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The Prediction of Solid-Liquid Diagram Topology of Ternary Systems for the Solution of Problems Related to Materials Science

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Abstract

It is convenient to separate the problem connected with the investigation and description of phase diagrams of three-component systems into two parts: a) investigation of the topology of phase diagram, b) its quantitative description. Both parts have their own specific features. The paper presents the examples of two topological tasks solved. The first task is the description of $x_1 - x_2 - T$ phase diagram topology at sufficient initial information. The algorithm of building up a graph of the phase diagram is described for the system GeTe – Sb_2Te_3 – Te, the graph containing complete information on the system's topology in a compact form. The second task is the construction of different versions of the topological images of the phase diagram which are in agreement with the set of initial data when they are insufficient. As examples, four versions of phase diagram for the system $Li_2O \cdot B_2O_3 - Li_2O \cdot MoO_3 - MoO_3 - B_2O_3$ are built that agree with the set of experimental data available. Discriminating experiments are planned according to the results of the analysis performed; on this basis, a correct scheme is selected for the liquidus surface of the system under consideration.

INTRODUCTION

The data on phase diagrams are necessary for the elaboration of new materials, solution of different problems in metallurgy, chemical technology, mineralogy, ecology and other areas of science and technology. It should meet the demands of completeness, reliability and compatibility [1]. A user going to apply primary and reference data for the solution of scientific and applied tasks often meets the problem how to evaluate the quality of literature information concerning the phase diagram. It is most easily solved for unary and binary systems. For ternary systems, this task is complicated by the fragmentary character of the information concerning their phase diagrams reported in primary communications, reference books and databases. The items presented usually include the projections of liquidus surface onto the composition plane, isothermal and polythermal sections. This presentation of the diagram puts forward several questions:

– are the fragments presented sufficient to provide a complete description of the phase diagram of a three-component systems?

– what should be done if a user needs the data on the structure of a region not present in the published fragments of the diagrams?

– are the fragments of the diagram described in primary literature compatible with each others?

– what should be done in case of the evident lack of information concerning phase diagrams?

In order to find answers to these questions, it is reasonable to separate two tasks. One of them is the investigation and description of the phase diagram as a complicated geometric structure in three-dimensional space ($T - x_1 - x_2$ and $P - x_1 - x_2$) or four-dimensional one ($P - T - x_1 - x_2$). The second task is quantitative description of the diagram. A result of solving the first

task is the construction of the topological image of phase diagram. The solution of the second task leads to the construction of its metric image [1]. In the present paper we describe two examples of the solutions of topological tasks. One of them demonstrates how one can build up a topological image of the phase diagram using its fragments in the case when the initial information is complete. The problem is solved for the subsystem GeTe – Sb_2Te_3 – Te which is a part of the three-component system Ge – Sb – Te. The solution of this task is a part of the prediction of phase diagrams. The second example relates to the investigation of the topology of phase diagram under the conditions of the lack of initial information for the subsystem $Li_2O \cdot B_2O_3$ – $Li_2O \cdot MoO_3$ – MoO_3 – B_2O_3 which is a part of the system B_2O_3 – Li_2O – MoO_3.

THE GeTe – Sb_2Te_3 – Te SYSTEM

The system Ge – Sb– Te is of practical interest because it contains a series of double and ternary phases with thermoelectric properties. This system involves a quasibinary section GeTe – Sb_2Te_3 which gives the possibility to study the subsystems GeTe – Sb_2Te_3 – Te and Ge – GeTe – Sb_2Te_3 – Te separately. The authors of [2] built up 4 polythermal sections (isopleths) of the phase diagram of the second subsystem by means of DTA. Using experimental isopleths and the data on boundary binary systems, the authors built up several isothermal sections, a scheme of the liquidus surface and flow diagram (a scheme of phase reactions) for this system. The designations for phases in this system will be as follows [3]: α-Sb_2Te_3 = α, α-, β- and γ-GeTe = α^*, β^* and γ^*, $Ge_3Sb_2Te_6$ = A, $GeSb_2Te_4$ = B, $GeSb_4Te_7$ = C.

