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Statistical approach to study of lithium magnesium metaborate glasses

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Abstract: Alkali borate glasses and alkaline earth borate glasses are commonly used materials in the field of optoelectronics. Infrared (FTIR) and Raman spectroscopy are valuable tools for structural investigation of borate glass networks. The compositional and structural variety of lithium magnesium metaborate glasses is usually determined by traditional instrumental methods. In this study a data set is classified by structural and physicochemical parameters (FTIR, Raman spectra, glass transition temperature-Tg). Characterisation of magnesium containing metaborate glasses by multivariate statistics (hierarchical cluster analysis) to reveal potential relationships (similarity or dissimilarity) between the type of glasses included in the data set using specific structural features available in the literature is conducted. The clustering of the glass objects indicates a good separation of different magnesium containing borate glass compositions. The grouping of variables concerning Tg and structural data for BO_3 and BO_4 linkage confirms that BO_4/BO_3 ratios strongly affect Tg. Additionally, patterns of similarity could be detected not only between the glass composition but also between the features (variables) describing the glasses. The proposed approach can be further used as an expert tool for glass properties prediction or fingerprinting (identification of unknown compositions).

Keywords: borate glasses, BO_4/BO_3 ratio, spectroscopy, multivariate statistics, cluster analysis

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1 Introduction

The glasses are inorganic products of fusion which have cooled to a rigid condition without any crystallisation. The optimisation of glass properties as a function of composition and other processing parameters requires a detailed knowledge and understanding of the microscopic glass structure [1, 2].

B_2O_3 is one of the most significant glass forming oxides and has been incorporated into various kinds of glass systems to obtain desired physical and chemical properties. Alkali borate glasses [3-10] and alkaline earth borate glasses [2, 12-21], are commonly used materials in the field of opto-acoustical electronics, optical fibres, optical filters, laser hosts, photonic and nonlinear devices, piezoelectric actuators, and so forth. Infrared and Raman spectroscopy are valuable tools for structural investigation of borate glass networks. In comparison of available data of state of the art for alkali borate glasses [3-11], relatively few vibrational studies have been published for alkaline earth borate glasses [12-16]. The boron atom in borate crystals and borate glasses is usually coordinated with either three or four oxygen atoms forming the structural groups [BO_3] or [BO_4] depending on the composition. When various ratios of BO_4/BO_3 are combined, superstructural units such as a boroxol ring, metaborate, pentaborate, triborate, tetraborate, diborate, etc. can be obtained.

Lithium metaborate glasses $xLi_2O{\cdot}(1\text{-}x)B_2O_3$ are one of the most studied borate glasses. Their local structure is determined mainly by the isomerization between metaborate triangles $BØ_2O^-$ (Ø - oxygen atom bridging two boron centres; O - nonbridging oxygen atom) and tetrahedra $BØ^-_4$. The study of $LiBO_2$- glasses has indicated that approximately 40% of its boron centres are in fourfold coordination, and the remaining 60% are triangular $BØ_2O^-$ units. The transformation of $BØ_3$ to $BØ^-_4$ leads toan increase in the number of tetrahedral boron units found at ($0 \le x \le 0.40$). Subsequent destruction for non-bridging oxygen-bearing units is observed after $x \ge 0.40$. The quantity of BO_4 has impact on Tg, rigidity and density of borate glass [3-8].

Studies of alkaline earth borate glasses $xMO\cdot(1-x)B_2O_3$ have shown that at low contents of MO (alkaline earth oxide), alkaline earth ions behave like alkali modifier ions and the fraction of BO_4 units follows the trend observed in alkali borates. BO_4 structural units are decreased to further increase the ion field strength of the metal ion modifier for a fixed glass composition. This trend is opposite to that exhibited by alkali borate glasses [12-16]. At higher MO contents the M^{2+} ions network forming ability starts, and this is manifested by decreasing their coordination number with oxygen atoms. All alkali earth borate glasses are characterised with a reduced conversion rate of BO_3 to BO_4, narrow glass forming range and higher Tg compared to the alkali borate glasses. This phenomenon is strongly evident for borate glasses containing MgO ($0.45\leq x\leq 0.55$) [12].

