

# Atomistic simulation on the site preference and mechanical properties of $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$ and $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$

Ping Qian<sup>a,b,\*</sup>, Hui-Jun Tian<sup>b</sup>, Nan-Xian Chen<sup>a,c</sup>, Jiang Shen<sup>a</sup>

<sup>a</sup>*Institute of Applied Physics, Beijing University of Science and Technology, Beijing 100083, China*

<sup>b</sup>*School of Physics, Beijing University of Chemical Technology, Beijing 100029, China*

<sup>c</sup>*Department of Physics, Tsinghua University, Beijing 100084, China*

Received 7 September 2007; received in revised form 4 January 2008; accepted 7 January 2008

Available online 12 January 2008

## Abstract

An atomistic study is presented on the phase stability, site preference and lattice constants of the actinide intermetallic compounds  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$ . Calculations are based on a series of interatomic pair potentials related to the actinides and transition metals, which are obtained by a strict lattice inversion method. The lattice constants of  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$  are calculated for different values of  $x$ . The site preference of Co atoms at Al sites is also evaluated and the order is given as  $6h$ ,  $4f$ ,  $2b$  and  $12k$  for  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$ , and  $6h$ ,  $4f$ ,  $12k$  and  $2b$  for  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$ . In addition, some simple mechanical properties such as the elastic constants and bulk modulus are investigated for the actinide compounds with complex structures.

© 2008 Elsevier Inc. All rights reserved.

PACS: 34.20.Cf; 81.05.Zx; 61.66.-f; 61.43.Bn

Keywords: Interatomic potentials; Actinide compounds; Crystal structure; Mechanical properties

## 1. Introduction

During the past three decades, U-based intermetallic compounds have been revealed to be a continuous source of materials for the study of unusual physical properties [1–5]. They may exhibit a wide variety of electronic phenomena including heavy fermion behavior, Kondo effect, valence fluctuation, coexistence of magnetism and superconductivity, which still constitutes an important challenge for theory. In theoretical research, Chen et al. have performed studies on the structural properties of 1:5-type compounds and their derivatives [6–17] from the viewpoint of energy. The method combining interatomic potentials with different crystal structures is a shortcut, but can be an effective way of investigating structural stability and site preference. It is accepted that the local atomic

environment determines if the energy of a compound is low enough to form a compound with a certain structure. Now, we extend our study to the  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$  compounds. In this paper, interatomic potentials are used to investigate the structural and mechanical properties of actinide compounds  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$ .

## 2. Methodology

### 2.1. Lattice inversion method

The atomistic simulation has been widely used in the investigation of the structures, defects, and thermodynamic properties of various materials. The key problem with this technique is how to determine the interatomic potentials. In the mid-1990s, Chen used the Möbius inversion theorem in the number theory to obtain interatomic potentials [18,19]. With the lattice inversion theorem, we can do without complicated fitting and parameter adjustment when obtaining the interatomic potentials. Some details

\*Corresponding author at: Institute of Applied Physics, Beijing University of Science and Technology, Beijing 100083, China.

Fax: +86 10 62322872.

E-mail address: [qianpinghu@sohu.com](mailto:qianpinghu@sohu.com) (P. Qian).

of the method for obtaining the potentials are given in our previous works [6–17]. The inverted pair potentials are approximately expressed as a Morse function:

$$\Phi(x) = D_0(e^{[-\gamma(x/R_0-1)]} - 2e^{[-(\gamma/2)(x/R_0-1)]}), \quad (1)$$

where  $D_0$ ,  $R_0$ ,  $\gamma$  are potential parameters. For the reader's convenience, several important potential parameters are listed in Table 1.

## 2.2. Second derivative method

There are three basic methods available for calculating mechanical properties in the Cerius2 [20] procedure provided by Materials Simulation Incorporation: second derivative, constant stress minimization and constant strain minimization. All these techniques can be used to obtain the stiffness matrix as well as its inverse, called the compliance matrix. These two matrices are then used to derive the other properties, such as Young's modulus, bulk modulus, Poisson's ratio, and so on. In this work, we use the second derivative method to acquire the mechanical properties of actinide intermetallics.

The second derivative method uses a single-point energy calculation to obtain the second derivatives of the lattice energy with respect to the lattice parameters and the atomic coordinates. The following energy expression is used:

$$U = U_0 + \sum_i \frac{\partial U}{\partial \varepsilon_i} \varepsilon_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j, \quad (2)$$

where  $U_0$  is the equilibrium energy and  $\varepsilon$  is the strain.

