MOLTEN SALT PHASE DIAGRAMS CALCULATION USING ARTIFICIAL NEURAL NETWORK OR PATTERN RECOGNITION-BOND PARAMETERS①

Part 2. Prediction of phase diagrams of ternary molten salt systems

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ABSTRACT Using pattern recognition method or the three layered artificial neural network (ANN) method with back propagation algorithm, and with chemical bond parameters as features or inputs, the properties or characteristics of the phase diagrams of some ternary molten salt systems have been investigated. The trained ANN was used to predict the formability of ternary intermediate compound, the type of phase diagram. Moreover, the results of computerized prediction for two unknown systems are confirmed by experimental work.

Key words phase diagram calculation artificial neural netwrok pattern recognition bond parameter ternary molten salt system

1 INTRODUCTION

The CALPHAD of thermodynamic method has been used for the estimation of the unknown ternary molten salt phase diagrams based on the data of binary molten salt phase diagrams. The functions of CALPHAD are as follows. First, it can calculate and plot some phase diagrams of binary or ternary systems with the known thermodynamic functions. Second, it can predict the properties of the unmeasured parts in some phase diagrams. Third, it may test the reliability of the phase diagrams measures. Fourth, it can make a probable prediction for the unknown systems. So, most of the scholars thought that the CALPHAD method is a supplement of experimental method for phase diagram construction, and the combination of two methods can construct an accurate phase diagram with less experimental work. However, the CALPHAD method is faced with two problems, one is that thermodynamic functions, excess thermodynamic functions are insufficient. Before the CALPHAD method deals with ternary systems, the three binary system phase diagrams must have been measured, and the functions must be regressed by experimental results. The other is that the CALPHAD method can not predict the formability of the ternary intermediate compounds of the unknown ternary systems, based on the data of the binary phase diagrams only. The CALPHAD method presumes that ternary

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systems do not form new ternary intermediate compounds or phases when it predicts the properties of systems and calculates ternary phase diagrams using the measured binary systems. But new ternary intermediate compounds or phases formation will lead to large difference for the equilibrium relations of ternary phase diagrams.

In this paper, the regularity and prediction of the formability of intermediate compound, the type (continuous solid solution or eutectic mixture) of some ternary system phase diagrams are reported with pattern recognition or ANN-chemical bond parameters method[1-4], as a complementary work for CALPHAD method. In addition, some predicted results were confirmed by our experimental work.

2 FORMABILITY OF TERNARY INTERMEDIATE COMPOUND

Molten salt ternary systems include common anion additive system Me, Me', Me"|X, common cation additive system Me|X, X', X", and ternary reciprocal system Me, Me'|X, X' (here Me, Me', Me" denote metallic elements, X, X', X" denote anion-forming elements or radicals). The ternary system data from the handbooks of ternary system phase diagrams[5-7], the journal of inorganic chemistry (in Russian) after 1980 and all the handbooks (phase diagrams of ceramist) of the American ceramic society were used as training sets.

2.1 Additive ternary systems

Using the data of 299 ternary systems with common cations or common anions for computation, it can conclude that: (1) Me^+, Me'^+, $Me"^+ | X^-$ type systems have no record of ternary compound formation; (2) Me^+, Me'^{2+}, $Me"^{2+} | X^-$ systems usually do not form ternary compound with a few exceptions; (3) common cation systems $Me^+ | X^-$, X'^-, $X"^-$ have also no record of ternary compound formation; (4) the most of the known ternary compounds distribute in Me^+, Me'^+, $Me"^{n+} | X^-$ type systems.