A structural study carried out for a pseudobinary glass system indicated metaborate stoichiometry and $LiBO_2$ as one end member. Thus, in the mixed alkali family $xNaBO_2\cdot(1-x)LiBO_2$ ($0\leq x\leq 0.75$), the substitution of part of Li^+ by Na^+, leads to broadening of the glass formation region, induces monotonic decrease of BO_4 groups and decreases the amount of Tg [7, 17]. Therefore, in the classification by Angell [18] alkali mixing was supposed to render "strength" to the rather "fragile" $LiBO_2$ glass. The available studies of mixed lithium metaborate metal aluminate glasses $LiAlO_2\cdot(1-x)LiBO_2$ ($0\leq x\leq 0.42$) have found that for aluminium a tetrahedral coordination $AlØ^-_4$ is assumed. The presence of AlO_4 in the structure of the glass causes a displacement of the equilibrium towards $BØ_2O^-$ species and therefore the amount of BO_4 is reduced. As a result, the glass formation stops when the fraction of the aluminate tetrahedral becomes equal to the quantity of boron tetrahedral structural units in mixed borate glass [19, 20].

As a continuation of the studies mentioned above, the synthesis and structural characterization by infrared and Raman spectroscopy are reported for other mixed cations metaborate glasses $xMgO\cdot(1-x)Li_2O\cdot B_2O_3$ where Li^+ is substituted by Mg^{2+} in the range ($0\leq x\leq 1$) [21]. It is known that contrary to the $xLi_2O\cdot(1-x)B_2O_3$ system the binary $xMgO\cdot(1-x)B_2O_3$ system exhibits a narrow range of glass formation located around the metaborate stoichiometry (MgB_2O_4). Magnesium oxide is supposed to play an "amphoteric" role in glass, varying between participation in the covalent glass network and ionic modification [2, 13]. It was therefore expected that the lithium magnesium metaborate system would offer a thick glass forming range and exhibit structural trends intermediate to those of the lithium sodium metaborate and lithium metaborate metaaluminate systems.

The compositional and structural variety of lithium magnesium metaborate glasses is usually determined by traditional instrumental methods, and here is applied to new compositions. The purpose of the present study is to classify a data set constructed by structural and physicochemical parameters (FTIR, Raman spectra, Tg). The characterization of magnesium containing metaborate glasses by multivariate statistics (hierarchical cluster analysis) is used to reveal potential relationships (similarity or dissimilarity) between the type of glasses included in the data set using specific structural features available in the literature. Additionally, patterns of similarity could be detected not only between the glass composition but also between the features (variables) describing the glasses. The proposed approach can be further used as an expert tool for glass properties prediction or fingerprinting (identification of unknown compositions).

2 Experimental

The set for the statistical intelligent data analysis was collected from already published infrared or Raman spectra and glass transition temperatures (Tg) for the following metaborate glass systems $xMgO\cdot(1-x)B_2O_3$ [12] and $xMgO\cdot(1-x)Li_2O\cdot B_2O_3$ [21]. The used dataset shown in Table 1; consists of 16 glass compositions (conditionally named "cases" or "objects") and 14 features or parameters ("variables").

The parameter Ar can be defined by the ratio of the integrated infrared absorptions in the ranges relating to BO_4 and BO_3 structural groups. The value of N_4 is related to Ar via the relationship $N_4=Ar/(\alpha+Ar)$, where α is a constant representing the relative infrared extinction coefficient of borate tetrahedral versus triangular [7, 12, 16, 21].

For the data mining, an already classical method of multivariate statistics (hierarchical cluster analysis) was applied. Cluster analysis is a typical chemometric unsupervised method aiming to detect patterns of similarity (clusters) in a data set. The similarity could be detected and proven either between objects of interest (e.g. glass compositions) or between the features (chemical and physicochemical variables) characterizing the objects.

In general, cluster analysis follows several steps in the process of data mining [23]:

- standardization of the input data to eliminate differences in variable dimension; usually, z-transform mode is applied;
- calculation of the similarity distances; in the present study the squared Euclidean distances were chosen as a similarity measure;
- linkage of the objects into clusters by Ward's method of linkage;

Table 1: Datasets depending on the glass composition for $xMgO\cdot(1-x)B_2O_3$ and $xMgO\cdot(1-x)Li_2O\cdot B_2O_3$.

