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Structure and radiative properties of aluminophosphate glasses

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The structure and radiative properties of aluminophosphate glasses in the system $K_2O–Al_2O_3–P_2O_5$ and $BaO–Al_2O_3–P_2O_5$ were investigated. The structural changes in glasses with the addition of alumina were investigated by using FTIR spectroscopy and NMR spectroscopy. In the case of the $K_2O–Al_2O_3–P_2O_5$ glasses, the aluminium atoms were mainly octahedrally coordinated and acted as network modifiers. The decrease in the spontaneous emission rate of $K_2O–Al_2O_3–P_2O_5$ glasses was due to the tightening of chains in terms of the addition of alumina to the glasses. The increase in effective linewidth was probably due to the increase of end groups in the glasses. In the case of $BaO–Al_2O_3–P_2O_5$ glasses, the addition of alumina had little effect on the radiative properties, probably due to the small structural change which occurred on its addition.

1. Introduction

Phosphate glasses have been of interest because of their application in the high power Nd: glass laser system [1–3]. In recent years, the development of high average power solid state laser has encouraged research into the development of a new active medium with higher laser performance and good thermomechanical properties, which are required for increasing the power and the repetition rate [4, 5]. However, in general, phosphate glasses have low thermomechanical properties compared with silicate glasses.

In order to improve the thermomechanical properties of phosphate glasses, several types of new laser glasses have been investigated [6–8]. Aluminophosphate glasses were investigated as one of the candidate materials as they seemed to meet the required thermomechanical properties [7]. However, the role of aluminium atoms in phosphate glasses in terms of the relation between radiative properties and the glass structure has not been studied in detail. It is important to understand the role of aluminium atoms in the phosphate glass structure because the radiative properties of glasses are closely related to their structure [9].

There have been several research projects on the structural role of aluminium atoms in phosphate glasses. Tallant and Nelson [10] studied the structure of $NaPO_3$ glass with the addition of Al_2O_3 by Raman spectroscopy. They suggested that the aluminium atoms were mainly co-ordinated tetrahedrally when small amounts of alumina were present, but an increase in alumina content led to aluminium atoms being mainly octahedrally coordinated.

Brow *et al.* [11] studied the structure of $x\mathrm{Al_2O_3} - (1 - x)\mathrm{NaPO_3}$ glasses by NMR spectroscopy. They found that the aluminium atoms were mainly octahedrally coordinated in the glasses containing a small amount of alumina. However, the tetrahedrally coordinated Al^{3+} species became dominant as the alumina content was increased. Other studies by NMR spectroscopy showed similar results [12, 13]. This short perusal of the literature suggests that there are contradictory views on the role of aluminium atoms in phosphate glass structure. Therefore, the aim of this investigation was to study the effect of aluminium atoms in $K_2O–Al_2O_3–P_2O_5$ and $BaO–Al_2O_3–P_2O_5$ glasses in terms of the structure of the glasses and on the radiative properties of neodymium in the glasses.

2. Experimental procedure

The composition of the $K_2O–Al_2O_3–P_2O_5$ (K-series) and $BaO–Al_2O_3–P_2O_5$ (B-series) glasses prepared are listed in Table I. Alumina content was increased in both series, while the ratio of $P_2O_5:K_2O$ or $P_2O_5:BaO$ were kept constant at 4.0. For all glass compositions, Nd_2O_3 was added at 3 wt %.

Batches were made from K_2CO_3, $BaCO_3$, Al_2O_3, Nd_2O_3 and $NH_4H_2PO_4$. Each batch was calcined at 500 °C for 4 h and then melted at 1200 or 1300 °C, depending upon the glass compositions, for 1 h. After

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TABLE I Composition of K_2O–Al_2O_3–P_2O_5 (K-series) and BaO–Al_2O_3–P_2O_5 (B-series) glasses (mol %)

	K_2O	BaO	Al_2O_3	P_2O_5
K-series	18	–	10	72
	17	–	15	68
	16	–	20	64
B-series	–	18	10	72
	–	17	15	68
	–	16	20	64

melting, the glass melt was poured into the graphite mould and annealed at an appropriate temperature.

