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Synthesis and structure of glasses in the system BaO–MnO–SiO_2

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Glasses corresponding in composition to $BaMnSiO_4$ and $BaMnSi_2O_6$ crystalline phases synthesized previously, have been obtained in the region with low SiO_2 content of the BaO–MnO–SiO_2 system. The glass structures were investigated by electron spin resonance, ultraviolet–visible and infrared spectroscopy, X-ray diffraction methods, etc. The trend to a complex ortho-silicate structure owing to the transformations into diortho-groups and silicate rings, has been established. The R_1 (0.186–0.177 nm) maxima of the total pair correlation functions are related to the mean Si–O and Mn–O distances, while the R_2 (0.283–0.278 nm) maxima refer to the Ba–O distance. Conclusions are drawn concerning the formation of Mn–O and Ba–O polyhedra. It is assumed that several kinds of structural polyhedra participate in the formation of the glass network.

1. Introduction

The BaO–MnO–SiO_2 system has not been subjected to systematic studies. Some data on the region of glass formation and on the properties of the glasses obtained have been reported [1]. However, data on the structure of glasses with the above composition have not been published. Until recently, the only known ternary compound in the BaO–MnO–SiO_2 system was the melilite analogue $Ba_2MnSi_2O_7$ synthesized by Brisi and Abbattista in 1961 [2]. The phase was confirmed by Scheet *et al.* [3]. As a result of our studies, other ternary crystalline phases, such as $Ba_3MnSi_2O_8$, $BaMnSiO_4$ [4] and a phase with the probable composition $BaMnSi_2O_6$, were established.

The purpose of the present investigation was to establish the structure and the short-range order of glasses in the BaO–MnO–SiO_2 system that correspond in composition to some of the ternary crystalline phases found earlier [4].

2. Experimental procedure

Batches containing $BaCO_3$, $MnCO_3$ and amorphous SiO_2 were used for preparing the glasses. The above components were taken in ratios corresponding to stoichiometric $BaO \cdot MnO \cdot SiO_2$ and $BaO \cdot MnO \cdot 2SiO_2$. Melting was performed in an electric chamber furnace under air. In order to reduce the interaction of the melts with the corundum crucibles, the batches were introduced into the furnace at 1440–1460 °C and held at these temperatures for 30 min. The melts were shock-chilled by pouring on to a copper plate.

The infrared spectra were recorded with a SPECORD–M80 (Carl Zeiss, Jena) two-beam spectrophotometer in the 1300–300 cm^{-1} range. The samples were studied photometrically as suspensions in liquid paraffin.

The diffraction patterns were obtained with a DRON–1IM diffractometer in the angular 2θ range 10°–110° using CuK_α radiation, a quartz monochromator for the diffracted beam, and a pulse height analyser. The diffraction data were utilized for obtaining the total pair correlation functions in the glasses under consideration.

The transmittance ultra violet–visible (UV–VIS) spectra were recorded with a SPECORD UV–VIS (Carl Zeiss, Jena) spectrophotometer in the 200–800 nm (50 000–13 000 cm^{-1}) range. The thickness of the samples was 25–30 μm.

The ESR spectra were obtained using a Bruker B–ER 420 spectrometer with a microwave frequency of 9.48 GHz. The magnetic field was scanned between 500 and 5000 G, and a DPPH standard with $g = 2.0036$ was used.

The emission spectral analysis was carried out with a Q 24 (Carl Zeiss, Jena) spectrograph in order to establish how far the interaction of the melt with the corundum crucible had affected the composition. An aluminium content of the order of 0.3 wt % was found in the glass with the composition $BaO \cdot MnO \cdot SiO_2$.

3. Results and discussion

The microscope observations showed the samples to be isotropic and homogeneous. The glasses obtained were dark in colour, that with the composition $BaO \cdot MnO \cdot SiO_2$ having a thin iridescent crust, which is often the case with manganese-containing glasses [1]. The brown-red colour is indicative of partial oxidation of the Mn^{2+} ions. Electron spin resonance (ESR) and UV–VIS spectroscopic studies were performed with a view to determining the valency state of manganese. The ESR spectrum of the glass with the composition $BaO \cdot MnO \cdot SiO_2$ presented

