http://dx.doi.org/10.17159/2411-9717/2015/v115n8a14

Measuring and modelling of density for selected $CaO-Al_2O_3-MgO$ slags

by J.F. Xu*, K. Wan*, J.Y. Zhang†, Y. Chen*, and M.Q. Sheng*

Synopsis

The densities of selected $CaO-Al_2O_3-MgO$ slag systems were measured at 1823K by the Archimedean method. Thirteen different slag compositions were chosen based on different levels of the MgO content and the mass ratio of CaO/Al_2O_3. The results indicated that the density of the slag decreases with increasing MgO content (from 0–3.78 mass%), but increases with further increases in MgO content up to 11.33 mass%. At a fixed MgO content of 5.5%, the trend of density change with CaO/Al_2O_3 in the slag is similar to that for changes in MgO content. On the basis of the regular solution approximation rules of excess molar quantities, an attempt was made to estimate the molar volume of the slags investigated. The application of the molar volume model confirmed that the present expanded approximation rules are applicable to predict the molar volumes of the melts discussed.

Keywords

slag density, $CaO-Al_2O_3-MgO$ system, molar volume, modelling.

Introduction

Density is one of the most important fundamental properties of slags, which influences metallurgicaly phenomena in many ways. Density is sensitive to the nature of the chemical bonds and the species in the melt, and is of great importance not only for theoretical research on the structural properties of molten slags, but also for industrial applications. Density is also required to estimate other key properties used to assess the behaviour of high-temperature molten oxides, *e.g.* viscosity, surface tension, and thermal conductivity.

Liquid calcium aluminate slags that contain magnesia are the basis of most ladle slags for secondary refining processes. The $CaO-Al_2O_3$ binary phase diagram (Hallstedt , 1990) shows the eutectic composition (50 wt% CaO and wt% Al_2O_3) has the lowest melting temperature. The main emphasis of this study is on the $12CaO{\cdot}7Al_2O_3$ refining slag with MgO additions. The $CaO-Al_2O_3-MgO$ ternary system is of considerable importance in industrial metallurgical processes, and is fundamental to the understanding of metallurgical slags, ceramic materials, and geological phenomena. Many researchers have reported on the optimization of the ternary $CaO-Al_2O_3-MgO$ system (Hallstedt, 1995; Jung, Degterov, and Pelton, 2004). It has been shown that the liquidus temperature of the slag is lower than 1823K when the addition of MgO to $12CaO{\cdot}7Al_2O_3$ is less than 10 wt%. The density of the $CaO-Al_2O_3-MgO$ system has not been systematically investigated experimentally, and few experimental studies of density have been reported in the $CaO-Al_2O_3-MgO$ system (Slag Atlas, 1995). Due to the difficulty of experimental measurements at high temperature, the existing data covers only a limited composition and temperature range. In our previous work, the viscosity of the selected $CaO-Al_2O_3-MgO$ slag system was measured by using the rotating cylinder method and the effects of temperature, the MgO content, and the mass ratio of CaO/Al_2O_3 were studied. The results indicated that both the MgO content and the mass ratio of CaO/Al_2O_3 influence the viscosity of the slag (Xu *et al.*, 2011). The aim of the present work is to investigate the effect of MgO additions on the density of $12CaO{\cdot}7Al_2O_3$ slag. The effects of the MgO content and the mass ratio of CaO/Al_2O_3 were studied. On the basis of the regular solution approximation rules of excess molar quantities, an attempt was made to estimate the molar volumes of selected $CaO-Al_2O_3-MgO$ slags investigated.

Experimental

Sample preparation and characterization

The $CaO-Al_2O_3-MgO$ equilibrium phase diagram from Verlag Stahleisen (Slag Atlas, 1995) is shown in Figure 1. Table I shows the nominal chemical compositions of samples used in the present work. The samples were divided into two groups. In the first group,

* *Shagang School of Iron and Steel, Soochow University, China.*

† *Shanghai Key Lab. of Modern Metallurgy and Material Processing, Shanghai University, China.*

