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ON THE STUDY OF SOLID-LIQUID STABLE-METASTABLE PHASE EQUILIBRIA

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ABSTRACT

In many cases we need to distinguish the regions of existence of stable and metastable phases. The recommended approach is to subdivide the phase diagram into simpler subsystems by extrapolating boundary lines. In this connection the usibility of static (X-ray diffraction) and dynamic (DTA) methods are discussed.

INTRODUCTION

Although equilibrium diagrams specify what composition and relative amount of each phase are present at equilibrium, they do not show the metastable non-equilibrium phases to the produced when equilibrium formation is prevented. The interpretation of the data experimentally obtained depends upon the aim of our study. We can determine an equilibrium phase boundary by using static (zero heating rate) conditions, although quasistatic (non-zero heating rate) conditions are actually applied. The result is "quasiequilibrium" phase diagram in which a certain degree of non-equilibrium exists depending upon the true rate of the temperature change. However, analysing the existing experimental data in more details, we can try to differentiate stable and metastable phase boundaries /1/.

RESULTS AND DISCUSSION

The determination of stable and metastable phases can be conveniently documented on the system PbO-Ga_2O_3 /2/ which was investigated by three independent techniques:

Indirect dynamic method of DTA, where the changes of the state of the system are indicated by the detection of temperature changes between the sample and the reference indicating the enthalpy changes due to phase transitions in the material (o).

Direct dynamic method of high temperature microscopy observing the phase creation and/or disappearance (+).

Indirect static method of X-ray diffraction indicating the existence of individual phases (■, ▲) and their characterization for the samples prepared either by quenching of high temperature structures or by very slow cooling as used in the crystal growth by flux method. The results are collectively shown in the Fig. 1.

It can be seen that a good coincidence exists along the solidus and liquidus of PbO-rich compositions, whereas certain deviations in the peritectic region can be noticed. The phase boundary derived exclusively from DTA measu-

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rements [+)] can thus be misleading. A good coincidence between DTA and high-temperature microscopy is exhibited for liquidus curves, except that for the peritectic region.

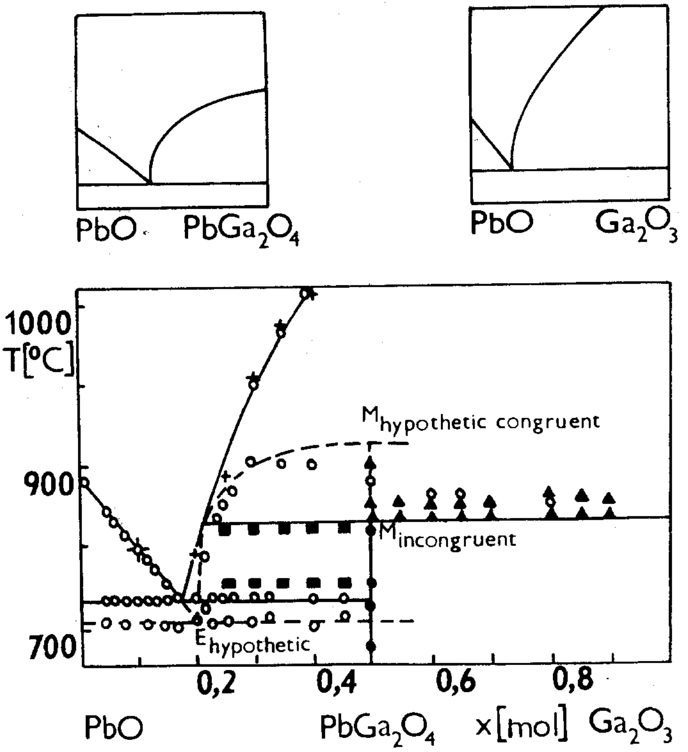

Fig. 1: Phase diagram of PbO-Ga_2O_3 system, experimentally obtained by DTA (o), X-ray diffraction analysis (■ , ▲) and high-temperature microscopy (+).

[+)] It is worth noting that the sensitivity of DTA measurements is closely related on the type of reaction and the enthalpy production. The indicated peak area is thus dependent upon both the compositions investigated and the positioning of this composition to the invariant points. The heat extent of a transition is given by the ratio resulting from the lever rule so that the interpretation of data obtained for the compositions falling in the regions with a small amount of solid phase is difficult.

The discrepancies are, probably, caused by the difference virtually inherent in the static X-ray and the dynamic DTA methods. The open circles corresponding to DTA data show higher temperatures of the peritectic phase transition than that determined by X-ray diffraction (solid squares and triangles). This hysteresis can be explained by kinetic reasons which prevent the formation of the stable phase so that the metastable phase can be created later on.

In this sense we attempted to analyse the phase diagram in Fig. 1. Such a phase diagram can be imagined as a superposition of two simple phase diagrams of an eutectic type, one within PbO-Ga_2O_3 and the other PbO-$PbGa_2O_4$, having so the independent stable compound $PbGa_2O_4$. Their synthesis within common temperature-concentration axis produce our diagram with a peritectic region of metastable $PbGa_2O_4$. Such approach retains the boundary lines even in metastable regions which are drawn dashed. They intersect in the hypothetical invariant points of congruent melting, M, and the hypothetic eutectic melting, E.

These boundaries can be mathematically evaluated similarly to those for stable phase diagrams as already shown in the previous studies /3–6/.

CONCLUSIONS

The success of phase analysis is conditioned by our capacity to distinguish equilibrium and non-equilibrium states resulting from our experimental inability to secure ideally equilibrium measurements. This is a typical case of thermal analysis, where particularly DTA is widely employed to determine phase boundaries. Therefore, it is necessary to adopt a certain strategy /1/: The shape of individual DTA peaks characterizes preliminarily the type of processes in question. From the characteristic temperatures evaluated for the peak onsets and apexes of individual compositions we can preconstruct the phase diagram regions. For a more precise localization of the invariant point the method of linear extrapolation of the heat amount versus the composition is recommendable. For the delimination of metastable phase regions a complementary independent method must be used preferably that of the direct method of X-ray diffraction phase analysis. In the case of existence of metastable regions we can try to subdivide the phase diagram into the simpler subsystems by extrapolating the boundary lines. The course of metastable lines can now be calculated similarly to the practice of ordinary phase diagrams assuming the thermodynamic data of individually chosen subsystems are known.

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