**Glass transition temperatures and structures of multicomponent borate glasses:
Influence of modifier cation field strengths**

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Abstract

Glass transition temperatures, T_g , are determined for a series of multicomponent borate glasses with composition $x\text{PbO} \cdot (33.33-x)\text{Na}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot 1.3y\text{SiO}_2 \cdot (66.67-2.3y)\text{B}_2\text{O}_3$, (where x and y take values from 0 up to 13.5 mol%, and from 0 up to 5.3 mol%, respectively). For this purpose, differential scanning calorimetry is used while the structure of these glasses containing two kinds of modifier oxides - Na_2O and PbO , is investigated by infrared spectroscopy. A detailed analysis of the infrared spectra reveals that at constant total content of the glass-forming oxides (B_2O_3 , SiO_2 and Al_2O_3) in the glasses investigated, the borate network progressively depolymerizes when Na_2O is substituted for PbO . This substitution favors the destruction of the more rigid structural units and the formation at their expense of units with a lower degree of connectivity. The macroscopic manifestation of these structural changes is the steep decrease in the glass transition temperature of the glasses investigated at increasing PbO concentration. This tendency for depolymerization of the borate network is explained by the influence of the Pb^{2+} -cations possessing substantially higher ionic field strength as compared to that of the Na^+ -cations.

Keywords: Borate glasses, DSC, Glass transition temperature, Infrared spectroscopy, Glass structure

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1. Introduction

Borate glasses have been an object of many years of research since depending on their composition these glasses have already found or could find various applications, e.g. as low melting solders and enamels [1-4], as effective gamma-ray shielding materials [5-7] and solid electrolytes [8, 9] as well as photo conversion layers for solar cells [4, 10-12] etc. Moreover, a large number of studies has been devoted to the structure of borate glasses. The reasons for this interest are two peculiarities in the behavior of boron in boron containing glasses [13-18]. The first peculiarity is that, in contrast to the silicate glasses, the addition of a network modifier to vitreous B_2O_3 leads initially to the conversion of BO_3 -triangles into BO_4 -tetrahedra, i.e. to the formation of more compact and rigid regions in the structure of borate glasses. The second peculiarity is that the network of borate glasses is not built up by randomly distributed BO_3 - and BO_4 groups, but by the so called superstructural units which consist of well-defined and rigid arrangements of the basic BO_3 and BO_4 groups [13, 15-18]. Moreover, it has been established that the properties of borate glasses depend to a greater extent on the kind and concentration of these superstructural units rather than on the concentrations of the BO_3 and BO_4 groups themselves [13, 15-18]. Due to these peculiarities in the boron behavior, the interpretation of the composition-structure-properties relationships of boron containing glasses is a difficult task. This problem becomes even more complicated in respect to the multicomponent borate glasses because of the mutual influence between the different glass ingredients. One of the ways to overcome this problem is to reveal in the first place which changes in the composition significantly affect the glass property of interest. To answer to this question it will be very helpful to use results of previous investigations on binary or ternary glass systems which resemble in some respect the composition of the glasses investigated. This strategy, as shown in the present contribution, turned out to be very useful

in interpreting the dependence between the glass transition temperature, T_g , and the composition of a series of multicomponent lead containing borate glasses.

