STUDIES ON THE PROCESS OF $Bi_{12}MO_{20}$ (M=Ti, Ge, Si) FORMATION FROM OXIDES

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Using DSC technique, the chemical interaction in Bi_2O_3+MO_2 mixtures resulting the $Bi_{12}MO_{20}$ phase, (M=Ti, Ge and Si) was monitored. Kinetic parameters for the primary stage of interaction were yielded by the non-isothermal method of kinetic evaluation of experimental heat flux DSC curves. The model of three-dimensional diffusion according to Jander was fitted as the best in a statistical sense.

Keywords: bismuth oxide, ceramics, electronic materials technology, kinetic parameters

Introduction

Bismuth oxide is of interest because of its increasing importance in the ceramic fields and electronic materials technology. In Bi_2O_3-MO_2 (M=Ti, Ge, Si) systems the compounds $Bi_{12}MO_{20}$, crystallizing in cubic system (space symmetry group 123), are formed [1, 2]. The single crystals of these compounds are strongly piezoelectric, optically active and manifest photoconductivity properties.

The aim of the present paper has been to elucidate the character and the temperature ranges of processes leading to $Bi_{12}MO_{20}$ formation using DSC technique.

The results of studies on the thermal behaviour of mixtures of Bi_2O_3 with TiO_2, GeO_2 and SiO_2 (mole ratio 6:1) by DSC are presented. The DSC measurements of the reacting mixtures were evaluated by means of the non-isothermal kinetic method. The results of kinetic evaluation were compared with the results obtained in [3, 4] by the isothermal kinetic method.

Experimental

The reagents Bi_2O_3, GeO_2, TiO_2 and SiO_2 of high purity (99.99 mass.%) were mixed in the stoichiometric ratio $Bi_2O_3:MO_2=6:1$ and finely ground using a Retzsch grinding mill. The starting oxides were preliminarily calcined at 500°C. Powdered samples were pressed into pellets of about 1 mm thickness and 5 mm in diameter; the weight of the pellets varied from 250 to 350 mg.

The studies were carried out using a Netzsch model DSC 404 calorimeter, equipped with a platinum furnace capable of operating to 1500°C and platinum/rhodium sample carrier. Data acquisition and instrument control were accomplished using a 16/32 bit computer system with peripheral units and the appropriate software.

The specific heat values were obtained from DSC measurements of three scans, accordingly, the first run is for empty sample pan, to get a baseline, the second one with sapphire as a standard serves to determine the sensitivity curve of the sample carrier, and the third run is for studying the sample. DSC measurements were conducted at heating rates of 2.5 and 10 deg·min^{-1} from 150° to 950°C.

The kinetic evaluation of the thermal measurements was done by a Netzsch Thermokinetic Analysis software including calculation by multiple linear regression based on the modified Friedman equation and nonlinear regression applying the Runge-Kutta-algorithm of fourth degree in a modified Marquardt-method. The kinetic equations corresponding to the appropriate reaction types were solved and the kinetic parameters, namely the frequency factor A, activation energy E and reaction order n, were calculated.

The X-ray diffraction patterns of the samples were obtained using a Geigerflex X-ray diffractometer with CuK$_\alpha$ radiation.

Results and discussion

In the DSC experiments starting with the unreacted mixtures, the samples were scanned at different heating rates up to the temperature of reaction completion. The course of the DSC curves for GeO_2, SiO_2 and TiO_2 containing mixtures was quite different (Fig. 1a, b, c).

As can be seen from Fig. 1c, the DSC curve of the mixture with TiO_2 shows two endothermic peaks: the first, at 729°C, corresponding to the $\alpha \rightarrow \delta$ Bi_2O_3 phase transition, and the second, at 853°C, associated with the decomposition of incongruently melting $Bi_{12}TiO_{20}$. The course of the DSC curve before the latter peak was endothermic, and at high heating rates the small peak at 825°C associated with Bi_2O_3 melting could be sometimes observed.