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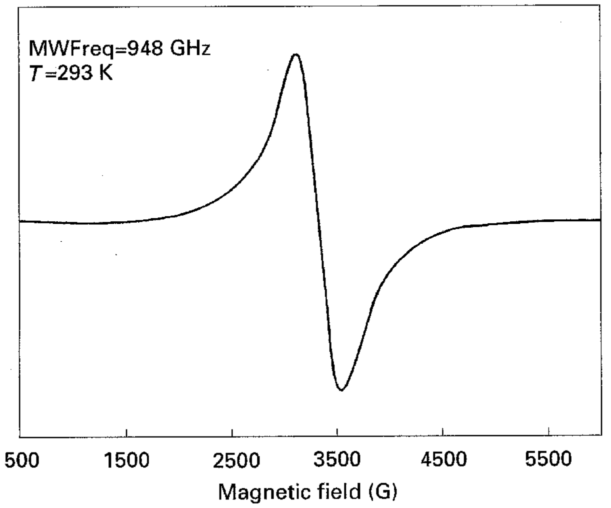

Figure 1 ESR spectrum of a glass with the composition $BaO \cdot MnO \cdot SiO_2$.

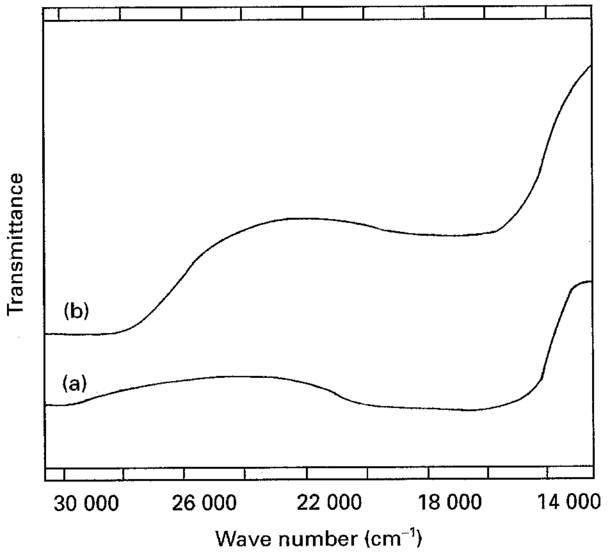

Figure 2 Visible spectra of the glasses.

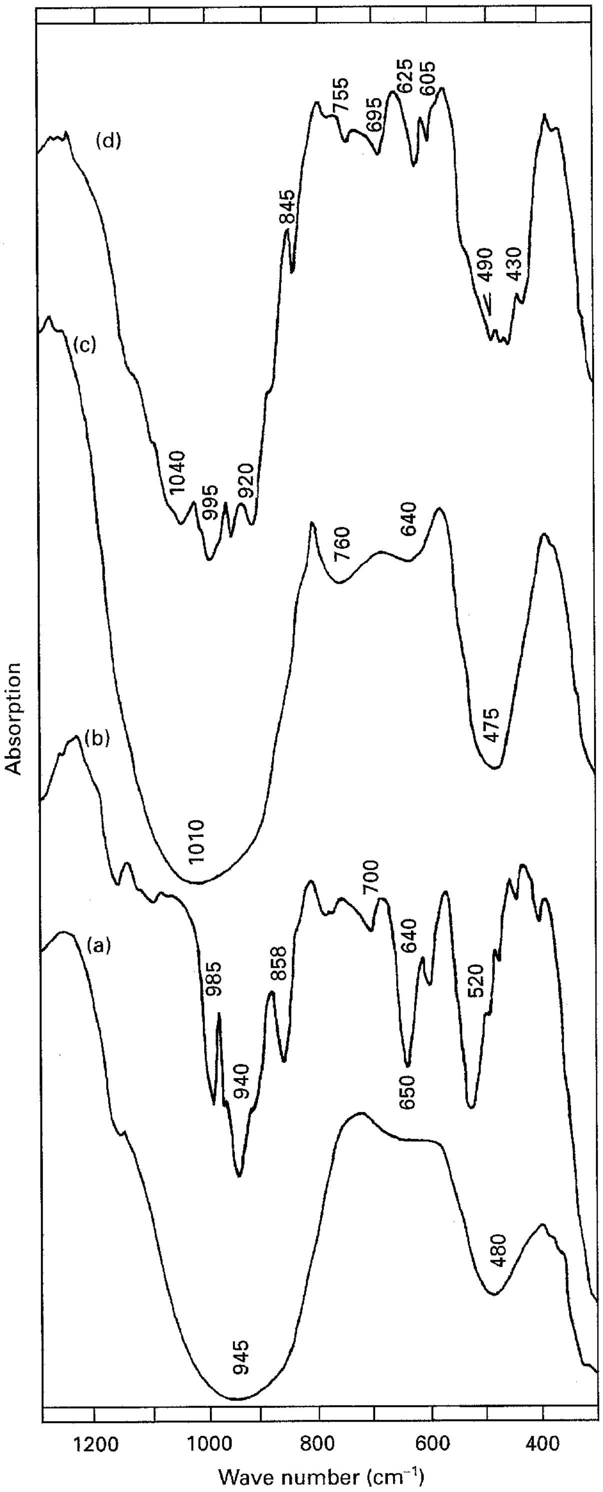

Figure 3 Infrared spectra of glasses and crystalline samples.