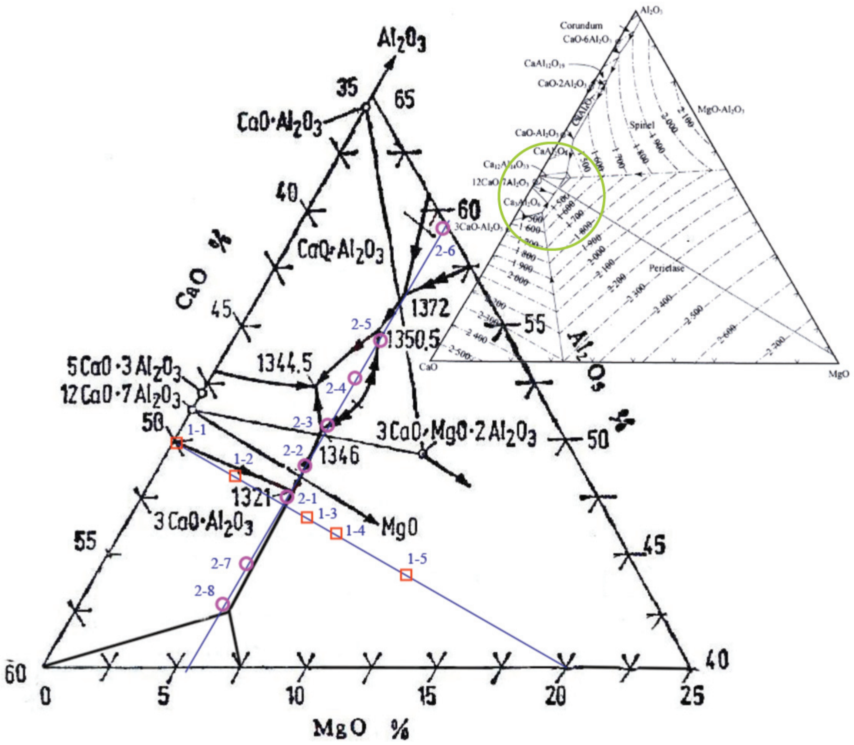

Figure 1 – Liquidus projection of $CaO-Al_2O_3-MgO$ slag system (Slag Atlas)

comprising five samples, the mass ratios of CaO/Al_2O_3 were equal to unity, while the MgO content was varied from zero to 12 wt%. The eight samples in the second group had MgO contents of 5.5 wt%, and the mass ratio of CaO/Al_2O_3 was varied from 0.60 to 1.20.

Samples were prepared from CP (chemically pure) grade CaO (≥99.0 wt%), Al_2O_3 (≥99.5 wt%), and MgO (≥99.0 wt%) powders, which were dried at 373K for 24 hours. The method for preparation of the slag samples has been reported in detail elsewhere (Xu *et al.*, 2012). The powders were ground and weighed to the desired compositions and mixed in a mortar, and the mixtures were melted in a graphite crucible in an air induction furnace for 30 minutes at 1773K. The fused slag samples were poured onto the surface of a cold steel plate. For further homogenization, these samples were then crushed and ground to fine powders. The powder samples were placed in a corundum crucible and were dried and decarburized at 1223K for 30 hours in a muffle furnace in air. Finally, the chemical compositions of the samples were analysed; the results are reported in Table I.

Table I

Nominal and analysed chemical compositions of slag samples, wt%

Sample no.	Nominal				Analysed				Density
	CaO	Al_2O_3	MgO	R*	CaO	Al_2O_3	MgO	R	g/cm^3
1-1	50.00	50.00	0.00	1.00	49.80	49.46	0.39	1.01	2.70
1-2	48.00	48.00	4.00	1.00	48.02	48.43	3.78	0.99	2.47
1-3	47.00	47.00	6.00	1.00	46.61	46.90	5.79	0.99	2.72
1-4	46.00	46.00	8.00	1.00	46.26	45.58	7.60	1.01	2.78
1-5	44.00	44.00	12.00	1.00	44.16	43.84	11.33	1.01	3.51
2-1	47.00	47.50	5.50	0.99	46.62	47.53	5.24	0.98	3.22
2-2	46.00	48.50	5.50	0.95	47.08	47.96	4.86	0.98	2.70
2-3	44.00	50.50	5.50	0.87	44.29	50.26	5.05	0.88	2.75
2-4	42.00	52.50	5.50	0.80	42.83	52.36	4.96	0.82	3.14
2-5	40.00	54.50	5.50	0.73	41.00	53.54	4.91	0.77	2.93
2-6	35.44	59.06	5.50	0.60	35.25	58.60	5.14	0.60	3.50
2-7	49.50	45.00	5.50	1.10	51.14	43.58	5.50	1.17	3.32
2-8	51.54	42.96	5.50	1.20	52.40	40.94	5.24	1.28	3.49

