KINETICS AND MECHANISM
OF CRYSTALLIZATION OF BOROPHOSPHATE
GLASSES OF THE ZnO-B$_2$O$_3$-P$_2$O$_5$ SYSTEM

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Borophosphate glasses of the ZnO -B$_2$O$_3$ -P$_2$O$_5$ system were prepared by cooling the melt from 1230 °C. Their crystallization was studied by DSC and X-ray diffraction. The crystallization takes place mostly at 600–800 °C giving at least two crystalline phases with BPO$_4$ as one of the products. The kinetics of the crystallization of borophosphate glass 58.3 ZnO -8.3 B$_2$O$_3$ -33.4 P$_2$O$_5$ can be described by the Šesták–Berggren model, while that of 50 ZnO -50 B$_2$O$_3$ is better described by the Johnson–Mehl Avrami model. The analysis of the shape and position of the crystallization peak for different sizes of glass powders lead to the conclusion that surface crystallization prevails for the borophosphate glass, while for the borate glass surface crystallization dominates only when the particle size is under 300 μm, but internal crystallization prevails in the bulk glass.

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Introduction

Boron oxide and phosphorus oxide are known as glass-forming oxides which form glasses also with other modifying oxides. In the B_2O_3–P_2O_5 system no stable homogeneous glasses are formed, but with the addition of other oxides various glass-forming systems were prepared [1]. Borophosphate glasses are suitable for applications as glass seals, glass enamels and in glass frits for pastes for screen printing of hybrid integrated circuits. The reason for this applications is especially their good chemical resistance and low melting temperatures of some borophosphate systems [2]. Phase separation was observed in some MO–B_2O_3 systems, especially where M is the alkaline earth metal [3]. Shartsis et al. [4] found that additions of other metals to the MO–B_2O_3 glasses can eliminate phase separation. In the ZnO–B_2O_3–P_2O_5 glasses homogeneous glasses are formed in the composition region close to ZnO–P_2O_5 system [5,6]. Their structure and physical properties were determined and reported in paper [6]. This study is devoted to the kinetics and mechanism of the crystallization of ZnO–B_2O_3–P_2O_5 glasses, which is important for their applications in enamels or ceramic materials.

Experimental

Glasses of the ZnO–B_2O_3–P_2O_5 were prepared by the reaction of ZnO with H_3BO_3 and H_3PO_4 and heating slowly the reaction mixture up to 1230 °C in a Pt crucible. The obtained melt was then cooled by pouring on a steel plate. In this way 16 samples of homogeneous glasses were obtained. Their thermal behavior was investigated with a Perkin-Elmer DTA 1700 equipment in the DSC mode within the temperature range of 20 – 900 °C. For this study glass powders of the medium diameter of 80 μm were used. X-ray diffraction analysis was carried out on an X-ray diffractometer HZG4 (Freiberger Präzisionsmechanik) with Cu K(á) radiation.

Results and Discussion

The samples of ZnO–B_2O_3–P_2O_5 glasses crystallize under heating at the rate of 10 K min^{-1} within the temperature range of 600 – 800 °C mostly in two steps. Therefore, for the kinetic studies of their crystallization we chose 2 samples of glasses revealing only 1 crystallization peak: (A) $58.3\,ZnO$–$8.3\,B_2O_3$–$33.4\,P_2O_5$ (B) $50\,ZnO$–$50\,B_2O_3$.

The modified kinetic equation applied to studies of crystallization of glasses is usually adopted in the following form [7]

$$\Phi = \Delta H A \exp(-\varepsilon)f(\alpha) \qquad (1)$$

where Φ is the heat flow, ΔH is the enthalpy of the crystallization process, A is the pre-exponential factor, á is the degree of crystallization, and $\varepsilon = E/RT$ is the reduced activation energy. The function of $f(\alpha)$ represents the mathematical expression of the phenomenological kinetic model.

For the description of the kinetics of crystallization in glasses the most frequently applied kinetic equations are the Johnson–Mehl–Avrami (JMA) equation and the Šesták–Berggren (SB) equation. The JMA equation [8,9] has the form of

$$f(\alpha) = m(1 - \alpha)[-\ln(1 - \alpha)]^{1 - 1/m} \tag{2}$$

the SB equation [10] has the form of

$$f(\alpha) = \alpha^M (1 - \alpha)^N \tag{3}$$

Because of the mutual interdependence of A and B in Eq. (1) multiple-scan method is usually applied taking several sets of kinetic data at various heating rates. For the calculations of activation energy E the methods of both Friedmann [11] and Kissinger [12] were applied.

