FORMABILITY OF TERNARY INTERMEDIATE COMPOUNDS IN SOME MOLTEN SALT PHASE DIAGRAMS①

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ABSTRACT By chemical bond parameters and pattern recognition or artificial neural network method, the regularity and criterion of formability of ternary intermediate compounds in some molten salt phase diagram have been studied.

Key words: molten salt phase diagram ternary compounds forming criterion

1 INTRODUCTION

Thermodynamic methods can be used for the estimation of the unknown molten salt phase diagram based on the data of binary molten salt phase diagrams. However, when ternary system form ternary compound which does not exist in binary systems, it is difficult to predict unknown ternary phase diagram or reciprocal ternary systems based on the data of binary phase diagrams only. In this paper, the regularity of formability of intermediate compounds in these kinds of phase diagrams is investigated by chemical bond parameter method and pattern recognition or artificial neural networks[1-3], as a complementary work for ternary phase diagram prediction.

2 MODEL AND METHOD OF COMPUTATION

The chemical bond of ternary compounds in molten salt systems is chiefly ionic bond with different degree of partial covalency. The lattice energy of these compounds should be some function of chemical bond parameters including the ionic charge (z_i), the ionic radius (r_i), the ionic charge-radius ratio (z/r_i), and the electronegativity (x_i) of elements. Using these chemical bond parameters, the regularity of the fomability of ternary compounds has been studied. These parameters were used as the inputs of the artificial neural network or features for pattern recognition, and the criterion of formability of ternary compounds was searched.

The computer program of principal component analysis (PCA)[4] of pattern recognition method was used in our work.

A three-layered artificial neural network[5] was also used in our work with chemical bond parameters mentioned above as inputs and the formability data as output (output "1" denotes ternary compound formation, and output "0" denotes absence of ternary compound). Applying BP algorithm and tanh x transfer function, the artificial neural network program of Neuralware Inc. was used. The computation was carried out on a 486 microcomputer.

3 RESULTS AND DISCUSSION

Molten salt ternary systems include com-

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mon-anion system Me, Me′, Me″ | X, common-cation system Me | X, X′, X″ (here Me, Me′, Me″ denote metallic elements, X, X′, X″ denote anion-forming elements or radicals), and ternary reciprocal system Me, Me′ | X, X′. The ternary system data from the handbooks of Посыайко[6] and Воскренсенсая[7] were used as training sets, the results of training and prediction are described in following paragraphs.

3. 1 *Ternary Systems With Common Anion or Cation*

Using the data of 299 ternary systems with common cations or common anions for computation, it can be concluded that: (1) Me^{+}, Me'^{+}, Me''^{+} | X^{-} type systems (here Me^{+}, Me'^{+}, Me''^{+} denote monovalent cations, and X^{-} denotes monovalent anions) have no record of ternary compound formation; (2) Me^{+}, Me'^{2+}, Me''^{2+} | X^{-} systems usually form no ternary compounds with a few of exceptions. Most of the known ternary compounds form in the systems of Me^{+}, Me'^{+}, Me''^{n+} | X^{-} type and Me^{+}, Me'^{+}, Me''^{2+} | X^{2-} type. The common cation system of Me^{+} | X^{-}, X'^{-}, X''^{-} type also has no record of ternary compound formation.

Me^{+}, Me'^{+}, Me''^{n+} | X^{-} (here $n = 2, 3, 4$ etc.) systems often form ternary compounds, for example, $Li_3AlF_6 \cdot 2Cs_3AlF_6$, $NaAlCl_4 \cdot 3CsAlCl_4$, $Na_3AlF_6 \cdot K_3AlF_6$, $7LiBiCl_4 \cdot 3NaBiCl_4$, etc.. We have used the data of Li, Cs, Al | F, Na, K, Al | F, Li, Rb, Al | F, Li, Na, Be | F, Na, Rb, Be | F, Na, K, Cr | Cl, Na, Rb, Cr | Cl, Na, K, Sm | Cl, Na, K, Y | Cl, Na, K, Zr | F, Na, Cs, Al | Cl, Li, Cs, U | F, Na, Cs, V | F, Li, Na, Bi | Cl systems (these systems form ternary compounds), and 64 systems without ternary compound formation[6, 7] as training set, and chemical bond parameters (the ionic radii of Me^{+}, Me'^{+}, Me''^{n+}, X^{-}, the electronegativity of elements, the charge number of ions and charge-radius ratio of ions) are used as inputs of artificial neural networks. And the formability of ternary compounds is used as output ("0" denotes no-compound-formation and "1" denotes ternary compound formation). After training, the trained artificial neural network is used to predict the ternary compound formation in seven systems (Na, K, Be | F, Li, Na, Ti | F, Li, Na, Cd | Cl, Na, Tl, Cd | Cl, K, Cs, Mg | F, Li, Cs, Sr | Cl and Li, Na, Ba | Cl) which are not included in training set. The results of prediction indicate that two systems (Na, K, Be | F and Li, Na, Ti | F) form ternary compounds, and other systems have no ternary compound formation. These results are confirmed by experimental works. Using the same training set, PCA method is also applied for classification. The ternary-compound-forming systems and the systems without compound formation distribute into different regions, as shown in Fig. 1. PCA method is also used for prediction, with good results.