* R is the mass ratio of CaO/Al_2O_3

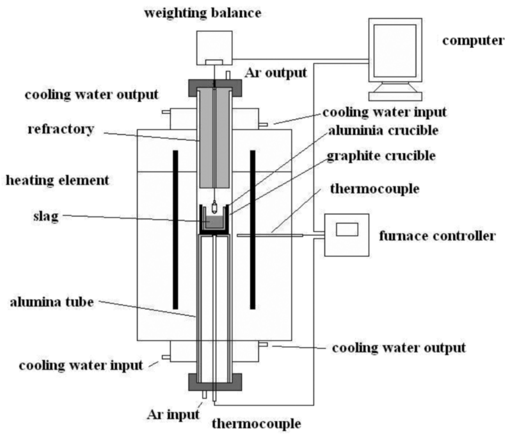

Figure 2 – Schematic of experimental apparatus

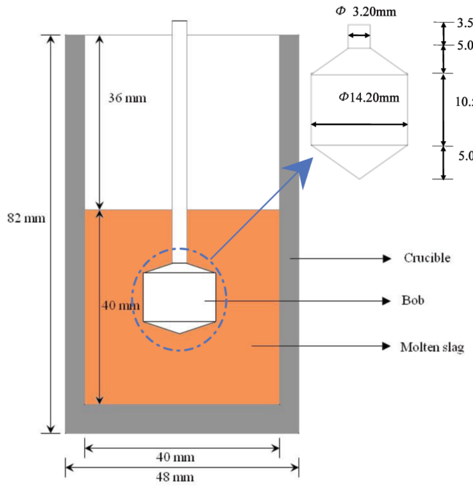

Figure 3 – Dimensions of crucible and bob

Density measurements

The densities were measured at 1823K by the Archimedean method using the RTW-08 type testing instrument . The experimental set-up and procedure have been described in detail in an earlier publication (Xu *et al.*, 2012). In this section, a brief description of the method is given. The furnace (Figure 2) had a maximum temperature of 1873K. The temperature was measured by a Pt-30Rh/Pt-6Rh thermocouple touching the crucible bottom from outside. The metal bob for measurement was made of molybdenum, which has a melting point of 2896K. The volume of the bob at high temperature was calculated from the values measured in pure water in the temperature range 283–308K and the coefficient of thermal expansion of molybdenum. Dimensions of the crucible and bob are presented in Figure 3. The size of bob had to be carefully designed so that it was applicable in the required measurement range. Purified argon gas (0.2 L/min) was introduced into the reaction chamber during the entire process. The graphite crucible was filled with 120 g slag and placed in the furnace, and the furnace was programmed to heat up to 1823K at a heating rate of 10K/min. The furnace was kept at the target temperature at least for 30 minutes. The densities of the slags were then measured at the

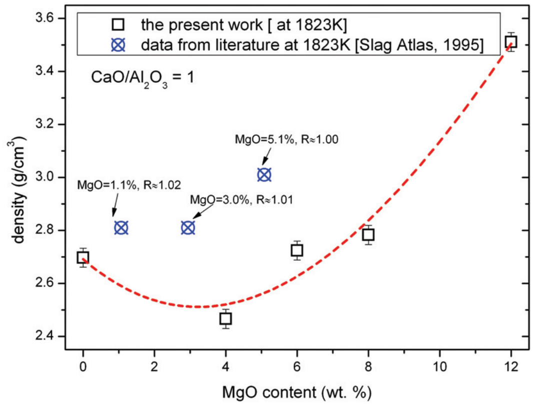

Figure 4 – Relationship between density and MgO content

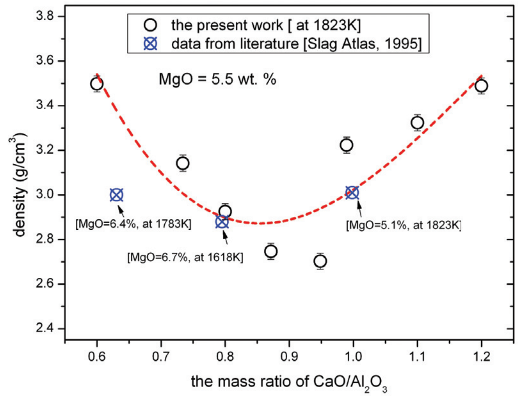

Figure 5 – Relationship between density and ratio of CaO/Al_2O_3

predetermined temperature, and the measurements were repeated several times until the values were stable, at which the error was about $\pm 1\times10^{-3}$ g. After measurement was complete, the furnace was allowed to cool.