	Composition (mol fraction)	IR Shift (cm^{-1})					Raman Shift (cm^{-1})								
		V1	V2	V3	V4	V5	V6	V7	V8	V9	V10	V11	V12	V13	V14
	$xMgO\text{-}(1\text{-}x)B_2O_3$	IR1	IR2	IR3	IR4	IR5	R1	R2	R3	R4	R5	R6	Tg(°C)	Ar	N4
C1	B_2O_3	0	725	0	1275	1450	0	800	0	0	1275	0	525	0	0
C2	$0.45MgO\text{-}0.55B_2O_3$	395	700	975	1275	1450	675	795	850	1000	0	1470	908	0,49	0,2
C3	$0.47MgO\text{-}0.53B_2O_3$	395	700	975	1275	1450	675	795	850	1000	0	1470	910	0,51	0,21
C4	$0.50MgO\text{-}0.25B_2O_3$	400	700	975	1275	1450	700	795	850	1000	1290	1445	925	0,49	0,2
C5	$0.52MgO\text{-}0.48B_2O_3$	425	700	975	1275	1450	700	795	850	1000	1290	1445	913	0,47	0,19
C6	$0.55MgO\text{-}0.45B_2O_3$	425	700	975	1250	1450	700	795	850	1000	1290	1445	913	0,35	0,16
	$xMgO\cdot(1\text{-}x)Li_2O\cdot B_2O_3$														
C7	$Li_2O\text{-}B2O3$	471	726	1055	1236	1423	550	766		959	0	1488	420	0,9	0,37
C8	$0.1MgO\text{-}0.9Li_2O\cdot B_2O_3$	459	724	1056	1242	1423,5	545	768	833	959	0	1487	424	0,97	0,38
C9	$0.2MgO\text{-}0.8Li_2O\cdot B_2O_3$	440	720	1058	1250	1424	543	770	834	959	0	1486	434	0,95	0,36
C10	$0.25MgO\text{-}0.75Li_2O\cdot B_2O_3$	430	719	1059	1257	1424,5	543	772	935	959	0	1485	439	0,93	0,35
C11	$0.33MgO\text{-}0.67Li_2O\cdot B_2O_3$	420	718	1060	1261	1425	543	774	836	958	0	1484	452	0,84	0,33
C12	$0.5MgO\text{-}0.5Li_2O\cdot B_2O_3$	410	717	1062	1265	1425,5	543	778	837	958	0	1483	483	0,82	0,31
C13	$0.67MgO\text{-}0.33Li_2O\cdot B_2O_3$	400	716	1064	1267	1426	543	780	838	957	0	1482	514	0,72	0,28
C14	$0.75MgO\text{-}0.25Li_2O\cdot B_2O_3$	390	715	1066	1269	1426,5	543	784	839	956	0	1481	541	0,7	0,27
C15	$0.9MgO\text{-}0.1Li_2O\cdot B_2O_3$	383	714	1068	1272	1427	543	788	840	956	0	1480	590	0,57	0,25
C16	$MgO\text{-}B_2O_3$	380	713	1069	1275	1427,5	543	792	840	956	0	1479	646	0,49	0,2

- determination of the cluster significance by Sneath's criterion (1/3 or 2/3 of the maximal distance of linkage;
- graphical representation of the clustering by hierarchical dendrogram.
- All statistical calculations were performed by the STATISTICA 8.0 software package.

3 Results and discussion

The hierarchical clustering was performed with two major goals:

- determination of the similarity patterns (clusters) within the objects of interest (different magnesium borate glass systems);
- determination of the similarity patterns (clusters) between the variables describing the objects (spectral and physicochemical characteristics).

In Figs. 1 and 2 the dendrograms for linkage of objects (Fig. 1) and variables (Fig. 2) are presented.

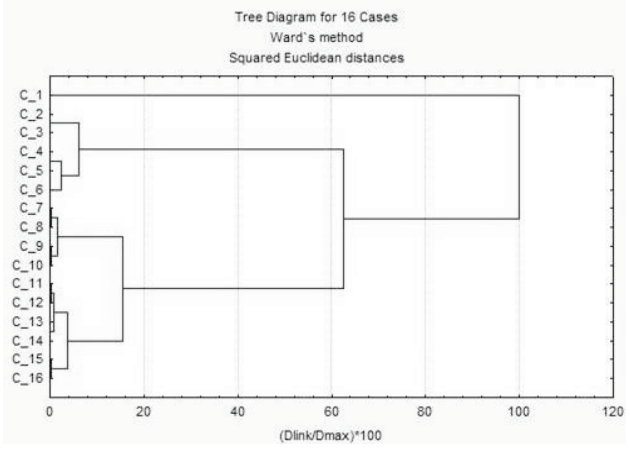

Figure 1: Hierarchical dendrogram of 16 glass objects with different glass composition.

The dendrogram of the objects (Fig. 1) indicates three major clusters. The first cluster includes cases of C2 to C6, which are the compositions of the system $xMgO\cdot(1\text{-}x)B_2O_3$, where x= 0.45 to 0.55 MgO. Within this cluster, two subclusters could be found (C2, C3, C4) and (C5 and C6).