FTIR spectra of glasses were measured using Perkin-Elmer Model 1800 FTIR spectrometer. Powdered samples were mixed and pressed with KBr powders to form pellets which could be spectrally investigated using a KBr pellet method.

Absorption spectra from 450 to 950 nm were measured at room temperature. Emission spectra in the 1.05 μm region were obtained using the monochromator, and the effective linewidths were determined by integrating the fluorescence-line shape and dividing by the intensity at peak wavelength after calibrating the sensitivity of the detector. The spontaneous emission rate and the stimulated emission cross-section for the $^4F_{3/2}$–$^4I_{11/2}$ transition were calculated by the Judd–Ofelt model developed by Krupke [14].

The ^{27}Al NMR spectra were collected at 78.206 MHz at magnetic field strength, H_0, of 7.05 T using an AM 300 spectrometer (Bruker Co.). Spinning speeds were generally > 3 kHz; 5.0 μs pulses, which corresponded to 55° and 3.0 s recycle times were used. The chemical shifts were measured relative to an external standard of $AlCl_3$ solution for all glasses.

3. Results

3.1. FTIR spectra of glasses

Figs 1 and 2 show the FTIR spectra of the K- and B-series glasses, respectively. Four groups of stretching vibrations were mainly observed in both spectra. They were assigned to ν_{as}(OPO) at ca. 1280 cm^{-1}, ν_s(OPO) at 1090 cm^{-1}, ν_{as}(POP) at 1050–850 cm^{-1} and ν_s(POP) at ca. 770 cm^{-1} where ν_s and ν_{as} express the symmetry and asymmetry modes, respectively [15–17].

As shown in Fig. 1 and 2, there were several differences in the changes in the FTIR spectra in terms of the addition of alumina to the K- and B-series glasses.

For K-series glasses, the intensity of the vibrational mode at ca. 1090 cm^{-1} increased as the alumina content increased. The vibrational mode at ca. 1150 cm^{-1} also increased in intensity as the alumina content increased further; this band was assigned to the vibrational mode of end groups in phosphate glasses [15, 17]. Therefore, this increase in intensity indicated that the chain length decreased as the alumina content increased.

For B-series glasses, the spectra were generally similar to the FTIR spectra of metaphosphate glasses [15]. As the alumina content increased the band at ca. 1150 cm^{-1} increased in intensity. However, the intensity was less than that for K-series glasses; possibly indicating that the B-series glasses had longer chain lengths than the K-series glasses.

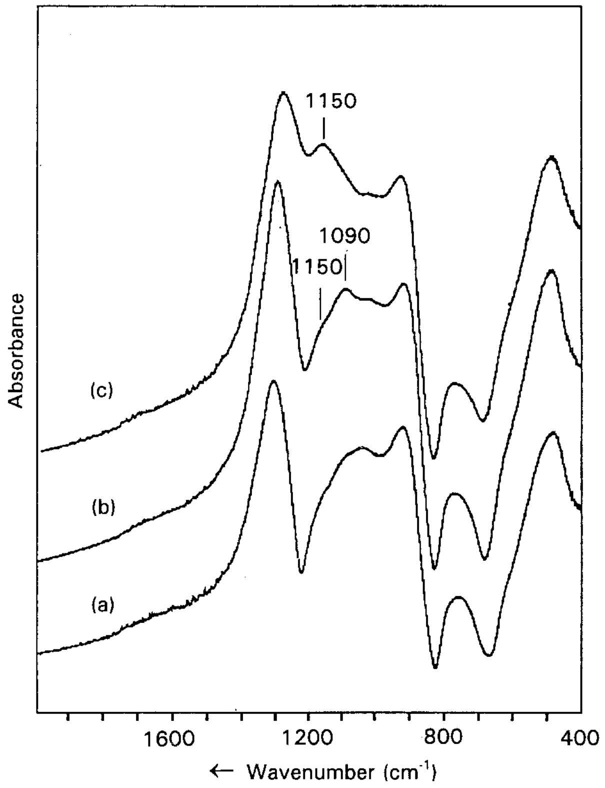

Figure 1 FTIR spectra of K-series glasses. (a) Al_2O_3 = 10 mol %; (b) Al_2O_3 = 15 mol %; (c) Al_2O_3 = 20 mol %.

