

Electrical transport properties of Cu₂Se dispersed and Na-doped Bi₂Ba₂Co₂O_y thermoelectric composites

Senlin Leng^{1,a}, Wei Shi^{1,b} and Hongzhang Song^{2,c}

¹College of Material and Chemical Engineering, Tongren University, Tongren 554300, China.

²Key Laboratory of Material Physics of Ministry of Education, and Physical Engineering College, Zhengzhou University, Zhengzhou 450052, China.

^alengsenlin@sohu.com, ^bwzlsbdb@hotmail.com, ^cstar@zzu.edu.cn

Keywords: Bi₂Ba₂Co₂O_y ceramics; Cu₂Se dispersant; Na-doping; electrical transport properties.

Abstract. The Cu_{2-x}Se nanopowder was synthesized by the hydrothermal method. The electrical transport properties of Bi_{1.975}Na_{0.025}Ba₂Co₂O_y + *x*wt% Cu₂Se (*x* = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50) ceramic samples prepared by the solid-state reaction method were investigated from 300 K to 898 K. The Cu_{2-x}Se dispersant with an appropriate amount played an important role in reducing resistivity. Although the Seebeck coefficients decreased slightly, the power factors of the doped samples got a significant improvement. Ultimately, the Bi_{1.975}Na_{0.025}Ba₂Co₂O_y + 0.25wt% Cu₂Se sample exhibited a better power factors (*PF*) of 191.8 (10⁻⁶W⁻¹mK⁻²) at 898 K, which was improved by 31% compared with the un-doped Bi₂Ba₂Co₂O_y sample.

Introduction

In recent years, the development of energy conversion technologies has become a key topic of scientific research because of the deterioration of environmental problems. Thermoelectric (TE) conversion technology can convert heat into electricity directly and relieve the environmental pollution. The dimensionless TE figure of merit (*ZT*), a key parameter for the TE material conversion efficiency, is defined by the equation $ZT = S^2 T / \rho \kappa$, where *S* is Seebeck coefficients, ρ is electrical resistivity, κ is thermal conductivity, and *T* is absolute temperature. Moreover, the power factor (*PF*) is defined as $PF = S^2 / \rho$, which represents the properties of electrical transport.

Cu₂Se, as a competitive thermoelectric material, got more attention, since the conception of the Phonon Liquid-Electron Crystal (PLEC) was proposed. Element doping and nanotechnology are two most popular means to increase the *ZT* values of the TE materials [1,2]. The *ZT* value of Cu₂Se nano materials prepared by plasma sintering technology reached 1.8 at 850 K [3]. The *ZT* value of Cu₂Se fabricated by high-energy ball grinding reached 2.1 at 973 K [4]. What's more, the hydrothermal synthesis is a good method to prepare nanopowders. Recently, the Chinese Academy of Sciences and other units prepared Cu₂Se_{0.5}S_{0.5} materials by the solid solution, whose *ZT* value could reach 2.3 [5-7]. However, the volatilization of selenium was found at high temperature, and Cu₂Se was easy to be oxidized.

Since NaCo₂O₄ thermoelectric materials were found, owing to the high chemical and thermal stability, the cobalt base oxides become a key topic of research [8-10]. The properties of oxide can make up the shortcomings of easy oxidation of Cu₂Se. Cu₂Se is a p-type semiconductor. Bi₂Ba₂Co₂O_y (BBCO) is also a kind of p-type with better thermoelectric performance among cobalt oxide. In this paper, the Cu₂Se nanopowder synthesized by the hydrothermal method was dispersed in the Na element doped Bi_{1.975}Na_{0.025}Ba₂Co₂O_y materials according to a certain mass ratio. The dispersion effects of Cu₂Se on the electrical transport properties of Bi_{1.975}Na_{0.025}Ba₂Co₂O_y were explored.