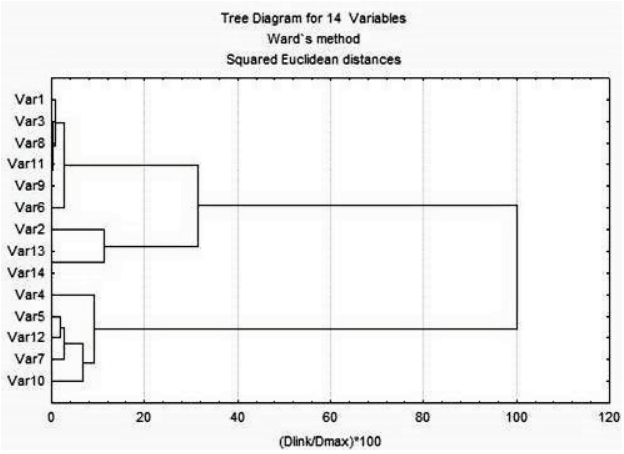

Figure 2: Hierarchical dendrogram of 14 variables describing different glass composition.

The first subcluster consists of objects with slight increase of MgO in the compositions. The objects C5 and C6 are grouped separately in the second subcluster due to the increased content of Mg^{2+} in their composition. It can be seen that case C4 is a boundary system with 0.5 MgO. MgO in low concentrations acts as a modifier and as a result metaborate ionic glasses are obtained. Major structural changesoccurred in glass compositions containing above 50 mol% MgO. As a result, it starts to bind covalently in the borate network showing properties of glass formatting oxide [12]. The object C1 is an outlier. The reasoning is based on an absence of MgO in the composition. Although B_2O_3 is one of the components in the magnesium borate system, the structure of pure B_2O_3 glass is radically different compared to that of the modified borate glass.

The compositions of C7 to C16 belong to the system $xMgO{\cdot}(1\text{-}x)Li_2O{\cdot}B_2O_3$ where x= 0 to 1 MgO. They are grouped in two clusters (second and third) according to the MgO content. The second cluster of the dendrogram is composed of objects C7 to C10. It is known that the presence of alkaline oxide in magnesium borate glass systems leads to expansion of the glass formation field. A content of MgO below 25 mol% does not affect the metaborate glass network but at higher concentrations of MgO a process of depolymerization occurs [13, 16, 21]. The results of cluster analysis confirm this assumption as shown by case C10 being a boundary case for this system. Further addition of Mg^{2+} is associated with significant structural changes evident in the next cluster. The third cluster (objects C11 to C16) is subdivided into two groups of similarity (C11 and C12) and (C15 and C16). The object C13 (67 mol% MgO) shows similarities with both of these groups, while object C14 has specific behaviour. The group of similarity concerning the $xMgO{\cdot}(1\text{-}x)B_2O_3$ system is associated with that for $xMgO{\cdot}(1\text{-}x)Li_2O{\cdot}B_2O_3$ due to compositional and structural properties. The major participant of the glass system, B_2O_3, is common to both systems, presented mainly as a metaborate structural unit which is dependent on metal oxides type and quantity.

Infrared and Raman spectroscopy are important analytical tools for understanding the structure and dynamics of amorphous materials. They are also used to assign the observed absorption peaks to the proper vibration of the atoms in geometric groupings. The vibrational modes of the borate network are mainly active in three infrared regions: 1200-1500 cm^{-1} (B-O stretching of BO_3 units), 800-1200 cm^{-1} B-O (stretching of BO_4 unit) and around 600-800 cm^{-1} (bending vibrations for B-O-B bonds in various borate segments). For the glassy B_2O_3, it is well known that the content of boroxol rings (1270 cm^{-1}) and all independent BO_3 triangles (700 cm^{-1}) exhibit no infrared active modes between 800 and 1200 cm^{-1}. The Raman frequency regions of borate glasses are 500 – 1100 cm^{-1} concerning BO_3 groups and 1250-2000 cm^{-1} being related to BO_4. The absorptions bands involved in far range Raman and Infrared regions (250–500 cm^{-1} and 350-500 cm^{-1}, respectively) are tied to the modifying metal ions frequencies. Table 2 presents the values of characteristic infrared and Raman absorption bands corresponding to different borate structural groups and B-O-B bonds [3, 5, 8, 10-16, 19-22].

The results of cluster analysis based on data of Tg, IR and Raman spectroscopies are shown in Fig. 2. The dendrogram consists of three clusters. The first of them is composed of variables V1, V3, V8, V11, V9, V6 being structural data only (see Table 1 and Table 2). These Infrared and Raman frequencies are related to BO_4 (V3, V9,) and BO_3 (V8, V11, V6) structural groups as well as to B-O-B bonds between them especially of meta- and pyro-borates. V1 is associated with the region of Mg-O vibrations. It is known that magnesium oxide is supposed to play an "amphoteric" role in the glass when coordinated to MgO_4 as a glass forming agent and ionic modificator when MgO_6. Thus, depending on the metal ion concentration the glass structure is affected, and BO_4/BO_3 ratio is changed [2, 16, 13].