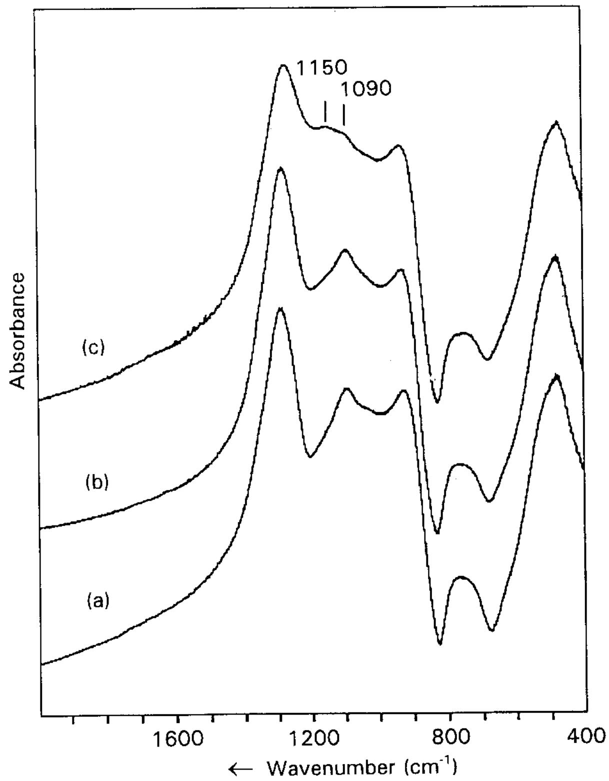

Figure 2 FTIR spectra of B-series glasses. (a) Al_2O_3 = 10 mol %; (b) Al_2O_3 = 15 mol %; (c) Al_2O_3 = 20 mol %.

3.2. NMR spectra

The ^{27}Al NMR spectra of K- and B-series glasses are shown in Figs 3 and 4, respectively. For both series, the peak at ca. -20 ppm appeared to be the dominant peak. This peak was assigned to $Al(OP)_6$ species in the glasses [11].

In the case of K-series glasses, the peak at ca. 18 ppm was assigned to $Al(OP)_5$ species. As the alumina content increased small peaks at ca. 5 and 30–40 ppm could be observed. These peaks were assigned to $Al(OAl)_6$ and $Al(OP)_4$ species, respectively [11].

For the B-series glasses, similar peaks were observed. However, the peak at ca. 5 ppm could be observed in glasses containing a low concentration of alumina, whereas it was observed only in glasses containing a high concentration of alumina in the K-series. The peak at ca. 30 ppm was higher in intensity than for K-series glasses.

3.3. Radiative property

The stimulated emission cross-section is expressed as

$$\sigma = \frac{\lambda^4}{8\pi c n^2 \Delta\lambda_{\mathrm{eff}}} A_{II'} \qquad (1)$$

