Advanced Glass Science
(4016101)

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GLASS-LAB@NPRU

Course Outline:

Week 10: Glass composition, structures and applications (1)

- Boric Glass
- Alkali Boric Glass
- *Case studies from international publications*

Book:
A.K., Varshneya. ***Fundamentals of inorganic glasses***
A., Paul A, ***Chemistry of glasses***
J.E. Shelby, ***Introduction to glass science and technology***

Boric Glass or Borate Glass

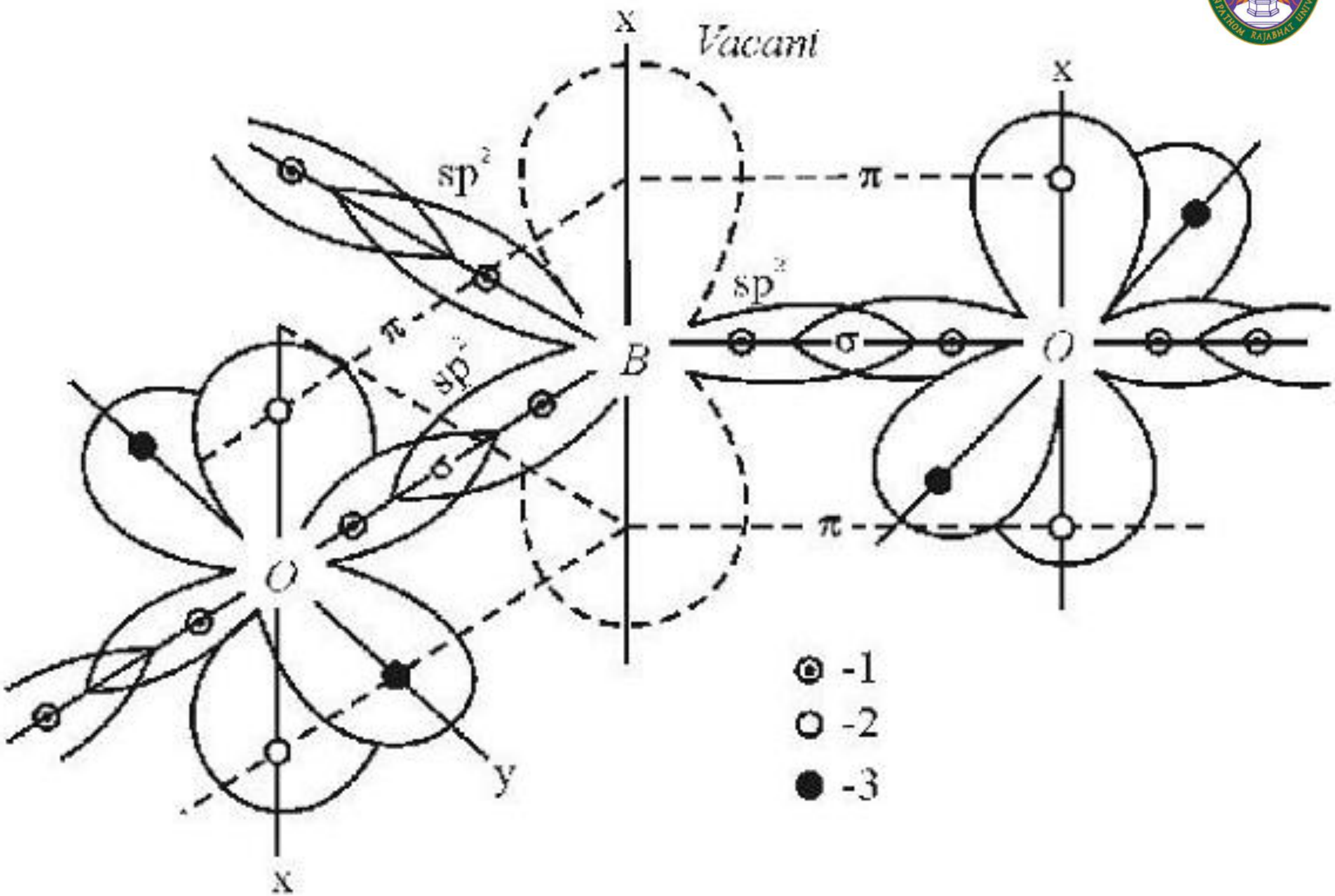


Fig. 1 The superposition of orbitals in B_2O_3: (1) σ-electrons (2) π-electrons (3) lone pair electrons

Structure of Borate glasses

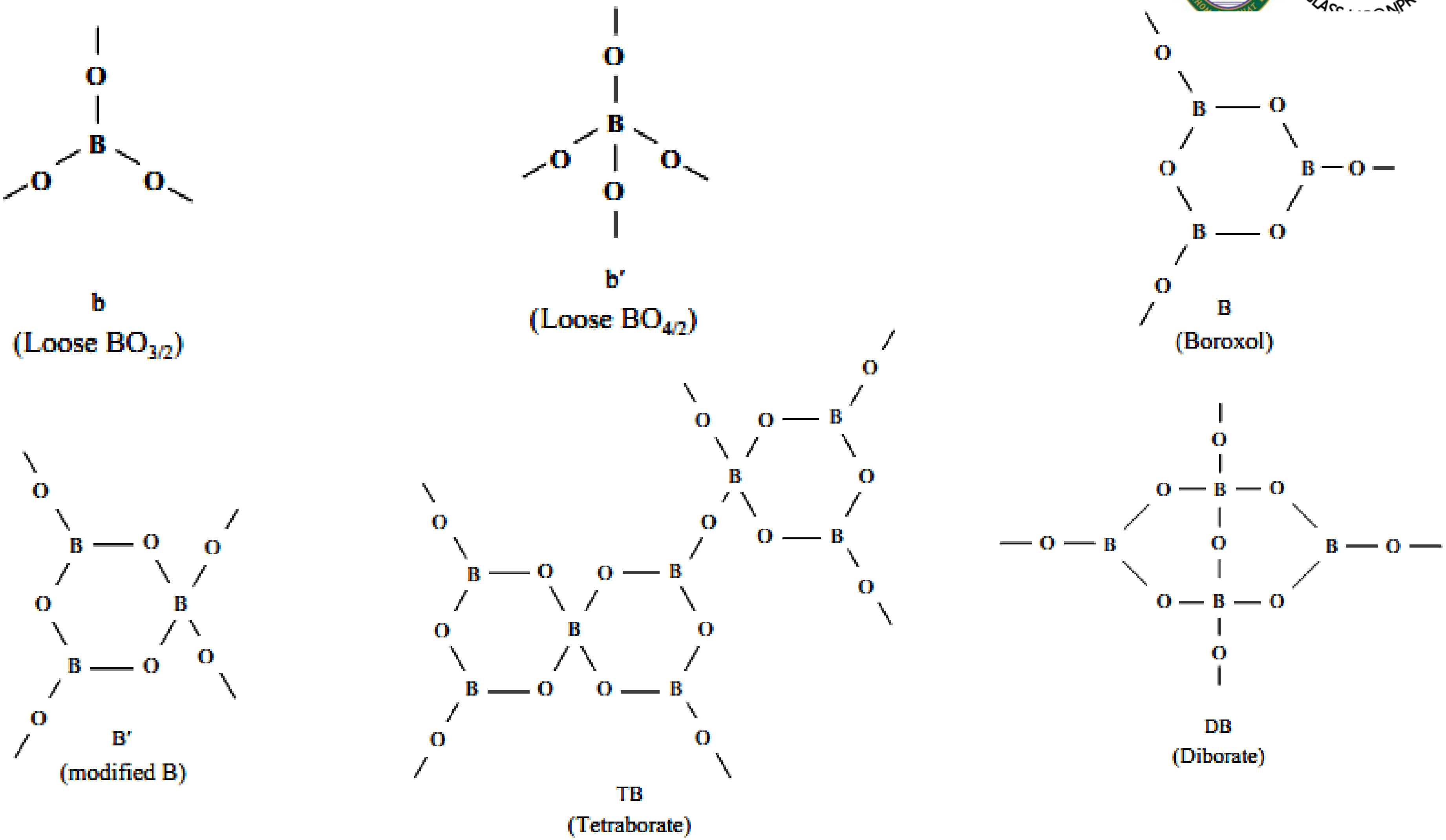
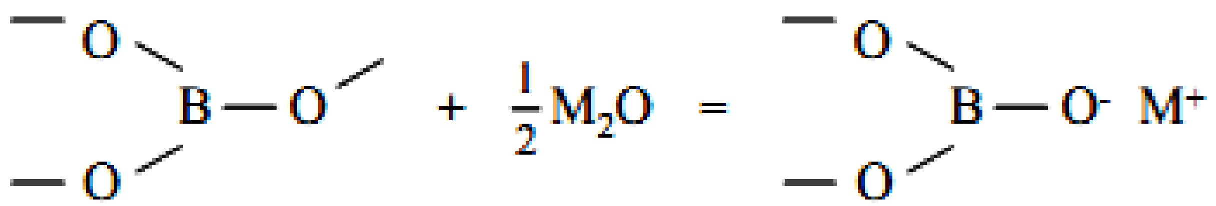


Fig. 2 Different structural units present in alkali borate glasses

Alkali Borate Glasses

(a) Create a nonbridging oxygen (NBO), as in the silicate glasses, by forming $BO_{2/2}O^{-}M^{+}$. (The " / 2" subscript is denoted for the connection between a bridging oxygen and two borate ion.



(b) Convert boron from a 3 - coordination state ("B_3 state") to a 4 - coodination state ("B_4 state"). Tetrahedral borate, B_4 is commonly found in alkali and alkali earth borate glass.