Experimental

The high-purity Bi₂O₃, Na₂CO₃, BaCO₃ and Co₃O₄ powders were used to prepare the polycrystalline ceramic samples of Bi_{1.975}Na_{0.025}Ba₂Co₂O_y by the conventional solid phase method. After full blending, the powders were heated to 1043 K and kept at this temperature for 20 h, and then nature cooled to

room temperature. The Cu_2Se nanopowder prepared by hydrothermal synthesis was dispersed in the sintered powders according to the quality rate. Regrind and pressed into bar shape and tablets, the pressed samples were heated to 1053 K and kept at this temperature for 20 h, and then nature cooled to room temperature slowly. The phase composition and crystal structure of the samples were examined by X-ray diffraction (XRD; X'pert Pro system using $\text{Cu K}\alpha$ radiation; Panalytical, Holland). The micro morphology of the samples was observed by the SEM (JSM6700F, JEOL). LSR-3/800 Seebeck coefficient/electrical resistivity measuring system (LINSEIS, Germany) was carried out to measure the electrical resistivity (ρ) and Seebeck coefficients (S) simultaneously.

Results and Discussion

The XRD patterns at room temperature of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + x\text{wt}\% \text{Cu}_2\text{Se}$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples were shown in Fig. 1. It can be seen that all of samples show the $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$ layered structure and no obvious impurity phase exists in the figure. Due to the radii of Na^+ (1.02 \AA) approached to Bi^{3+} (1.03 \AA), therefore, lattice parameters have little change compare with the $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$ [10], the diffraction patterns of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$ is in complete conformity with the $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$. Moreover, the diffraction patterns of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + x\text{wt}\% \text{Cu}_2\text{Se}$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) have little shift with the increasing of Cu_2Se dispersant amount, which indicates that the dispersion of Cu_2Se and the doping of Na have no effect on the lattice parameters of $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$.

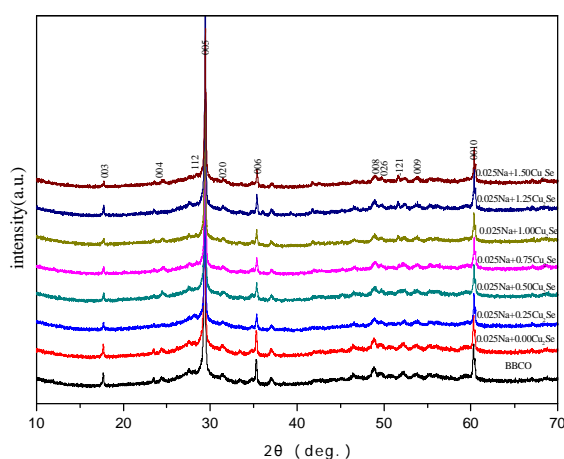


Fig. 1. The XRD patterns of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + x\text{wt}\% \text{Cu}_2\text{Se}$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples.

The SEM micrographs and the EDS of samples were shown in Fig. 2. Fig. 2(a), (b) and (c) shows the SEM micrographs of $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$, $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$ and $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + 1.50\text{wt}\% \text{Cu}_2\text{Se}$ ceramic samples respectively, the EDS of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + 1.50\text{wt}\% \text{Cu}_2\text{Se}$ ceramic sample was shown in Fig. 2(d). The $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$ sample has sheet microstructures consistent with $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$ and there is no substantial grain growth or morphological change due to the Na doping. Grain sizes of $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$ and $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$ samples are in the range of $1\text{--}10 \mu\text{m}$. However, the grain and morphology of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + x\text{wt}\% \text{Cu}_2\text{Se}$ ($x = 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) change largely compared with the non-dispersed samples. According to the Refs. [10,11], the mixed nanoparticles are scattered around the microstructure. The Cu_{2-x}Se nanoparticles dispersed around the $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$ grains lead to samples denser at high temperature. In addition, the cross-sectional morphology of samples appears some layered structure, which would contribute to optimize the electronic and thermal transport properties of $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$ samples.

