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Regularities of melting behavior of intermediate compounds in halide molten salt systems①

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[Abstract] The regularities of melting behavior for nine kinds of stoichiometries including 311 compounds were discussed by pattern recognition method with bond parameters as features. The compounds of the nine kinds of stoichiometries were $MeMe'X_2$, $MeMe'X_3$, $Me_2Me'X_4$, $MeMe'X_4$, $MeMe'_2X_5$, $MeMe'X_5$, $Me_2Me'X_6$, Me_3MeX_6 and $MeMe'_2X_7$ respectively (Me, Me′ denote metallic elements, X denotes halogen). It has been found that the congruent or incongruent melting of intermediate compounds in molten salt systems distribute in different regions. In addition, four general regularities for melting behavior of halides were summarized on the basis of the nine semi-empirical models obtained from the known phase diagrams.

[Key words] intermediate compound; melting behavior; molten salt system
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1 INTRODUCTION

The melting behavior (including congruent melting or incongruent melting) of intermediate compounds is an important property of phase diagrams, the first one creates one peak at the point of intermediate phase, the second one causes a peritectic reaction. However, the phase diagram theory and structural chemistry theory still can not be used to determinate the melting types of intermediate compounds. In recent years, we have used pattern recognition method with parameters as features to find the regularities of melting behaviors of some binary alloy phases[1,2], and discuss the properties of phase diagrams of some molten salt systems[3~5].

In this paper, the same method is again used to summarize the semi-empirical regularities of melting behaviors of intermediate compounds for halide molten salt systems, based on the known data. We would discuss nine kinds of stoichiometries including 311 intermediate compounds, formed in MeX-Me′X, $MeX-Me'X_2$, $MeX-Me'X_3$ and $MeX-Me'X_4$ systems, the compounds of nine kinds of stoichiometries were $MeMe'X_2$, $MeMe'X_3$, $Me_2Me'X_4$, $MeMe'X_4$, $MeMe'_2X_5$, $MeMe'X_5$, $Me_2Me'X_6$, Me_3MeX_6 and $MeMe'_2X_7$ respectively. The aim of this paper is to investigate the factor affecting melting behavior of the compounds, discuss the physical nature of melting processes and conclude the rules of melting behavior.

2 METHOD OF COMPUTATION

An incongruent melting process (or peritetic reaction) involves the transformation of one crystal lattice into another crystal lattice and a liquid phase. The relative stability of these two lattices (or the difference of the lattice energy) should have a great influence on the occurrence of incongruent melting. It is well known that there are three factors affecting the lattice energy of ionic crystal: geometrical factor, polarizable factor and charge-transfer factor. So it is reasonable to use the chemical bond parameters, such as ionic radii, charge numbers, electronegativities and polarizabilities, in order to find the regularities of melting types of compounds. These parameters was used to span a multi-dimensional space and could be used to find semi-empirical models from the known experimental data by pattern recognition in this space. The pattern recognition methods used here are computational methods mapping the patterns in multi-dimensional space to two-dimensional figures, along with some techniques for mapping the two-dimensional figures back to original multi-dimensional space[6]. The partial least squares (PLS)[7] method of pattern recognition was used in our work.

All data of melting types of intermediate compounds used in this paper were quoted from Refs.[8, 9], and all phase diagrams handbooks of ceramist, edited by the American Ceramic Society. The chemical bond parameters were quoted from Ref.[10].

3 RESULTS OF COMPUTATION

Eleven $MeMe'X_2$ compounds such as $CsAgCl_2$, $CsLiF_2$ and others, were used as the training set for pattern recognition, $r_{Me}/r_{Me'}$ (the ratio of ionic radius, definite $r_{Me} > r_{Me'}$), r_- (anionic radius) and $\chi_{Me'}$ (electronegativity of metallic ion Me′) were used

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to span a three-dimensional space. The $MeMe'X_2$ compounds were classified according to their melting behaviors. Fig.1 is the linear mapping figure in the two dimensional plane by PLS method (in the figures, "●" denotes congruent melting compound, "-" denotes incongruent melting compound). It illustrates that the representative points of congruent melting and those of incongruent melting distribute in different regions, and the compounds of congruent melting are found in the region with large $r_{Me}/r_{Me'}$, $\chi_{Me'}$ and small r_-.