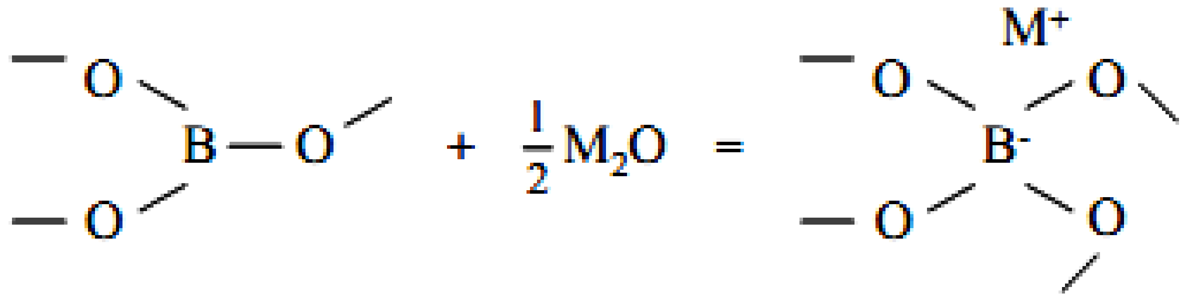


Fig. 3 (a) Creation of NBO when introduction of modifier to borate glass
(b) Structure change from B3 to B4 introduction of modifier to borate glass

Alkali Borate Glasses

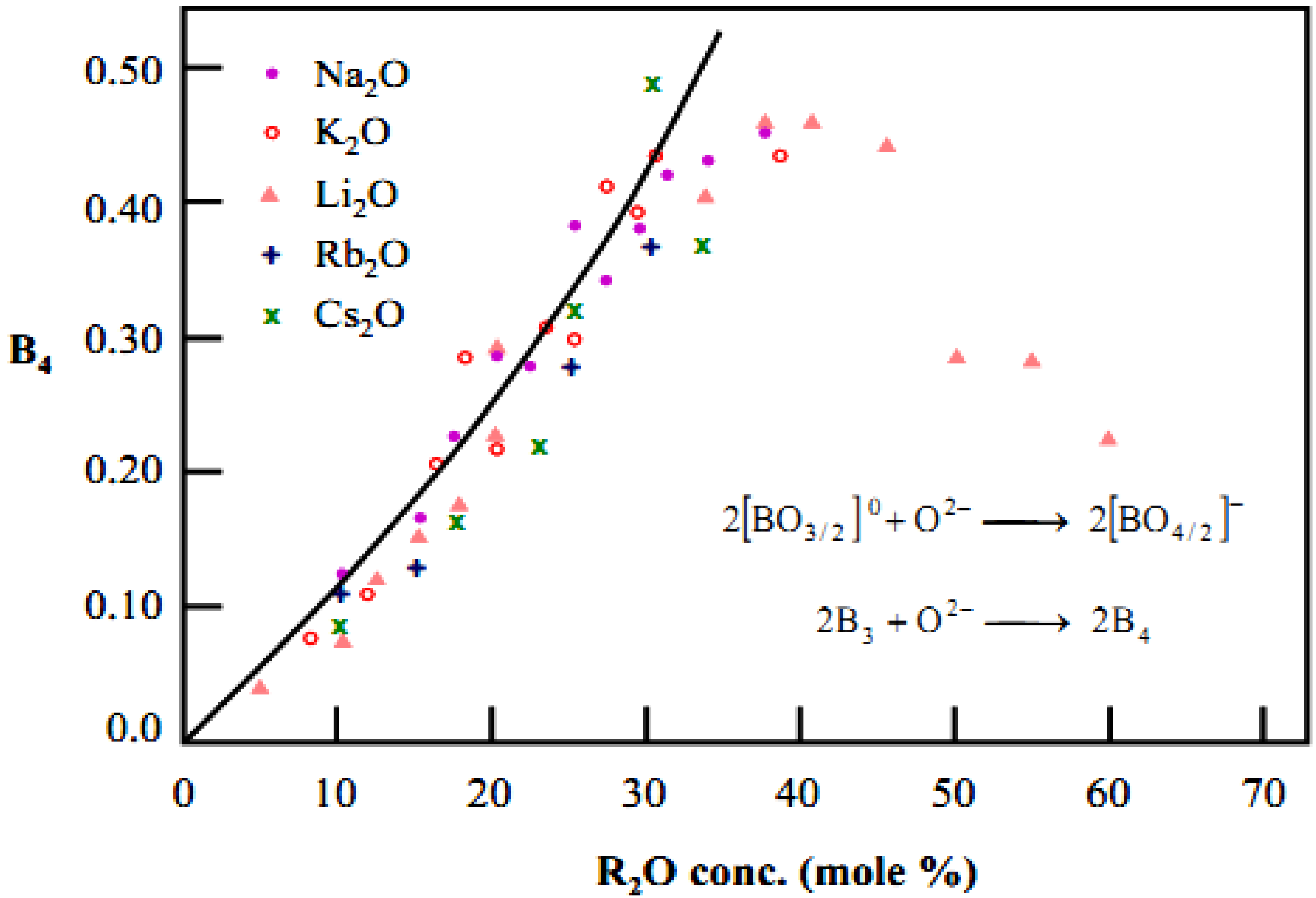


Fig. 4 Variation of B_4 with R_2O concentration

Alkali Borate Glasses

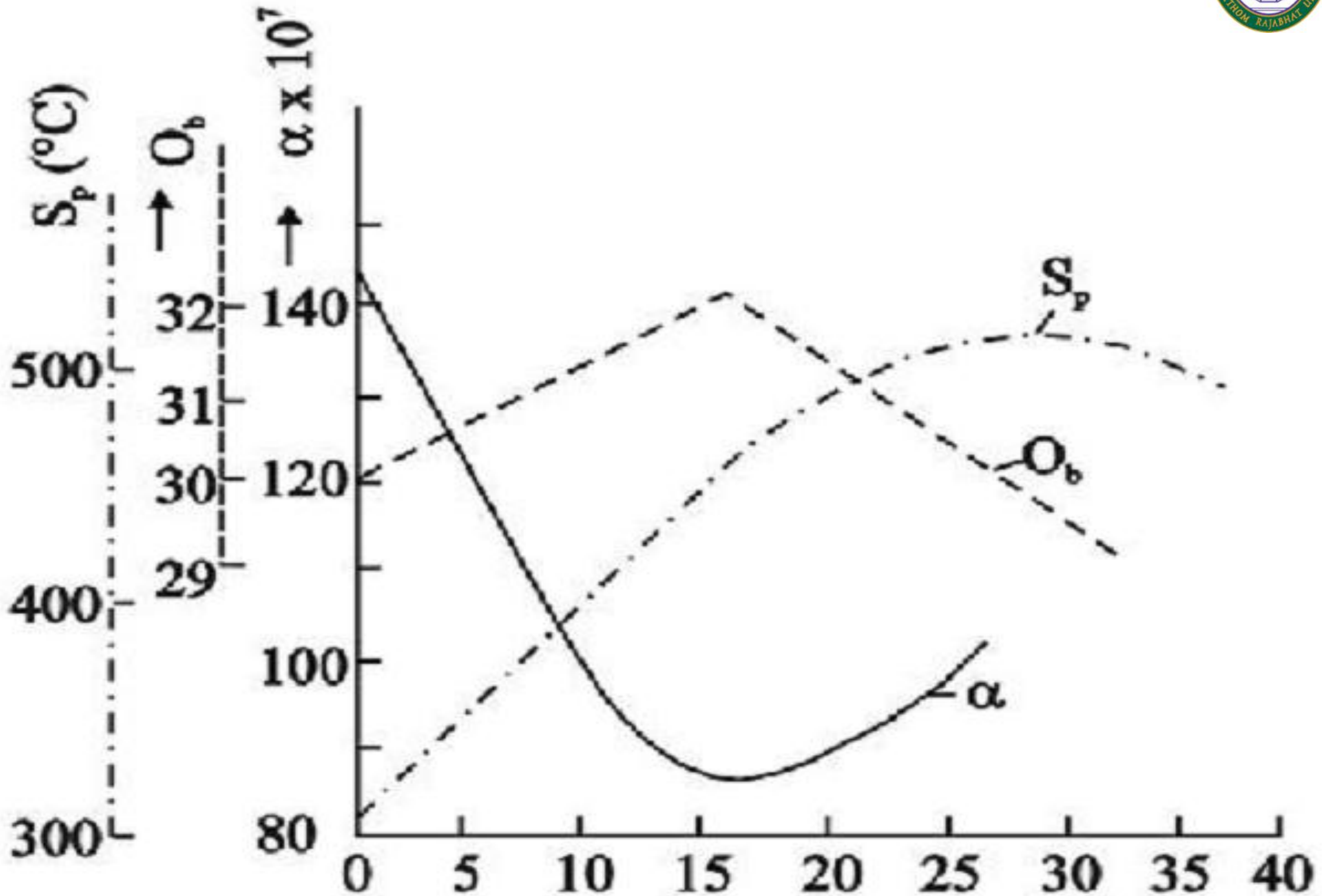


Fig. 5 Variation in the number of bridging oxygen atoms (O_b), the coefficient of thermal expansion (αT) and the softening temperature (S_p) as a function of alkali-oxide concentration in a B_2O_3-containing binary glass

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Coordination and valence state of transition metal ions in alkali-borate glasses

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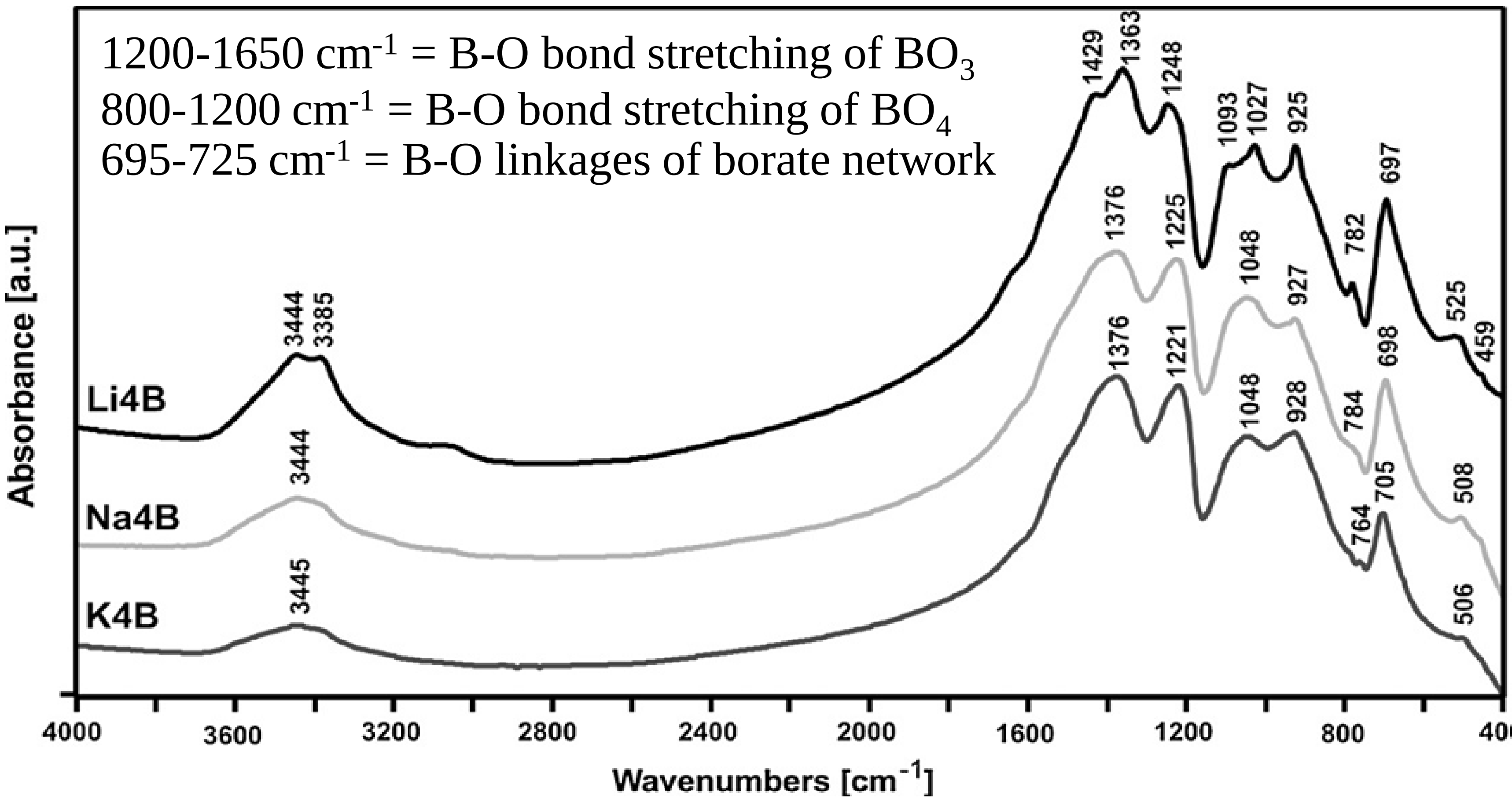