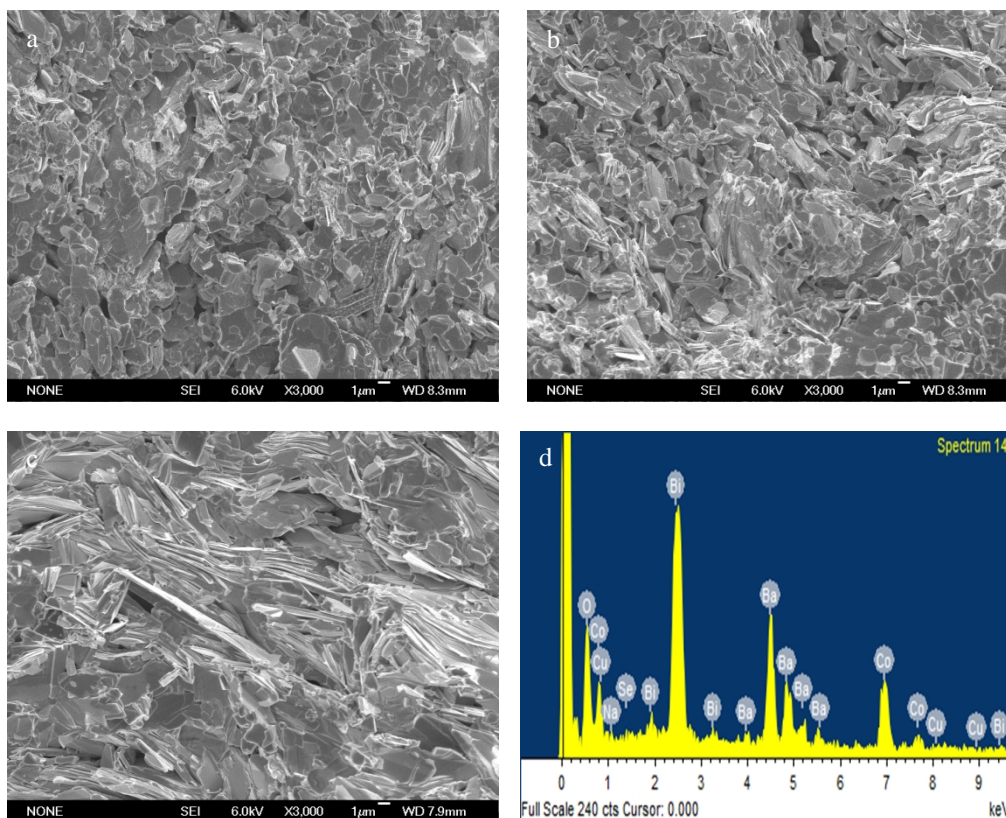


Fig. 2 (a), (b) and (c) SEM micrographs of the $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$, $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$ and $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + 1.50\text{wt}\% \text{Cu}_2\text{Se}$ ceramic samples, respectively, (d) EDS of the $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + 1.50\text{wt}\% \text{Cu}_2\text{Se}$ ceramic sample.

The electrical resistivity of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + x\text{wt}\% \text{Cu}_2\text{Se}$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples were shown in Fig. 3 from room temperature to 898 K. It can be seen that the electrical resistivity of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$ is lower than the electrical resistivity of $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$, which suggests that Na-doping can decrease the electrical resistivity of $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$ effectively. This is consistent with our earlier study [10,12,13]. Except for a few points at low temperature, the electrical resistivity of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + 0.25\text{wt}\% \text{Cu}_2\text{Se}$ sample is lower than the electrical resistivity of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$, which attribute to the increasing of carrier concentration. In addition, for $0.50 \leq x \leq 1.50$ samples, the electrical resistivity increases for the reducing of carrier mobility. Ultimately, the $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + 0.25\text{wt}\% \text{Cu}_2\text{Se}$ sample has the lowest electrical resistivity: $153.3 (10^{-6} \text{w}^{-1} \text{mk}^{-2})$ at 898 K. In short, both Na-doping and the Cu_{2-x}Se dispersion can reduce the resistivity by increasing the carrier concentration moderately.

The variety trend of the Seebeck coefficients of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + x\text{wt}\% \text{Cu}_2\text{Se}$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples with temperature is shown in Fig. 4. Obviously, the Seebeck coefficients of all samples increase with the increasing of temperature and all the values are positive, which indicated that $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + x\text{wt}\% \text{Cu}_2\text{Se}$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) samples are p-type semiconductors. However, the Seebeck coefficients of all samples are very close. This suggested that the dispersion of Cu_2Se has litter effect on the Seebeck coefficients. Form the formula of Seebeck coefficients [14], the Seebeck coefficients is related to the effective mass of carrier, concentration of carrier and Fermi level. It is possible that the Seebeck coefficients change slightly for these parameters interact with each other, which is needed further exploration.