Me^+, Me'^+, $Me"^{n+} | X^-$ (here n= 2, 3, 4) systems often form ternary compounds, for example, $Li_3AlF_6 \cdot 2Cs_3AlF_6$, $NaAlCl_4 \cdot 3CsAlCl_4$, $7LiBiCl_4 \cdot 3NaBiCl_4$. The sixty four systems were used as training set, they were Li^+, Cs^+, $Al^{3+} | F^-$; Na^+, K^+ $Al^{3+} | F^-$; Li^+, Rb^+, $Al^{3+} | F^-$; Na^+, K^+, $Be^{2+} | F^-$; Li^+, Na^+, $Be^{2+} | F^-$; Na^+, Rb^+, $Be^{2+} | F^-$; Na^+, K^+, $Cr^{3+} | Cl^-$; Na^+, K^+, $Sm^{3+} | Cl^-$; Na^+, K^+, $Y^{3+} | Cl^-$; Na^+, K^+, $Zr^{4+} | F^-$; Na^+, Cs^+, $Al^{3+} | Cl^-$, Li^+, Cs^+, $V^{3+} | F^-$; Na^+, Cs^+, $V^{3+} | F^-$; Li^+, Na^+, $Bi^{3+} | Cl^-$ and Na^+, K^+, $Cd^{2+} | Cl^-$; Li^+, K^+, $Cd^{2+} | Cl^-$; Cs^+, Tl^+, $Cd^{2+} | Br^-$; K^+, Cs^+, $Cd^{2+} | I^-$; Na^+, K^+, $Ca^{2+} | F^-$; K^+, Rb^+, $Ca^{2+} | Cl^-$; Li^+, Na^+, $Ca^{2+} | NO_3^-$; Rb^+, Tl^+, $Ca^{2+} | NO_3^-$; K^+, Cs^+, $Cd^{2+} | Br^-$; Na^+, Cs^+, $Cd^{2+} | Br^-$; Na^+, Cs^+, $Cd^{2+} | Cl^-$; Na^+, Cs^+, $Cd^{2+} | I^-$; Cs^+, Tl^+, $Cd^{2+} | Br^-$; K^+, Na^+, $Cd^{2+} | Br^-$; K^+, Cs^+, $Mn^{2+} | F^-$; K^+, Cs^+, $Pb^{2+} | Br^-$; Li^+, Cs^+, $La^{3+} | F^-$; Li^+, Cs^+, $Mg^{2+} | NO_3^-$; Na^+, Cs^+, $Mg^{2+} | F^-$; Li^+, Cs^+, $Y^{3+} | F^-$; K^+, Ag^+, $Mg^{2+} | NO_3^-$; Tl^+, Ag^+, $Pb^{2+} | Cl^-$; Na^+, Cs^+, $Al^{3+} | Br^-$; Na^+, Cs^+, $Ba^{2+} | Cl^-$; Na^+, Cs^+, $Ba^{2+} | F^-$; Li^+, K^+, $Ba^{2+} | Cl^-$; Na^+, K^+, $Ba^{2+} | Cl^-$; Li^+, Na^+, $Ba^+ | Cl^-$; Na^+, Rb^+, $Ba^{2+} | Cl^-$; Li^+, Cs^+, $Ca^{2+} | F^-$; Na^+, Cs^+, $Ca^{2+} | F^-$; Li^+, Na^+, $Ca^{2+} | Cl^-$; Li^+, Na^+, $Ca^{2+} | F^-$; Rb^+, Tl^+, $Pb^{2+} | Cl^-$; Na^+, Tl^+, $Pb^{2+} | Cl^-$; Na^+, Tl^+, $Pb^{2+} | I^-$; Li^+, Rb^+, $Sr^{2+} | Cl^-$; Li^+, Rb^+, $Sr^{2+} | NO_3^-$; Li^+, Na^+, $Sr^+ | F^-$; Li^+, Rb^+, $Mg^{2+} | NO_3^-$; K^+, Tl^+, $Pb^{2+} | I^-$; Na^+, K^+, $Ti^{2+} | Cl^-$; Na^+, K^+, $Pb^{2+} | I^-$; Na^+, K^+, $Mn^{2+} | Cl^-$; Li^+, K^+, $Pb^{2+} | Br^-$; Li^+, K^+, $Mn^{2+} | F^-$; Li^+, K^+, $Mg^+ | Cl^-$; Na^+, K^+, $Fe^{2+} | Cl^-$; Cs^+, Tl^+, $Pb^{2+} | Cl^-$ and Na^+, Cs^+, $Sr^+ | NO_3^-$. Ten chemical bond parameters were used as the inputs of ANN, and the formability of ternary compound was used as the output ("1" denotes ternary compound formation and "2" denotes no ternary compound formation), the hidden nodes were four. After training, the trained ANN was used to predict the ternary compound formation