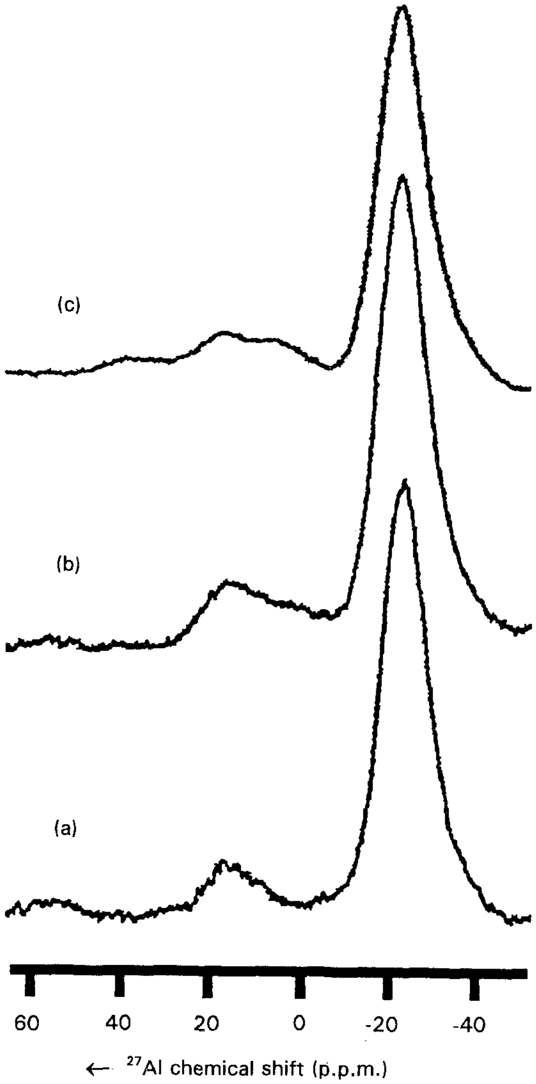

Figure 3 ^{27}Al MAS NMR spectra of K-series glasses. (a) $Al_2O_3 = 10$ mol %; (b) $Al_2O_3 = 15$ mol %; (c) $Al_2O_3 = 20$ mol %.

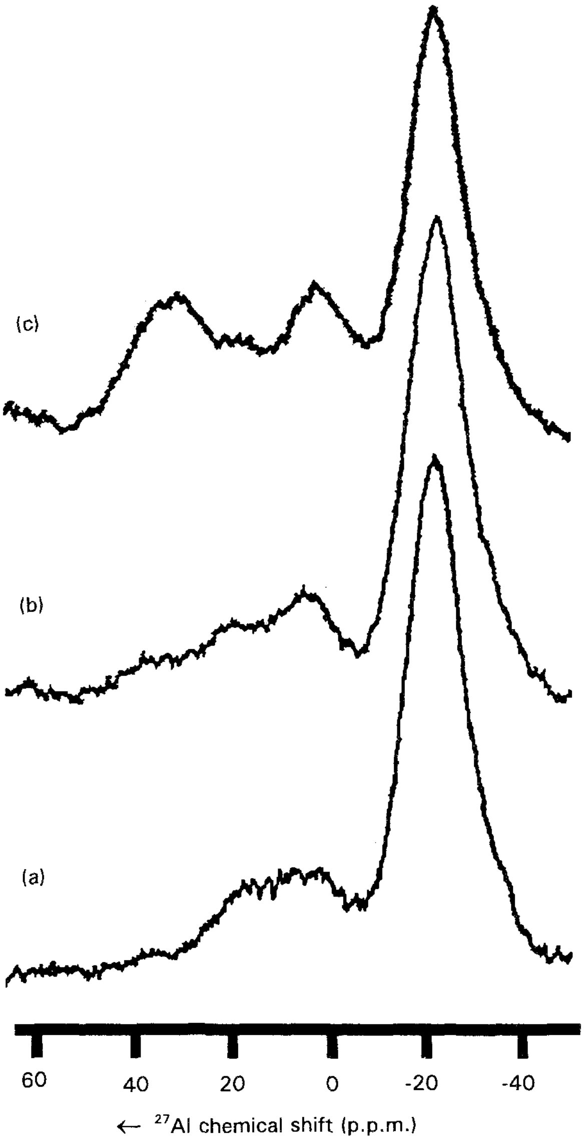

Figure 4 ^{27}Al MAS NMR spectra of B-series glasses. (a) $Al_2O_3 = 10$ mol %; (b) $Al_2O_3 = 15$ mol %; (c) $Al_2O_3 = 20$ mol %.

where λ is the mean wavelength of fluorescence, $\Delta\lambda_{\mathrm{eff}}$ is the effective linewidth of the fluorescence spectra, n is the refractive index of the glass and $A_{II'}$ is the spontaneous emission rate between two I, I' states [1].

The spontaneous emission rate from an initial J manifold to final J' manifold can be shown as follows:

$$A_{II'} = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} \frac{n(n^2+2)^2}{9} \times \sum_{\lambda=2,4,6} \Omega_\lambda |\langle (S,L)J \| U^{(\lambda)} \| (S',L')J' \rangle|^2 \qquad (2)$$

where Ω_2, Ω_4 and Ω_6 are the intensity parameters and $\langle \| U^{(\lambda)} \| \rangle$ is the doubly reduced matrix element of unit tensor operator [1].