in Fig. 1, has a singlet line with a g factor of 2.034, which indicates the presence of a prevailent amount of Mn^{2+} in the sample. The spectra in the visible region (Fig. 2) exhibit a broad absorption maximum between 16 000 and 21 000 cm^{-1}. According to level [5], this maximum can be ascribed to a $^5T_{2g}$–^5E_g electron transition, which is valid for Mn^{3+} in an octahedral coordination. Hence, it can be assumed that the manganese in the samples investigated is present as Mn^{2+} and Mn^{3+}, but the predominance of the divalent ions is significant.

The infrared spectrum of the glass with the composition $BaO \cdot MnO \cdot SiO_2$ (Fig. 3a) is characterized by a main maximum at 945 cm^{-1}, a shoulder at 650 cm^{-1} and a mean intensity absorption at 480 cm^{-1}. As is shown elsewhere [6, 7], the position of the main maximum in this region is established with silicates in cases when the crystal has an orthosilicate structure.

In association with the absorption maximum at 650 cm^{-1}, it is known that a mean or low-intensity band in this region characterizes the $(SiO_4)^{4-}$ to $(Si_2O_7)^{6-}$ transition and is attributed to vibrations caused by splitting of the full symmetric vibration of the $(SiO_4)^{4-}$ ortho-group [8]. The absorption bands in the infrared spectra of pure orthosilicates are below 650 cm^{-1}, and between 800 and 650 cm^{-1}, no bands are observed [6]. The band at 480 cm^{-1} corresponds to a bending mode of the silicon–oxygen tetrahedron. On the basis of these data it may be assumed that the shape of the infrared spectrum depends mainly on the low polymerization degree of the silicon–oxygen tetrahedra. The presence of isolated $(SiO_4)^{4-}$ tetrahedra is also probable. The existence of $(Si_2O_7)^{6-}$ diortho-groups should not be neglected, especially as the size of the diortho-groups agrees well with the edges of the polyhedra around the large barium cations in barium silicates [9].

The infrared spectrum of the glass with the composition $BaO \cdot MnO \cdot 2SiO_2$ shown in Fig. 3(c) displays a shift of the main absorption band from 945 cm^{-1} to 1010 cm^{-1}. A new band at 760 cm^{-1} appears. The other two bands, at 640 and 475 cm^{-1}, correspond to those found in the spectrum of a glass with the orthosilicate composition, $BaO \cdot MnO \cdot SiO_2$. The shift of the main maximum to a higher frequency is due to the higher degree of binding of the silicon–oxygen tetrahedra. As is pointed out elsewhere [6], the bands between 1200 and 800 cm^{-1} move to the high-frequency region during the transition from island-to chain-, layered- and skeleton-type silicates and are most informative with respect to the binding degree of the silicon–oxygen tetrahedra.

Undoubtedly, the band appearing at 760 cm^{-1} is of special interest. A number of investigators [6] assume this band to be characteristic of the presence of rings of silicon–oxygen tetrahedra in the crystalline structure of the silicates. The band at 830–740 cm^{-1}, observed in the reflectance and transmission spectra of two-component glasses [6], is interpreted in an analogous way. There are also other interpretations, e.g. a similar band in the infrared spectra of lead–silicate glasses is ascribed [7] to the presence of crystallites of free SiO_2. The existence of rings of connected silicon–oxygen tetrahedra in the $BaO \cdot MnO \cdot 2SiO_2$ glass under consideration should not be excluded either. Examination of the crystalline structures of barium silicates shows that the rings of silicon–oxygen tetrahedra are characteristic for them. Four-, six- and eight-fold rings, and two-, four-layer, etc., rings are found [9]. In addition, the main structural unit in these cases is the diortho-group again, and the shortest parameter of the unit cell corresponds very often to a distance of 0.46 nm, which characterizes both the diortho-group and the edge of the barium polyhedron.

On the basis of the foregoing it may be concluded that with increasing SiO_2 content from the $BaO \cdot MnO \cdot SiO_2$ to the $BaO \cdot MnO \cdot 2SiO_2$ composition, the polymerization degree of the silicon–oxygen tetrahedra increases, leading from isolated tetrahedra and/or diortho-groups towards ring and probably chain structures that result from binding of diortho-groups.