For mixtures containing SiO_2 and GeO_2 (Fig. 1a, b), three endothermic peaks, characterizing the $\alpha \rightarrow \delta$ Bi_2O_3 phase transition, and melting processes of δ-Bi_2O_3 and of the $Bi_{12}MO_{20}$ formed were observed. As for the exothermic peaks, the effects at 851°C for SiO_2 mixtures and at 868°C for GeO_2 represented, evidently, the interaction between bismuth oxide melt and unreacted silicon and germanium dioxides, which yielded $Bi_{12}SiO_{20}$. The exothermic peak at 787°C for the germanium-containing mixture as well as the complex character of the DSC curve before the beginning of all the peaks, reflects some peculiarities of interaction with germanium oxide.
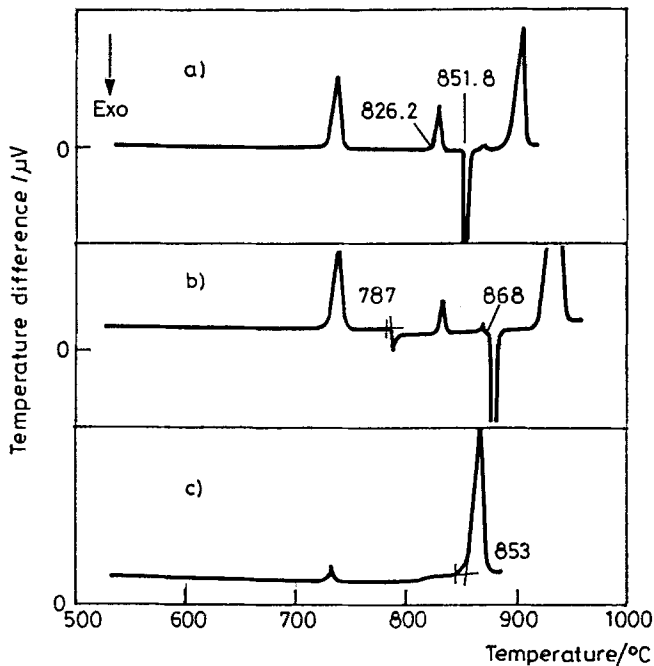

Fig. 1 Experimental DSC curves of Bi_2O_3+MO_2 mixtures: (a) M=Si; (b) M=Ge; (c) M=Ti

Since the XRPD (X-ray powder diffraction) analysis of the samples, heated to this temperature, did not identify any other phases except $Bi_{12}GeO_{20}$ and Bi_2O_3, the effect at 787°C was assumed to characterize one of the intermediates of interaction. This may be possible because the temperature increase induced changes in the atomic mobility connected with the atom distribution along the phase boundaries.

Analysis of interaction processes

For detailed kinetic analysis of DSC curves, it is necessary to identify the main stages of the process. For this purpose we have investigated the following characteristics of the process, observed while heating unreacted mixtures:

(i) the enthalpy changes during the $\alpha \rightarrow \delta$ Bi_2O_3 phase transformation and melting of Bi_2O_3

(ii) the specific heat dhanges before, during and after the $\alpha \rightarrow \delta$ Bi_2O_3 transition;

(iii) the specific heat curves of virgin mixture and reacted one, obtained at heating rates of 2 and 10 deg·min^{-1}.

Results obtained for (i) and (ii) are presented in Table 1

The enthalpy changes of phase transformations in Bi_2O_3 may be a measure of the degree of conversion of Bi_2O_3 to $Bi_{12}MO_{20}$. It can be seen in Table 1 that the enthalpy changes of the $\alpha \rightarrow \delta$ Bi_2O_3 transition for SiO_2- and GeO_2-containing mixtures are very close to each other, whereas for TiO_2-containing one it is three times smaller, evidently because of the higher degree of chemical conversion of Bi_2O_3. As for specific heat changes, Table 1 shows that the heating of mixtures in the temperature range of 290°–710°C and during the polymorphous transition of Bi_2O_3 was accompanied by the exothermal process which occurred in the samples and, therefore, caused the specific heat to decrease.

Table 1 The specific heat changes ($J·g^{-1}K^{-1}$) and the enthalpy changes ($J·g^{-1}$) for $Bi_2O_3+MO_2$ mixtures studied; the heating rate was 2 deg·min^{-1}

$T / °C$	ΔC_p 290–710	$\Delta H_{\alpha \rightarrow \delta}$	ΔC_p 720–750	ΔC_p 750–815	ΔH_m	ΔC_p 815–835
MO_2:						
SiO_2	–0.26	60	–0.05	–0.11	22	–0.22
GeO_2	–0.26	62	–0.08	–0.42	11	–0.58
TiO_2	–0.50	20	–0.18	+0.27	2	+0.23

On further heating within the temperature range of 750°–815°C, the specific heat change of the TiO_2-containing mixture became positive, and thus revealed the elimination of the exothermic process. Thus, two main stages of the formation process of $Bi_{12}TiO_{20}$ were determined, namely an interaction in the temperature range of 290°–710°C and the $\alpha \rightarrow \delta$ Bi_2O_3 transition. The XRPD patterns of specimens heated to 500° and 700°C, have evidenced the presence of $Bi_{12}TiO_{20}$ and small amount of Bi_2O_3. Heating to 840°C resulted in the complete

conversion to sillenite. We have seen no evidence of the formation of any other mixed bismuth-titanium oxides.

As for SiO_2- and GeO_2-containing mixtures, the data of Table 1 testify several additional stages of the interaction.