for seven "unknown" systems which were not included in the training set. The predicted results are listed in Table 1. The results of prediction indicate that two systems (Li^+, Na^+, Ti^{4+} | F^- and Na^+, Rb^+, Cr^{3+} | Cl^-) form ternary compounds, and other five systems have no ternary compound formation. These results are confirmed by refs. [6, 7].

Using seventy one systems (including seven testing systems above) as learning set, and the ten parameters as features, PCA method was also applied for classification. The ternary compound forming systems and the systems without ternary compound formation distribute into two regions as shown in Fig. 1. The result of PCA method indicates that the large $(Z/r)_{n+}$ of $Me"^{n+}$ ion, small ionic radius of X^- ion favor ternary compound formation. This fact implies that large $(Z/r)_{n+}$ of $Me"^{n+}$ and small X^- ion favor the stability of polyvalent complex anion. So ternary compound can be considered as the double salt consisting of Me^+, Me'^+ cation and a complex ion $[Me"X_m]^{[m-n]-}$.

2.2 Reciprocal ternary systems

A reciprocal ternary salt system is one consisting of two kinds of anions and two kinds of cations. The systems of Me^+, Me'^+ | X^-, X'^- type and these of Me^+, Me'^+ | X^-, X'^{2-} type have no record of ternary compound formation. The most of the reciprocal ternary compounds discovered distribute in Me^+, Me'^{2+} | X^-, X'^{2-} type. We used the data of K^+, Mg^{2+} | Br^-, SO_4^{2-}; K^+, Mg^{2+} | Cl^-, SO_4^{2-}; K^+, Mn^{2+} | Cl^-, SO_4^{2-}; Cs^+, Zn^{2+} | Cl^-, SO_4^{2-}; K^+, Zn^{2+} | Br^-, SO_4^{2-}; K^+, Zn^{2+} | Cl^-, SO_4^{2-}; K^+, Zn^{2+} | I^-, SO_4^{2-}; Rb^+, Mg^{2+} | Cl^-, SO_4^{2-}; Cs^+, Zn^{2+} | Br^-, SO_4^{2-}; Tl^+, Zn^{2+} | Br^-, SO_4^{2-}; Tl^+, Zn^{2+} | Cl^-, SO_4^{2-}; Tl^+, Zn^{2+} | I^-, SO_4^{2-} and Ag^+, Cd^{2+} | Cl^-, SO_4^{2-}; K^+, Ba^{2+} | Cl^-, SO_4^{2-}; Na^+, Ba^{2+} | Cl^-, CO_3^{2-}; K^+, Ca^{2+} | Cl^-, SO_4^{2-}; K^+, Ca^{2+} | NO_3^-, SO_4^{2-}; Na^+, Cd^{2+} | Cl^-, SO_4^{2-}; Li^+, Co^{2+} | Cl^-, SO_4^{2-}; K^+, Pb^{2+}, | Cl^-, SO_4^{2-}; Li^+, Sr^{2+} | Cl^-, SO_4^{2-}; Li^+, Mg^{2+} | Cl^-, SO_4^{2-}; Na^+, Mg^{2+} | Cl^-, SO_4^{2-}; Na^+, Zn^{2+} | Cl^-, SO_4^{2-} systems as

