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On effective use of existing experimental data in glass science

O. V. Mazurin[1]

Joint-Stock Company "Thermex", 86 Sredniy Prospect, St. Petersburg, Russia

Yu. Gankin

MDL Information Systems, Inc.

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Two large glass property databases have been on the market for nearly ten years. Nevertheless, even now their use by specialists in glass science and technology is surprisingly limited. In this communication we try to demonstrate the importance of using such databases in the course of experimental work, selecting a recent publication in Physics and Chemistry of Glasses *as an example.*

From the last quarter of 19th century to the present time a great body of experimental data on properties of glasses and glass forming melts has been obtained by thousands of scientists. Most of the data were obtained in the period beginning in the 1930s.[(1)] At that time, the techniques for most glass property measurements had reached quite a reasonable level. Besides, scientists were not as pressed for time as they are now. As a result, the average quality of the glass property data published over the last 75 years has either remained on the same level or even decreased with time.[(1,2)] This means that we can and should try to make use of practically all glass property data published so far in the scientific literature.

It is well known that the use of glass property data taken from only one source, uncorroborated by other researches, is always open to the possibility that the applied data are erroneous. Even when authors report errors of their measurements, these values can characterise only random errors of measurement, yet systematic errors can be many times higher than the random ones. The only way to approach the true value of a property of a given glass composition is to collect as many data taken from independent sources as possible, and then to perform the statistical evaluation of all these data. It is similar to the approach applied in the Round Robin tests. However, in the case now discussed, it is impossible to perform a preliminary selection of "reliable' and "unreliable" sources. If the number of data points and the number of independent sources is large enough, and property–composition dependencies are smooth, then the outlier data points can be found by the statistical evaluation of the whole dataset, and can be eliminated, if necessary, prior to final data approximation. This approach is strongly recommended for determination of the most probable composition–property dependencies in binary glass systems. The results of such an approach have been demonstrated and discussed in a number of publications.[(1, 2, 3, 4)]

Meanwhile collection, comparison, normalisation and evaluation of a great body of data taken from different sources require great effort. Even the well known glass property handbooks[(5, 6)] can help scientists to only a limited extent. Now thanks to the availability of two glass property databases[(7, 8)] this task can be fulfilled quite easily. A proper use of already published glass property data can in many cases lead to a substantial decrease in the time needed and the cost of experimental work, and to a simultaneous increase in the quality of the results. In the present communication, we demonstrate this by giving one example, which from our point of view could be of a considerable interest for glass scientists desiring to organise their work in the most rational way.

The main objective of the recent study by Singh *et al*[(9)] was to determine the possibilities of using barium and calcium borate glasses as shielding materials for x-rays and gamma rays. Accordingly, the authors concentrated their attention on the measurements of attenuation of incident γ-rays. At the same time they had to measure the densities of all the glasses studied, because correct density values are essential for such investigations. According to the authors, "the density

[1] Corresponding author. Email address: mazurin@itcwin.com

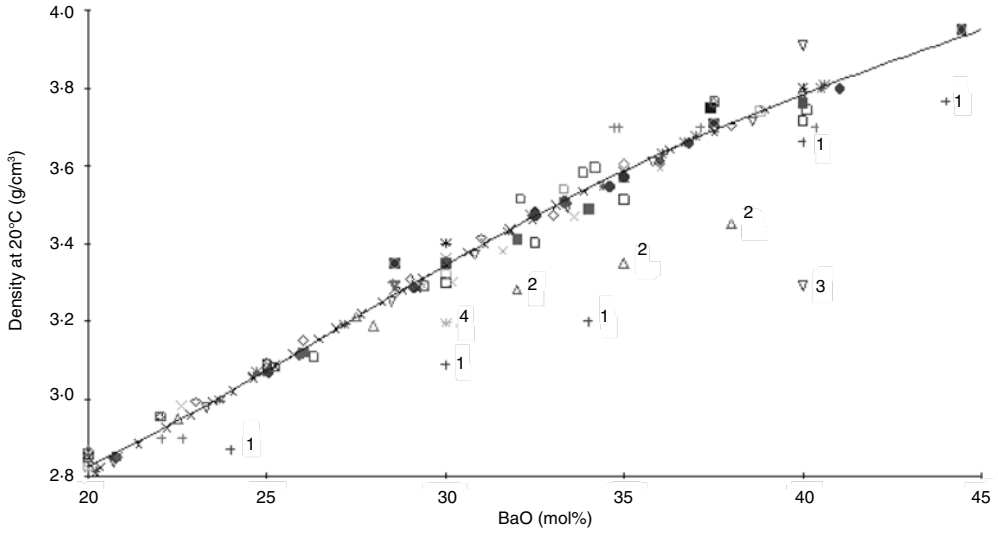

Figure 1. Composition dependencies of density at room temperature for glasses of the system $BaO–B_2O_3$. The solid line represents the root mean square approximation results. The outliers belong to the following sources: 1 – Ref. 9, 2 – Ref. 10, 3 – Ref. 11, 4 – Ref. 12