Fig. 6 FTIR spectra of base alkali-borate glasses modified with Li, Na and K oxides. Recorded at room temperature.

Table. 1 Band positions (mmax) in the absorption spectra and optical basicity of the alkali-borate glasses doped with cobalt ions in octahedral and tetrahedral coordination spheres.

Oxide modifier R_2O	Optical basicity, Λ_{cal}	Band position (Co^{2+}), ν (cm^{-1})		
		Octahedral	Tetrahedral	
		$\nu_1 = \nu_2 = {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	$\nu_3 = {}^4A_2(F) \rightarrow {}^4T_1(P)$	Molar extinction coefficient, ε
Li_2O	0426	19 960 17 889 (501 nm) (559 nm)	–	28,421[a]
Na_2O	0427	19 960 17 986 (501 nm) (556 nm)	–	20,016[a]
K_2O	0432	19 881 17 575 (503 nm) (569 nm)	15 748 (635 nm)	24,456[a]

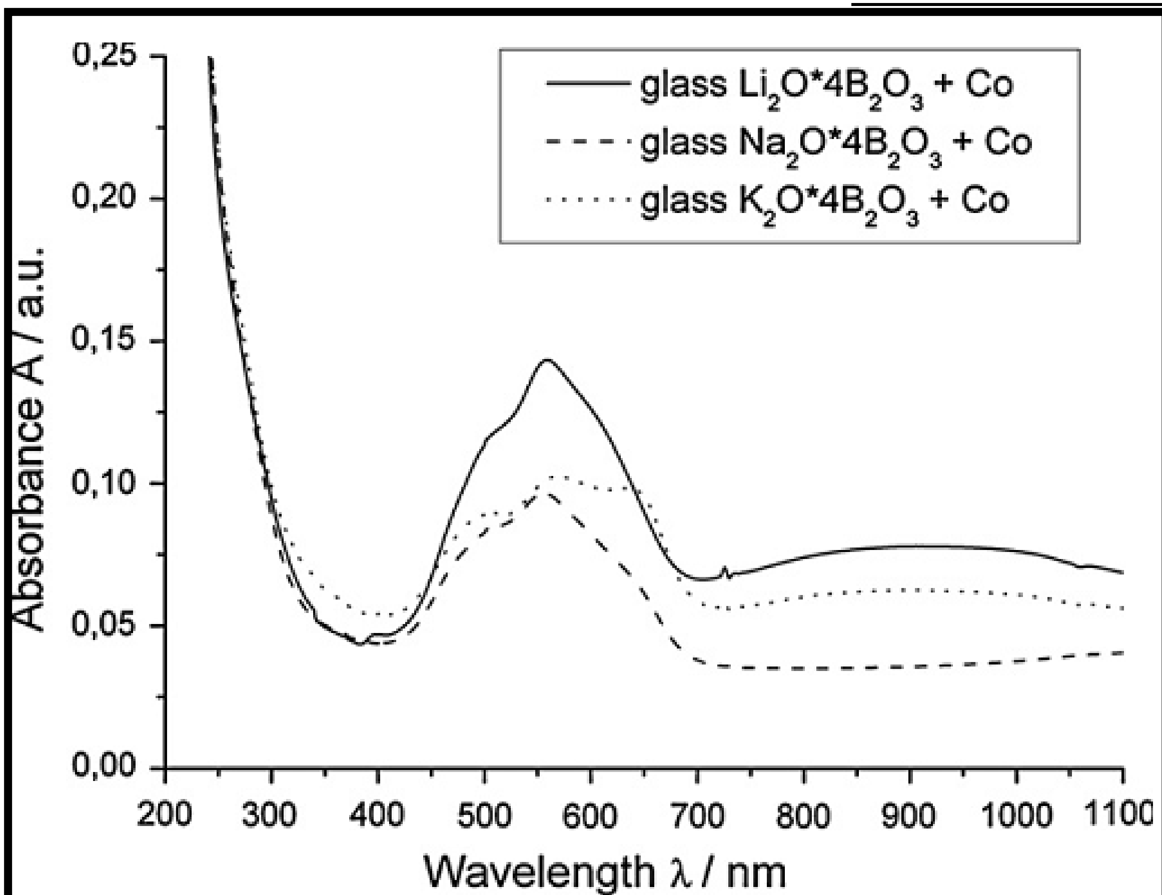

Fig. 7 Absorption spectra of the borate glasses modified with Li, Na or K oxides and doped with Co ions.

Table. 2 Band positions (mmax) in the absorption spectra and optical basicity of the alkali-borate glasses doped with Nikle ions in octahedral and tetrahedral coordination spheres.

Oxide modifier R_2O	Optical basicity, Λ_{cal}	Band position (Ni^{2+}, octahedral), ν_{max} (cm^{-1})		
		$\nu_1 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	$\nu_2 = {}^3A_{2g}(F) \rightarrow {}^1E_g(D)$ ca. 755 nm	Molar extinction coefficient, ε
Li_2O	0.426	24,039 (416 nm)	Shoulder	11,821[a]
Na_2O	0.427	24,213 (413 nm)	Shoulder	12,183[a]
K_2O	0.432	24,156 (414 nm)	Shoulder	12,013[a]

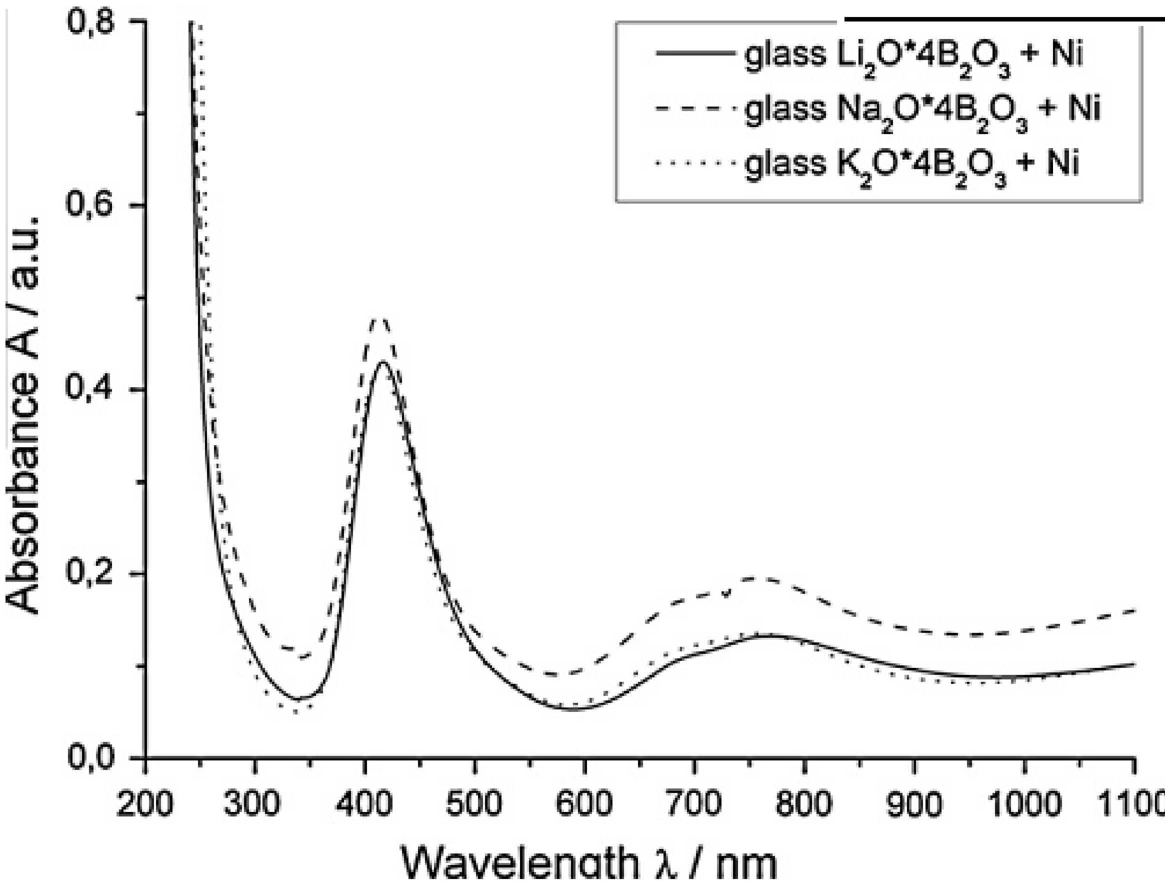

Fig. 8 Absorption spectra of the borate glasses modified with Li, Na or K oxides and doped with Ni ions.

Table. 3 Band positions (mmax) in the absorption spectra and optical basicity of the alkali-borate glasses doped with chromium ions in octahedral and tetrahedral coordination spheres.