When the structure is at the energy minimum (i.e., all first derivatives of the lattice energy are zero), the second derivative term can be used to calculate the components  $C_{ij}$  of the stiffness matrix:

$$C_{ij} = \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j}. \quad (3)$$

The stiffness matrix computed by this method is always symmetric, that is,  $C_{ij} = C_{ji}$ . Then the compliance matrix,  $S$ , is calculated as the inverse of the stiffness matrix:

$$S = C^{-1}. \quad (4)$$

Table 1  
Part of Morse parameters of the converted pair potentials

	$R_0$ (Å)	$D_0$ (eV)	$\Gamma$
U–U	3.9415	0.6624	7.3445
Al–Al	3.0059	0.4232	8.9191
Co–Co	2.7087	0.6766	8.9030
Th–Th	4.4270	0.5873	7.2648
U–Al	3.4682	0.5915	8.8707
U–Co	3.2024	0.8835	8.6841
Th–Co	3.2856	0.7465	8.6819

The volume compressibility is calculated from the compliance matrix as follows:

$$\beta = S(1, 1) + S(2, 2) + S(3, 3) + 2[S(3, 1) + S(2, 1) + S(3, 2)] \quad (5)$$

and the bulk modulus is the inverse of the volume compressibility:

$$B = \frac{1}{\beta}. \quad (6)$$

## 3. Calculated results

### 3.1. Preferential site occupation of Co

The basic features of the crystal structure of the hexagonal  $Gd_3Ru_4Al_{12}$  type were first determined by Gladyshevskii [21].  $Th_3Co_{4+x}Al_{12-x}$  and  $U_3Co_{4+x}Al_{12-x}$  crystallize in the hexagonal system with a  $Gd_3Ru_4Al_{12}$ -type structure in which 32 metal atoms are located at the  $2a$ ,  $6g$ ,  $2b$ ,  $4f$ ,  $6h$  and  $12k$  symmetry sites of space group  $P6_3/mmc$ . Actinide atoms are most reasonably placed at  $6h$  sites. The site preference of Co atoms in  $Th_3Co_{4+x}Al_{12-x}$  and  $U_3Co_{4+x}Al_{12-x}$  has been investigated. The calculation unit of  $Th_3Co_{4+x}Al_{12-x}$  and  $U_3Co_{4+x}Al_{12-x}$  was a  $3 \times 3 \times 3$  cell (1026 atoms in total) expanded from the  $Gd_3Ru_4Al_{12}$  unit cell. Firstly, we substituted Co atoms for Al at each site with different concentrations. Then, the energy-minimization method was applied to let the ternary system relax under the applied potentials. The average energy was taken as a criterion of the stability. Calculations were performed on 30 samples in each case, with the equivalent Al sites randomly occupied by Co atoms. Fig. 1 shows the calculated average energy of  $Th_3Co_{4+x}Al_{12-x}$  and  $U_3Co_{4+x}Al_{12-x}$  compositions with  $Gd_3Ru_4Al_{12}$ -type structure. The error bars in Fig. 1 represent the ranges of the root-mean-square errors. It can be seen from Fig. 1 that the substitution of Co for Al at all the four sites  $2b$ ,  $4f$ ,  $6h$  and  $12k$  decreases the cohesive energy of  $Th_3Co_{4+x}Al_{12-x}$  and  $U_3Co_{4+x}Al_{12-x}$ , which means that the Co atoms can play a role in stabilizing the structure. Furthermore, the Co atoms strongly prefer  $6h$  sites, which can easily be concluded from Fig. 1 because the average energy decreases more significantly after Co substitution for Al. The order of the site preference is  $6h$ ,  $4f$ ,  $2b$  and  $12k$  for  $Th_3Co_{4+x}Al_{12-x}$ , and  $6h$ ,  $4f$ ,  $12k$  and  $2b$  for  $U_3Co_{4+x}Al_{12-x}$ .

### 3.2. Crystal structure and phase stability of $Th_3Co_{4+x}Al_{12-x}$ and $U_3Co_{4+x}Al_{12-x}$

According to the results of the site preference, using the conjugate gradient method the lattice constants and interatomic distances of  $Th_3Co_{4+x}Al_{12-x}$  and  $U_3Co_{4+x}Al_{12-x}$  are calculated. The calculated results are presented in Table 2 and Fig. 2. From Table 2, one can find that our calculated results for the uranium system are close to the experimental results [22]. However, so far, there are no