In the Friedmann method the activation energy is calculated from the logarithmic form of equation (1)

$$\ln\Phi = \ln[\Delta HAf(\alpha)] - \frac{E}{RT} \tag{4}$$

as the slope of the plot of the normalized heat flow at a given crystallization degree, plotted vs. the reciprocal temperature.

The Kissinger method is based on the condition for the maximum of DSC peak

$$\ln\frac{\beta}{T_p^2} = \ln\left[-\frac{f(\alpha_p)AR}{E}\right] - \frac{E}{RT_p} \tag{5}$$

where T_p and α_p are the peak temperatures and the crystallization degree at the DSC peak, respectively, and β is the heating rate.

The calculations of the value of activation energy by the Friedmann method gave the values of 269 ± 24 KJ mol^{-1} (A glass) and 338 ± 38 KJ mol^{-1} (B glass), whereas Kissinger method gave the values 318 ± 8 KJ mol^{-1} (A) and 308 ± 12 KJ mol^{-1} (B). For the kinetic calculations, only the values of E obtained

by the Kissinger method were used, because the dependence of E on the degree of conversion α is not linear in the range of $\alpha \in \langle 0.3, 0.7 \rangle$ [13].

In the next step, normalized functions of $z(\alpha)$ and $y(\alpha)$ [13], suitable for the differentiation among various kinetic models, were calculated. The $z(\alpha)$ function is defined as

$$z(\alpha) = \frac{\pi(\varepsilon)\Phi T}{\beta} \tag{6}$$

where $\pi(\varepsilon)$ is an approximation of the temperature integral, introduced for the solution to equation (1), which cannot be integrated analytically.

The $y(\alpha)$ function is defined [13] as

$$y(\alpha) = \Phi \exp(\varepsilon) \tag{7}$$

The courses of the functions $y(\alpha)$ and $z(\alpha)$ do not depend on the experimental procedure of the thermal analysis. From their shapes and the values of their maxima α_M and α_p^∞, respectively, it is possible to choose a proper kinetic model [13]. The values of α_M are important also for the calculation of the kinetic exponent in the corresponding kinetic model.

When the maximum of the $y(\alpha)$ function is at $\alpha_M \in (0, \alpha_p)$, kinetic data can be described by the SB(M, N) or JMA ($m > 1$) model [13]. The value of the maximum of the $z(\alpha)$ function (α_p^∞) is used for deciding between SB and JMA models. For the application of JMA model the maximum of the $z(\alpha)$ function should lie at 0.632 [7,13]; lower values of α_p^∞ correspond to the application of SB model for the description of the crystallization process.

The course of $y(\alpha)$ and $z(\alpha)$ for the borophosphate glass (A) is shown in Fig. 1. For the borophosphate glass (A) the maximum of the $y(\alpha)$ function lies at $\alpha_M = 0.34 \pm 0.04$ and that of $z(\alpha)$ function lies at $\alpha_p^\infty \cong 0.57$. It means that the SB model is more convenient than the JMA model for the description of the crystallization of borophosphate glass. Thus the overall crystallization of the borophosphate glass can be described by the empirical SB model for the following kinetic parameters

$$\_ \quad M = 0.59 \pm 0.15, \quad N = 1.12 \pm 0.08 \quad \text{and} \quad \ln A = (41.21 \pm 0.36)\text{s}^.$$