Besides PbO, the glasses studied also contained Na₂O in order to investigate the role of Pb²⁺ cations as modifiers of the borate network in competition with another kind of modifier cations, different in their chemical nature as well as in their ionic field strength like Na⁺ cations. To the best of our knowledge, this aspect of behavior of Pb²⁺-cations in borate glasses has not been completely elucidated, yet. The main reason is that up to now borate glasses with a high PbO content (higher than 30 mol %) have been predominantly studied [1, 4, 5, 7, 19]. At so high PbO concentration, it has been established that Pb²⁺ cations begin to play the role of network formers and change their coordination number from six to four [20 - 22]. Moreover, the efforts have been mainly concentrated on Li₂O-PbO-B₂O₃-glasses possessing a high total concentration of Li₂O and PbO in order to guarantee the formation of glass structures with a low degree of connectivity and high ionic conductivity [23-28]. For the present, several publications are known, only, in which the structure and properties of borate glasses simultaneously containing PbO and Na₂O have been studied [6, 29-34]. In the cited works, optical, mechanical, electrical and gamma shielding properties of glasses have been mainly investigated. However, to the best of our knowledge, there are two papers, only, in which the compositional dependence of glass transition temperature T_g have been systematically investigated in borate glasses simultaneously containing PbO and Na₂O [31, 32]. The following glass series have been used for these investigations: pseudo-binary glasses with compositions $x\text{PbO} \cdot (1-x) \text{Na}_2\text{B}_4\text{O}_7$, where $x = 0,25, 0,5, 0,67$ and $0,79$ [31] and multicomponent borate glasses with a general formula $x\text{PbO} \cdot y\text{Na}_2\text{B}_4\text{O}_7 \cdot (100-x-y) \cdot \text{CAS}$ ($0,49\text{CaO} \cdot 0,21\text{Al}_2\text{O}_3 \cdot 0,3\text{SiO}_2$) with $0 \leq x \leq 50$ and $y = 50$ or 75 mol% [32]. As seen, the content of PbO in the above glass series increases keeping a constant ratio between the concentrations of Na₂O and B₂O₃. However, this way of compositional variation is connected

with a continuous change of the ratio R between the modifier and network former oxides. That is why in the present contribution, a series of glasses with compositions $x\text{PbO} \cdot (33.33 - x)\text{Na}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot 1.3y\text{SiO}_2 \cdot (66.67 - 2.3y)\text{B}_2\text{O}_3$ (where x and y take values from 0 up to 13.5 mol% and from 0 up to 5.3 mol%, respectively) was investigated. According to the above formula, all glasses studied can be considered as obtained from sodium diborate glass $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ by equimolar substitution of Na_2O by PbO and of B_2O_3 by Al_2O_3 and SiO_2 . This model of compositional changes ensured a constant value of 0.5 for the ratio R between the total concentrations of modifier oxides (Na_2O and PbO) and network former oxides (B_2O_3 , SiO_2 and Al_2O_3). Moreover, accounting for the low content of PbO (≤ 13.5 mol %) in the glasses investigated, the Pb^{2+} cations should play the role of modifier of the glass network, only, and not of network former, and to possess a coordination number of six, respectively [22].

2. Experimental

The glasses investigated were synthesized employing conventional melt quenching method. The nominal compositions of the glasses are given in Table 1. Reagent grade sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), lead oxide (Pb_3O_4), boric acid (H_3BO_3), silica (SiO_2) and aluminum hydroxide ($\text{Al}(\text{OH})_3$) were used for the synthesis. Appropriate amounts of chemicals were thoroughly mixed. The bathes thus obtained were heated in a platinum crucible in an electrical muffle furnace at 450°C for several hours to remove water. After that the temperature was gradually raised to 900°C to decarbonize the batches. The batches were melted at temperatures between 1000 and 1100°C depending on the glass compositions. For better homogenization, the melts were occasionally mixed by swirling. The glass melts were poured onto a steel plate and pressed by another steel plate to form thin disc samples with a

thickness of about 0.5 mm. According to the results of X-ray diffraction studies the glasses thus synthesized were fully amorphous.

Small pieces of these disc samples with a weight of about 30 mg were used for determination of the glass transition temperatures, T_g . For this purpose differential scanning calorimetry (DSC) was employed. The measurements were carried out on a DDSC7, Perkin Elmer calorimeter.

Our DSC experiments were performed as follows. For each of the glass compositions studied, at least two samples were independently investigated. The following heating/cooling program consisting of two runs was applied for determination of the glass transition temperatures, T_g : In the first heating/cooling run, the sample was heated up to a temperature T_x which was at least 50 K higher than the expected T_g value, held for 10 min at this temperature to destroy the sample thermal history. Afterwards the sample was cooled down at a rate of 10 K min^{-1} to a temperature T_y of about 50 K lower than T_g . In the second run, the sample was heated at the same rate of 10 K min^{-1} up to the respective temperature T_x . The T_g value was determined from the onset point of the heat flow curve recorded during the second heating run as this is illustrated on Fig.1.

