centred at 1.68 \AA^{-1} corresponding to correlations of 3.74 \AA . Doping with neodymium ions causes the emergence of two straddling broad maxima centred at 1.01 and 2.84 \AA^{-1} . When the gel is doped with only praseodymium ions, the additional maxima are observed at 1.10 and 3.02 \AA^{-1} originating from correlations of 5.71 and 2.08 \AA , respectively. For gels having both dopants, the broad diffuse maximum shifts to a slightly lower value of Q due to correlations at about 3.79 \AA . Each pattern also shows a pre-peak at around 0.4 \AA^{-1} in Q -space which may be related to a correlation length of 15 \AA . Thus, the X-ray data clearly relates to real space correlations between 2 and 6 \AA as well as from 15 \AA . A detailed Fourier-transform analysis of the data was not executed on account of the relatively low Q_{max} of 5.25 \AA^{-1} leading to poor real space resolution.

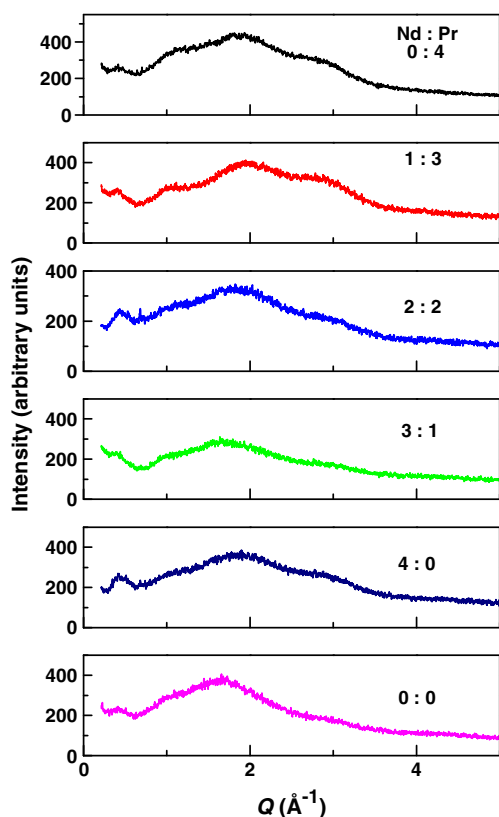


Figure 14. XRD patterns of PVA gels with varying Nd:Pr ratio.

3.7 Small angle neutron scattering

As shown in figure 15, the intensities for all the three gels are closely similar except at the higher end of the Q range. It may be noted that although all other gels reported in this work contained the rare-earths as nitrates, the similarities reported here for the SANS data on the rare-earth chlorides would also have held for rare-earth nitrates.

Analysis using SASfit software (Kohlbrecher 2010) showed that the data agreed with the Debye–Bueche and Ornstein–Zernike approximations, given by the relations $I(Q) = I(0)/(1 + \xi^2 Q^2)^2$ and $I(Q) = I(0)/(1 + \xi^2 Q^2)$, respectively, in the regions with $Q < 0.07$ and $Q > 0.07 \text{ \AA}^{-1}$. In the above equations, ξ is the correlation length and $I(0)$ is the forward scattering, i.e. the scattering intensity at $Q = 0$. For the sake of clarity, the fitted curve is shown in figure 16, only for the undoped sample. The goodness of fit for the other samples was similar.

The undoped gel and the gels with neodymium and praseodymium were, respectively, found to have correlation lengths of 31 , 30 and 32 \AA in the Debye–Bueche region and 10 , 7 and 8 \AA in the Ornstein–Zernike region. The forward scattering values were, respectively, found to be 6 , 6 and 7 cm^{-1} (Debye–Bueche) and 0.3 , 0.2 and 0.3 cm^{-1} (Ornstein–Zernike). It is known that crystallites are the cross-linking points in PVA gels (Kanaya et al 1994). Since the correlation length ξ may be related to the inter-crystallite distance, it is concluded that doping does not change the spacing between crystallites. Thus, there appear to be no structural changes in the nanometric size range when the gels are doped with the rare-earth ions.

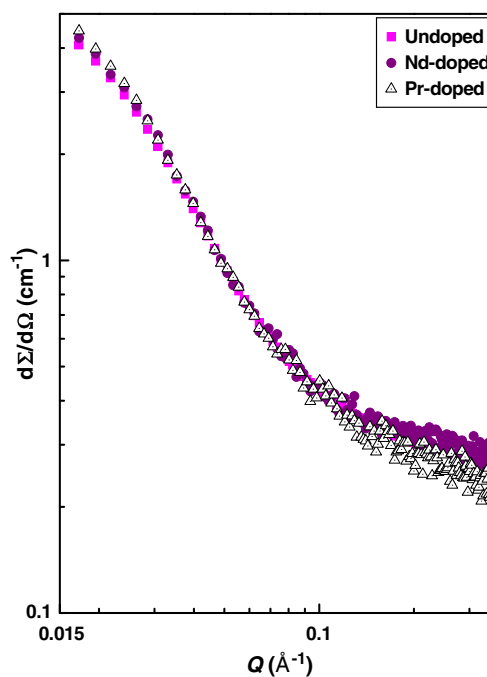


Figure 15. SANS intensity data for the undoped and doped PVA gels.

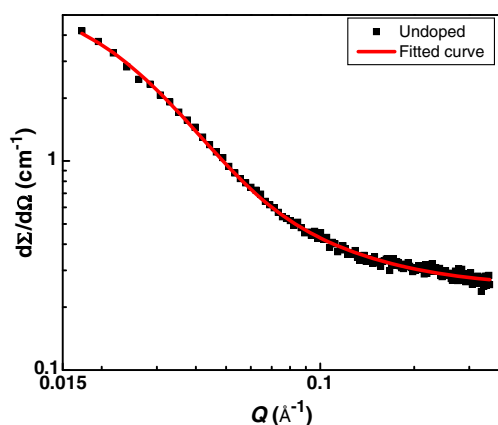


Figure 16. SANS intensity data of the undoped gel fitted with Debye–Bueche and Ornstein–Zernike approximations.

4. Conclusions

A set of rare-earth ions have been incorporated in a PVA–borax gel matrix. The gel-like nature of the samples has been confirmed through rheological measurements. UV–visible data reveal that gels containing two different rare-earth elements show frequencies of absorptions due to $4f$ electronic transitions from both the ion types.

FTIR data on the doped gels support the view that the rare-earth ions do not form an integral part of PVA chain structure but rather agglomerate separately. DSC measurements indicate the glass transition temperature in these rare-earth doped gels to be about 60 °C. Intermediate order structural studies by X-ray diffraction show features due to correlations in 2–6 Å as well as 15 Å regions of these gels.

SANS measurements show that doping with either neodymium and praseodymium ions does not alter the structure of the gels in the measured range of correlation lengths. The dopant ions are thus likely to form large clusters with correlations greater than about 400 Å. They would be detected at Q values lower than the minimum of the instrument.

When the gels are excited in the UV at 220 nm, emission spectra in the visible are observed which display absorption features of UV–vis spectra superimposed on the emission bands. Emissions in the 800–900 nm range result from excitations at the various absorption peaks of the visible

wavelength range. Thus, initial UV excitation at 220 nm ultimately results in near IR emissions. The maximum of the emission band due to Pr appears to be increased when the second rare-earth ion viz. Nd is present in the gel. The possibility of spectrally shaping these bands thus exists through the choice of rare-earth types and their relative proportions.

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