For the borate glass (B) the maximum of the $y(\alpha)$ function lies at $\alpha_M = 0.50 \pm 0.03$ and that of $z(\alpha)$ function lies at $\alpha_p^\infty \cong 0.63$. It means that the JMA model is more convenient than the SB model for the description of the
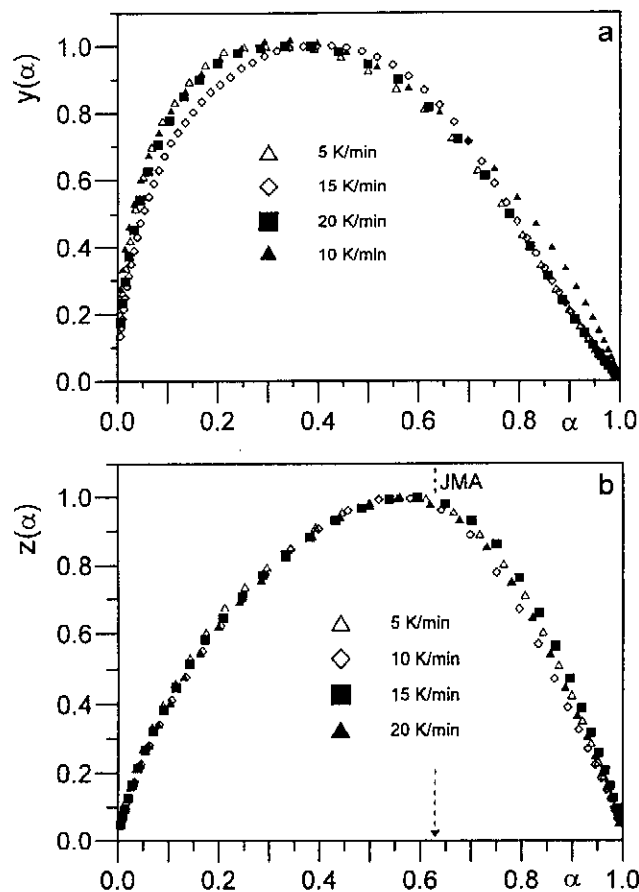
Fig. 1 Normalized functions of $y(\alpha)$ and $z(\alpha)$ for the crystallization of the borophosphate glass of the composition $58.3\,ZnO-8.3\,B_2O_3-33.4\,P_2O_5$ for 4 different heating rates

crystallization of borate glass. The calculated kinetic parameters for this model are

$$m = 3.25 \pm 0.41 \quad \text{and} \quad \ln A = (32.57 \pm 0.09)\,s^{-1}$$

These conclusions obtained for both glasses correspond to the fit presented in Figs 2 and 3 for the borophosphate glass (A) and borate glass (B), respectively. These pictures show better agreement between experimental and theoretical curves for the SB model in the case of the borophosphate glass (Fig. 2), whereas for the borate glass the JMA model gives better fit of the experimental data (Fig. 3). When we tried to calculate parameters of the JMA model for the borophosphate glass, we obtained

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$$m = 1.58 \pm 0.06 \quad \text{and} \quad \ln A = (40.54 \pm 0.15)\,s^{-1}$$

The parameter m in the JMA model corresponds to a dimensionality of the crystal growth in the glasses. As the value of m in the borate glass is close to 3, it sindicates prevailing three-dimensional growth after saturation of nucleation sites in this glass. The value of $m = 1.58$ obtained for the borophosphate glass salso indicates participation of one- or two-dimensional growth of crystals in this glass.
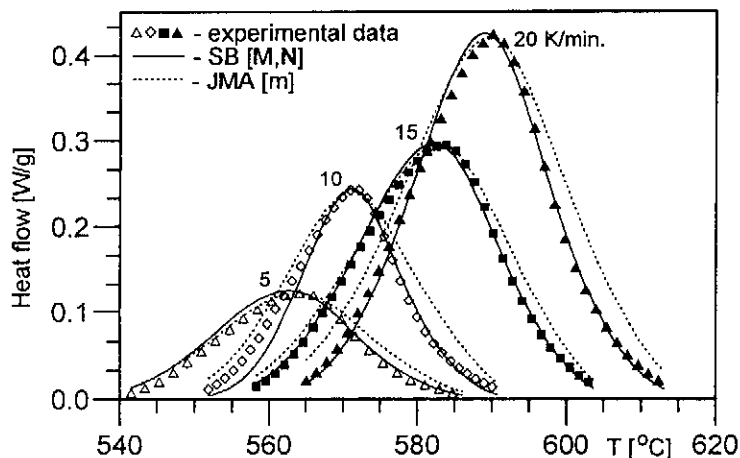

Fig. 2 Experimental DSC curves (points) and calculated DSC curves for the SB kinetic model (Solid line) and JMA model (dotted line) corresponding to the crystallization of the borophosphate glass of the composition $58.3\,ZnO-8.3\,B_2O_3-33.4\,P_2O_5$ for the heating rates of 5, 10, 15 and 20 K min^{-1}

We also tried to evaluate the mechanism of crystallization in these two glasses from the curves of thermal analysis as proposed in Refs [14,15]. This method makes it possible to evaluate crystallization mechanism (surface or volume) from the changes in the shape and position of the crystallization peak on the DTA or DSC curves with changes in the particle size of glass powder used for the analysis.