The specific heat curves according to (iii)

The specific heat data of the $Bi_2O_3+TiO_2$ mixture, are presented in Fig. 2. The specific heat curves of unreacted mixtures demonstrate the exothermal effect of sintering between 190° and 290°C, as well as the $C_p(T)$ curve of pure Bi_2O_3. Although the dispersity degree of powdered samples was not controlled, precautions were made to use equal duration and intensity of grinding for all the mixtures studied.
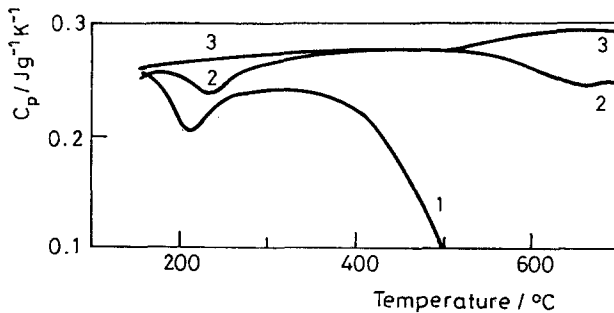

Fig. 2 Specific heat of the unreacted mixture of Bi_2O_3 and TiO_2 at various heating rate: 2 deg·min^{-1} (curve 1); 10 deg·min^{-1} (curve 2); and of the reaction products at 10 deg·min^{-1} (curve 3)

The increase in the specific heat values after the ending of the sintering process was followed by a further decrease which became clearly noticeable in the case of a heating rate of 10 deg·min^{-1}, from about 520°C (curve 2, Fig. 2). After cure in the calorimeter, the sample was cooled and reheated to give the temperature dependence of the specific heat of the products formed after the first DSC experiment (curve 3, Fig. 2). The specific heat curve obtained in the second scan had a normal character with a gradual increase of the C_p values which differs from the curve obtained in the first scan.

For the $C_p(T)$ curve obtained at a heating rate of 2 deg·min^{-1}, the starting C_p values at 150°–170°C are higher than those of samples obtained after the exothermic effect of sintering at 250°–350°C. The course of the $C_p(T)$ curve, taking into account the starting values at 150°–170°C, cannot be associated with the normal course of C_p curve. Evidently, the exothermic sintering process is accompanied by some other exothermic process. It seems reasonable to assume that during the physical process of sintering not only changes in the size and shape of solid particles, resulting in the phase boundary formation occur, but

also the primary stage of interaction takes place. Thus, the initial temperature of interaction at a heating rate of 2 deg·min^{-1} is shifted towards the sintering temperature range. Similar data were obtained for other mixtures showing the beginning of the interaction process.

Kinetic analysis

Non-isothermal kinetic analysis was used to obtain kinetic parameters of processes from the results of thermal analysis. To estimate the kinetic parameters, the heat-flux-DSC measurement was used.

For the stage proceeding after the sintering process, the best model for data evaluation from the statistical point of view was the model of three-dimensional diffusion of Jander's type. This estimate agreed well with the results of studies [3] in which the diffusion model was also proposed as the best for this temperature range.

Table 2 Kinetic parameters evaluated using non-linear regression with the 3-dimension (D3) model of Jander's type

MO$_2$	Correlation coefficient	lg (A×s)	E / kJ·mol^{-1}
SiO$_2$	0.9971	1.96±0.29	89.6±4.5
GeO$_2$	0.9862	3.71±0.37	124.1±5.8
TiO$_2$	0.9985	4.59±0.41	135.1±6.3

In Table 2 the results of kinetic evaluation obtained using the non-isothermal kinetics method, are given. As seen from Table 2, the correlation coefficients are quite good for SiO$_2$- and TiO$_2$-containing mixtures. The data obtained for these mixtures allow the conclusion that the rate constant of the reaction with titanium dioxide is higher than that of the reaction with silicon dioxide. This conclusion agrees well with the results of the thermochemical analysis of mixtures and, therefore, confirms the suitability of the diffusion model for kinetic evaluation in this temperature range.

Conclusion

Thus, in the present paper the formation processes of Bi$_{12}$MO$_{20}$ (M=Ge, Si, Ti) were studied and the temperature ranges of the primary stages of interaction

were determined. The data obtained by non-isothermal treatment revealed the beginning and the maximum rate of the reactions, and thus might be used to optimize the temperature programme of solid state synthesis of compounds of sillenite type.

References

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Zusammenfassung — Mittels DSC wurde die Bildung von $Bi_{12}MO_{20}$-Phasen aus Bi_2O_3+ MO_2-Gemischen (mit M= Ti, Ge uns Si) untersucht. Die kinetischen Parameter für den ersten Schritt der Reaktion erhielt man mittels einer nichtisothermen Methode der kinetischen Auswertung der experimentellen Wärmefluß-DSC-Diagramme. Als bestes Modell zur Beschreibung des Vorganges ergab sich das dreidimensionale Diffusionsmodell von Jander.