In the density measurements several sources of error may occur. As mentioned above, a deviation in the volume of the bob caused an error of ±0.5% in density, the determination of the temperature with an accuracy of ±5K introduced an error of ±0.3% in density, and the accuracy of $\pm 1\times10^{-3}$ g in the weighting balance caused an additional error of ±0.3% in density. Since the effect of surface tension on the density measurement is difficult to estimate, no corrections were made for the effect of surface tension of the melt acting on the thin section of the spindle. This has been calculated to cause an error of about 2.0% in the density measurement (Nakanishi *et al.*, 1998). The total error in the determination of the density was less than ±3.1%.

Results and discussion

The density of the selected CaO-Al_2O_3-MgO slag system was measured at 1823K. Thirteen different slag compositions were chosen based on different levels of MgO content and mass ratios of CaO/Al_2O_3. The MgO content was varied from 0.39 to 11.33 wt.%, and CaO/Al_2O_3 mass ratios varied between 0.60 and 1.28. The effects of MgO content and CaO/Al_2O_3 ratio on the density are shown Figure 4 and Figure 5 respectively.

The data for corresponding slags from the literature (Slag Atlas, 1995) is also shown in Figures 4 and Figure 5. Comparison reveals that although the values obtained in the present study may be higher or lower than those from the literature, the density trends are similar. The differences in densities could be related to slag composition and experimental design and procedure. It should be noted that there are difficulties in retrieving reliable experimental density values.

Effect of MgO content on density

The measured densities at a constant mass ratio of CaO/Al_2O_3 and various amounts of MgO (0.39–11.33%) at 1823K are shown in Figure 4. The results indicate that the density of the slag decreased for low additions of MgO, with a minimum value of 2.47g/cm^3 at 1823K at an MgO content of 3.78%. This was followed by a sharp increase in density with further additions of MgO.

An additive method for the estimation of density in alloys and slags has been widely used for some time. The densities of the pure components CaO, MgO, and Al_2O_3 are 3.32, 3.50, and 3.97g/cm^3 respectively (Lide, 2003). Since the density of MgO is much lower than that of Al_2O_3, slag density will decrease with small increases in MgO content. On the other hand, the addition of metal oxides has a strong impact on the physical properties of molten slag systems. The effect of cations on the structure is commonly related to the charge of the cations as well as the radius. In order to estimate the effect of different cations, the ratios z/r or z/r^2 are used, where z is the valence and r is the cation radius. Slags are composed of cations and complex anions, and the forces of attraction between ions directly affect slag density (Cui *et al.*, 1996). When MgO is added to 12CaO·7Al_2O_3-type slags, the complex polymers of aluminum such as AlO_4^{5-} tetrahedra break down into smaller units, decreasing the degree of polymerization, and the radius of the ions decreases; then the force of attraction between ions and the density of the slag increase (Cui *et al.*, 1996; Mills, 1993). Furthermore, the molar masses of CaO, MgO, and Al_2O_3 are 56.08, 40.31, and 101.96 g/mol, respectively. Since the molar mass of MgO is lower than that of the other metal oxide components of the slags, when MgO replaces part of the CaO and Al_2O_3 content in 12CaO·7Al_2O_3, the total number of ions in the molten slag will increase. This also increases the forces of attraction between the ions, and thus increases the density of the slag.

Effect of CaO/Al_2O_3 on density

The effect of the mass ratio of CaO/Al_2O_3 (in the range 0.6–1.28) on density at different temperatures and a constant MgO content of 5.5 wt.% is shown in Figure 5. The effect of CaO/Al_2O_3 mass ratio on density was the same as the effect of MgO content; density decreases at first, and then increases with increasing the mass ratio of CaO/Al_2O_3. The minimum density at 1823K was 2.70g/cm^3 at a CaO/Al_2O_3 mass ratio of 0.98.