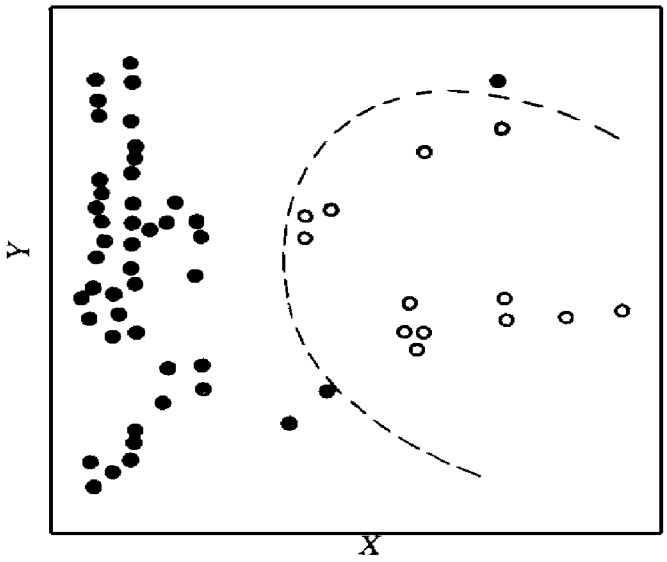

Fig. 1 Ternary compound in Me^+, Me'^+, $Me"^{n+}$ | X^- systems

(○—Ternary compound forming;
●—No ternary compound forming)

$$X = -0.01r_+ - 0.18r_{n+} + 0.62Z_{n+} - 0.05r_- - 0.14\chi'_+ + 0.02\chi_{n+} + 0.04\chi_- + 0.76(Z/r)_{n+}$$

$$Y = 0.23r_+ + 0.06r'_+ - 0.09r_{n+} + 0.67r_- - 0.17\chi_+ + 0.11\chi'_+ + 0.33\chi_{n+} - 0.58\chi_- + 0.04(Z/r)_{n+}$$

Table 1 Prediction of formability of ternary compound in Me^+, Me'^+, $Me"^{n+}$ | X^- systems

Systems	r_+	r'_+	r_{n+}	Z	r_-	χ_+	χ'_+	χ_{n+}	χ_-	$(Z/r)_{n+}$	Output
Li^+, Na^+, Ti^{4+} | F^-	0.60	0.95	0.68	4	1.36	1.0	0.9	1.6	3.9	5.90	0.9964
Na^+, Rb^+, Cr^{3+} | Cl^-	0.95	1.48	0.64	3	1.81	0.9	0.8	1.6	3.1	4.69	0.9720
Li^+, K^+, Cd^{2+} | Cl^-	0.60	1.33	0.97	2	1.81	1.0	0.8	1.7	3.1	2.06	2.0033
Na^+, Tl^+, Cd^{2+} | Cl^-	0.95	1.40	0.97	2	1.81	0.9	1.4	1.7	3.1	2.06	1.9881
K^+, Cs^+, Mg^{2+} | F^-	1.33	1.69	0.65	2	1.36	0.8	0.7	1.2	3.9	3.08	2.0252
Li^+, Cs^+, Sr^{2+} | Cl^-	0.60	1.69	1.13	2	1.81	1.0	0.7	1.0	3.1	1.77	1.9986
Li^+, Na^+, Ba^{2+} | F^-	0.60	0.95	1.35	2	1.36	1.0	0.9	0.9	3.9	1.48	1.9951

training set. PCA method was applied for classification. Fig. 2 illustrates that the ternary compound forming systems and the systems without ternary compound formation distribute into different regions. The criterion of formability is as follows:

$$D = -0.01 + 0.29\chi_+ - 0.12\chi_{2+} - 0.53r_+ + 1.51r_{2+} - 1.20r_- + 0.67r_{2-}$$

where D is criterion, $D < 0$ denotes ternary compound formation, and $D > 0$ denotes no ternary compound formation. The results of PCA method indicates that ionic radii are dominating factors for ternary compound formation. Small Me^{2+} ion and large X^-, Me^+ ion favor ternary compound formation. On these ground, we designed two new reciprocal ternary salt systems Cs^+, Mn^{2+} | Cl^-, SO_4^{2-} and K^-, Mn^{2+} | Br^-, SO_4^{2-} which are not reported up to now. The pattern recognition predicts that these systems form new ternary compounds, the predicted results were also obtained from D value of criterion equation or the trained ANN.