Oxide modifier R_2O	Optical basicity, Λ_{cal}	Band position (Cr^{3+}, octahedral), ν_{max} (cm^{-1})	
		$\nu_1 = {}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$	Molar extinction coefficient, ε
Li_2O	0.426	16,234 (616 nm)	8329[a]
Na_2O	0.427	16,234 (616 nm)	6166[a]
K_2O	0.432	16,313 (613 nm)	4351[a]

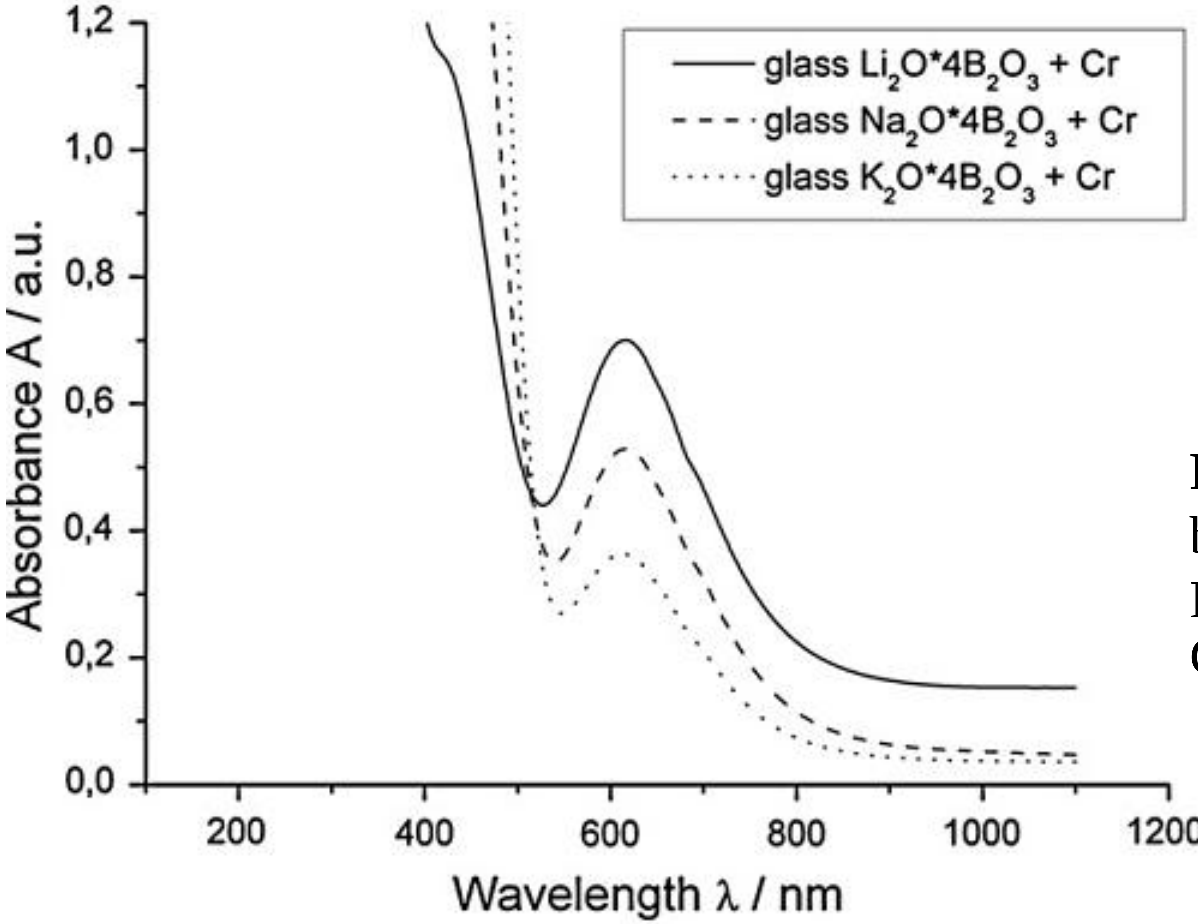

Fig. 9 Absorption spectra of the borate glasses modified with Li, Na or K oxides and doped with Cr ions.

Table. 4 Band positions (mmax) in the absorption spectra and optical basicity of the alkali-borate glasses doped with manganese ions in octahedral and tetrahedral coordination spheres.

Oxide modifier R_2O	Optical basicity, Λ_{cal}	Band position of Mn ions, ν_{max} (cm^{-1})	
			Molar extinction coefficient, ε
Li_2O	0.426	21,322 (469 nm)	8752[a]
Na_2O	0.427	21,186 (472 nm)	12,883[a]
K_2O	0.432	21,008 (476 nm)	29,452[a]

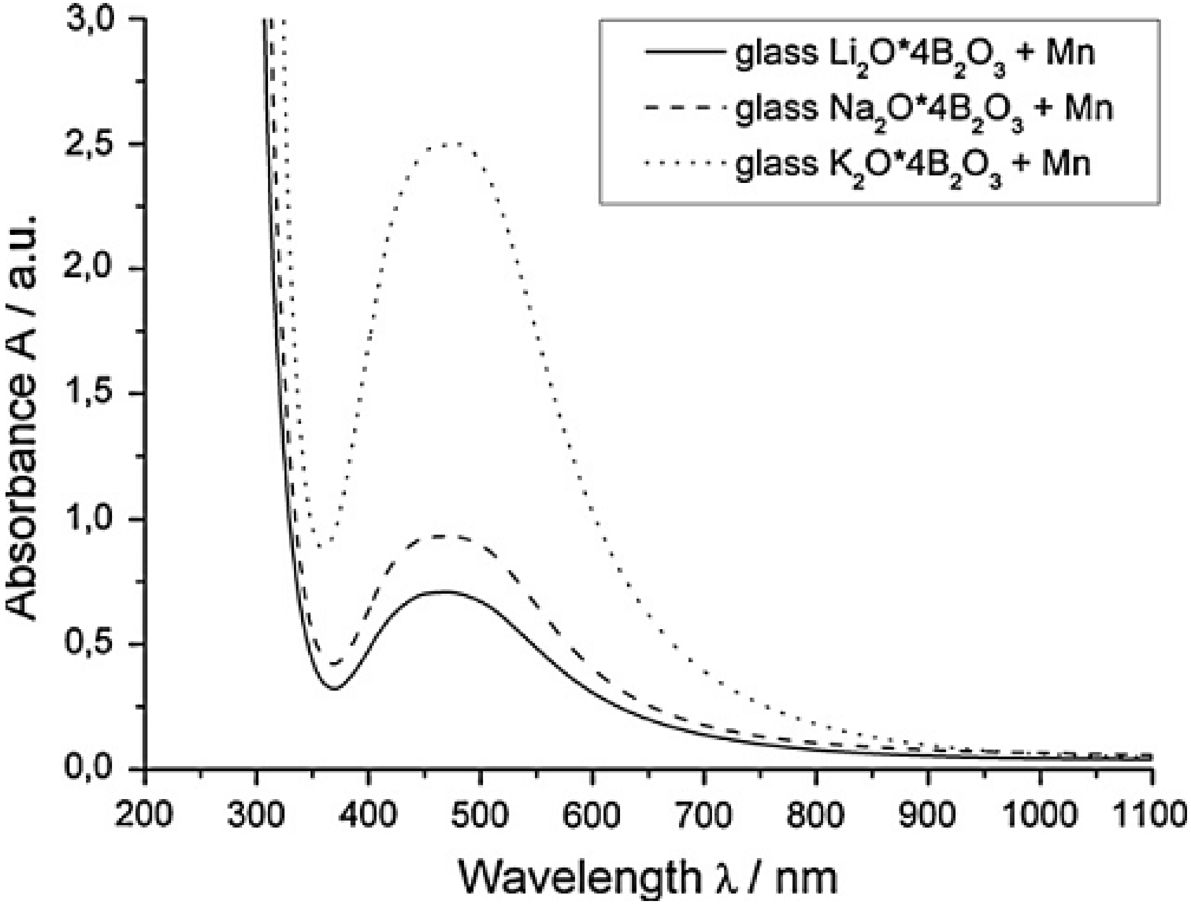

Fig. 10 Absorption spectra of the borate glasses modified with Li, Na or K oxides and doped with Mn ions.

Structure and properties of alkaline earth borate glasses

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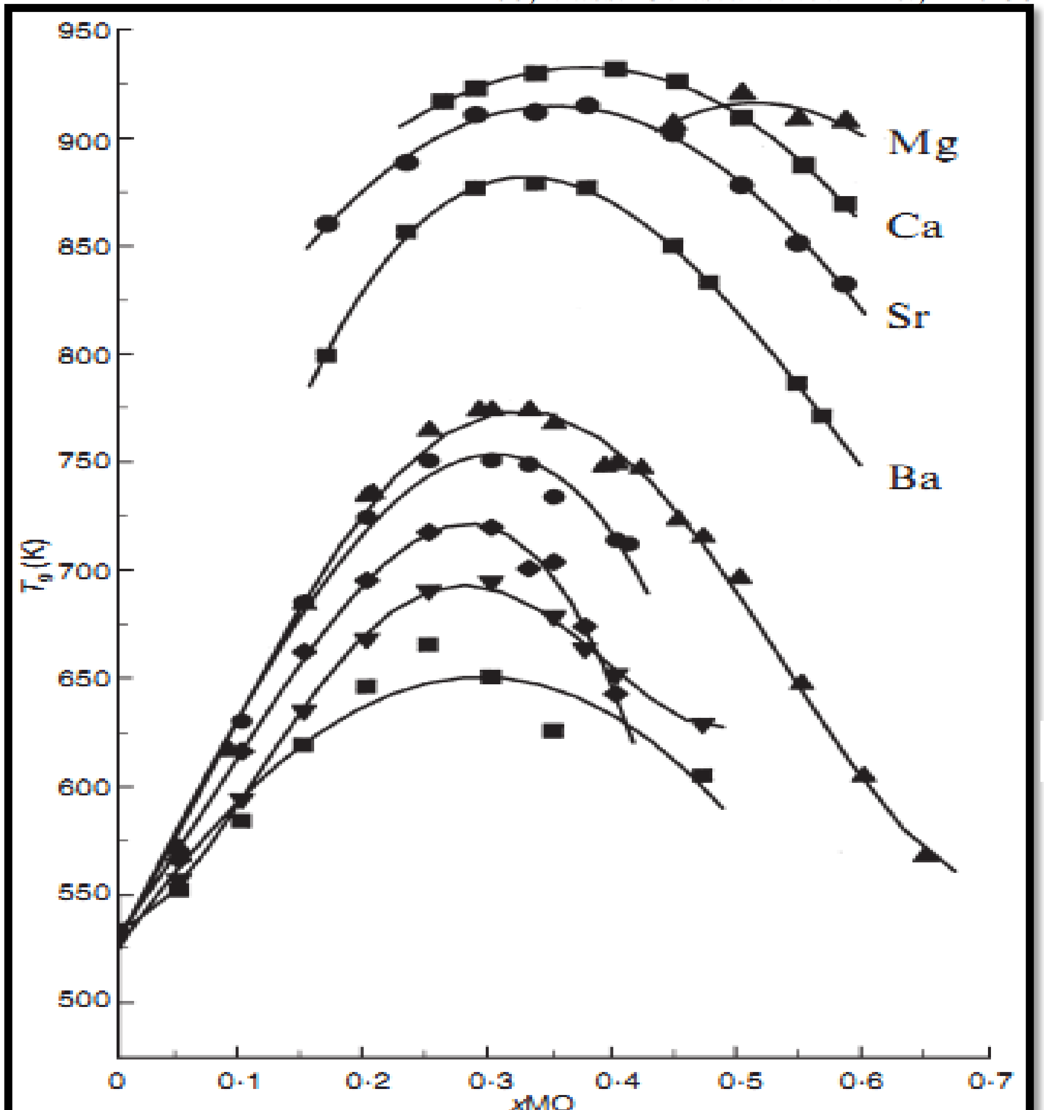