The results of PCA method indicate that large z/r_k of Me''^{n+} ion, small ionic radius of X^{-} ion favor ternary compound formation. This fact implies that larger z/r_k of Me'^{n+} and small radius of X^{-} favor the stability of polyvalent complex anion. So the ternary compound can be considered as a double salt consisting of Me^{+}, Me'^{+} cation and complex an ion $[Me''X_m]^{[m-n]-}$. It is well - known that

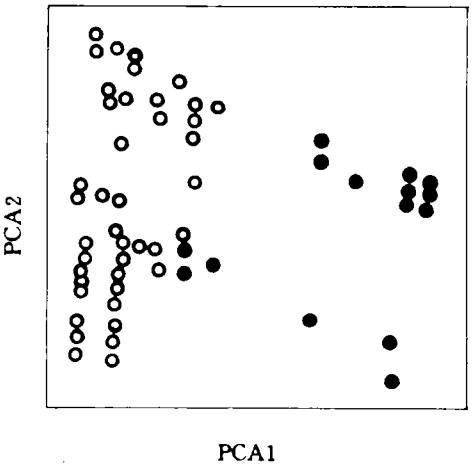

Fig. 1 Formability of ternary compound in Me^{+}, Me'^{+}, Me''^{n+} | X^{-} systmes (PCA method)

●—ternary compound be formed;
○—no ternary compound

many polyvalent anions for double salt with two monovalent cations, such as $Li_2SO_4 \cdot K_2SO_4$ etc. Me^+, Me'^+, $Me''^{2+}|X^{2-}$ type systems also form many ternary compounds (here Me^+, Me'^+ are two monovalent cations, Me''^{2+} is divalent cation, X^{2-} is divalent anion). We take ternary compound forming systems including K, Na, Zn $|SO_4$, Li, Na, Cd $|SO_4$, K, Na, Cd $|SO_4$, Li, K, Cd $|SO_4$ and 9 systems ternary without ternary compound formation as training set, and use PCA method to find the regularities. The results are illustrated in Fig. 2.

3.2 *Reciprocal Ternary Systems*

Molten salt systems consisting of two kinds of anions and two kinds of cations are called reciprocal ternary systems. The compound formed by four kinds of ions is also called ternary compound[8]. Systems of Me^+, $Me'^+|X^-$, X'^- type and that of Me^+, $Me'^+|X^-$, X'^{2-} type have no record of ternary compound formation. Most of ternary compounds discovered distribute in Me^+, $Me'^{2+}|X^-$, X'^{2-} type and Me^+, $Me'^{3+}|X^-$, X'^- type systems. Fig. 3 illustrates the regularity of the formability of ternary compounds (general formula is

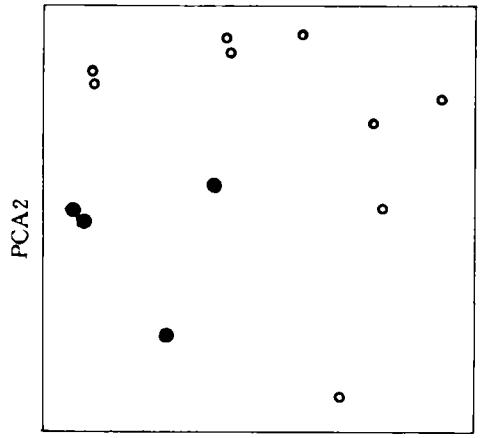

Fig. 2 Formability of ternary compound in Me, Me'^+, $Me''^{2+}|X^{2-}$ systems (PCA method)
●—ternary compound be formed;
○—no ternary compound

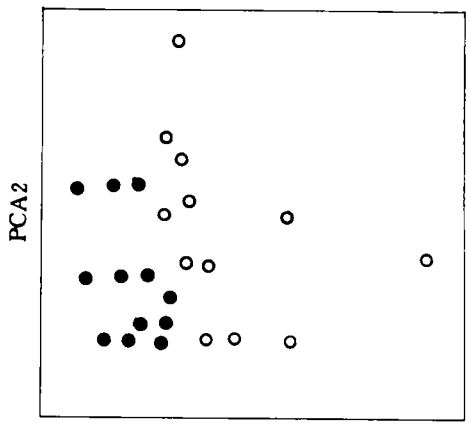

Fig. 3 Formability of ternary compound of Me^+, $Me'^{2+}|X^-$, SO_4^{2-} systems (PCA method)
●—ternary compound be formed;
○—no ternary compound

$MeX \cdot Me'SO_4$ or $MeMe'SO_4X$) by PCA method. The results of PCA method indicate that ionic radii are dominating factors for $MeX \cdot Me'SO_4$ type compound formation. Small Me^{2+} ion and large X^- ion favor the ternary compound formation.

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