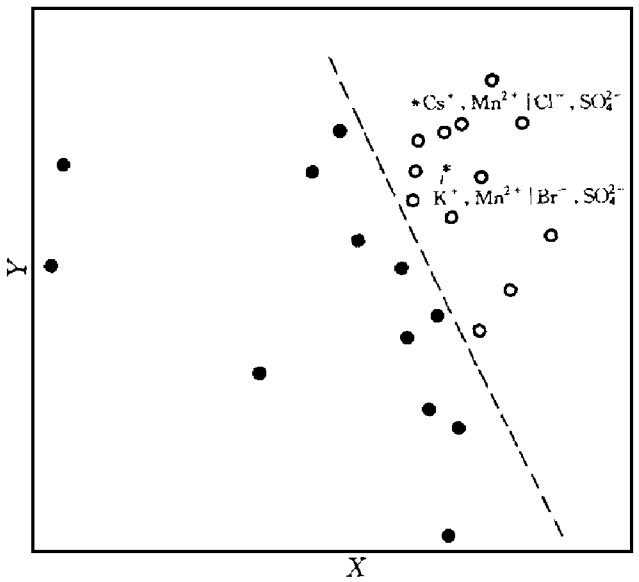

Fig. 2 Ternary compound in Me^+, Me'^{2+} | X^-, X'^{2-} systems

(○—Ternary compound forming;
●—No ternary compound formation;
*—Predicted point)

$$X = 0.16\chi_+ + 0.50\chi_{2+} + 0.17r_+ - 0.55r_{2+} + 0.29r_- + 0.55r_{2-}$$

$$Y = -0.55\chi_+ - 0.28\chi_{2+} + 0.67r_+ - 0.10r_{2+} + 0.38r_- - 0.08r_{2-}$$

2.3 Confirmation of new ternary compounds

In order to confirm the predicted results, five samples containing CsCl (C. P.) and $MnSO_4$(C. P.), with the mole ratios of CsCl to $MnSO_4$ 2∶1, 3∶2, 1∶1, 2∶3, 1∶2, and the other five samples containing KBr (C. P.) and $MnSO_4$(C. P.), with the same mole ratios of KBr to $MnSO_4$, were mixed respectively, and molten by heating for eight hours. After cooling, these ten samples were analysed by X-ray diffraction. The data of the sample that mole ratio of CsCl to $MnSO_4$ was 1∶1 are different from ones of pure CsCl and $MnSO_4$, and the data of the sample that mole ratio of KBr to $MnSO_4$ was 2∶3 are also different from ones of pure KBr and $MnSO_4$. It may be thought that there exist new compounds. The data of rest samples are overlapped between the data of new compounds diffraction spectrum and ones of CsCl or KBr or $MnSO_4$. Moreover, the experimental liquidus curves of a cross section of the phase diagrams in CsCl-$MnSO_4$ and KBr-$MnSO_4$ system were measured, there is a peak when CsCl∶$MnSO_4$ is 1∶1 or KBr∶$MnSO_4$ was 2∶3. The results indicate that there exist two congruent melting ternary compounds, the formulae of the new ternary compounds are CsCl·$MnSO_4$ and 2KBr·3$MnSO_4$. Their data of X-ray diffraction spectrum are 2.82 (s), 3.88(s), 3.09(m), 7.33 (w) and 3.17(s), 3.04(w), 2.79(w), 1.86 (w), 1.75(s), 1.73(s) respectively.