of each sample was measured separately with a high precision method based on Archimedes' principle", the error in the measurement being ±0·006 g/cm^3. At the same time, it seems likely that the authors did not compare their results with any previously published data.

By using the latest version of the SciGlass database[8] we have compiled the data on the density of $BaO–B_2O_3$ glasses published to date. The results are shown in Figure 1 (the most densely populated part of the dependence is shown).

In this graph, 169 data points taken from 34 various sources of information are shown. It is worth noting that the most precise results were published by Kodama.[13] In this publication the data for 28 various glasses are given. The standard deviation of the experimental points from the curve fitting all data-points presented in the graph (except the outliers) is equal to 0·00335 g/cm^3. At the same time, among the mentioned 34 sources one can find four sources containing seemingly erroneous data points. These data points are marked by numbers in Figure 1. Note that the data from the paper by Singh *et al*[9] fall into this category. The standard deviation for the data published in this present paper is equal to 0·231 g/cm^3. It is nearly 40 times higher than the error reported by Singh *et al*.

Figure 2 shows similar results for glasses of the $CaO–B_2O_3$ system. Here only 32 data points taken from 12 sources have been found, and the scatter of

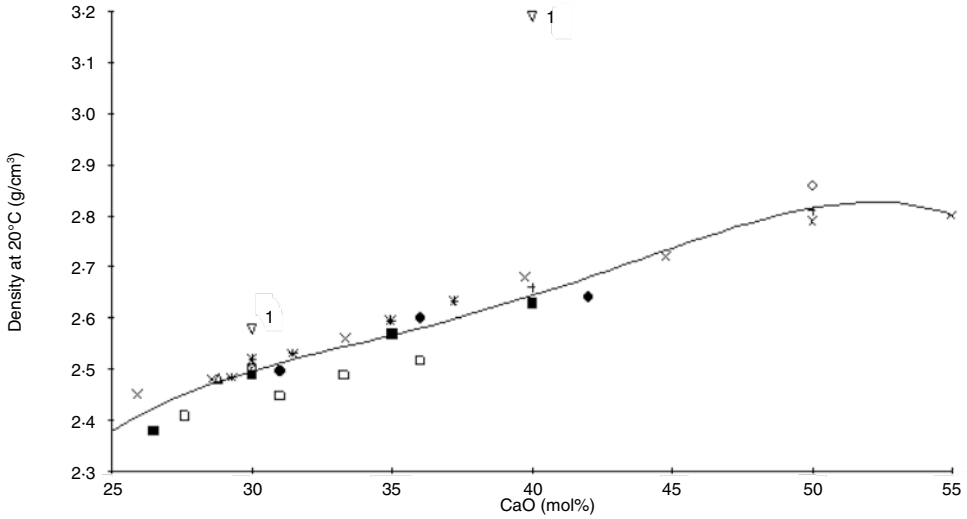

Figure 2. Composition dependencies of density at room temperature for glasses of the system $CaO–B_2O_3$. The solid line is described by the approximating polynomial of the fourth order. The outliers marked by number 1 belong to the publication by Singh et al[9]

the points is greater than in the $BaO–B_2O_3$ system. However, the position of the most reliable dependence is obvious enough. In this system, the values published by Singh *et al* also show great deviations from the best fit curve. The deviation for the glass containing 40% CaO is so great that it is probably not an experimental error but just a misprint.

Now let us suppose that the authors[9] had one of the existing databases at their disposal. Owing to the fact that the Interglad database is more oriented towards the needs of the large scale glass industry, the total number of binary glasses that has been compiled in that database is so far considerably smaller than that in SciGlass. However, even the number of data points contained in Interglad should be enough to establish the general density–composition relations for both systems in question. In the case of SciGlass, the best fit curves are especially reliable because of the large number of data points. It could have take only several minutes to draw graphs like those presented in Figures 1 and 2 and to obtain reliable values of densities of all glasses needed in the study of the attenuation coefficients. Then there would be no need to perform any density measurements at all. This recommendation will be correct in cases where authors are sure that they know the exact compositions of the glasses studied.

