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CHEMICAL INTERACTIONS IN THE SYSTEMS $BaCuO_2$ - PbO AND $YBa_2Cu_3O_7$ - PbO

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Chemical interactions were found to occur in the systems $BaCuO_2$ - PbO and $YBa_2Cu_3O_7$ - PbO at 600-800°C. The chemical peculiarities of these reactions are explained on the basis of redox transformations, with formation of the phase $BaPbO_3$.

We earlier reported the formation of the phase $BaPbO_3$ in the system $BaCuO_2$ - PbO [1]. In the present work, the chemical reactions of lead oxide in two systems have been studied by means of thermal analysis and X-ray analysis.

Experimental

The compound $BaCuO_2$ was synthesized from $BaCO_3$ and CuO by sintering at 950-970° during 6 hours with three times grinding. The compound $YBa_2Cu_3O_7$ was prepared by the usual method [2]. In all experiments, the lead oxide was of analytical grade purity.

Chemical analysis of the studied compounds was performed by customary methods [3-5].

Thermoanalytical investigations were carried out by means of a Q-1500-D Derivatograph (MOM, Hungary). The sample mass was 400-500 mg; the heating and cooling rates were 10 deg/min; the crucible was a home-made one consisting of high-density aluminium oxide; atmosphere: air.

X-ray analysis of the final products in tablet form was carried out by means of a DRON-UMI, DRON-3M, with filtered Cu-radiation. Sample

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resistance was measured as a function of temperature by the standard 4 points method at constant current (1-40 mA).

Results and discussion

Thermoanalytical curves of the interactions of PbO with $BaCuO_2$ and with $YBa_2Cu_3O_7$ are shown in Fig. 1. The reactions take place with sample mass increase at 600-800°. It is evident that the mass increase can result only from oxygen uptake. Lead can exist in two oxidation states: Pb^{2+} and Pb^{4+}. The highest oxide, PbO_2, is thermally stable up to 400°. It is worth noting that the quantity of absorbed oxygen (calculated from the PbO quantity and the mass increase) is in accordance with only half of the oxygen amount necessary for the oxidation $Pb^{2+} \rightarrow Pb^{4+}$. It is possible to explain this on the basis of the high reduction properties of lead oxide, with such chemicel reactions as stage I (without mass change): $BaCuO_2 + PbO \rightarrow BaPbO_3 + Cu$; stage II (with mass increase): $2\ Cu + 0.5\ O_2 \rightarrow Cu_2O$.

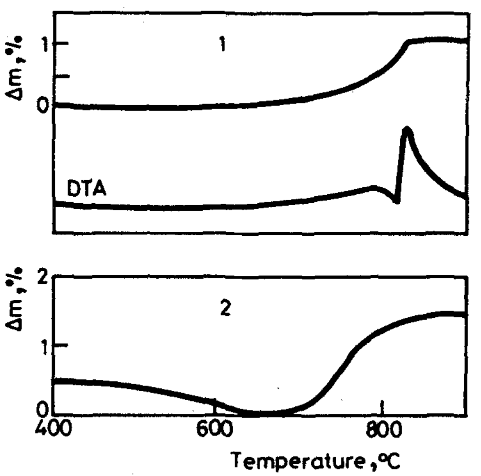

Fig. 1 Thermoanalytical curves of the chemical interaction: 1. $BaCuO_2$ +0.5 PbO; 2. $YBa_2Cu_3O_7$ +PbO

These chemical reactions are valid for a quantitative explanation of the mass increase without the direct oxidation $Pb^{2+} \rightarrow Pb^{4+}$.

The kinetics of these chemical interactions was studied. The experiment was carried out with a plate-like holder, at a heating rate of 5 deg/min. The best description of the curve is the equation of three-dimensional diffusion, with $E = 120$ kJ and $\log A = 2.2$. It is not clear what the rate-limiting step is: oxygen diffusion to the grain contacts, or chemical diffusion in the solid state. Chemical diffusion in the solid state seems to be the more preferable explanation, as the melting process sharply promotes the oxidation reaction: the endo peak of melting ($t^{o}_{max} = 820^{o}$) changes sharply to an exo peak of fast oxidation (DTA curve in Fig. 1). The limiting step seems to be stage I ($BaCuO_2$ + PbO $\rightarrow BaPbO_3$ + Cu). The extent of the slow reaction before melting decreases when the heating rate is increased (from 5 to 10 deg/min), and the proportion of the fast process (with a large exo effect) increases.