Unambiguous data on the phase diagram of a three-component system can be obtained from a complete set of topologically different isothermal sections ordered over temperature. It is convenient to select the first section at any temperature at which only melt exists in the system (Fig. 1). The decrease of temperature leads to the phase reaction involving crystallization of germanium telluride from the three-component melt: $L \rightarrow \beta^*$. This reaction starts at the invariant point of the Ge – Te system. This causes the changes in isothermal section of the diagram. Then it remains similar till one more phase reaction starts in the system: $L + \beta^* \rightarrow A$. So, the topology of isothermal section changes as a result of phase reactions at invariant points of the phase diagram that lead to the appearance and/or disappearance of the existence fields for some two- and three-phase complexes in the isothermal section. Figure 1

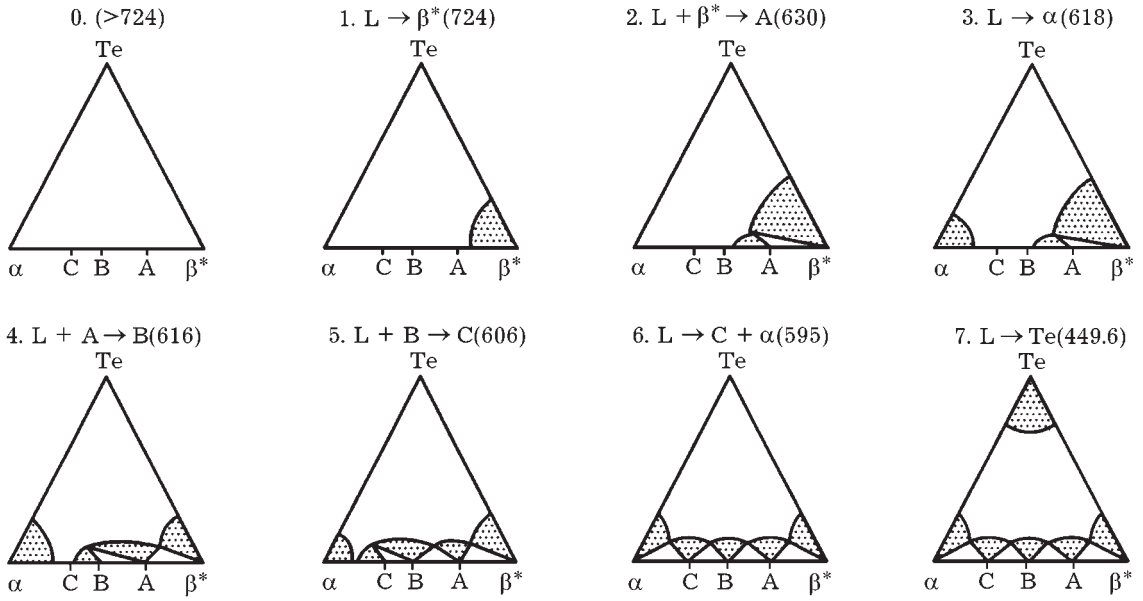

Fig. 1. Transformation of isothermal sections of the subsystem GeTe – Sb_2Te_3 – Te under temperature decrease as a result of the first seven phase reactions with the participation of the melt. The temperatures of phase reactions (in °C) are given in parentheses (according to [2]).