In addition, we used the melting points of the known ternary compounds, including KCl·$MgSO_4$, KI·$ZnSO_4$, KCl·$ZnSO_4$, KCl·$MnSO_4$, CsBr·$ZnSO_4$, RbCl·$MgSO_4$, KBr·$ZnSO_4$, TlCl·$ZnSO_4$ compounds, as the outputs of ANN. T (the average melting point value of two constituents), r_-, r_+/r_{2+} were used as inputs of ANN, the number of hidden nodes was two. After training, the trained ANN was used to predict the melting point of CsCl·$MnSO_4$. The predicted value was 677 ℃, the experimental value was 634 ℃ by our measurement. The relative error was 6.7%.

Therefore, the experimental results illustrate that the predictions of pattern recognition or ANN with chemical parameters method for

the formability and the melting point of ternary compounds are reasonable.

3 CLASSIFICATION OF SIMPLE PHASE DIAGRAMS

The fifty two phase diagrams of the simple additive ternary systems which three binary systems have no intermediate compound formation, were collected from handbooks. They are Na^+, Cd^{2+}, Pb^{2+} | Br^-; Na^+, K^+, Cs^+ | Br^-; Ag^+, Cd^{2+}, Pb^{2+} | Cl^-; Li^+, Na^+, Ba^{2+} | Cl^-; Na^+, Ca^{2+}, Pb^{2+} | Cl^-; Ca^{2+}, U^{3+}, Pu^{3+} | Cl^-, Na^+, Co^{2+}, Te^{4+} | Cl^-; Cu^+, Hg^{2+}, Te^{4+} | Cl^-; Ta^{5+}, Fe^{3+}, Mn^{2+} | Cl^-; W^{6+}, Fe^{3+}, Mn^{2+} | Cl^-; W^{6+}, Mo^{3+}, Fe^{3+} | Cl^-; W^{6+}, Nb^{5+}, Fe^{3+} | Cl^-; W^{6+}, Ta^{5+}, Fe^{3+} | Cl^-; Li^+, Na^+, K^+ | Cl^-; Na^+, K^+, Rb^+ | Cl^-; Li^+, Na^+, Sr^{2+} | Cl^-; Li^+, Na^+, U^{3+} | Cl^-; Mg^{2+}, U^{3+}, Pu^{3+} | Cl^-; W^{6+}, Ta^{5+}, Mn^{2+} | Cl^-; Na^+, K^+, Cs^+ | I^-; K^+, Tl^+, Cs^+ | I^-; Na^+, Tl^+, Cs^+ | I^-; Rb^+, Tl^+, Cs^+ | I^-; Na^+, K^+, Tl^+ | I^-; Na^+, Rb^+, Tl^+ | I^-; Mo^{5+}, Si^{4+}, Te^{4+} | Cl^-; Li^+, Mg^{2+}, Ca^{2+} | F^-; Li^+, Na^+, Ca^{2+} | F^-; Li^+, Sr^+, Ca^{2+} | F^-; Li^+, Na^+, K^+ | F^-; Li^+, K^+, Sr^{2+} | F^-; Na^+, K^+, Sr^{2+} | F^-; Li^+, Mg^{2+}, Sr^{2+} | F^-; Li^+, Na^+, Sr^{2+} | F^- and K^+, Rb^+, Cs^+ | Br^-; Si^{4+}, Ge^{4+}, Sn^{4+} | Br^-; Si^{4+}, Ge^{4+}, Ti^{4+} | Br^-; Ge^{4+}, Sn^{4+}, Ti^{4+} | Br^-; Na^+, K^+, Rb^+ | Br^-; K^+, Rb^+, Tl^+ | Br^-; Rb^+, Tl^+, Cs^+ | Cl^-; Ge^{4+}, Sn^{4+}, Fe^{3+} | Cl^-; Mo^{5+}, Ta^{5+}, Fe^{3+} | Cl^-; Mo^{5+}, Si^{4+}, Ge^{4+} | Cl^-; Si^{4+}, Ge^{4+}, Sn^{4+} | Cl^-; Si^{4+}, Ti^{4+}, Ge^{4+} | Cl^-; Ge^{4+}, Sn^{4+}, Te^{4+} | Cl^-; Ti^{4+}, Ge^{4+}, Sn^{4+} | Cl^-; W^{6+}, Nb^{5+}, Mo^{5+} | Cl^-, Mo^{5+}, W^{5+}, Re^{5+} | Cl^-; W^{6+}, Mo^{5+}, Ta^{5+} | Cl^-; Na^+, K^+, Rb^+ | I^-. These systems were used as training set for pattern recognition. The $r_1 - r_2 (x_1)$, $r_1 - r_3 (x_2)$, $r_2 - r_3 (x_3)$ (definite $r_1 > r_2 > r_3$, subscript i (i= 1, 2, 3) denotes the metallic elements), $|Z_1 - Z_2| (x_4)$, $|Z_1 - Z_3| (x_5)$, $|Z_2 - Z_3| (x_6)$, $|X_1 - X_2| (x_7)$, $|X_1 - X_3| (x_8)$, $|X_2 - X_3| (x_9)$, $r_- (x_{10})$ were used as features. Fig. 3 is the classified figure according to ternary continuous solid solution or eutectics by partial least squares method. It illustrates that the representative points of the two types phase diagrams distribute in different regions, but Ca^{2+}, U^{3+}, Pu^{3+} | Cl^- and Rb^+, Tl^+, Cs^+ | I^- situate in boundary line. The calculated results indicate that the small radius difference, the ionic charge difference, the electronegativity difference of the either two of the three metallic ions, and the large radius of X ion favor to form the ternary continuous solid solution. These results are in agreement with the binary systems.