For this study the glass powder of the samples (A) and (B) was screened into five fractions with the average particle sizes of 81.5, 150, 300, 515 and 715 μm. DSC curves of crystallization were measured at the heating rate of 10 K min^{-1} in the temperature region of $90 - 800$ °C. The obtained crystallization peaks were analyzed in terms of parameters denoted in Fig. 4. These parameters are the peak temperature T_p, its maximum height $(\delta T)_p$, the width at the half-peak maximum $(\Delta T)_p$. In this method either $(\delta T)_p$ or $T_p^2/(\Delta T)_p$ are plotted as a function of particle
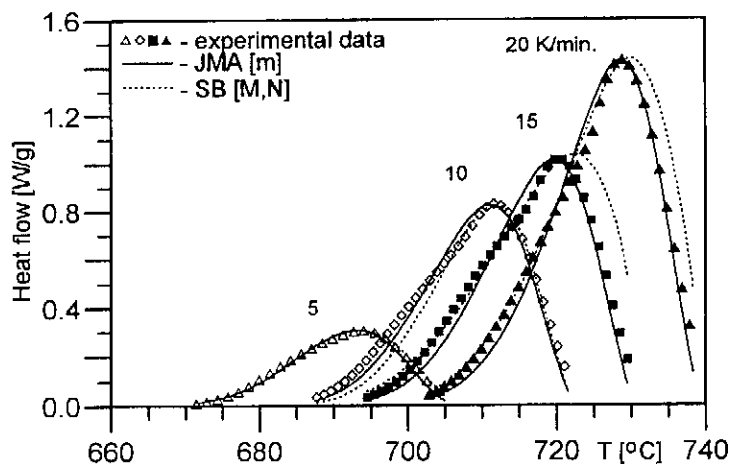
Fig. 3 Experimental DSC curves (points) and calculated DSC curves for the JMA kinetic model (solid line) and SB model (dotted line) corresponding to the crystallization of the borate glass of the composition $50\,ZnO-50\,B_2O_3$ for the heating rates of 5, 10, 15 and 20 K min^{-1}
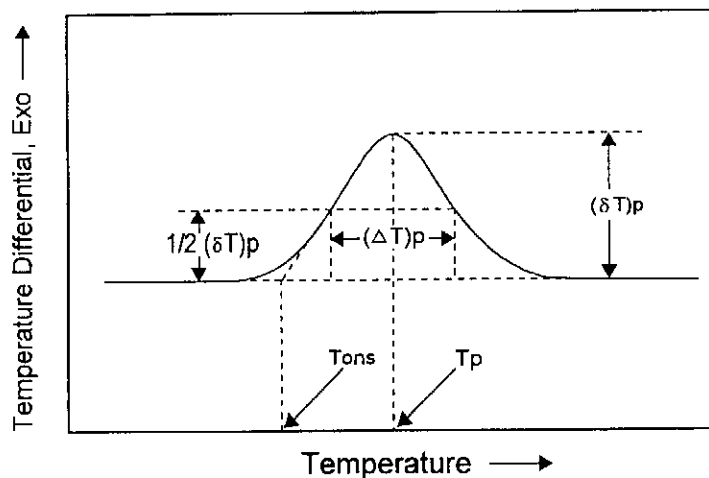

Fig. 4 Parameters of the exothermic peak on the DSC curve of a crystallizing glass

size because both $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ should depend on specific mechanism of crystallization.