In the case of the work by Singh *et al* the reason for deviation of experimental results from the best fit dependence is yet to be explained. The analysis of the glasses studied was not performed. In principle, the deviations in question can be related either to measurement errors, to the specific thermal history of the glasses, or to the differences between nominal and actual compositions. The comparison of Figures 1 and 2 shows that for glasses belonging to different systems the deviations of the measured values from the reliable ones had opposite signs. Thus, most likely, these deviations were not connected with the quality of density measurements, and the measurement errors reported by the authors were probably correct. The largest effect of a thermal history on density can be found in glasses belonging to systems with a tendency to metastable phase separation.[14] However, even in this case, the range of density changes does not exceed 0·02–0·03 g/cm^3.

In our case the deviations are much larger. Thus, there seems no escaping the conclusion that something was wrong with the process of glass synthesis. From our point of view one can consider the following possibility. In the work by Singh *et al* there was no information on the material of crucibles used for glass synthesis. However, it was mentioned that "the glasses were prepared by a melt quenching technique as described by Khanna" (see Ref. 15). Khanna used porcelain crucibles. Thus, presumably, Singh *et al* used the same kind of crucibles. These crucibles can be severely corroded by barium borate melts.

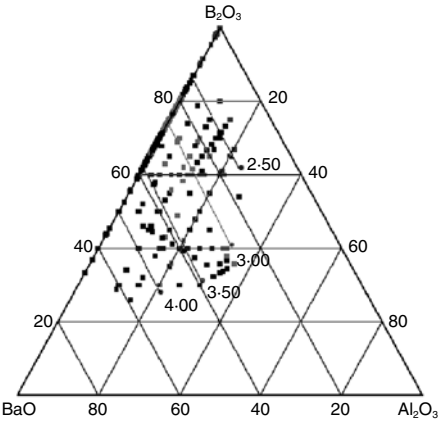

Figure 3. Density at 20°C of glasses in the system $BaO–Al_2O_3–B_2O_3$. The graph was drawn by using the SciGlass Information System on the base of 338 points taken from 47 sources. Numbers at isolines mean density in g/cm^3

Figure 3 shows the influence of composition on the density of ternary $BaO–Al_2O_3–B_2O_3$ glasses. It is clear that addition of Al_2O_3 to a barium borate glass decreases its density, while exchange of B_2O_3 for Al_2O_3 does not influence its density at all. Accordingly, if for example in the glass with a nominal composition of 40% BaO and 60% B_2O_3, additional Al_2O_3 is dissolved in the course of synthesis, then the density of the glass with the composition of 37·5% BaO, 6·25% Al_2O_3, 56·25% B_2O_3 should practically coincide with the value corresponding to the best fit dependency. Certainly, one should be aware of the possible volatility losses, as well. However, of the 30 sources where the reported data are near enough to the best fit curve shown in Figure 1 only nine sources reported compositions determined by analysis. In 21 sources, compositions were determined by batch (note that in most cases platinum crucibles were used for glass synthesis).

If our reasoning is correct, this means that the compositions of the glasses that were measured by Singh *et al* were different from those expected and then reported. The content of BaO in these glasses can be determined very easily with the help of the density data obtained by the authors. One should only use the best fit curve shown in Figure 1.

We have discussed here only one out of hundreds of similar examples that can be encountered in highly ranked journals in the last few decades. This example shows that glass scientists should be aware of the simple and quick way of checking the quality of their experimental techniques by using corresponding databases.

We may also consider another aspect of the same problem. In principle, it is not particularly dangerous for a glass community to encounter papers with erroneous data for properties of glass systems that have

already been reported in many other information sources. In such cases, the only necessary precaution is to refer to the glass property database. However, when inexperienced authors publish results for the glasses not yet studied, the level of the resulting "information noise" may impact on the future of the glass science. From our point of view, anyone publishing experimental studies of selected glass properties has only one safe way to eliminate such dangers. The author should select one or two glasses belonging to well studied systems whose compositions must be as close as possible to the compositions of the main set of glasses under study. Comparison of the results of new measurements of such "reference" glasses with the numerous data of previous studies will permit evaluation of the reliability of the selected experimental procedure. In some ways, this is similar to the use of the standard glass samples of NITS. However, the additional advantage of the proposed approach is the fact that in this case not only the correctness of property measurements will be tested, but also the correctness of glass synthesis, glass analysis and sample preparation will also be included in the testing procedure. The comparison of new results with the whole set of the already available data is a straightforward way of improving the quality of experimental data in future publications.

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