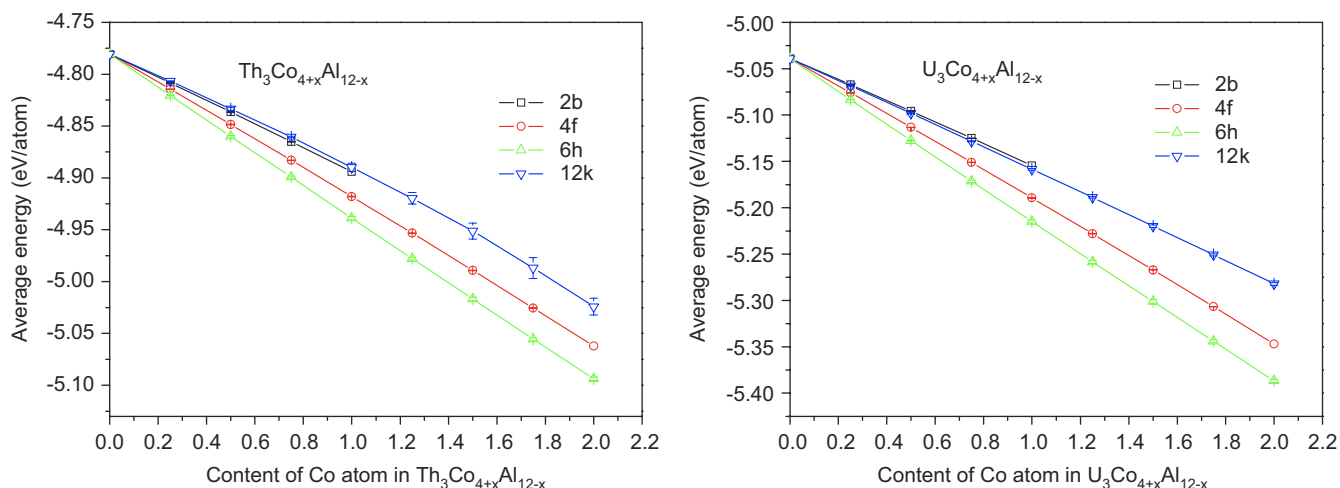


Fig. 1. Calculated cohesive energy variation with  $x$  when Co atoms occupy different sites in  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$ .

Table 2

Selected interatomic distance (Å) in  $\text{U}_3\text{Co}_{4.55}\text{Al}_{11.45}$  and  $\text{Th}_3\text{Co}_{4.55}\text{Al}_{11.45}$

U(1)/Th(1)–Al(4)	3.062(2.967 <sup>a</sup> )/3.114	Al(2)–Co(2) × 2	2.540(2.508 <sup>a</sup> )/2.602
U(1)/Th(1)–Al(2) × 2	3.066(3.012 <sup>a</sup> )/3.170	Al(2)–Al(2) × 2	2.660(2.658 <sup>a</sup> )/2.654
U(1)/Th(1)–Al(3) × 2	3.147(3.021 <sup>a</sup> )/3.309	Al(2)–Al(1) × 4	2.767(2.743 <sup>a</sup> )/2.810
U(1)/Th(1)–Al(1) × 2	3.142(3.103 <sup>a</sup> )/3.208		
U(1)/Th(1)–Al(1) × 4	3.188(3.157 <sup>a</sup> )/3.271	Al(3)–Co(2) × 3	2.538(2.499 <sup>a</sup> )/2.582
U(1)/Th(1)–Co(2) × 4	3.241(3.263 <sup>a</sup> )/3.364	Al(3)–Al(1) × 3	2.693(2.701 <sup>a</sup> )/2.721
U(1)/Th(1)–U(1)/Th(1) × 2	3.506(3.512 <sup>a</sup> )/3.581	Al(3)–Al(2) × 3	2.731(2.841 <sup>a</sup> )/2.710
Al(1)–Co(1)	2.545(2.530 <sup>a</sup> )/2.576	Al(4)–Co(1) × 2	2.340(2.316 <sup>a</sup> )/2.383
Al(1)–Co(2) × 2	2.679(2.642 <sup>a</sup> )/2.740	Al(4)–Al(1) × 6	2.896(2.889 <sup>a</sup> )/2.924
Al(1)–Al(1) × 2	2.889(2.835 <sup>a</sup> )/2.965		

<sup>a</sup>Literature [22].