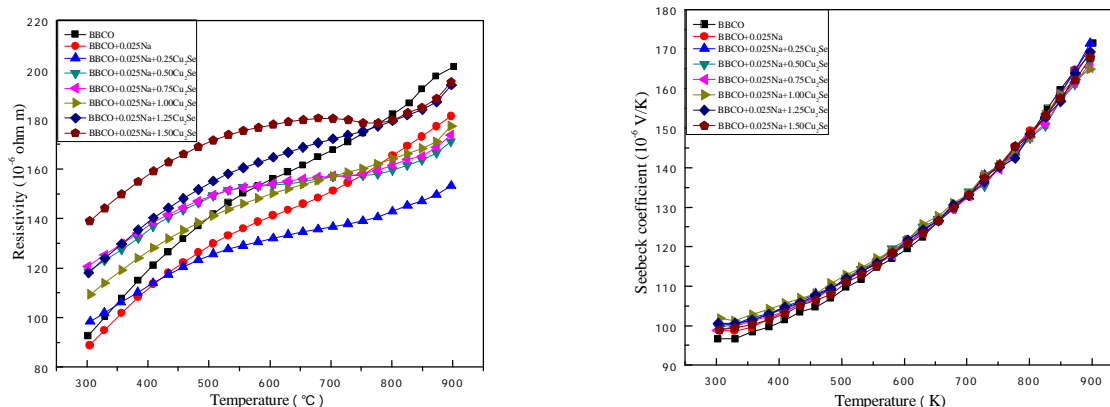


Fig. 3. The electrical resistivity of $Bi_{1.975}Na_{0.025}Ba_2Co_2O_y + xwt\% Cu_2Se$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples

Fig. 4. The Seebeck coefficients of $Bi_{1.975}Na_{0.025}Ba_2Co_2O_y + xwt\% Cu_2Se$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples

Fig. 5 shows the variety trend of the power factors of $Bi_{1.975}Na_{0.025}Ba_2Co_2O_y + xwt\% Cu_2Se$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples with temperature. The power factors ($PF=S^2/\rho$) calculated by the electrical resistivity and the Seebeck coefficients present the properties of electrical transport. The power factors of $Bi_{1.975}Na_{0.025}Ba_2Co_2O_y$ are higher than the power factors of $Bi_2Ba_2Co_2O_y$ for Na-doping decreases the electrical resistivity of sample. The power factors of the $Bi_{1.975}Na_{0.025}Ba_2Co_2O_y + xwt\% Cu_2Se$ ($x = 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples show the trend of first rising and followed decreasing with the increasing of the mixed amount of Cu_2Se , indicating that a proper amount of mixed Cu_2Se can effectively improve the electrical transport properties of the materials. Due to the $Bi_{1.975}Na_{0.025}Ba_2Co_2O_y + 0.25wt\% Cu_2Se$ sample has the lowest electrical resistivity and the dispersion of $Cu_{2-x}Se$ has little effect on the Seebeck coefficients, it has the highest power factors: $191.8 (10^{-6} W^{-1} m K^{-2})$ at 898 K in all samples, which increases by about 23% compare with the $Bi_{1.975}Na_{0.025}Ba_2Co_2O_y$, and increases by about 31% compare with the $Bi_2Ba_2Co_2O_y$ as well. This value is better than those of the Refs. [10,12]. The data show that the doping of Na element and the dispersion of Cu_2Se can improve the power factors of the materials independently. However, the effects of the dispersion of Cu_2Se combine with the Na-doping on optimize the electrical transport performance of the material are much better.

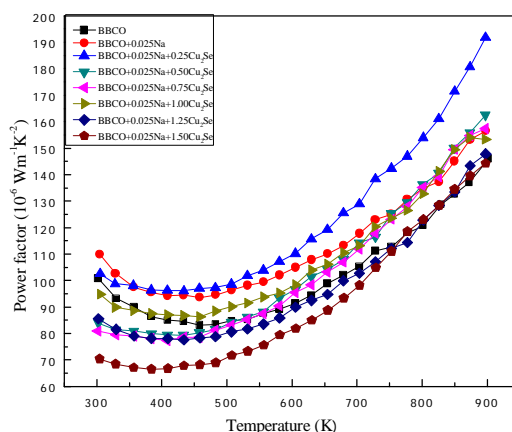


Fig. 5. The power factors of $Bi_{1.975}Na_{0.025}Ba_2Co_2O_y + xwt\% Cu_2Se$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples bulk samples