Since the density of pure CaO is lower than that of Al_2O_3, increasing CaO/Al_2O_3 decreases the slag density in line with the additive method of density calculation. On the other hand, with increasing mass ratio of CaO/Al_2O_3, the network-breaking cations (Ca^{2+}) present in slag increase, and the complex polymers of aluminum such as AlO_4^{5-} tetrahedra break down into smaller units, reducing the degree of polymerization, and the radius of ions decreases, thus increasing the attractive forces between ions. Furthermore, the total number of ions in the molten slag will also increase with increasing of the mass ratio of CaO/Al_2O_3. The lower degree of polymerization and the higher number of ions will enhance the attractive forces between ions, and the density of the slag will increase (Lide, 2003). Due to these effects, the density of slag at first decreases with increasing the mass ratio of CaO/Al_2O_3, followed by an increase in density with further increases in the mass ratio of CaO/Al_2O_3. The lower density values of slag at CaO/Al_2O_3 mass ratios in the range 0.9–1.0 could also be due to the fact that the slag compositions are between the two eutectic points in the CaO-Al_2O_3-MgO slag system, as shown in Figure 1.

Estimated molar volume of the selected slags

The molar volume, which the reciprocal of the density multiplied by the molar mass, is an important thermodynamic property. Due to the inherent difficulties associated with measurements at high temperature, it is necessary to have access to reliable models for estimating the molar volume of slags, which are reflective of the structure of the melt. There are many kinds of model cited in the literature (Zhang and Chou, 2010; Persson, Matsushita, and Zhang, 2007; Bottinga, Weill, and Richet, 1982; Mills, Yuan, and Jones, 2011; Hayashi, Abas, and Seetharaman, 2004; Priven, 2004; Nakajima, 1994; Vadasz, Havlik, and Danek, 2006; Shu, 2007; Zhang and Chou, 2009) for estimating the molar volume of slag, including physical models and semi-empirical models. Physical models, which are based on the structure of atoms and molecules, can give a clear physical picture of the practical solution. The semi-empirical models combine both theoretical considerations and practical thermodynamics; these models can give more reasonable data and be suitable for many systems with larger compositional ranges.

In order to estimate molar volumes for multi-component silicate melts, expanded approximation rules are proposed, on the basis of the regular solution approximation rules of excess molar quantities for a binary system melt (Vadasz, Havlik, and Danek, 2006). A brief description of the model is given below. Detailed discussions about this method can be found in Vadasz, Havlik, and Danek, (2006).

The molar volume of slags is calculated from Equation [1]:

$$V_m = \sum x_i V_i^* + V^E \qquad [1]$$

where V_m is the molar volume of the slag and V_i^* is the molar volume of the pure componet i, x_i is the mole fraction of component i, and V^E is the excess molar volume of the slag.

The molar volume of slags can be expressed by the following equation:

$$V_m = \frac{\sum x_i M_i}{\rho} \qquad [2]$$

Here, x_i is the mole fraction of component i, M_i is the molecular weight of component i, and ρ is the measured density of the slag.

We have to obtain the relation between the excess molar volume and composition. The regular solution approximation rule is most widely used (Shu, 2007). The excess molar volume can be expressed as follows:

$$V^E = \sum_{j \neq i} a_{ij} x_i x_j + \sum_{j \neq i \neq k} a_{ijk} x_i x_j x_k \quad [3]$$

where a_{ij} represents the parameters for components i and j, which can be obtained by optimizing an appropriate amount of experimental data in a certain compositional and temperature range. x_i and x_j indicate the mole fractions of component i and j, respectively.

The average error of all calculated values can be assessed by using Equations [4] and [5]. δ_n is the percentage difference between the calculated and measured values. $\Delta(\%)$ is calculated by taking the summation of all absolute values of δ_n and dividing by the total number of data.

$$\delta_n = \frac{(V_{m\ cal})_n - (V_{m\ mea})_n}{(V_{m\ mea})_n} \times 100 \quad [4]$$

$$\Delta = \frac{1}{N} \sum_{n=1}^{N} |\delta_n| \quad [5]$$

The molar volumes of the pure oxides (Table II) recommended by Mills *et al.* were used in the present model. Now that all necessary data has been collected, using the experimental data in the CaO-MgO-Al$_2$O$_3$ slag system and its subsystem, the optimized parameters are shown in Table III.