The second cluster contains two variables which are associated with the qualitative (V2) and quantitative (V13) infrared characteristics. The bands around 700 cm^{-1} are related to BO_3 groups of orthoborate or boroxol rings containing the BO_4 group, as well as to B-O-B bonds formed between BO_3 and BO_4 groups. The clustering of V2 and V13 assumed that BO_4/BO_3 ratios strongly depend on the number of connected BO_3 and BO_4 groups in magnesium-containing metaborate glasses.

The variable V14 has radically different behaviour and does not show similarity with the other features. This is

Table 2: Infrared and Raman absorption bands of borate structural units.

Band position (cm^{-1})		Band assignments	
IR	**Raman**	**IR**	**Raman**
670-725	670-800	B-O-B bending vibrations of (orthoborate, and linked BO_3 and BO_4 group)	Ring breathing vibration of boroxol ring contains both BO_3 triangles and BO_4 tetrahedral
975	830-850	Stretching vibration of B-O linkage of BO_4 groups	BO_3 of (pyroborate dimers, meta and diborates)
1055-1070	950-1100	Vibration of B-O bonding of BO_4 groups of superstructural units	Vibration of B-O bonds of BO_4 groups of superstructurel units
1250-1275	1210-1290	B-O stretching vibration of $(BO_3)_3$-units of (metaborate chains, ortho, pyroborates)	$B\text{-}O^-$ stretching of BO_3 of (pyroborate dimers)
1420-1450	1445-1490	Antisymmetrical stretching vibrations with three non-bridging oxygens of B-O-B linkage (ortho, methaborates)	Stretching of B-O bonds attached to large number of BO_3 groups (methaborate chains)

most likely because it is a calculated parameter depending on the ratio of the integrated infrared absorptions concerning BO_4 and BO_3 structural groups.

The third cluster consists of V12, V4, V5, V7, V10 variables concerning Tg, infrared and Raman structural data. Infrared bands around 1450 cm^{-1} and Raman around 790 cm^{-1} are assigned to BO_3 groups of ortho, meta and more complicated borates structures as well as to boroxol rings containing BO_4 groups. The behaviour of V4 is quite different compared to the other intragroup of similarity in the cluster. V4 is corresponding to infrared frequencies around 1275 cm^{-1} related to BO_3 groups only. The presence of V12 in this group assumes that Tg depends on the number of BO_4 groups and mainly of those linked to BO_3. It can be concluded that the presence of isolated BO_3 groups (orthoborate) or BO_3 bonded dimers (pyroborate) and BO_3 bonded chains (metaborate) do not strongly affected Tg. Decrease of BO_4 groups leads to an increase of Tg in magnesium metaborate glasses, and its MgO content. Coexistence of boroxol rings and pyroborate dimers $B\text{Ø}O_2^{2-}$ in the glass below the metaborate stoichiometry case C4 (x=0.50) and case C10 (x=0.25) can be attributed to the depolymerization of the metaborate networks.

The results obtained by cluster analysis are correlated with those in the literature. The structural changes of borate glass [13-16, 20, 21] are due either to isomerization reactions between metaborate triangles ($B\text{Ø}_2O^-$) and tetrahedra (BO_4) or to the following disproportional equilibrium of metaborate ($Ø_3B\text{-}O\text{-}B\text{Ø}O^-$) leading to the local pyroborate ($B\text{Ø}O_2^{2-}$) and orthoborate $B\text{Ø}_3$ species. These are activated by the high field strength of Mg^{2+} ion that requires sites of high anionic charge density for their coordination. The charged oxygen atoms of obtained pyroborate are very suitable ligand for coordination of Mg^{2+}.

4 Conclusions

The cluster analysis carried out has indicated that the unsupervised pattern recognition approach could contribute to better interpretation of experimentally obtained structural or physicochemical data for lithium magnesium metaborate glasses. The clustering of the glass objects shows a good separation of different magnesium containing borate glass compositions. The systems in consideration $xMgO\cdot(1\text{-}x)B_2O_3$ and $xMgO\cdot(1\text{-}x)Li_2O\cdot B_2O_3$ are forming two distinct patterns of similarity and in such a way a good discriminative method for compositional and intimate structural recognition of the systems could be proposed.

The grouping of variables concerning Tg and structural data for BO_3 and BO_4 linkage confirms that BO_4/BO_3 ratios strongly affect Tg.

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