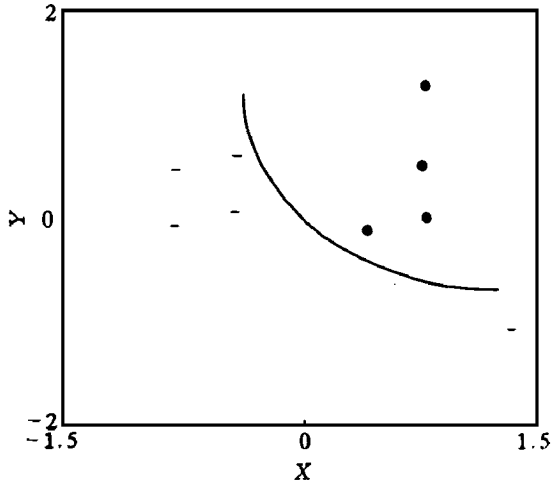

Fig.1 Melting type of $Me'MeX$
$X = 0.02\, r_{Me}/r_{Me'} - 0.82\, r_- + 0.58\, \chi_{Me'}$;
$Y = 0.98\, r_{Me}/r_{Me'} - 0.29\, r_- + 0.51\, \chi_{Me'}$

The melting behavior of $MeMe'X_3$, $Me_2Me'X_4$, $MeMe'X_4$, $MeMe'_2X_5$, $MeMe'X_5$, $Me_2Me'X_6$, Me_3MeX_6 and $MeMe'_2X_7$ compounds were discussed respectively by PLS method, and the classified figures of eight stoichiometries compounds according to their melting behavior in a multi-dimensional space are given in Fig.2 ~ Fig.9. The calculated results indicate that there is a clear-cut boundary between congruent and incongruent melting compounds for every stoichiometry.

In addition, there is only fluoride for $Me_3Me'X_7$ compounds. Cs_3SiF_7, Cs_3ZrF_7, K_3SnF_7, K_3ZrF_7, Rb_3SiF_7, Cs_3HfF_7, K_3ThF_7, Na_3HfF_7, Na_3UF_7, Li_3ThF_7, Cs_3TiF_7, K_3SiF_7, K_3TiF_7, Na_3ZrF_7 are all congruent melting except Tl_3ThF_7. The cause may be that the electronegativity for Tl is larger than other outer layer ions.

4 RESULTS AND DISCUSSION

In this section, we obtained four general regularities for the melting behavior of intermediate compounds based on the summarization of nine figures.

There are two arrangements in the crystal of intermediate compound, the arrangement between the Me'^{n+} and X^- in complex $[Me'X_n]^{(m-n)-}$ is a

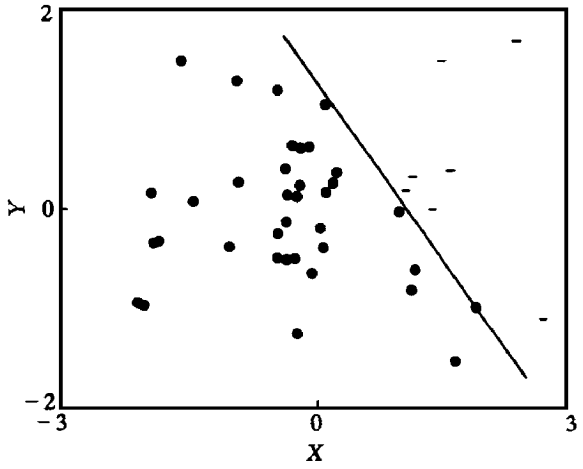

Fig.2 Melting type of $MeMe'X_3$
$X = -0.37\, r_{2+}/r_+ - 0.77\, r_{2+}/r_- + 0.39\, r_- - 0.36\, r_+$;
$Y = 0.40\, r_{2+}/r_+ - 0.04\, r_{2+}/r_- + 0.33\, r_- - 0.92\, r_+$