Fig.1. Heat flow curve in the glass transition region of one of the glasses investigated containing 13.5 mol% PbO (glass F). The figure illustrates the way for determination of the glass transition temperature, T_g .

The heating/cooling program described was repeated at least three times with every sample investigated to prove the reproducibility of the measurements. Employing this way of experimentation we estimated that the error of the T_g determination was about ± 2 K.

The structure of the multicomponent borate glasses was investigated by infrared spectroscopy at room temperature. The infrared absorption spectra were recorded on a Bruker model IFS 25 Fourier transform interferometer with a resolution of 2 cm^{-1} at room temperature using KBr disc technique.

3. Results

Table 1 summarizes the data on the nominal compositions and the glass transition temperatures, T_g , of the glasses investigated. Here, the sodium diborate glass is denoted by letter A, while the other glasses from the series studied are indicated with letters from B to F as the content of PbO in them increases in the same direction. Since the structure and properties of the sodium diborate glass have been thoroughly investigated by many authors, further glass A will be used as a reference glass.

Fig.2. Heat flow curves of glasses A, B and F in the glass transition region.

Figure 2 shows three representative heat flow curves of the reference glass A and of glasses B and F, i.e. of the two glasses with the lowest and with the highest content of substituting oxides.

The next figure, Fig.3, presents the temperatures T_g as a function of the total concentrations, C_{tot} , of the substituting oxides PbO, Al₂O₃ and SiO₂. As seen in the figure, the glass transition temperature steeply decreases with C_{tot} .

Fig.3. The glass transition temperature, T_g , of the multicomponent borate glasses investigated as a function of the total concentration C_{tot} of the substituting oxides PbO, Al₂O₃ and SiO₂. The compositions of the glasses from A to F are given in Table 1

In Fig.4, the mid-infrared spectra of the multicomponent borate glasses (the glasses from B to F) and the reference binary Na₂O.2B₂O₃-glass (glass A) are shown. Three broad absorption bands are observed in the spectrum of glass A which can be assigned to the vibration modes of the borate network: 500 - 800 cm⁻¹ (bond bending vibrations of B-O-B linkages of the boron-oxygen network), 800 - 1200 cm⁻¹ (B-O asymmetric stretching vibrations of tetrahedral BO₄-units) and 1200 - 1600 cm⁻¹ (B-O asymmetric stretching vibrations of trigonal BO₃-units) [35]. Absorption bands in the same frequency regions are also visible in the spectra of glasses from B to F. Besides these three bands, inherent to the borate network, there is a small band at ca. 450 cm⁻¹ in the spectra of glasses from B to F

which is absent in the spectrum of glass A. The intensity of this band continuously increases with the total concentrations of the substituting oxides PbO, Al₂O₃ and SiO₂.

Moreover, other differences are observed between the spectrum of the reference glass A and the spectra of the glasses from B to F. The main difference is that the absorption envelopes in the 800 - 1200 cm⁻¹ and 1200 - 1600 cm⁻¹ frequency regions exhibit a more complex structure in the case of the multicomponent borate glasses. Going from glass B to glass F, i.e. increasing the concentration of the substituting oxides, the following changes can be detected in their spectra:

Fig.4. Infrared spectra of the glasses studied.

1. The absorption region of BO₄-units shows an overall decrease in intensity as compared to that of the BO₃-units.

2. A shoulder appears at ca. 1240 cm^{-1} in the BO_3 -absorption band which increases in intensity from glass B to glass F.
3. The very broad band at ca. 1000 cm^{-1} observed in the spectrum of glass B splits in the spectrum of glass C into two bands at ca. 960 cm^{-1} and 1050 cm^{-1} . Initially these two bands possess nearly equal intensities, while in the case of glass F the intensity of the band at 960 cm^{-1} becomes smaller as compared to that of the band at 1050 cm^{-1} .
4. The band centered at ca 1350 cm^{-1} systematically broadens and shifts to higher frequencies (from 1350 to 1380 cm^{-1}).