Conclusions

The Cu_2Se nanopowder prepared by the hydrothermal synthesis method was dispersed in $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$ by the solid-state reaction method. The dispersion of Cu_2Se changes the morphology of the samples, reduces the electrical resistivity of samples. However, the Seebeck coefficients of $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + x\text{wt}\% \text{Cu}_2\text{Se}$ ($x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25$, and 1.50) ceramic samples change slightly. Finally, the $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y + 0.25\text{wt}\% \text{Cu}_2\text{Se}$ sample has the lowest electrical resistivity and the dispersion of Cu_2Se has little effect on the Seebeck coefficients, so it has the highest power factors: $191.8 (10^{-6}\text{W}^{-1}\text{mK}^{-2})$ at 898 K in all samples, which increases by about 23% compare with the $\text{Bi}_{1.975}\text{Na}_{0.025}\text{Ba}_2\text{Co}_2\text{O}_y$, and increases by about 31% compare with the $\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y$.

Acknowledgements

This work was financially supported by Natural Science Foundation of China (51767021 and 51462030), the Provincial Key Disciplines of Chemical Engineering and Technology in Guizhou Province (ZDXK[2017]8), and the Key Programs for Science and Technology Development of Henan Province (182102210183 and 182102210594).

References

- [1] N. Zhou, G. Chen, X.S. Zhang, Y.C. Xu and B.R. Xu: RSC Adv. Vol. 4 (2013), p. 2427
- [2] J.Q. Li, S.P. Li, Q.B. Wang L. Wang, F.S. Liu and W.Q. Ao: J. Electron. Mater. Vol. 40 (2011), p. 2063.
- [3] L. Yang, Z.G. Chen, G. Han M. Hong, Y. Zou and J. Zou: Nano Energy Vol. 16 (2015), p. 367
- [4] B. Gahtori, S. Bathula, K. Tyagi, M. Jayasimhadri, A.K. Srivastava, S. Singh, R.C. Budhani and A. Dhar: Nano Energy Vol.13 (2015), p. 36
- [5] K. Zhao, P. Qiu, Q. Song, A.B. Blichfeld, E. Eikeland, D. Ren, B. Ge, B.B. Iversen, X. Shi and L. Chen: Mater. Today Phys. Vol. 1 (2017), p. 14
- [6] K. Zhao, A.B. Blichfeld, E. Eikeland, P. Qiu, D. Ren, B.B. Iversen, X. Shi and L. Chen: J. Mater. Chem. A Vol. 5 (2017), p. 34
- [7] K. Zhao, A.B. Blichfeld, H. Chen Q. Song, T. Zhang, C. Zhu, D. Ren, R. Hanus, P. Qiu, B.B. Iversen, F. Xu, G.J. Snyder, X. Shi and L. Chen: Chem. Mater. Vol. 29 (2017), p. 15
- [8] M.A. Madre, F.M. Costa, N.M. Ferreira, S.I.R. Costa, Sh. Rasekh, M.A. Torres, J.C. Diez, V.S. Amaral, J.S. Amaral and A. Sotelo: J. Eur. Ceram. Soc. Vol. 36 (2016), p. 67
- [9] H. Hao, H. Yang, Y. Liu and X. Hu: J. Mater. Sci. Tech. Vol. 27 (2011), p. 525
- [10] W. Gao, H. Chai, F. Wu, X. Li, X. Hu and H. Song: Ceram. Int. Vol. 43 (2017), p. 5723
- [11] S. Wang, Z. Bai, H. Wang, Q. Lv, J. Wang and G. Fu: J. Alloy Compd. Vol. 554 (2013), p. 254
- [12] W. Gao, G. Wang, X. Li, X. Hu and H. Song: Int. J. Mod. Phys. B Vol. 31 (2017), p. 1750042
- [13] Q.L. He, S.Y. Li, F. Gao, Z. Zhu, X. Hu and H.Z. Song: Mod. Phys. Lett. B Vol. 29 (2015), p. 1550159
- [14] X. Zhang and L.D Zhao: J. Materiomics Vol. 1 (2015), p. 92