The ratio of the volume to the total effective surface area of all glass particles increases with increasing particle size for a given amount of sample. Thus $(\delta T)_p$ and
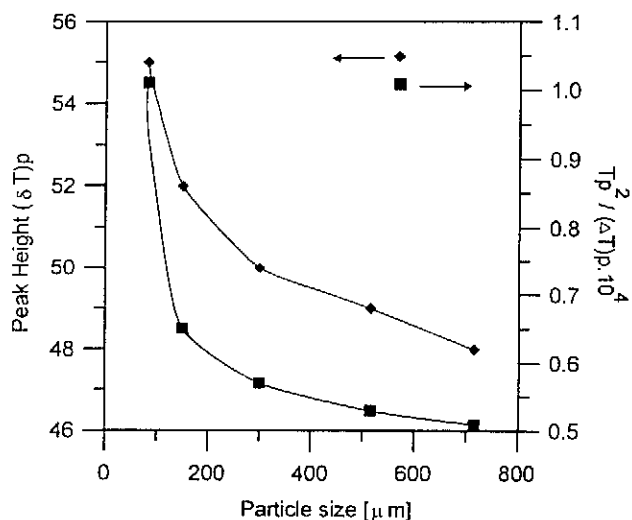
Fig. 5 $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ as a function of particle size for the borophosphate glass of the composition $58.3\,ZnO-8.3\,B_2O_3-33.4\,P_2O_5$. Heating rate 10 K min^{-1}, sample weight 100 mg
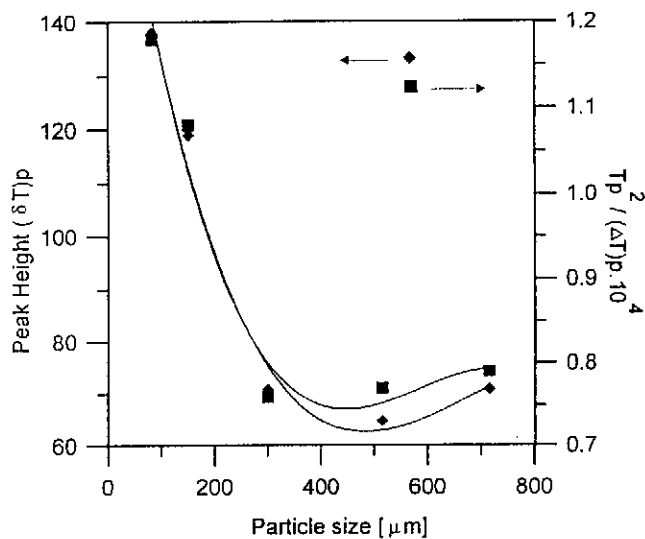

Fig. 6 $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ as a function of particle size for the borate glass of the composition $50\,ZnO-50\,B_2O_3$. Heating rate 10 K min^{-1}, sample weight 100 mg

$T_p^2/(\Delta T)_p$ should increase with increasing particle size when the internal crystallization predominates, while for the dominant surface crystallization the re-
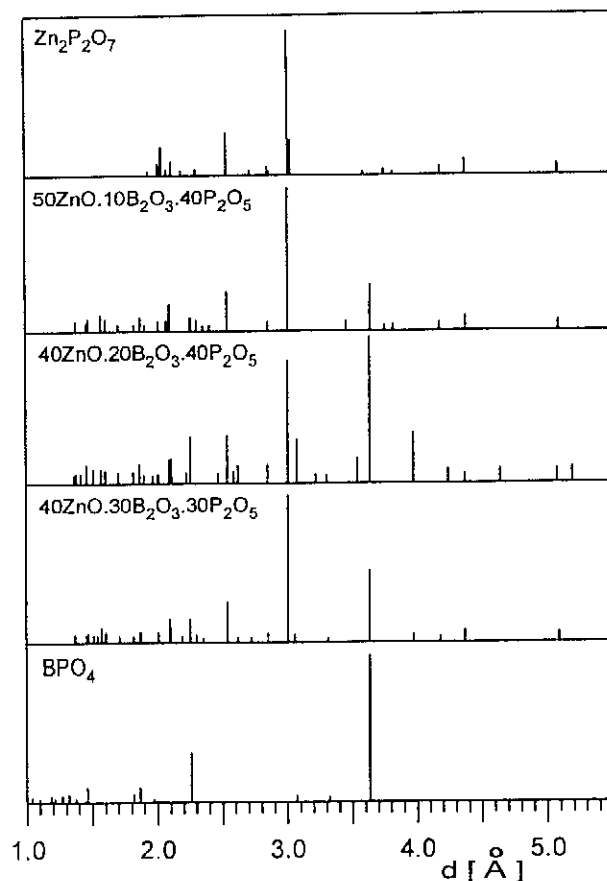
Fig. 7   X-ray diffraction diagrams of some borophosphate glasses and compounds $Zn_2P_2O_7$ and BPO_4

verse effect should be observed.