The estimated values using the present model were compared with the experimental data and the data for the CaO-Al$_2$O$_3$ system (Dou *et al.*, 2009; Slag Atlas, 1981; Ogino and Hara, 1977), MgO-Al$_2$O$_3$ system, and the CaO-MgO-Al$_2$O$_3$ system (Slag Atlas, 1995) from the literature to verify the model. The comparison of the experimental data with the model calculated molar volumes are shown in Figure 6. It can be seen that the estimated values agree with the experimental data, and for all calculated values the average error $\Delta(\%)$ is 2.20%. From the data for the CaO-MgO-Al$_2$O$_3$ slag system and its subsystem, the application of molar volume model confirmed that the present expanded approximation rules are applicable to predict the molar volume of the melts discussed.

Table II

Molar volumes of the pure components

Oxide	Temperature (K) dependence of molar volume (m^3/mol)
CaO	$20.7\times(1+1\times10^{-4}\times(T-1773))\times10^{-6}$
Al$_2$O$_3$	$(28.31+32x_{Al2O3}-31.45x^2_{Al2O3})\times(1+1\times10^{-4}\times(T-1773))\times10^{-6}$
MgO	$16.1\times(1+1\times10^{-4}\times(T-1773))\times10^{-6}$

Table III

Values of model parameters for selected slags

	a_{12}*	a_{13}	a_{23}	a_{123}
CaO-Al$_2$O$_3$ system	0.47	-	-	-
MgO-Al$_2$O$_3$ system	-	-	-5.42	-
CaO-MgO-Al$_2$O$_3$ system	0.47	2.93	-5.31	-202.00

* 1, 2 and 3 representative of CaO, Al$_2$O$_3$ and MgO, respectively.

Conclusions

Both of the MgO content and the mass ratio of CaO/Al$_2$O$_3$ had an influence on the density of the selected slag. With a mass ratio of CaO/Al$_2$O$_3$ of unity, the density at first decreased with increasing the MgO content, following by an increase.

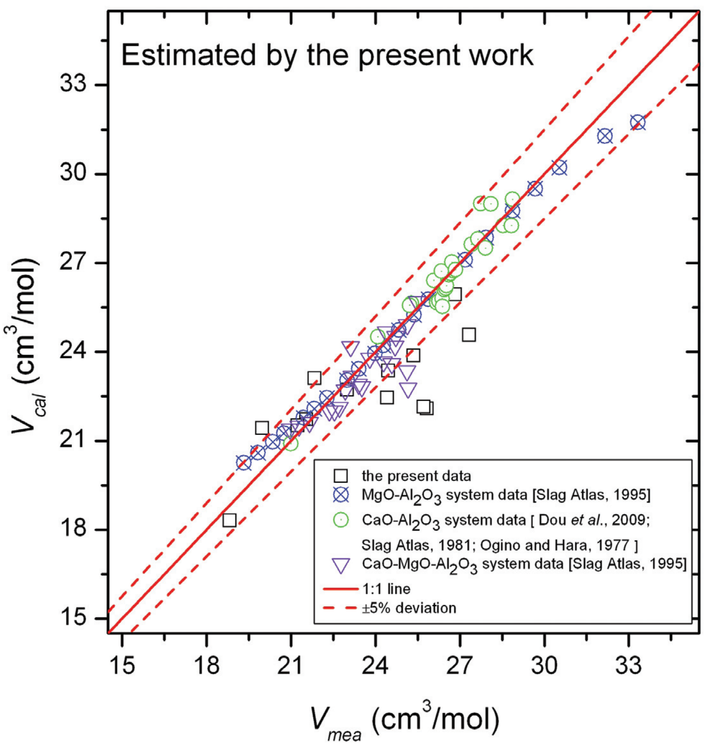

Figure 6 – Comparison between experimental data and predicated values

Changes in the mass ratio of CaO/Al_2O_3, at a constant MgO content of 5.5 wt.%, gave rise to a similar density trend as changes in the MgO content.

An attempt has been made to estimate the molar volume of the CaO-Al_2O_3-MgO slag investigated in the present work. Application of the molar volume model confirmed that the expanded approximation rules are applicable for predicting the molar volume of the melts discussed.

Acknowledgements

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (50874072, 51204115), the Natural Science Foundation of Jiangsu Province of China (BK20130308), and the China Postdoctoral Science Foundation (2014M561710).

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