The results of chemical analysis of the reaction products (after heating to 850^{o}) in the system $BaCuO_2$ - PbO confirms this chemical explanation. The quantity of Pb^{4+} is equal to approximately half of the starting Pb^{2+} quantity. Typical results on the mass change and the quantity of Pb^{4+} formed during the chemical interaction $BaCuO_2$ + PbO are given in Table 1.

Table 1

Starting materials, mg	Experimental mass increase, mg	Calculated mass increase (till $BaPbO_3$), mg
$BaCuO_2$ + PbO, 491	6.5	7.1

X-ray analysis shows that in the system $BaCuO_2$ - PbO after heating (in the concentration ratio range PbO : $BaCuO_2$ = 0.2-2.0) there is a decrease in the phase $BaCuO_2$ with increase of the added phase PbO. The diffraction pattern of $BaCuO_2$ disappears at PbO : $BaCuO_2$ = 1:1. The excess of PbO remains unreacted in the heated samples, while the phase CuO exists in all samples of the system.

The diffraction lines of $BaPbO_3$ are very strong in the patterns, but in the studied samples this phase does not have exactly cubic symmetry: the lines are markedly broadened, and splitting is observed.

The products in the system $YBa_2Cu_3O_7$ - PbO were studied too, at PbO : $YBa_2Cu_3O_7$ ratios of from 0.3 to 2.0. The intensities of the diffraction lines of $BaPbO_3$ and $YBa_2Cu_3O_7$ are comparable when this ratio is 0.5. There is only a trace of $YBa_2Cu_3O_7$ when the ratio is 1.0. Only two phases ($BaPbO_3$ and CuO) exist when the starting ratio is 2.0; there were no traces of $YBa_2Cu_3O_7$ and PbO.

The changes in the resistance of the samples obtained in the system $YBa_2Cu_3O_7$ - PbO on heating up to 850° are shown in Fig. 2. The temperature-dependence of the resistance changes sharply with increase of the PbO concentration in the starting sample; this points to chemical interaction in the system.

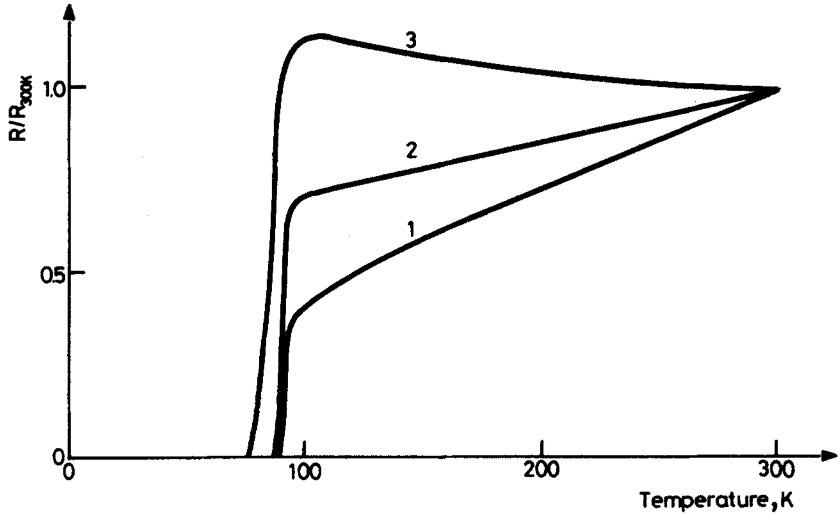

Fig. 2 Temperature-dependent resistance (in heated mixtures): 1. $YBa_2Cu_3O_7$ + 0.1 PbO; 2. $YBa_2Cu_3O_7$ + 0.3 PbO; 3. $YBa_2Cu_3O_7$ + PbO

Conclusions

Chemical interactions were found in the systems $BaCuO_2$ - PbO and $YBa_2Cu_3O_7$ - PbO in the temperature interval 600-800°. The chemical features of the reactions are explained on the basis of redox transformations, with formation of the phase $BaPbO_3$.

References

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Zusammenfassung — Bei 600-800°C konnte im System $BaCuO_2$ - PbO und $YBa_2Cu_3O_7$ - PbO eine chemische Wechselwirkung festgestellt werden. Die chemische Besonderheit der Reaktionen wurde mit Hilfe von Redoxumformungen unter Bildung der Phase $BaPbO_3$ erklärt.