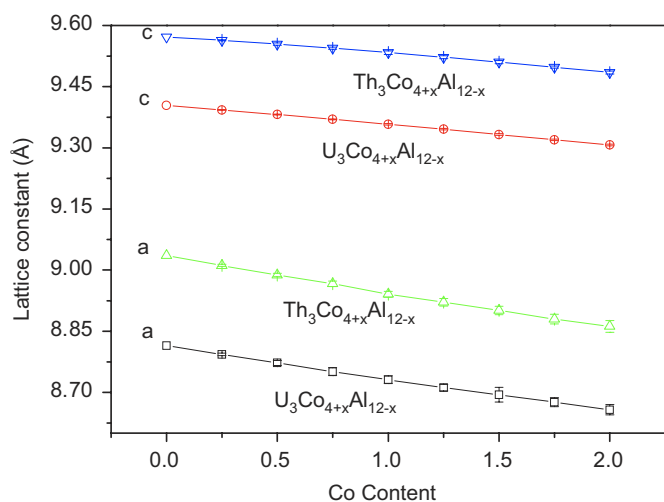


Fig. 2. Calculated lattice constants  $a$  and  $c$  variation with  $x$  in  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$ .

experimental results quoted for the thorium system. The interatomic distances are a little larger than the experimental data; however, deviations are less than 4%. Selected

interatomic distances (up to 3.506 Å) together with the number of near neighbors are given in Table 2. It can be seen from Table 2 that the Co–Al and Al–Al distances of  $\text{U}_3\text{Co}_{4.55}\text{Al}_{11.45}$  range from 2.340 to 2.679 Å and from 2.644 to 2.896 Å, respectively, consistent with strong Co–Al and Al–Al bonding interactions. The U–Al distances of  $\text{U}_3\text{Co}_{4.55}\text{Al}_{11.45}$  range from 3.062 to 3.188 Å and the U–Co distances are longer than 3.241 Å, reflecting weak bonding interactions between the U and Co atoms. In the  $\text{Th}_3\text{Co}_{4.55}\text{Al}_{11.45}$  compounds, the distribution of interatomic distances is similar to that in  $\text{U}_3\text{Co}_{4.55}\text{Al}_{11.45}$  mentioned above. However, all the interatomic distances of  $\text{Th}_3\text{Co}_{4.55}\text{Al}_{11.45}$  are longer than that of  $\text{U}_3\text{Co}_{4.55}\text{Al}_{11.45}$ , indicating weaker bonding interactions in the Th compound. It is found in Fig. 2 that the lattice constants  $a$  and  $c$  decrease with increasing Co content, and the lattice constants of  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  are larger than that of  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$ .

In order to check the stability of the calculated structure, further calculations were performed on the  $x = 0.55$  composition. Co atoms were randomly substituted for part of the Al atoms to give the correct stoichiometry. Each atom was randomly shifted 0.6 Å from its equilibrium

Table 3  
Elastic constants and bulk moduli of  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$

Compounds	Elastic constants $C_{ij}$ (GPa)						Bulk modulus (GPa)
	$C_{11}$	$C_{12}$	$C_{13}$	$C_{33}$	$C_{44}$	$C_{66}$	
$x$							
<i>Th<sub>3</sub>Co<sub>4+x</sub>Al<sub>12-x</sub></i>							
0.25	302	122	86	359	69	90	173
0.5	306	124	87	365	70	92	175
0.75	312	126	86	372	72	93	177
1	316	129	86	378	74	95	180
<i>U<sub>3</sub>Co<sub>4+x</sub>Al<sub>12-x</sub></i>							
0.25	356	130	95	413	87	113	197
0.5	362	132	97	420	89	115	199
0.75	367	135	97	427	91	116	202
1	373	137	97	434	93	118	205

position. After energy minimization, the final relaxed structures recovered the  $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ -type structure with  $P6_3/mmc$  symmetry. The lattice constants of the final structure were  $a = 8.9676 \text{ \AA}$ ,  $c = 9.5336 \text{ \AA}$  for  $\text{Th}_3\text{Co}_{4.55}\text{Al}_{11.45}$  and  $a = 8.7561 \text{ \AA}$ ,  $c = 9.361 \text{ \AA}$  for  $\text{U}_3\text{Co}_{4.55}\text{Al}_{11.45}$ . The results for  $\text{U}_3\text{Co}_{4.55}\text{Al}_{11.45}$  are consistent with the experimental data of  $a = 8.6518 \text{ \AA}$ ,  $c = 9.2620 \text{ \AA}$  [22] and suggest good stability for these structures.

### 3.3. Mechanical properties of $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$ and $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$

In order to probe into the mechanical properties of intermetallic compounds, the elastic constants and the bulk modulus of  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$  were studied at an atomistic level.