Comparison of infrared spectra of glasses with the compositions $BaO \cdot MnO \cdot SiO_2$ and $BaO \cdot MnO \cdot 2SiO_2$, and the crystalline phases with the same compositions (Fig. 3b, d), show good agreement, which may be an indication of the appearance of the main structural groups characterizing the crystalline phases.

The data on the total pair correlation functions obtained by X-ray investigations are given in Table I and Fig. 4. The first maximum, R_1, of the curves is probably a complex one and might be attributed to the shortest Mn–O and Si–O distances. Similar maxima in curves of total pair correlation functions are described elsewhere [10, 11]. The shift of the R_1 maximum for the glass having the composition $BaO \cdot MnO \cdot 2SiO_2$ is associated with the enhanced amount of SiO_2. It is known that the Si–O distance is relatively constant (0.163 ± 0.002 nm). According to data concerning the Mn^{2+} and Mn^{3+} contents in the known oxide and silicate phases, their most probable coordination is assumed to be the octahedral one [1]. An octahedral coordination is also ascribed to Mn^{2+} in silicate melts [11]. In crystalline phases, the mean Mn–O distance for Mn^{2+} in octahedral coordination is 0.221 nm, while in a tetrahedral coordination this distance is 0.202 nm for $Sr_2MnSi_2O_7$ and 0.204 nm for MnV_2O_4 [12]. More precise conclusions about the manganese coordination with respect to the oxygen in the glasses under investigation cannot be made because the Mn–O distance is affected by the spin state and the valency of manganese. In addition, due to the close Si–O and Mn–O distances, their total pair correlation functions overlap with the first R_1 peak.

TABLE I Interatomic distances in the network of glasses in the $BaO–MnO–SiO_2$ system

Composition	R_1(nm)	R_2(nm)	R_3(nm)	R_4(nm)	R_5(nm)
(a) $BaO \cdot MnO \cdot SiO_2$	0.186	0.283	0.381	0.460	0.568
(b) $BaO \cdot MnO \cdot 2SiO_2$	0.177	0.278	0.378	0.472	0.568

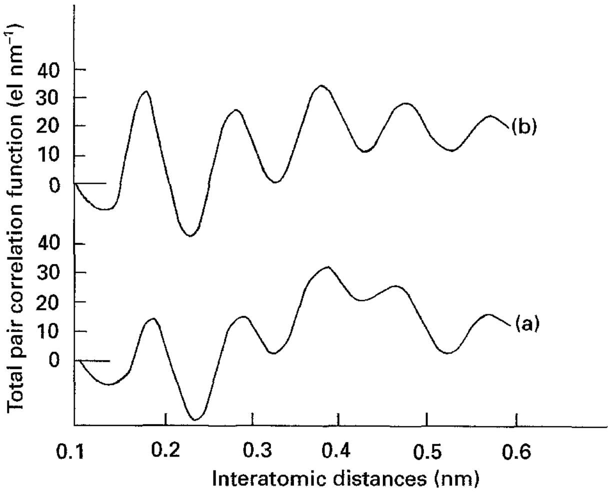

Figure 4 Total pair correlation functions of glasses in the $BaO–MnO–SiO_2$ system.

The second maximum, R_2, at 0.283–0.278 nm, is most probably associated with the Ba–O distance. In crystalline phases the mean Ba–O distance varies between 0.277 and 0.311 nm and the data obtained by us are comparable with the cited ones.

Owing to overlapping of many distances from the first and second coordination spheres, the interpretation of the maximum R_3 between 0.381 and 0.378 nm is difficult. The Mn–Mn, Mn–Si, Si–Si, etc., distances may have contributed to this maximum.

It is interesting that the R_4 distances (0.460 and 0.472 nm) on the correlation curves correspond to the period of repeatability of the pyroxenoid chain of $BaSiO_3$, which is assumed to be produced by binding of diortho-groups [13]. This is a distance that characterizes the silicon–oxygen tetrahedra forming diortho-groups, i.e. the edge of the barium polyhedron with which the diortho-group is coordinated.

The maximum R_5 at 0.568 nm is also complex. However, owing to the large mass and high electron density of the barium cation, this maximum is likely to depend mainly on the mean Ba–Ba distance. This assumption is also based on the fact that the Ba–Ba distance corresponds to the double Ba–O distance, as well as on the closeness of the unit cell parameters of $BaMgSiO_4$ and $BaZnSiO_4$ [14].

4. Conclusion

A glass with a low SiO_2 content (33 mol %) is obtained in the $BaO–MnO–SiO_2$ system. The investigations performed show that the short-range order of the glasses is determined by the formation of oxygen polyhedra with the participation of manganese and barium and silicon together. Therefore, the glassy network has a complex character and is determined by several different metal–oxygen structural units.

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