4. Discussion

In the interpretation of experimental results, first we tried to establish the limits within which the glass transition temperature, T_g , of sodium diborate glass (the reference glass A) would be influenced by equimolar substitution of B_2O_3 by small amounts of SiO_2 and Al_2O_3 . For this purpose, a comparison was made between the glass transition temperatures of glass A and the respective ternary sodium borosilicate and sodium aluminum borate glasses with comparable SiO_2 and Al_2O_3 concentrations to those of our glass F – the glass with the highest content of these oxides (7 and 5.31 mol %, respectively).

According to the investigations carried out with a series of ternary sodium borosilicate glasses of composition $33.33\text{Na}_2\text{O} \cdot y\text{SiO}_2 \cdot (66.67-y)\text{B}_2\text{O}_3$ [36], the equimolar substitution of B_2O_3 with several percents SiO_2 does not practically change T_g . To estimate the influence of Al_2O_3 substitution, data on T_g determined for ternary $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ glasses were used [37]. In the cited work [37], the dependence of T_g has been investigated for a series of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ glasses. Using the results of this investigation, it turned out that the equimolar substitution of B_2O_3 by about 5 mol % Al_2O_3 in the $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass would decrease T_g with about 15 K.

Based on the above considerations, it should be supposed that the observed steep decrease in T_g within the glass series investigated is mainly due to the equimolar substitution of Na_2O for PbO . To verify this assumption in the next figure (Fig.5), the T_g temperatures determined for the multicomponent borate glasses are presented as a function of their PbO content. In the same figure, the T_g data of one ternary sodium lead borate glass of composition $15.38 \text{ Na}_2\text{O} \cdot 15.38 \text{ PbO} \cdot 69.23 \text{ B}_2\text{O}_3$ is also given [38]. By its composition this glass could be considered as a three component analogue of our glass F. As seen in Fig.5, the T_g value of this sodium lead borate glass is very close to that determined for glass F which supports our assumption for the dominant role of PbO for the abrupt decrease of T_g .

Fig.5. Glass transition temperatures, T_g , of the multicomponent borate glasses studied vs. their PbO content (full circles). For comparison, the T_g value of one sodium-lead borate glass of composition $15.38\text{Na}_2\text{O} \cdot 15.38\text{PbO} \cdot 69.24\text{B}_2\text{O}_3$ is also given (the hollow circle) [38].

After elucidating the decisive role of the equimolar substitution of Na_2O for PbO for the steep decrease of T_g , it is important to reveal how the structure of the glasses changes within the glass series investigated. As known, the relations between the composition and the structure of boron containing glasses have been investigated by different methods: NMR, Raman and infrared spectroscopies, neutron scattering etc [13-18, 39 - 42]. In this respect, particular attention has been paid to the influence of modifier cation field strength on the

borate glass structure [39 - 42]. According to the cited works [39 - 42], the influence of modifier cations on the structure of borate glasses depends not only on their ionic field strength, but also on their concentration. At low modifier contents R , the concentration of four coordinated boron decreases and that of BO_3 -groups increases when modifier cations with lower field strength are substituted for cations with higher field strength. Moreover, the cations with higher field strength favor the formation of non-bridging oxygen atoms (NBO) at the borate groups as well as the formation of five and six-coordinated Al^{3+} -cations at the expense of the AlO_4 -groups. These effects have been explained assuming that the cations with higher field strength compensate better the negative charges at the non-bridging oxygen atoms rather than the partial negative charges at four coordinated boron atoms. However, at higher R -values a reverse tendency has been found. This effect has been related to the better stabilization of $^{[4]}\text{B-O-}^{[4]}\text{B}$ groups by the higher field strength cations in NBO-rich glasses.