Fig. 5 shows the stimulated emission cross-section for the K- and B-series of glasses. As shown in the figure, the stimulated emission cross-section of the K-series of glasses decreased as the alumina content increased. In the case of the B-series glasses, the stimulated emission cross-section was affected less than K-series glasses in terms of the addition of alumina.

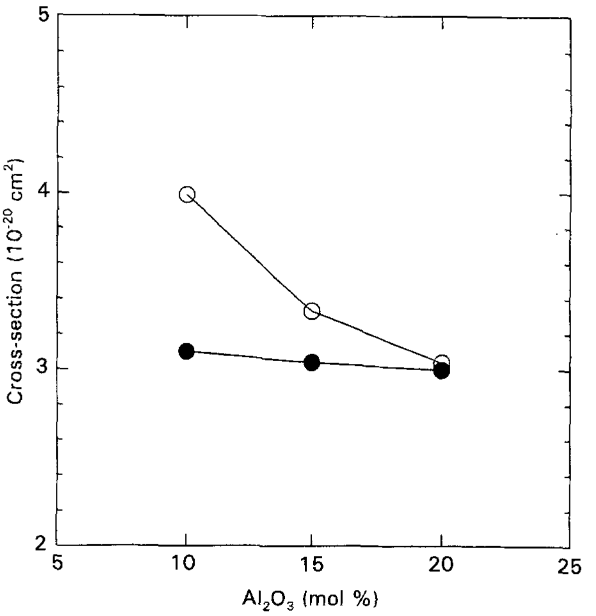

Figure 5 Stimulated emission cross-section of K- (○) and B-series (●) glasses.

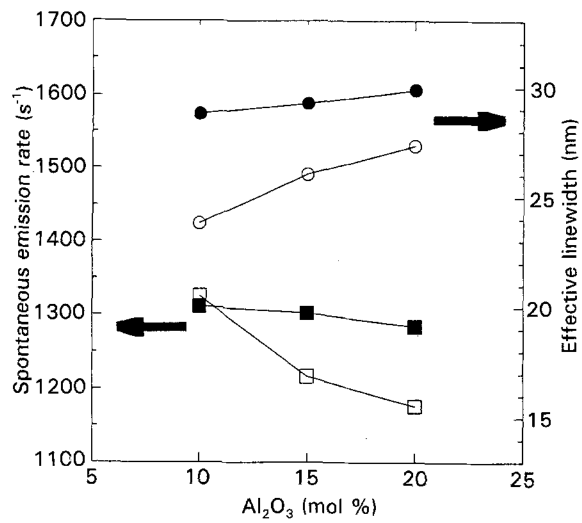

Figure 6 Spontaneous emission rate (□, ■) and effective linewidth (○, ●) of K- (□, ○) and B-series (■, ●) glasses, respectively.

Fig. 6 shows the spontaneous emission rate and effective linewidth of K- and B-series glasses. In the case of K-series of glasses, the spontaneous emission rate decreased and the effective linewidth increased, resulting in the decrease of the stimulated emission cross-section as the alumina content increased (see Equations 1 and 2). However, in the case of the B-series, those properties were affected less than in the K-series of glasses and, as a result, the stimulated emission cross-section was affected little in terms of the addition of alumina.

4. Discussion

4.1. FTIR and NMR spectra of glasses

The FTIR spectra of K- and B-series glasses are quite different, as shown in Figs 1 and 2. Firstly, the FTIR spectra of glasses containing 10 mol % of alumina differed markedly. The spectrum of a K-series glass containing 10 mol % alumina showed a similar spectrum to that of $AgO–2P_2O_5$ glass (reported by Bartholomew [5]), which may have shorter chain length with some cross-linking between chains compared to metaphosphate. As shown in the spectrum, the bands at ca. 1090 and 1150 cm^{-1}, which were assigned to the vibrational modes of ν_s(OPO) and the end groups, respectively, could be observed. In the case of a B-series glass containing 10 mol % alumina, the spectrum was rather similar to that of metaphosphate glasses [15]. Therefore, with 10 mol % of added alumina, it may be deduced that the K-series glass had a shorter chain length with some cross-linking between chains compared with the B-series glass.