In Figs 5 and 6 the values of $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ are plotted against particle size for the borophosphate glass (A) and borate glass (B), respectively. In the case of the borophosphate glass (Fig. 5) both parameters decrease with increasing particle size. These results indicate that the borophosphate glass (A) crystallizes primarily by surface crystallization. For the borate glass (B), $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ decrease initially with increasing particle size up to ~300 μm and then increase as the particle size increases (Fig. 6). These results obtained for the borate glass suggest that there is a tendency for surface crystallization when the particle size is less than 300 μm, but, in general, this glass crystallizes primarily by internal crystallization.

Peak temperatures T_p and temperatures corresponding to extrapolated onset of the crystallization peak, T_{ons}, increase with increasing particle size for both glass

Tab. I   Survey of crystalline products identified by X-ray diffraction analysis in the samples of $ZnO-B_2O_3-P_2O_5$ glasses annealed at 700 °C

Sample No.	ZnO mol %	B_2O_3 mol %	P_2O_5 mol %	Crystalline products
B25	40	0	60	$Zn(PO_3)_2$
B15	50	0	50	$Zn(PO_3)_2$
B45	60	0	40	ZnP_2O_7
B32	50	50	0	$ZnB_2O_4 + ZnB_4O_7$
B49	60	40	0	$ZnB_2O_4 + Zn_3B_2O_6$
B35	30	10	60	BPO_4 + glass
B37	30	30	40	$Zn_3(PO_4)_2 + BPO_4$
B40	30	60	10	$Zn_3(PO_4)_2 + BPO_4$
B26	40	10	50	$Zn_3(PO_4)_2 + BPO_4$
B27	40	20	40	$ZnP_2O_7 + BPO_4$
B28	40	30	30	$ZnP_2O_7 + BPO_4$
B21	50	10	40	$ZnP_2O_7 + BPO_4$
B22	60	20	30	$ZnP_2O_7 + BPO_4$
B46	60	10	30	$ZnP_2O_7 + BPO_4$
B1	58.3	8.3	33.4	$ZnP_2O_7 + BPO_4$

types, but their increase is more pronounced in borophosphate glass (A) than in borate glass (B). The increase in T_p with increasing particle size reflects only a higher resistance of the glass to crystallization, but cannot clearly distinguish between surface and internal crystallizations [15].

The identification of crystallization products was carried out by X-ray diffraction analysis on the powder samples of glasses annealed at 700 °C for 2hr. The diffraction patterns obtained were compared with literature data on X-ray powder diffraction diagrams of possible crystalline compounds [16]. In this way we have found that borophosphate glasses after crystallization give at least 2 crystalline products. One of them is BPO_4 and the other is mostly one of zinc phosphates, the composition of which is given by the rest of $xZnO-yB_2O_3-zP_2O_5$ sample after separation of BPO_4. The supposed composition of the crystalline product in the glasses with the atomic ratio P/B < 1 is given by the equation:

$$xZnO-yB_2O_3-zP_2O_5 = 2yBPO_4 + xZnO-(z-y)P_2O_5 \qquad (8)$$
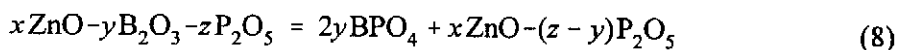
As an example, Fig. 6 shows X-ray diffraction patterns of the annealed samples of the composition $50\,ZnO-10\,B_2O_3-40\,P_2O_5$, $40\,ZnO-20\,B_2O_3-40\,P_2O_5$, and $40\,ZnO-30\,B_2O_3-30\,P_2O_5$ together with literature data on BPO_4 and $Zn_2P_2O_7$ compounds [16]. The survey of the crystallization products of annealed boro-phosphate glasses is given in Table I.

Acknowledgements

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