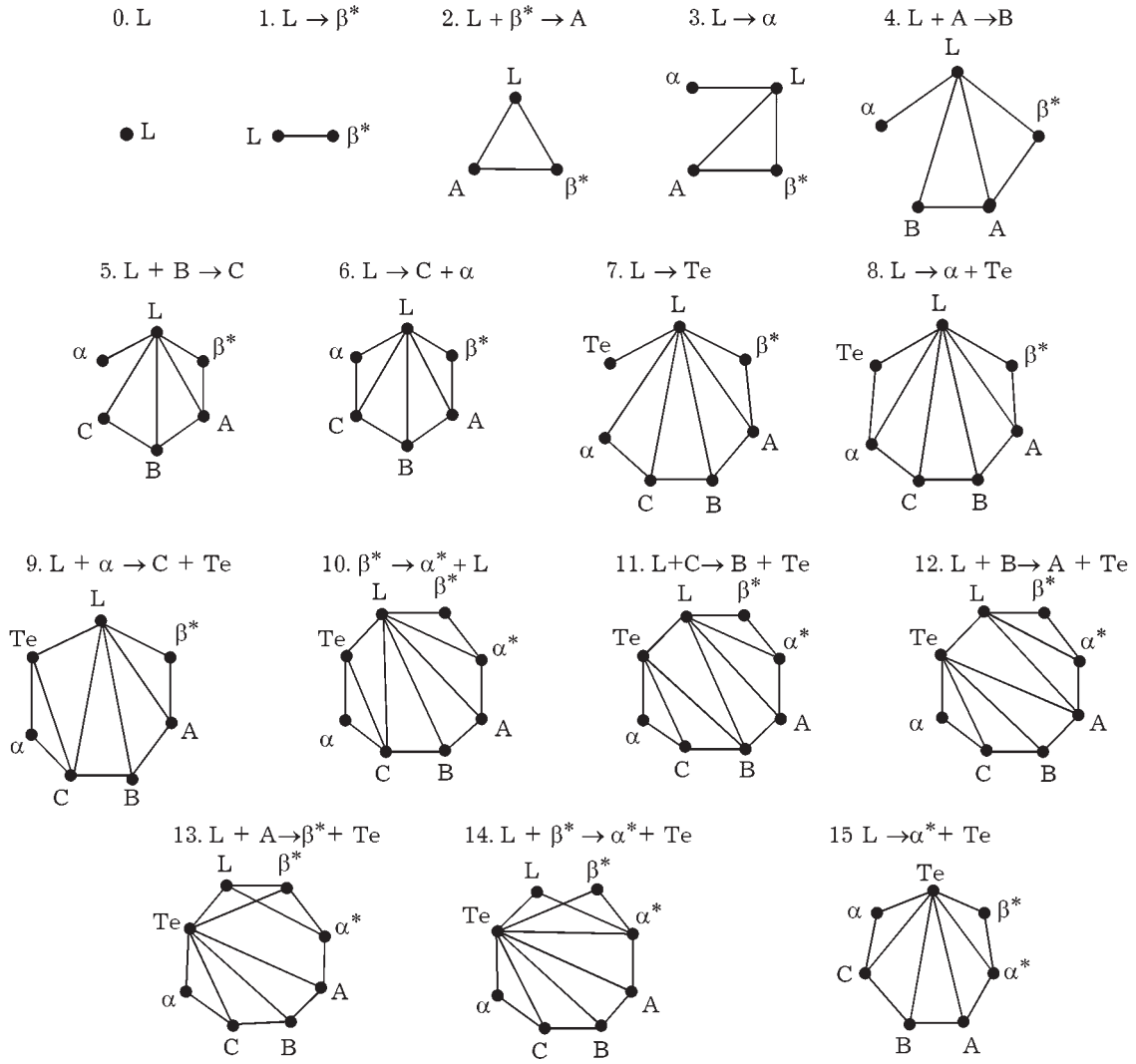

Fig. 2. The graphs of isothermal sections of the phase diagram of GeTe – Sb_2Te_3 – Te.

shows the transformation of the sections for the first seven reactions in the system GeTe – Sb_2Te_3 – Te.

If q phase reactions take place within the temperature range under consideration (*i. e.*, the same number of invariant points exists), the topology of the phase diagram is unambiguously described by $q + 1$ isothermal sections. Because of this, in order to describe the topology, it is sufficient to build up only one isothermal section of the diagram and compile a list of phase reactions ordered over temperature. It includes the lists of reactions occurring in binary edging systems Te – α, Te – β*, α – β* and the list of reactions in ternary system. All these reactions can be determined using the phase diagrams of binary systems and isopleths reported in [3].