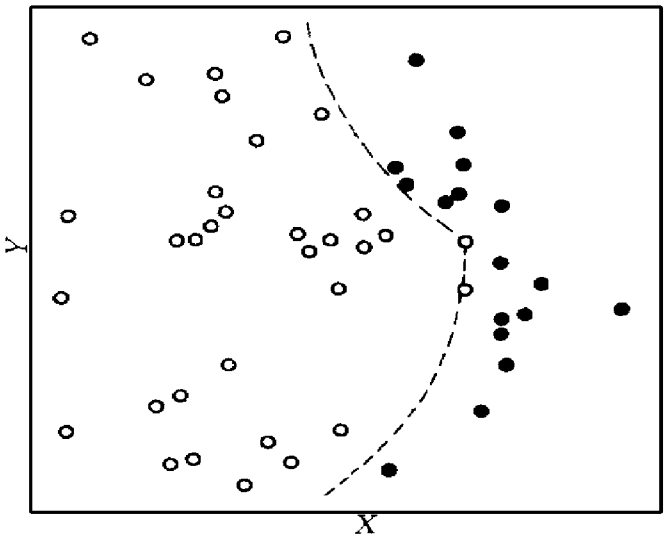

Fig. 3 Classification of eutectics and continuous solid solution in additive ternary systems

(○—Eutectics; ●—Continuous solid solution)

$$X = -0.33x_1 - 0.20x_2 - 0.34x_3 - 0.46x_4 - 0.12x_5 - 0.33x_6 - 0.40x_7 - 0.12x_8 - 0.40x_9 + 0.25x_{10}$$

$$Y = -0.21x_1 - 0.29x_2 + 0.31x_3 + 0.67x_4 - 0.04x_5 + 0.02x_6 - 0.49x_7 + 0.02x_8 + 0.06x_9 + 0.49x_{10}$$

The trained ANN had been used to predict the type of the five "unknown" ternary system phase diagrams[8], the predicted results are listed in Table 2.