The spectral changes with the increase of alumina in the glasses also showed some differences between the K- and B-series of glasses. In the case of the K-series, the number of end groups appeared to increase as the alumina content increased. In the case of the B-series of glasses, the number of end groups increased to a lesser extent than in the K-series of glasses. Also, in the case of the B-series of glasses the structure seemed to maintain a metaphosphate glass structure, whereas in the K-series the glass structure changed drastically with addition of alumina.

These differences of the spectral details of the K- and B-series of glasses may indicate the different structural role of aluminium atoms in the K- and B-series of glasses.

In the case of the K-series of glasses, the aluminium atoms appeared to be octahedrally coordinated and to act as network modifiers, as the number of end groups increased with the addition of alumina. Further, aluminium atoms in an octahedral oxygen environment are considered to be located at the interstitial phosphorous–oxygen framework [18].

The interpretation of the FTIR spectra of the K-series of glasses could be confirmed by the NMR spectra. The ^{27}Al NMR spectra of the K-series of glasses are shown in Fig. 3. It can be seen that the primary Al species in the K-series was octahedrally coordinated, since the peak at ca. − 20 ppm was dominant in the spectra. When the content of alumina was increased, the peaks which were assigned to $Al(OP)_4$ and $Al(OAl)_6$, respectively, were observed. However, the intensity of the peaks were very small. Therefore, the analyses of FTIR and NMR spectra of the K-series of glasses indicated that Al species were mainly octahedrally coordinated and acted as network modifiers.

In the case of the B-series of glasses, some of the aluminium atoms may not have acted as network modifiers, as the intensity of the vibrational mode of end groups was not increased as much as in the case of the K-series of glasses (see Fig. 2). There may be two possible explanations for this spectral difference. One is that some of the alumina in B-series glasses may not have been incorporated into the glasses and did not, therefore, form Al–O–P bonds, having little effect on the structure of the B-series glasses. The other is that some of the alumina may have been incorporated in the glass structure as network formers, so that the addition of alumina did not create as many end groups as in the K-series of glasses. According to the ^{27}Al NMR spectra (shown in Fig. 4) both explanations seem to be valid. As shown in Fig. 4, the Al species in the B-series of glasses were mainly octahedrally coordinated, as in the K-series. However, there were several differences in the NMR spectra of the K- and B-series of glasses. First of all, as shown in Fig. 4, the $Al(OAl)_6$ species were formed even with 10 mol % of alumina in the B-series; as the alumina content increased the peak at ca. 5 ppm showed a much greater intensity than in the K-series. This indicated that the aluminium atoms may not have formed as many Al–O–P bonds in the B-series glass structure as in the K-series one. Therefore, the addition of alumina may not have affected the structure of the B-series glasses as shown in the FTIR spectra.

Secondly, more $Al(OP)_4$ species seemed to be present in the B- than in the K-series of glasses when the alumina content was 20 mol % (see Figs 3 and 4). In other words, the aluminium atoms preferred to be tetrahedrally coordinated in the B-series, and therefore, the addition of alumina did not increase the number of end groups in K-series as much as in the B-series of glasses, as shown by the FTIR spectra.

From the analyses of FTIR and NMR spectra of K- and B-series glasses, the incorporation of aluminium atoms and the structural role of aluminium atoms in phosphate glass structure may be different in glasses containing different modifier ions. In other words, aluminium atoms seemed to be octahedrally coordinated and well incorporated in the K-series of glasses, while they appeared to be incorporated to such a great extent in the B-series of glasses, preferring to form $Al(OAl)_6$ species even with a small alumina content, forming more $Al(OP)_4$ species as the amount of alumina increased.