Fig.3 Melting type of $Me_2Me'X_4$
$X = -0.09\, r_{2+}/r_- + 0.26\, r_- + 0.24(\chi_{2+} - \chi_+) - 0.68\, r_+ - 0.64(\chi_- - \chi_{2+})$; $Y = 0.48\, r_{2+}/r_- - 0.47\, r_- - 0.29(\chi_{2+} - \chi_+) - 0.75\, r_+ - 0.09(\chi_- - \chi_{2+})$

stable short-range, and the one between outer layer ion Me^+ and X^- is an unstable long-range. In general, there are two arrangements in the crystal of intermediate compound, the arrangement between the Me'^{n+} and X^- in complex $[Me'X_n]^{(m-n)-}$ is a stable short-range, and the one between outer layer ion Me^+ and X^- is an unstable long-range. In general, the short-range arrangement is retained and the long-range arrangement is destroyed as an intermediate compound is heated. However, when the electronegativity of outer layer metallic ion Me^+ is too large or its radius is too small, the large polarizable force of the ion Me^+ acting on the complex anion $[Me'X_n]^{(m-n)-}$ causes to increase the distance between central ion Me'^{n+} and X^-, and finally destroy the complex anion structure, then the intermediate compound shows incongruent melting. In addition,

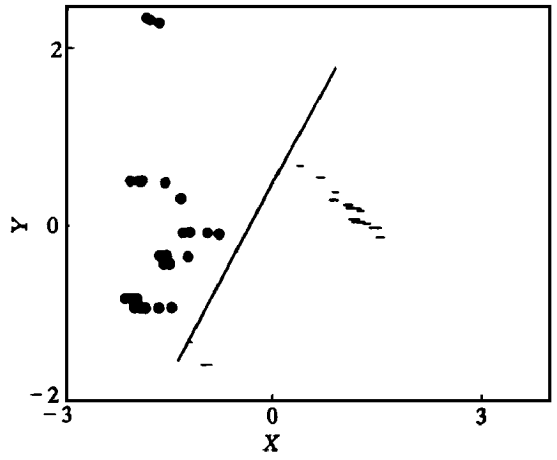

Fig.4 Melting type of $MeMe'X_4$
$X = -0.57r_- - 0.25r_+ - 0.63\chi_{3+} + 0.09r_+/r_- + 0.46r_{3+}/r_-$;
$Y = -0.79r_- - 0.06r_+ + 0.48\chi_{3+} + 0.08r_+/r_- - 0.36r_{3+}/r_-$

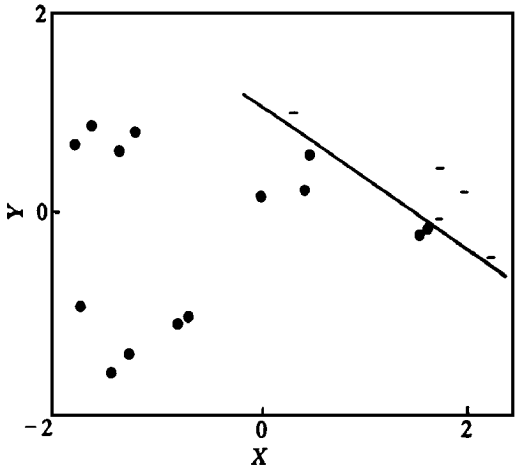

Fig.5 Melting type of $MeMe'_2X_5$
$X = 0.38r_{2+}/r_- + 0.33r_- - 0.63\chi_{2+} - 0.59(\chi_{2+} - \chi_+)$;
$Y = -0.83r_{2+}/r_- - 0.20r_- - 0.09\chi_{2+} - 0.65(\chi_{2+} - \chi_+)$

the complex anion $[Me'X_n]^{(m-n)-}$ which is of short-range arrangement can be regarded as a big globe in ionic crystal as the first approximation. Since the effective radius of complex anion is large relatively, so the complex anion can be only formation alized intermediate compound with the outer layer ion Me^+ of large radius, which has a high coordination number and high lattice energy. Therefore, the increase of outer layer metallic ionic radius favors to form the congruent melting compound. In the short-range arrangement of complex anion $[Me'X_n]^{(m-n)-}$, the electrostatic interaction between central ion Me' and halogen X will increase because of the decrease of central ionic radius, then the structure of complex anion