Fig. 11 Glass transition temperature, Tg, as a function of metal oxide content in borate glasses, $xMO(1-x)B_2O_3$. Tg data for alkali borate glasses (M= Li_2 to Cs_2)

▲ Li_2 ● Na_2 ◆ K_2 ▼ Rb_2 ■ Cs_2

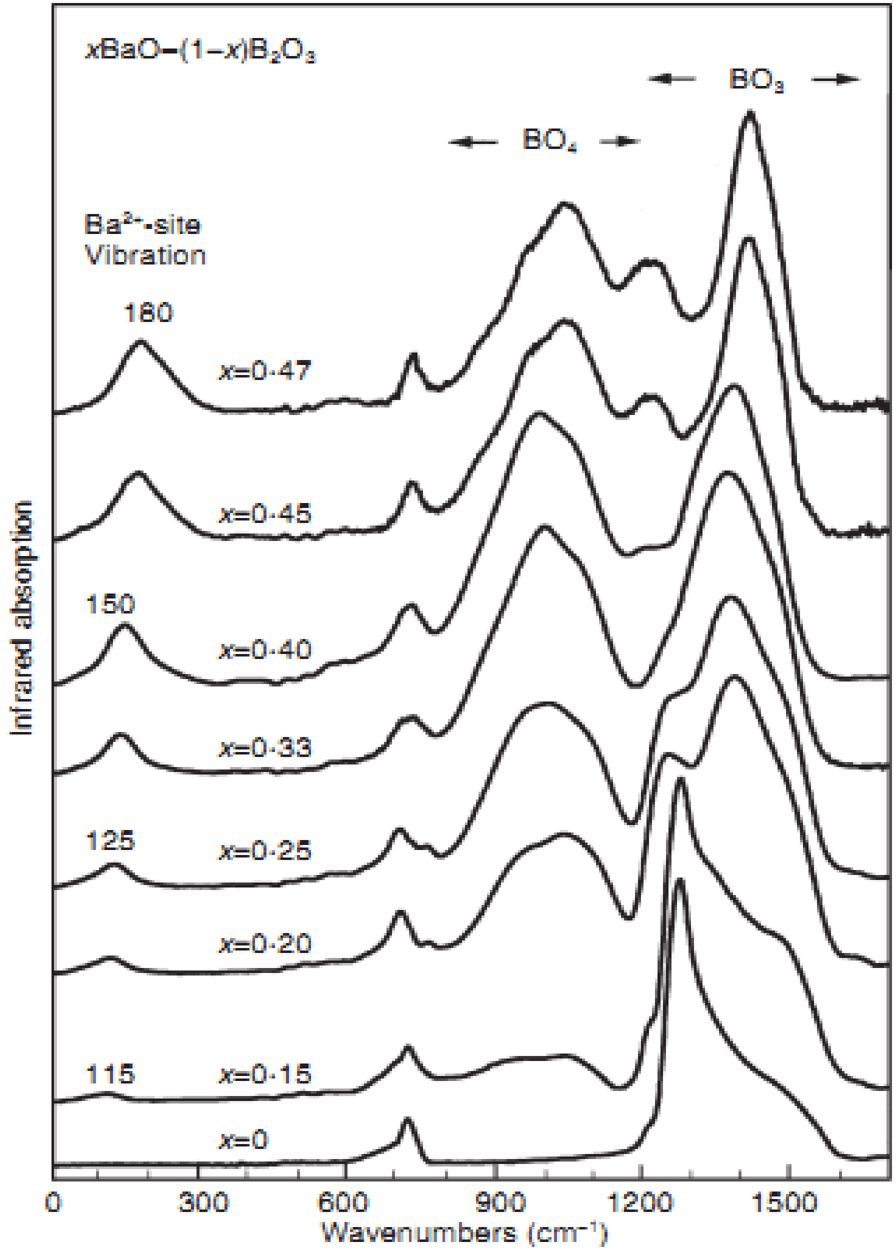

Fig. 12 Infrared absorption spectra of $xBaO.(1-x)B_2O_3$ glasses

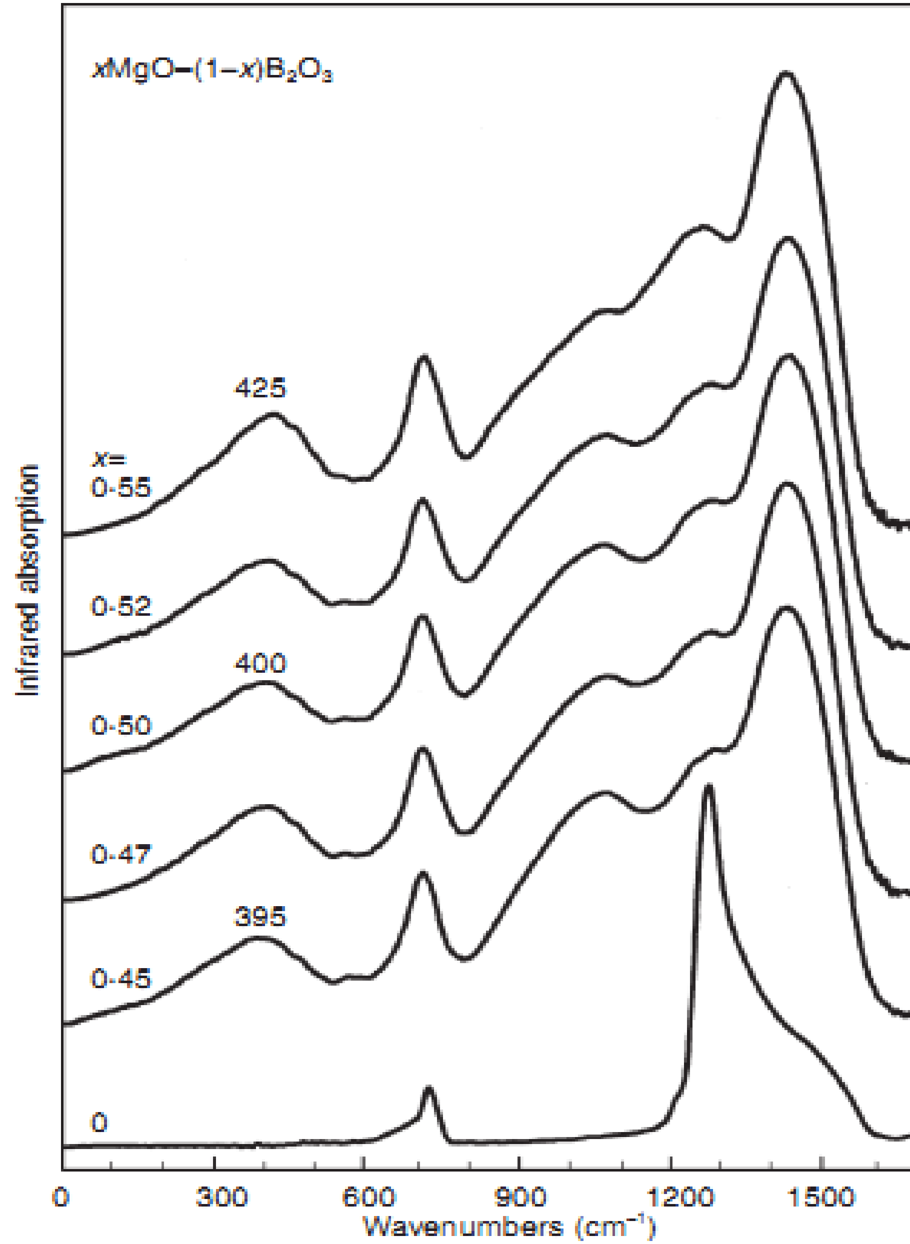

Fig. 13 Infrared absorption spectra of $xMgO.(1-x)B_2O_3$ glasses

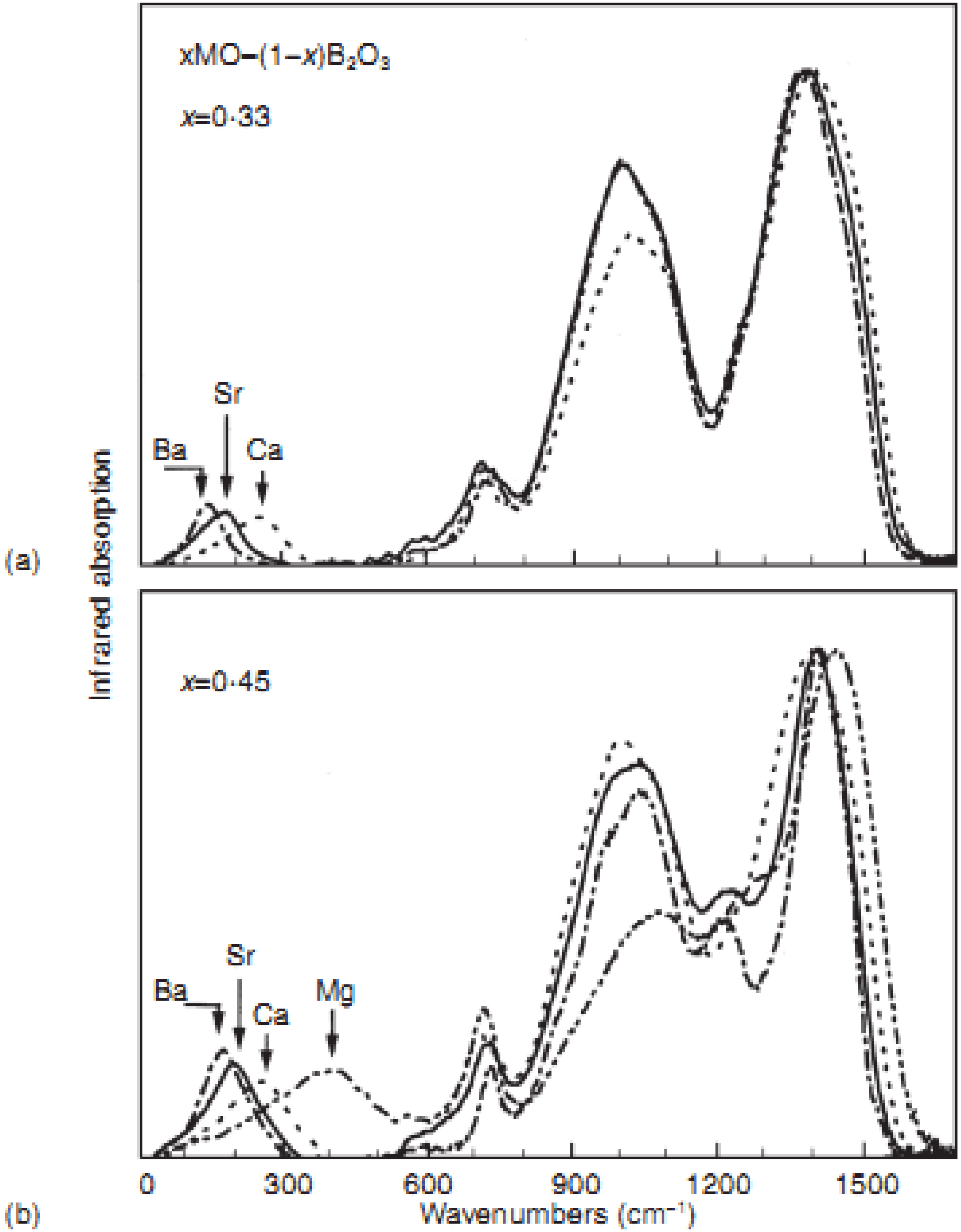

Fig. 14 Comparison of the infrared spectra of alkaline earth borate glasses, $xMO.(1\text{-}x)B_2O_3$, with (a) $x=0{\cdot}33$ and (b) $x=0{\cdot}45$