4 PREDICTION OF TERNARY EUTECTIC POINT

The temperatures and the compositions at

Table 2 Prediction of type of phase diagram and properties at eutectic point*

Predicted systems	Predicted results				Experimental results			
	Type	t / ℃	C_{1st} / %	C_{3rd} / %	Type	t / ℃	C_{1st} / %	C_{3rd} / %
Li^+, Ca^{2+}, Ce^{3+} | Cl^-	E	448	51	25	E	420	64	17
Li^+, Ca^{2+}, Pr^{3+} | Cl^-	E	441	51	26	E	420	50	27
Li^+, Nd^{3+}, Ca^{2+} | Cl^-	E	434	52	22	E	408	60	22
Mg^{2+}, Ca^{2+}, Ce^{3+} | Cl^-	E	512	37	27	E	527	38	23
Mg^{2+}, Ca^{2+}, Pr^{3+} | Cl^-	E	491	40	28	E	546	35	26

* Note: T, C_{1st}, C_{3rd} denote the temperature, the first and the third constituent composition at the eutectic point of ternary system, E denotes the eutectics type.

eutectic points of simple eutectic phase diagrams of additive ternary systems were predicted with ANN. The training set contained twenty-four systems, they were Na^+, Cd^{2+}, Pb^{2+} \| Br^-; Na^+, K^+, Cs^+ \| Br^-; Ag^+, Cd^{2+}, Pb^{2+} \| Cl^-; Li^+, Na^+, Ba^{2+} \| Cl^-; Na^+, Ca^{2+}, Pb^{2+} \| Cl^-; Ca^{2+}, U^{3+}, Pu^{3+} \| Cl^-; Na^+, Co^{2+}, Te^{4+} \| Cl^-; Cu^+, Hg^{2+}, Te^{4+} \| Cl^-; Ta^{5+}, Fe^{3+}, Mn^{2+} \| Cl^-; W^{6+}, Fe^{3+}, Mn^{2+} \| Cl^-; W^{6+}, Mo^{3+}, Fe^{3+} \| Cl^-; W^{6+}, Nb^{5+}, Fe^{3+} \| Cl^-; Li^+, Na^+, Sr^{2+} \| Cl^-; Li^+, Na^+, U^{3+} \| Cl^-; Mg^{2+}, U^{3+}, Pu^{3+} \| Cl^-; W^{6+}, Ta^{5+}, Mn^{2+} \| Cl^-, Na^+, K^+, Cs^+ \| Cl^-, W^{6+}, Ta^{5+}, Fe^{3+} \| Cl^-, Na^+, K^+, Cs^+ \| I^-; K^+, Tl^+, Cs^+ \| I^-; Na^+, Tl^+, Cs^+ \| I^-; Rb^+, Tl^+, Cs^+ \| I^-; Na^+, K^+, Tl^+ \| I^-; Na^+, Rb^+, Tl^+ \| I^-. The inputs of ANN were T_j (j = 1, 2, 3. T_j denotes the melting points of three constituents, definite $T_1 < T_2 < T_3$), $(Z/r)_i$, χ_i (i = 1, 2, 3. i denotes the metallic ions), r_-, χ_-. The number of hidden nodes was two. The outputs were the temperatures and compositions at eutectic points. The trained ANN was used to predict the properties of the "unknown" five systems[8], while their eutectics type had been predicted by the other trained ANN previously. The results are listed in Table 2.

It can be seen from Table 2 that the predicted results of the type of phase diagrams are in agreement with experimental results[8], and the adjusted ANN can be used for quantitative estimation of the temperatures and compositions at eutectic points of ternary molten salt systems, with a good result basically.

5 SUMMARY

The method has two advantages as compared with the CALPHAD of thermodynamics. First, the pattern recognition or ANN-chemical bond parameters method may not make experiment or need only to make a few confirmable experimental work, and need not to know the data of thermodynarnic in advance, it can predict many properties or characteristics of the unknown phase diagrams by training the known data of phase diagrams only. Second, the method can find some semi-empirical rules or formulae based on the known data, and the rules can not only predict some natures of the unknown phase diagrams, but also expand the structural chemistry theory and develop the phase diagram theory which lags behind reality.

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