Let us select an isothermal section of the phase diagram. The phases present in it will be designated as points and two-phase complexes as lines connecting these points. The scheme thus obtained is a graph of the isothermal section of the diagram. Let the first graph be number zero. Then, the graph No. 1 will be obtained from graph zero as a result of the reaction No. 1 (see Fig. 1). The numbering of the rest graphs coincides with the numbers in the list of temperature-ordered phase reactions. An equation of the reaction number n can be easily determined from the graphs No. $n - 1$ and n. The list of graphs of isothermal sections is shown in Fig. 2.

The graphs shown in Fig. 2 provide a complete description of the topology of the phase diagram for the system GeTe – Sb_2Te_3 – Te. However, this description is not compact. Having built a graph union shown in Fig. 2, we shall obtain a topological graph of the phase diagram (Fig. 3)

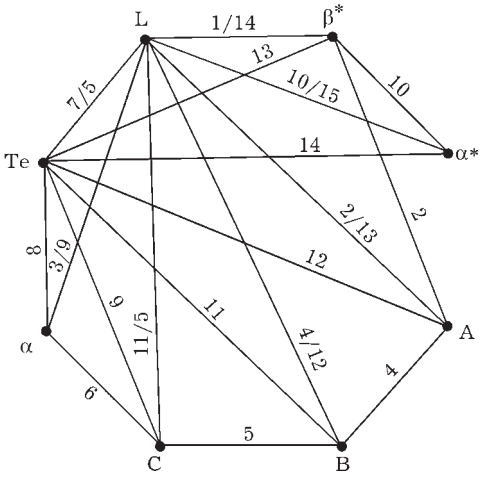

Fig. 3. Topological graph of the fusibility diagram for the system GeTe – Sb_2Te_3 – Te.

[3]. In order to conserve information on temperature sequence of phase reactions, the edges on the graph are marked. For example, see the edge L – A marked with the ratio 2/13. This means that the complex of the melt and phase A appeared in the phase diagram as a result of reaction 2 and disappeared as a result of reaction 13. Some edges are marked with only one figure which is a number of a reaction leading to the formation of the given two-phase complex. Such edges exist in the phase diagram at the lower border of the temperature range under consideration. It should be noted that the topological graph of the phase diagram can be used to solve such tasks as the determination of phase reaction at the given invariant point, building of the schemes of isothermal sections and isopleths, building of the liquidus surface scheme, *etc.* The algorithms of solving these tasks with the help of the topological graph are described in [3].

THE SYSTEM $Li_2O \cdot B_2O_3$ – $Li_2O \cdot MoO_3$ – MoO_3 – B_2O_3

This system is of interest for the growth of non-linear optical crystals of lithium triborate. The following designations will be used in the description of the composition of ingredients and compounds: B = B_2O_3, L = Li_2O, M = MoO_3. The liquid phase will be designated as *L*. In order to build up a topological image of the ternary system, we shall use the data of [4, 5] concerning phase diagrams of the systems B – L and B – M. Due to incompatibility of the data reported in different papers concerning the structure of the diagram for the system L – M, we studied this system by means of DTA. Besides, we used our own data on the crystallization regions for lithium borates in the ternary system [5], unpublished results of the DTA studies of the medium regions of LB_3 – M and LB_3 – L_2M_5 sections (they look like the fragments of diagram with simple eutectics; the temperatures of eutectics are 610 and 530invariant °C, respectively), as well as the LM – LB section which is quasibinary and separates the triangle of the compositions of the B – L – M system into two parts: L – LB – LM and LB – LM – M – B. The topology of each one of these subsystems can be investigated separately. In the present work we describe the results obtained for the second subsystem. The initial data for the topological analysis are shown in Fig. 4.