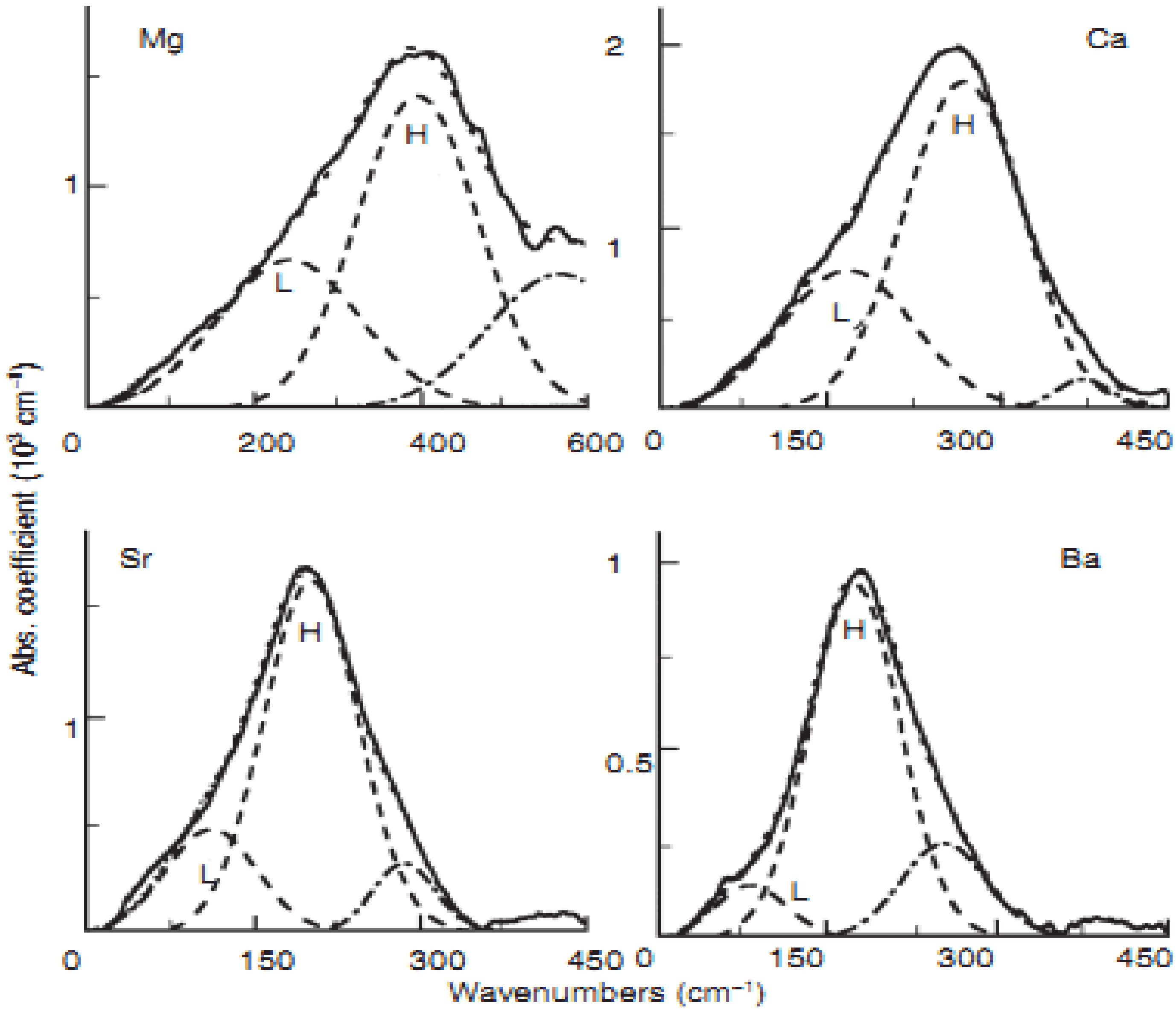

Fig. 15 Deconvoluted far infrared profiles of 0·45MO. 0·55B_2O_3 glasses (M=Mg, Ca, Sr, Ba). Experimental spectra are shown by continuous lines, Gaussian component bands by dashed lines and simulated spectra by dotted lines

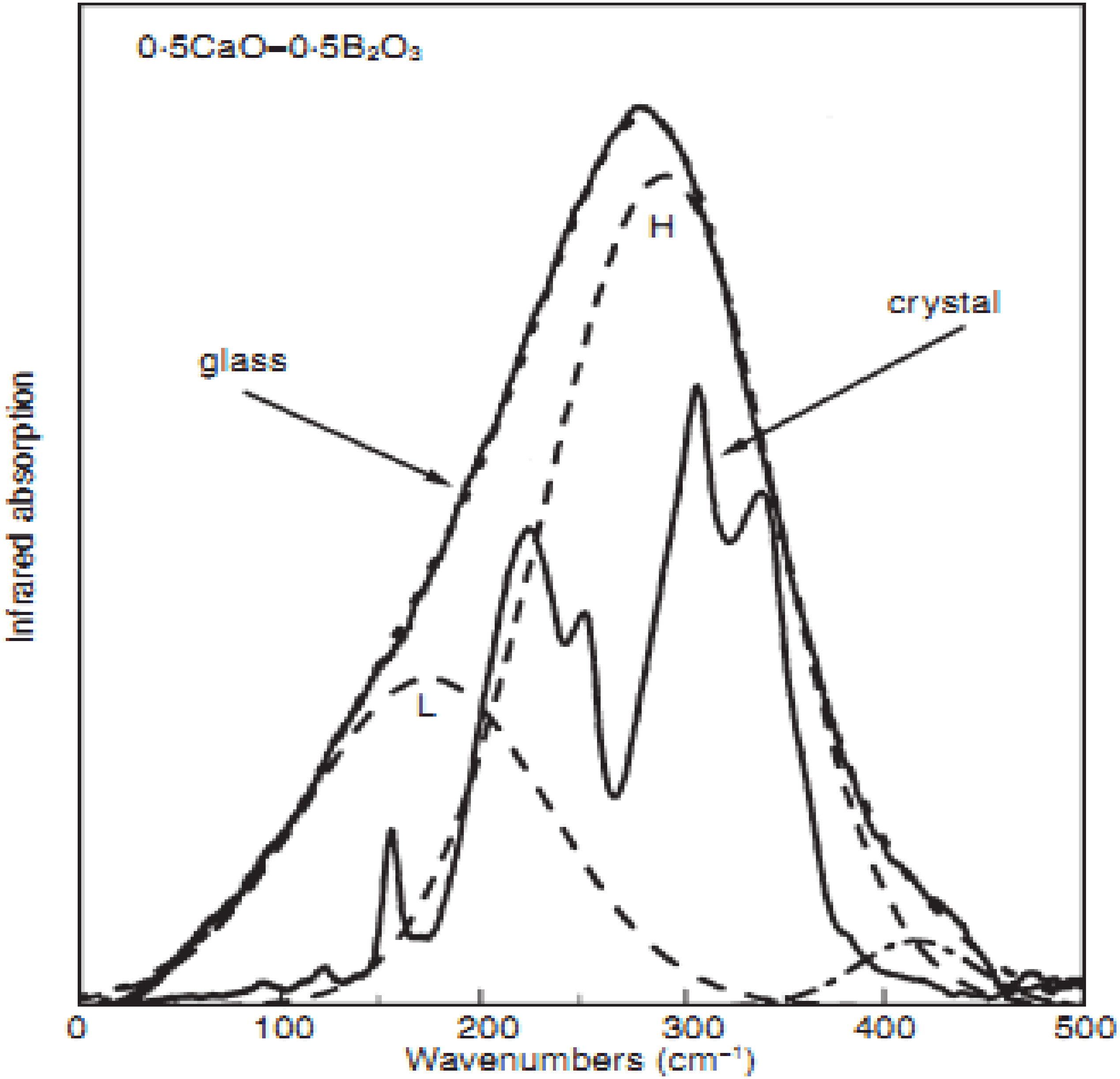

Fig. 16 Comparison of the far infrared spectra of glass and crystal with composition $0{\cdot}5CaO–0{\cdot}5B_2O_3$. Dashed component bands resulted from the deconvolution of the glass spectrum