According to the site preference results, Co atoms substitute for a randomly selected part of Al atoms at the  $6h$  sites, thus forming the  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$  systems. Under the influence of the inverted interatomic potentials, the second derivative method is used to acquire the mechanical properties of actinide intermetallics. The calculated results are listed in Table 3. From Table 3, it is noted that the values of the components of the elastic modulus increase for  $C_{11}$ ,  $C_{12}$ ,  $C_{33}$ ,  $C_{44}$  and  $C_{66}$  with increasing Co content, while for  $C_{13}$  there is no obvious change with  $x$ . Bulk modulus increases with increasing Co content consistent with a strengthening of bonding interactions in the system. This indicates that the Co atoms can improve the strength and atomic interaction of the system. In addition, the values for the bulk modulus and for all elastic constant components of  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$  are larger than that of  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$ .

## 4. Conclusion

An investigation of the structural properties of  $\text{Th}_3\text{Co}_{4+x}\text{Al}_{12-x}$  and  $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$  compounds has been

performed by a series of interatomic pair potentials obtained through the lattice inversion method. The calculated results demonstrate that the stabilizing element Co prefers to substitute for Al in  $6h$  sites. The calculated lattice parameters coincide with the experimental values for the U system. In addition, we have also utilized the same potentials to evaluate elastic constants and bulk modulus. This provides some information on the mechanical properties of the actinide intermetallics, which are difficult to calculate by more rigorous methods due to the low symmetry of structure.

## Acknowledgments

The authors would like to thank Professor F.M. Yang and Professor J.K. Liang at Institute of Physics in the Chinese Academy of Sciences for interesting discussions and encouragement. The work is supported by the 973 Project in China (No. 2006CB605101) and the Youthful Nature Science Foundation of Beijing University of Chemical Technology (No. QN0618).

## References

- [1] C. Geibel, A. Böhn, R. Caspary, K. Gloos, A. Grauel, P. Hellmann, R. Modler, C. Schank, G. Weber, F. Steglich, *Physica B* 186–188 (1993) 188–194.
- [2] G. André, F. Bourée, A. Oleoe, W. Sikora, B. Pene, A. Szytula, Z. Tomkowicz, *Solid State Commun.* 97 (1996) 923–929.
- [3] S. Pechev, T. Roisnel, B. Chevalier, B. Darriet, J. Etourneau, *Solid State Sci.* 2 (2000) 773–780.
- [4] O. Tougait, J. Stępień-Damm, V. Zaremba, H. Noël, R. Troc, *J. Solid State Chem.* 174 (2003) 152–158.
- [5] H. Noël, O. Tougait, R. Troc, V. Zaremba, *Solid State Sci.* 7 (2005) 780–783.
- [6] N.X. Chen, J. Shen, X.P. Su, *J. Phys.: Condens. Matter* 13 (2001) 2727–2736.
- [7] P. Qian, N.X. Chen, J. Shen, *Intermetallics* 13 (2005) 778–783.
- [8] J. Shen, P. Qian, N.X. Chen, *Model. Simul. Mater. Sci. Eng.* 12 (2004) 871–880.
- [9] P. Qian, Q.L. Wang, N.X. Chen, J. Shen, *J. Phys. D: Appl. Phys.* 39 (2006) 1197–1203.
- [10] H. Chang, N.X. Chen, J.K. Liang, G.H. Rao, *J. Phys: Condens. Matter* 14 (2002) 1.
- [11] P. Qian, N.X. Chen, J. Shen, *Phys. Lett. A* 335 (2005) 464–470.
- [12] P. Qian, N.X. Chen, J. Shen, *Solid State Commun.* 134 (2005) 771–776.
- [13] N.X. Chen, J. Shen, X.L. Wang, *J. Alloy Compd.* 359 (2003) 91–98.
- [14] W.X. Li, L.Z. Cao, J. Shen, N.X. Chen, B.D. Liu, J.L. Wang, G.H. Wu, F.M. Yang, Y.X. Li, *J. Appl. Phys.* 93 (2003) 6921.
- [15] S.Q. Hao, N.X. Chen, J. Shen, *J. Alloy Compd.* 343 (2002) 53–59.
- [16] L.Z. Cao, N.X. Chen, J. Shen, *J. Alloy Compd.* 336 (2002) 18–28.
- [17] Y.M. Kang, N.X. Chen, *J. Alloy Compd.* 349 (2003) 41–48.
- [18] N.X. Chen, G.B. Ren, *Phys. Rev. B* 45 (1992) 8177.
- [19] N.X. Chen, Z.D. Chen, Y.C. Wei, *Phys. Rev. E* 55 (1) (1997) R5.
- [20] <<http://www.accelrys.com/products/ceurus2/>>.
- [21] R.E. Gladyshevskii, O.R. Strusievicz, K. Cenzual, E. Parthé, *Acta Crystallogr. B* 49 (1993) 474–478.
- [22] O. Tougait, H. Noël, R. Troc, *Solid State Chem.* 177 (2004) 2053–2057.