Let us now consider the solution of the task concerning the determination of possible schemes of the topology of liquidus surface using this information and the data on the composition of the sections LB_3 – M and LB_3 – L_2M_5. One can see from Fig. 4 that the number of primary crystallization fields in the subsystem under consideration is 10. According to the phase rule, three solid phases and one liquid one coexist (*i. e.*, three fields of primary crystallization meet) at each invariant point of the liquidus surface. Because of this, 8 invariant points corresponding to the equilibrium of three solid phases and the melt should be present on the liquidus surface, together with 17 lines of two-phase crystallization. Reactions of the peritectic and eutectic types can occur during the crystallization of the melt at invariant points of the system under consideration: L + A → B + C and L → A + B + C, respectively. The first reaction results in the formation of a two-phase complex AB corresponding to a line on the scheme of subsolidus triangulation. In the second one, no complexes of this type are formed. If the number of solid phases on the scheme of subsolidus triangulation is 10, the number of two-phase complexes on this scheme will be 7. Compa-

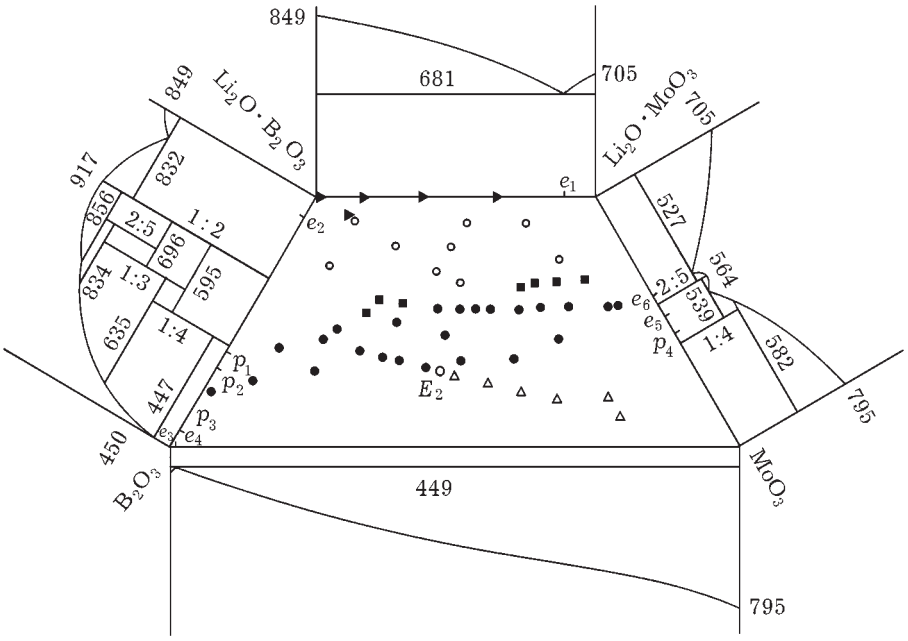

Fig. 4. Initial data for the topological analysis of the phase diagram of $Li_2O \cdot B_2O_3$ – $Li_2O \cdot MoO_3$ – MoO_3 – B_2O_3. Points indicate the compositions at which the phases crystallizing from the melt are determinhed: ▲ – LiB, ○ – LiB_2, ■ – Li_2B_5, ● – LiB_3, Δ – M.

ring this number with the number of invariant points, we find out that one point of the ternary eutectics and seven peritectic points can be present on the liquidus surface.

This conclusion is true if there are no degenerated invariant points on the liquidus surface. Comparing the temperatures of eutectics in the section LB_3 – M (610 °C) and the nearest invariant point in the system L – M (582 °C, see Fig. 4) one can conclude that the eutectic point on this section should be a pass one. So, it is degenerated and its vicinity looks like a "singular saddle". In this case, the two-phase complex LB_3 + M is formed according to the reaction that occurs in quasibinary eutectics, while two points of ternary eutectics are present on the liquidus surface. Taking account of the above, we can write down the following set of invariant reactions with the participation of the melt: L $\rightarrow$ LB_4 + B + M ($E_1 \approx 446$ °C), $L + LB_3 \rightarrow LB_4$ + M (U_1), $L \rightarrow LB_3$ + M (E_2, 610 °C), $L + M \rightarrow LB_3$ + LM_4 (U_2), $L + LM_4 \rightarrow LB_3 + L_2M_5$ (U_3). All the rest phase reactions cannot be deciphered unambiguously on the basis of the available information. Because of this, there are several versions of the topology of liquidus surface in the system in agreement with the available data. Further investigation involves the construction of these versions and planning of the simplest and cheapest discriminating experiments to choose a proper version.