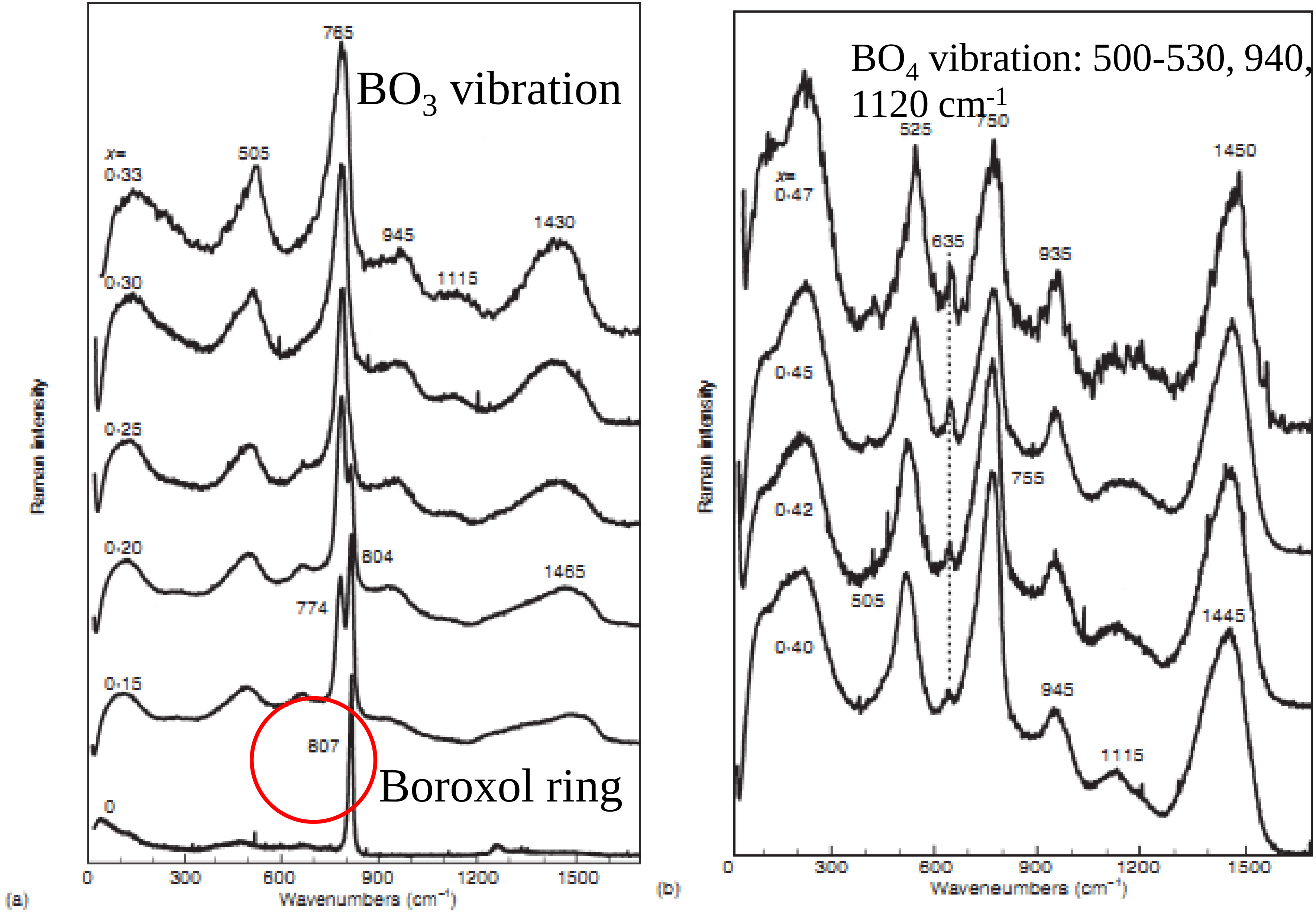

Fig. 17 Raman spectra of xBaO.(1-x)B_2O_3 glasses for (a) $0 \leq x \leq 0{\cdot}33$ and (b) $0{\cdot}40 \leq x \leq 0{\cdot}47$

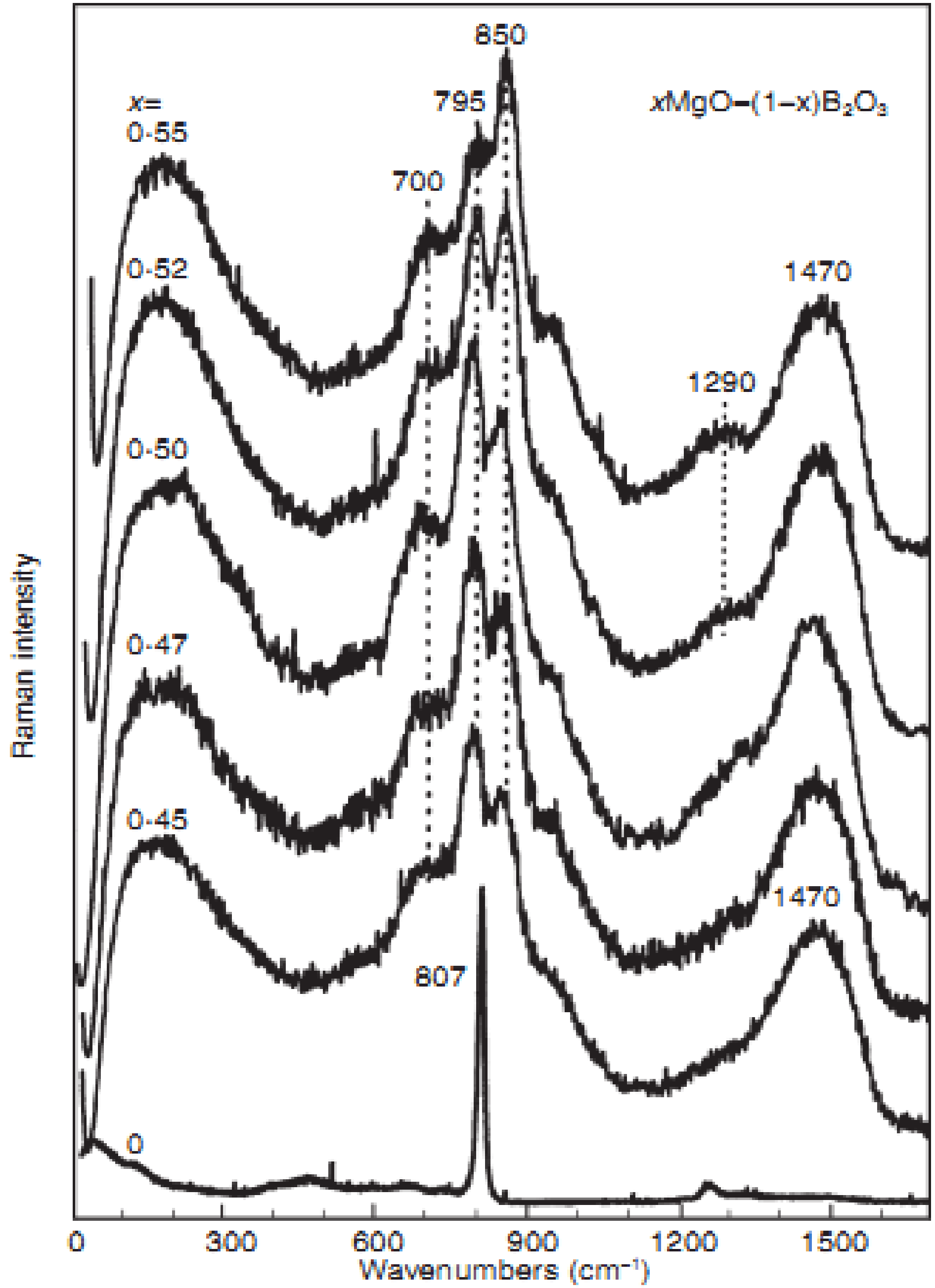

Fig. 18 Raman spectra of $xMgO.(1-x)B_2O_3$ glasses

Wavenumber (cm^{-1})	IR band assignments
~400–600	Bi–O–Bi and Bi–O in BiO_6 octahedral
~470	Total symmetric bending vibrations of BiO_3 units
~520	Bi–O bonds in BiO_6 units
~540	Doubly degenerating stretching vibrations of BiO_3 units
~726	B–O–B linkages
~950–980	Stretching vibrations of B–∅ bonds in $B\varnothing_4$ units from tri, tetra, and penta borate groups
1176–1500	B–O stretching vibrations of trigonal BO_3 units only
~1320–1470	B–O symmetric stretching vibrations of varied borate groups in BO_3 units
	$B–O^-$ symmetric stretching vibrations of varied borate groups in BO_2O^-

Table 5 IR band assignments for the borate glass

NOTE:

Raman and **FTIR** spectroscopy differ in some key fundamental ways. Raman spectroscopy depends on a **change in polarizability of a molecule**, whereas IR spectroscopy depends on **a change in the dipole moment**. Raman spectroscopy measures relative frequencies at which a sample scatters radiation, unlike IR spectroscopy which measures absolute frequencies at which a sample absorbs radiation.