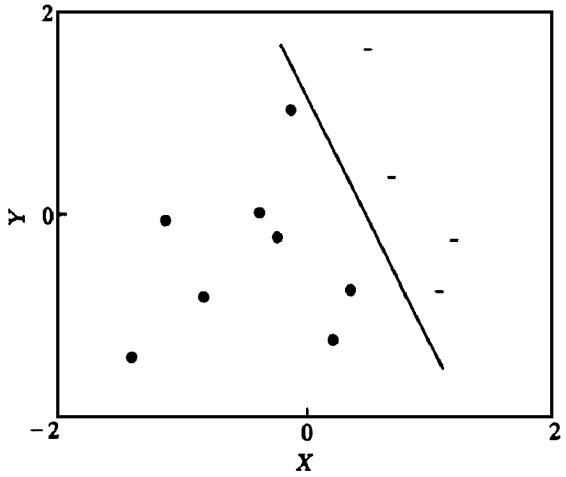

Fig.6 Melting type of $MeMe'X_5$
$X = -0.21r_+ + 0.77r_- - 0.61r_{4+}$;
$Y = -0.75r_+ - 0.34r_- - 0.63r_{4+}$

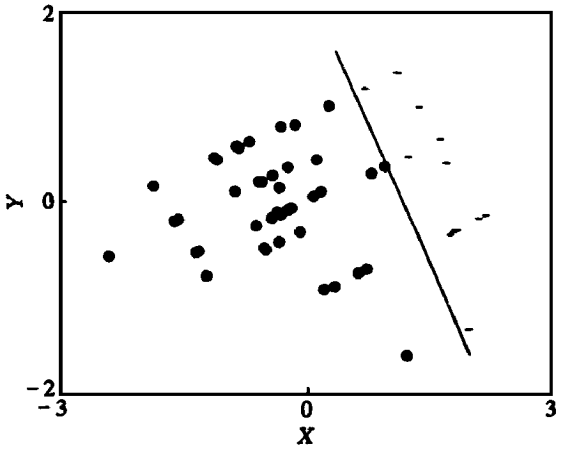

Fig.7 Melting type of $Me_2Me'X_6$
$X = 0.06\chi_+ - 0.39r_+ - 0.87r_- + 0.30r_{4+}$;
$Y = -0.19\chi_+ + 0.82r_+ - 0.53r_- + 0.21r_{4+}$

$[Me'X_n]^{(m-n)-}$ can not be destroyed easily when a compound is heated. The increase of central ionic electronegativity will strengthen the covalent interaction between two ions. So the decrease of central metallic ionic radius or increase of its electronegativity favors to form a stable complex anion, and the intermediate compounds will be a congruent melting. Some conclusions are obtained through the above calculations and discussions. First, increase of radius or decrease of electronegativity for outer layer metallic ion favors to form a congruent melting intermediate compound. Second, decrease of central metallic ionic radius or increase of its electronegativity favors to form a congruent melting compound. Third, increase of electronegativity difference of two metallic ions favors to form an intermediate compound with congruent melting. Forth, decrease of halogen ionic radius favors to form a congruent melting intermediate com-

Fig .8 Melting type of Me_3MeX_6
$X = -0.95 r_+ + 0.30 r_- + 0.11(Z/r_k)_{3+}$;
$Y = -0.16 r_+ - 0.61 r_- + 0.80(Z/r_k)_{3+}$

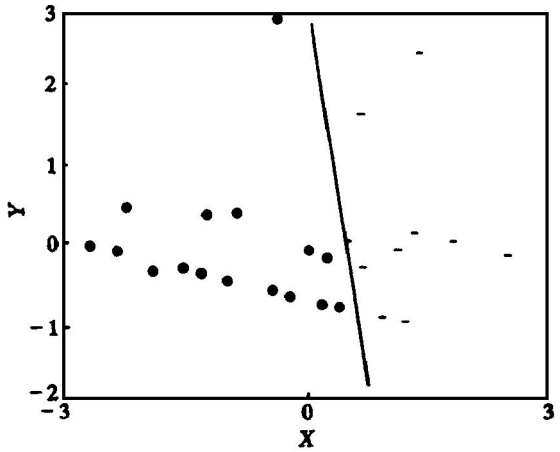

Fig .9 Melting type of $MeMe'_2X_7$
$X = 0.36 r_+ - 0.16 \chi_- + 0.64 r_{3+} - 0.66(Z/r_k)_{3+}$;
$Y = 0.38 r_+ - 0.89 \chi_- - 0.26 r_{3+} + 0.07(Z/r_k)_3$

pound when central ion is a hard acid or transitional metallic ion, and increase of halogen ionic radius favors to form an incongruent melting intermediate compound when central ion is a soft acid.

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