We know the positions of only four pieces out of seven on the scheme of subsolidus triangulation. There are 4 versions of the positions of other pieces in which the following three-phase complexes are present: 1) LB + LM + L_2M_5, L_2M_5 + LB + LB_2, LB_2 + L_2M_5 + L_2B_5; 2) LB + LM + LB_2, LB_2+ LM + L_2M_5, LB_2 + L_2B_5 +

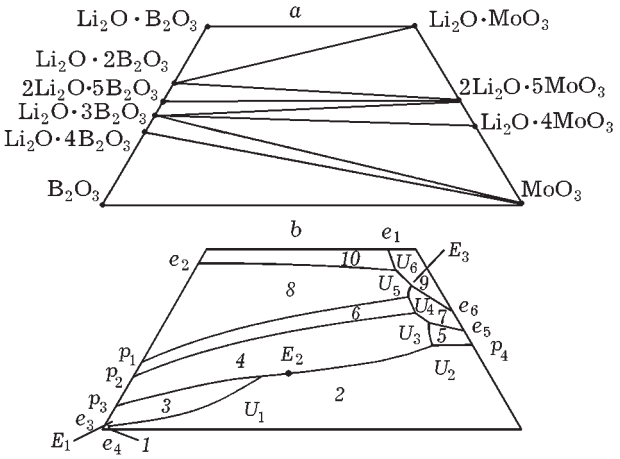

Fig. 5. The schemes of triangulation (*a*) and liquidus surface (*b*) of the subsystem $Li_2O \cdot B_2O_3$ – $Li_{12}O \cdot MoO_3$ – MoO_3 – B_2O_3 according to the data of topological analysis and discriminating experiment. The scheme *b* is shown out of the scale. The regions of primary crystallization of phases are marked: *1* – B_2O_3, *2* – MoO_3, *3* – $Li_2O \cdot 4B_2O_3$, *4* – $Li_2O \cdot 3B_2O_3$, *5* – $Li_2O \cdot 4MoO_3$, *6* – $2Li_2O \cdot 5B_2O_3$, *7* – $2Li_2O \cdot 5MoO_3$, *8* – $Li_2O \cdot 2B_2O_3$, *9* – $Li_2O \cdot MoO_3$, *10* – $Li_2O \cdot B_2O_3$.

L_2M_5; 3) LB + LM + LB_2, LB_2 + LM + L_2B_5, LM + L_2M_5 + L_2B_5; 4) LB + LM + LB_2, LB_2 + LM + L_2B_5, L_2B_5 + LM + LB_3. Each of them corresponds to its own topology of the liquidus surface. So, in order to choose a single version of the liquidus topology, it is sufficient to determine the triangulation of the subsystem under consideration at a temperature somewhat below the solidus. We performed the corresponding experiments and stated that the second version of triangulation is realized in the system. The scheme of liquidus surface topology corresponding to this version is shown in Fig. 5. It should be noted that starting from this scheme it is easy to make a complete list of phase reactions that proceed in the system till complete solidification of the melt, and to build up a topological scheme of the solid-liquid diagram. However, due to the lack of data, it is not possible to define exactly the temperature sequence of these reactions without additional experiments. Because of this, the graph of the system will provide a precise description of only the list of reactions and one of the possible versions of their sequence at the temperature decrease. In spite of the impossibility of final ordering of the phase reactions with respect to temperature, preliminary topological analysis and the liquidus surface scheme obtained on the basis of this analysis greatly simplify the planning of experiments directed at further investigation of the phase diagram.

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