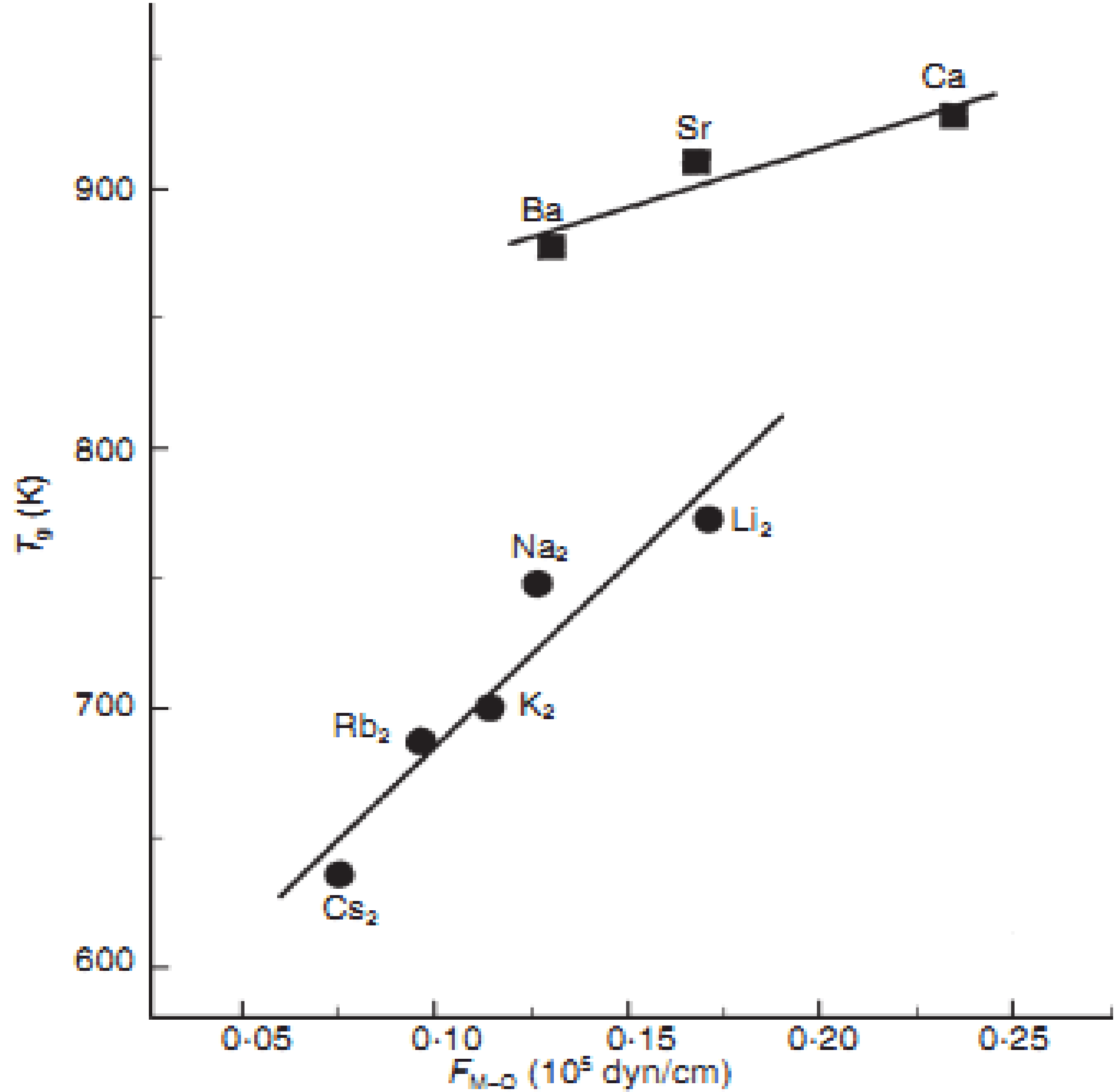

Fig. 19 Dependence of glass transition temperature, Tg, on the effective force constant, FM–O, of the metal ion oxygen bond in alkaline and alkali metal borate glasses of the diborate composition, $0{\cdot}33MO–0{\cdot}67B_2O_3$. Lines are least square fittings. A diborate glass is not formed in the Mg borate system

Effect of Nd^{3+} Concentration on the Physical and Absorption Properties of Sodium-Lead-Borate Glasses

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[b]Department of Physics, Guru Nanak Dev University, Amritsar, India

Glass	Composition in mol %			
	Na_2O	PbO	B_2O_3	Nd_2O_3
NPBN1	9.00	30	60	1.00
NPBN2	8.75	30	60	1.25
NPBN3	8.50	30	60	1.50
NPBN4	8.25	30	60	1.75
NPBN5	8.00	30	60	2.00

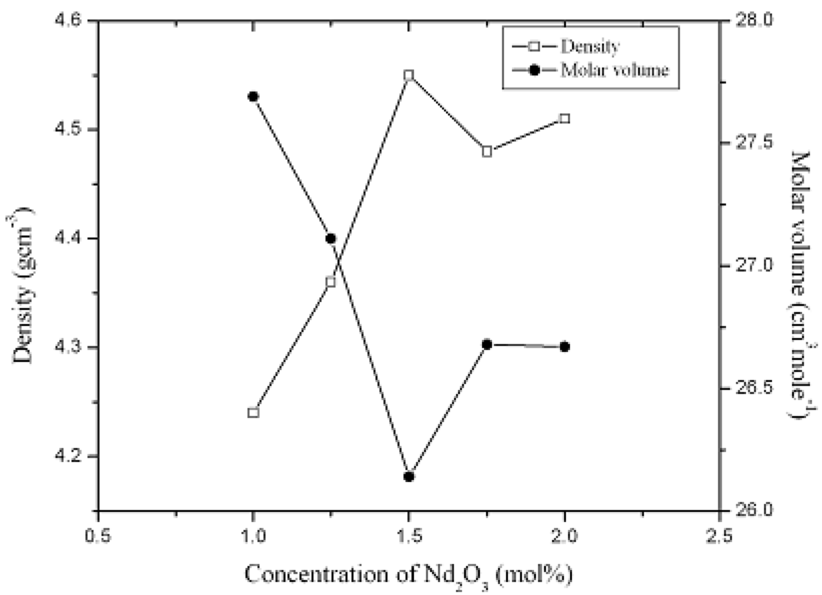

Fig. 20 Variation of density and molar volume with the concentration of Nd_2O_3

Physical property	Glass Sample				
	NPBN1	NPBN2	NPBN3	NPBN4	NPBN5
Refractive index (n)	1.652	1.652	1.652	1.652	1.652
Density (ρ) (g/cm^3)	4.24	4.36	4.55	4.48	4.51
Average molecular weight ($\overline{M}$) (g)	117.59	118.26	118.93	119.59	120.26
Molar Volume (V_M) (cm^3)	27.69	27.11	26.14	26.68	26.67
Ion concentration N ($\times 10^{20}$ ions/cm^3)	4.35	5.55	6.91	7.90	9.03
Ion concentration c(moles/liter)	0.72	0.92	1.15	1.31	1.50
Polaron radius r_p (Å)	5.32	4.90	4.56	4.36	4.17
Field Strength F ($\times 10^{15}$cm^2)	1.06	1.25	1.44	1.58	1.73
Inter nuclear distance r_i (Å)	13.20	12.16	11.31	10.81	10.34
Dielectric constant (ε)	2.73	2.73	2.73	2.73	2.73
Molar refraction (R_M)	10.12	9.91	9.56	9.76	9.75
Reflection losses (R %)	6.04	6.04	6.04	6.04	6.04

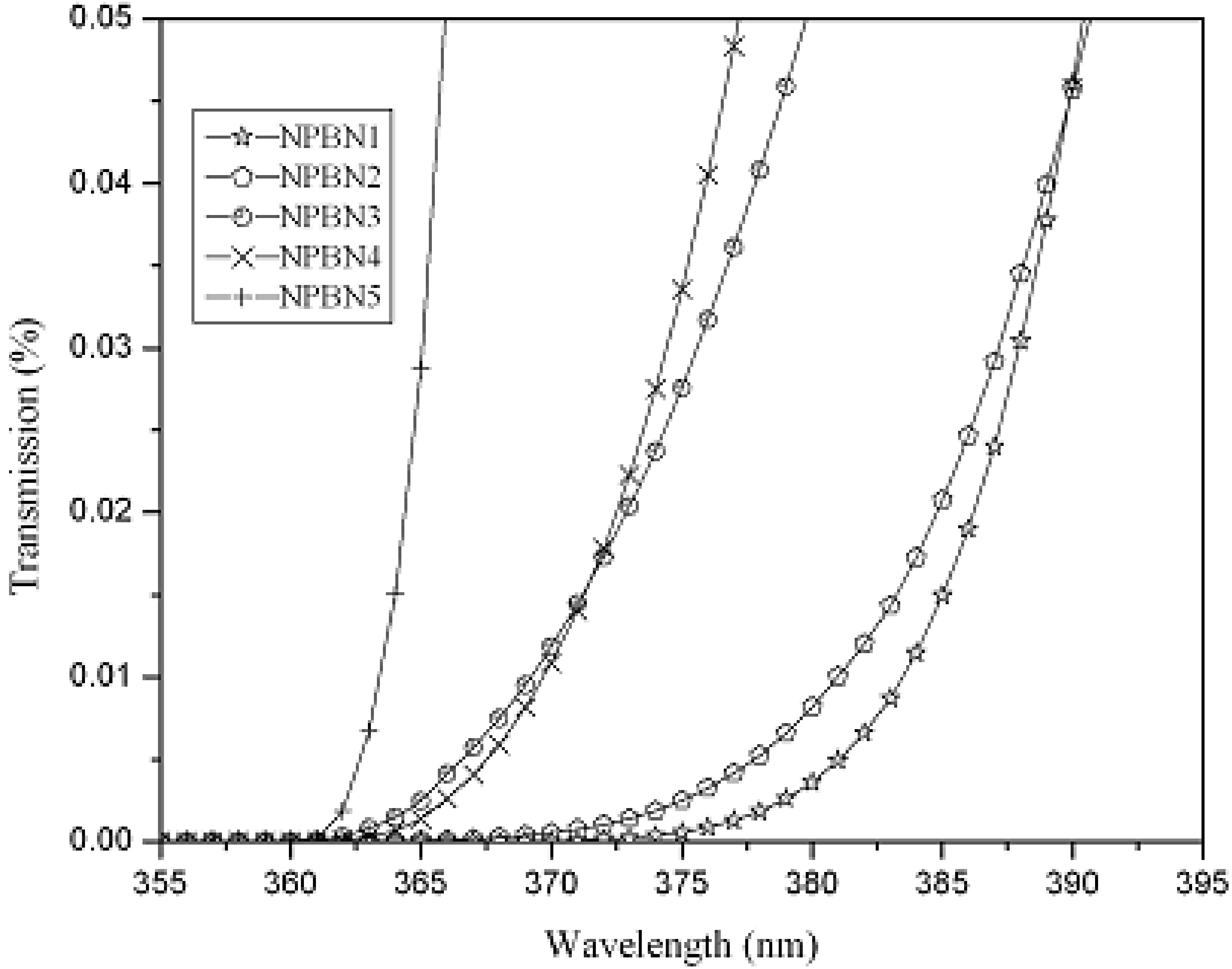

Fig. 21 Cut-off wavelength for sodium-lead-borate glasses containing varying amounts of Nd_2O_3

Next week

Course Outine:

Week 11: Glass composition, structures and applications (3)

- Phosphate Glass
- Alkali-and Phosphate Glass
- *Case studies from international publications*