4.2. Radiative properties and structure of glasses

The radiative properties of rare earth ions in glasses can be related to the structure of the glasses. It has been suggested by Izumitani *et al.* [9] that the effective linewidth and the spontaneous emission rate may be closely related to the structure of the glass. Izumitani *et al.* [9] and Dymnikov *et al.* [19] suggested that the effective linewidth could be related to the uniformity of the ensemble of neodymium centres. They also suggested that the effective linewidth increased with the increase of alkali content in glasses probably because the uniformity of the ensemble of neodymium centres decreased as the non-bridging oxygens, especially terminal groups, were increased. Izumitani *et al.* [9] also suggested that, in the case of phosphate glasses, the spontaneous emission rate may mainly be related to the asymmetry in the ligand field. They argued that the cage surrounding Nd^{3+} could easily be deformed in phosphate glasses and that the degree of symmetry in the ligand field could become considerably low compared with the silicate glasses, resulting in the larger intensity parameter and the spontaneous emission rate in phosphate glasses compared to the silicate glasses. With increasing field strength of modifying ions and the amount of modifying ions in phosphate glasses, they suggested that the asymmetry decreased due to the tightening of the chain structure in the phosphate glasses and, as a result, the intensity parameter and spontaneous emission rate decreased.

The decrease in the spontaneous emission rate of the K-series of glasses with the addition of alumina (see Fig. 6) can be explained by using the arguments suggested above. As shown in FTIR and NMR spectra of the K-series of glasses, the aluminium atoms were mainly octahedrally coordinated and acted as network modifiers in the interstitial phosphorous–oxygen framework. Therefore, the decrease in the spontaneous emission rate might have been due to the tightening of the chains with the addition of alumina to the glasses.

In the case of the B-series of glasses, the spontaneous emission rate changed to a lesser extent as the alumina content increased. As shown in the FTIR and NMR spectra, aluminium atoms were not incorporated as network modifiers in the B-series of glasses as much as in the K-series of glasses, which may have had less effect on the tightening of the chain structure. Also, more aluminium atoms seemed to be tetrahedrally coordinated in the B-series than in the K-series, which may again have had less effect on the tightening of chains in the glasses. Therefore, the addition of alumina seemed to have less effect on the changes of spontaneous emission rate in the B-series of glasses.

The increase of effective linewidth in the K-series of glasses with the addition of alumina may also be explained by Izumitani *et al.* [9] and Dymnikov *et al.* [19] suggestion. The uniformity of the ensemble of neodymium centres in phosphate glasses may have been decreased by the increase in end groups in the phosphate chain structure. As shown in the FTIR spectra of the K-series of glasses, the end groups increased sharply with the addition of alumina. Therefore, the increase in end groups in the phosphate chain structure may have been the main reason for the increase in the effective linewidth in the K-series of glasses.

In the case of the B-series glasses, the effective linewidth changed less with the addition of alumina compared with the K-series of glasses. As shown in the FTIR spectra, the end groups in the phosphate chain structure increased to a lesser extent in the B-series of glasses as the alumina content was increased. Therefore, the effective linewidth may have changed less due to the small increase in end groups in the glass structure than to the small change in structure with the addition of alumina in the B-series glasses.

5. Conclusions

The radiative properties and the structure of glasses seemed to be closely related to each other. The structural changes with the addition of alumina in glasses were different for the glasses containing different network modifiers. The alumina seemed to be well incorporated in K_2O–Al_2O_3–P_2O_5 glasses and the aluminium atoms seemed to be mainly octahedrally coordinated. In the case of $BaO-Al_2O_3-P_2O_5$ glasses, the addition of alumina had less effect on the formation of end groups in the glasses, due to the formation of $Al(OAl)_6$ and $Al(OP)_4$. The change in the spontaneous emission rate and the change of the effective linewidth could be explained by the effect of the addition of alumina on the structural changes in the glasses. In the case of the K-series of glasses, the aluminium atoms seemed to "tighten" the chain structure so that the spontaneous emission rate decreased. Also, the increase in end groups in the K-series glass structure with the addition of alumina may have been the main reason for the increase in effective linewidth. The radiative properties of the B-series of glasses were affected less by the addition of alumina than the K-series of glasses because the alumina was incorporated to a lesser extent in B-series and therefore had less effect on structural changes than in the K-series of glasses.

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