As seen in Fig.4, when Na_2O is substituted for PbO in the glass series investigated, the content of BO_3 -groups increases at the expense of that of the BO_4 -groups. This is for expectation accounting for the relatively low value of R ($R = 0.5$) in these glasses and that the ionic field strength of Pb^{2+} cations is substantially higher than that of the Na^+ cations. The ionic field strengths of Pb^{2+} and Na^+ cations are 0.27 and 0.19, respectively [43]. However, the above finding, namely that the content of BO_3 -groups increases at the expense of BO_4 groups shows the general tendency, only, and gives no information for the specific borate groups formed in the glass series investigated. For a more detailed interpretation, the infrared spectra of our glasses were compared with those of the following two glass series: $x\text{Na}_2\text{O} \cdot (33.33-x) \cdot \text{MgO} \cdot 66.67\text{B}_2\text{O}_3$ and $x\text{Na}_2\text{O} \cdot (30-\text{CaO}) \cdot 70\text{B}_2\text{O}_3$ [35, 44]. As seen, the glasses of these two series possess equal or nearly equal R value to that our glasses and besides Na^+ cations also contain a second kind of modifier cations with substantially higher field strengths, like Mg^{2+} and Ca^{2+} cations. The field strengths of Ca^{2+} and Mg^{2+} cations are 0.33

and 0.45, respectively [43]. It is important to note that all field strength values cited here are related for one and the same coordination number of six as for the typical modifier cations Na^+ and Ca^{2+} as well as for the Pb^{2+} and Mg^{2+} cations. As well known, the Pb^{2+} and Mg^{2+} cations depending on their concentrations can change their coordination number and thus to transform their role in the glass structure: from network modifier at low concentrations into network former at higher concentrations. The problem with the coordination number of Mg^{2+} cations in the $\text{Na}_2\text{O-MgO-B}_2\text{O}_3$ glass series has been thoroughly investigated in [45]. It has been found that the character of magnesium-oxygen site interactions in these glasses to be primarily ionic and that these cations appears to be 6-coordinated [45]. Using X-ray diffraction and ^{11}B NMR techniques it has been established in [22] that at low PbO concentration ($\text{PbO} < 40 \text{ mol\%}$) the coordination number of Pb^{2+} cations in $\text{PbO-B}_2\text{O}_3$ glasses is about 6 indicating that PbO acts mainly as a network modifier.

Continuing the comparison between the infrared spectra of our glasses and those of $\text{Na}_2\text{O-MgO-B}_2\text{O}_3$ and $\text{Na}_2\text{O-CaO-B}_2\text{O}_3$ glass series it was established that the substitution of Na^+ -cations for Pb^{2+} -cations caused analogous changes in the spectra when Na^+ cations have been replaced by Mg^{2+} or Ca^{2+} -cations [35, 44]. Moreover, in [35], the structure of $\text{Na}_2\text{O-MgO-B}_2\text{O}_3$ -glasses has been also investigated by Raman spectroscopy which guaranteed a more precise and unequivocal interpretation of the infrared spectra of these glasses. Accounting for the results of this thorough investigation [45], the infrared spectra on Fig.4 can be interpreted as follows. In the spectrum of the $\text{Na}_2\text{O}.2\text{B}_2\text{O}_3$ glass, the dominant species are the diborate groups (1000 cm^{-1} band). Going from the spectrum of glass B to that of glass F, the appearance of the shoulder at 1240 cm^{-1} and the simultaneous decrease in intensity of the band at ca. 960 cm^{-1} indicate for a process of intensive destruction of diborate groups and for the formation at their expense of boroxol rings and possibly of tetraborate groups. Moreover, the two bands contributing to the BO_4 -region do not change in intensity at the

same rate: the diborate band at ca. 960 cm^{-1} decreases more quickly relative to that at 1055 cm^{-1} attributed to the tetraborate groups. The small peak at about 450 cm^{-1} is probably due to the bending vibrations of Si-O-Si and Al-O-Al bonds [34]. The peak at about 730 cm^{-1} in the spectrum of $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass is assigned to bond-bending vibrations of oxygen bridges between two trigonal boron atoms [35]. As seen in Fig.4, going from glass B to glass F, the position of this peak is downshifting in frequency and increasing in relative intensity.

According to the above considerations, the substitution of Na^+ -cations for Pb^{2+} -cations leads to substantial changes in the structure of the glasses investigated. This substitution favors the destruction of the more rigid superstructural groups like the diborate groups and the formation at their expense of groups characterized with a lower degree of connectivity. Moreover, the large frequency upshift (from 1340 to 1380 cm^{-1}) and the broadening of the high frequency band suggest as discussed in [35] the formation of non-bridging oxygen atoms. Hence, the replacement of Na^+ cations by Pb^{2+} -cations in the glass series investigated substantially lowers the cross-linking of the borate network.

After establishing that the substitution of Na_2O by PbO as well as by MgO or CaO leads to similar changes in the structure of the borate network, it is important to compare the influence of these compositional changes on the glass transition temperature in the respective glass series. For this purpose, in Fig.6 the glass transition temperatures of $x\text{Na}_2\text{O} \cdot (33.33 - x)\text{MgO} \cdot 66.67\text{B}_2\text{O}_3$ and $y\text{Na}_2\text{O} \cdot z\text{CaO} \cdot (100 - y - z)\text{B}_2\text{O}_3$ (where y and z take values from 0 up to 30 mol% and from 0 up to 33.33 mol%, respectively) glasses are given as a function of the concentration C_{MO} of MgO or CaO oxides [38, 46-48]. Comparing Figs.5 and 6 it is seen that in contrast to our glasses, the glass transition temperature of the above two glass series increases when Na_2O is substituted by MgO or CaO . This comparison demonstrates that the connectivity of borate network is not the single factor influencing the glass transition temperature. Besides the cross-linking of borate network itself, it has also to be accounted for

the number and strength of the coordinate links between the oxygen anions and the respective modifier cations as this problem has been considered in detail in [49]. Taking into account that the field strengths of Mg^{2+} and Ca^{2+} cations are higher than that of Pb^{2+} cations at one and the same coordination number of 6, the interaction between Mg^{2+} and Ca^{2+} cations and oxygen anions has also to be stronger.

Fig.6. Glass transition temperatures, T_g , of two glass series of the systems $\text{Na}_2\text{O-MgO-B}_2\text{O}_3$ and $\text{Na}_2\text{O-CaO-B}_2\text{O}_3$ vs. the concentration C_{MO} of MgO or CaO in the respective glasses. Circles - $\text{Na}_2\text{O-MgO-B}_2\text{O}_3$ -glasses, triangles - $\text{Na}_2\text{O-CaO-B}_2\text{O}_3$ -glasses. The curves are given as a guide for the eye, only.

Moreover, the results in Fig.6 indicate that the coordinate links between Mg^{2+} and Ca^{2+} cations and oxygen anions are so strong that the lowering effect on T_g caused by the decreased borate network cross-linking is overcompensated. As a result the substitution of Na_2O by MgO or CaO leads to a continuous increase in T_g . On the contrary, in the case of multicomponent borate glass series investigated, the progressive decrease in connectivity of borate network due to the substitution of Na_2O by PbO has a dominant effect and determines the observed steep decrease of glass transition temperature.

5. Conclusions

The compositional dependence of glass transition temperature, T_g and the structure of a series of multicomponent $x\text{PbO} \cdot (33.33-x)\text{Na}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot 1.3y\text{SiO}_2 \cdot (66.67-2.3y)\text{B}_2\text{O}_3$ borate glasses were investigated. According to the analysis carried out the steep decrease in T_g of the glasses investigated is mainly due to the equimolar substitution of Na_2O for PbO . This substitution, as proven by the results of the infrared spectroscopy, progressively decreases the concentration of the more rigid superstructural borate groups and leads to the formation on their expense of groups with a lower degree of connectivity and containing non-bridging oxygen atoms. These structural changes reflecting in the observed steep decrease in T_g are explained by the influence of the Pb^{2+} -cations possessing a substantially higher ion field strength in comparison with the Na^+ -cations.

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TABLE

Table 1. Nominal compositions (in mol %) and glass transition temperatures, T_g (in K) of the glasses investigated.

Glass	Na ₂ O	PbO	B ₂ O ₃	Al ₂ O ₃	SiO ₂	T _g
A	33.33	0.00	66,67	0.00	0.00	735 $\pm$ 2
B	31.33	2.00	64,9	0.77	1.00	715 $\pm$ 2
C	28.83	4.50	63,13	1.54	2.00	697 $\pm$ 2
D	26.33	7.00	60,48	2.69	3.50	681 $\pm$ 2
E	23.33	10.00	57,82	3.85	5.00	674 $\pm$ 2
F	19.83	13.50	54,36	5.31	7.00	674 $\pm$ 2