Y. Zhang et al.: Two-dimensional TiC nanocrystals produced

Yanli Zhang^{a,b}, Zhen Dai^a, Dongming Niu^a, Baoyan Liang^{a,b}, Qisong Li^a, Li Yang^b

^aMaterials and Chemical Engineering School, Zhongyuan University of Technology, Zhengzhou, P.R. China

^bFaculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, P.R. China

Two-dimensional TiC nanocrystals produced by molten salt treatment of carbon black and Ti₂AlC

Abstract: In this study, 2D TiC nanosheets were successfully synthesized by reacting carbon black and Ti₂AlC in a molten NaCl/KCl eutectic salt. The effects of salt content and ratio of raw materials on the phase composition and purity of TiC products were systematically investigated. Results showed that carbon black enhanced the total decomposition of Ti₂AlC to TiC, Al, and Al₃Ti at 1 100 °C. The introduction of molten salt ensured the formation of TiC nanosheets. Excess carbon influenced the synthesis of high TiC content by removing the Al and Al₃Ti by-products. TiC nanosheets had a thickness of approximately 10–20 nm and a length of approximately 150–200 nm. A possible synthesis mechanism of TiC nanosheets was proposed.

Keywords: MXene; TiC; Carbon black; Molten salt synthesis

1 Introduction

Two-dimensional (2D) materials have been widely investigated in materials science with the discovery of graphene [1]. In recent years, a new family of 2D materials, including transition metal carbides, nitrides, and carbonitrides, has emerged; these 2D materials are called MXenes [2, 3]. MXene materials can be obtained by etching MAX phases. MAX phases are a layered ternary metal carbide, nitride, or

carbonitride with the general formula of M_{n+1}AX_n ($n = 1-3$). In the MAX phase structure, M–X layers have strong bond energy, and the A atom layer has an active chemical activity. Therefore, the A atom can be removed by etching the MAX phase. Then, a graphene, like MXene materials, can be obtained [4, 5]. MXenes possess many special properties, making them suitable in many fields, such as energy storage [6], environment [7], catalysis [8], and biology [9].

Hydrofluoric acid (HF) etching from MAX phases is widely used to prepare MXenes. Naguib et al. successfully prepared Ti₃C₂ MXenes from the Ti₃AlC₂ phase by using this method [2]. HF acid has strong toxicity to the human body and environment. Therefore, many researchers used weak acids to replace HF etching. In 2014, Ghidlu et al. [10] prepared Ti₃C₂ MXenes using LiF and HCl mixed solution as an etchant. In the same year, Halim et al. [11] selected another etching agent (NH₄HF₂) to replace HF. In addition to acid etching methods, MXenes were prepared through a concentrated alkali method [12], an electrochemical method [13], molten salt etching [14], and other technologies [15].

MXenes are usually prepared using HF acid [2] or LiF–HCl acid [10] to etch MAX phase materials. However, large amounts of waste liquid produced in etching are harmful to the human body and environment. The functional groups formed on the surface of MXenes during acid etching reduce their performance. The preparation cost is extremely high. Therefore, exploring a new low-cost preparation tech-

nology that meets the preparation conditions without functional groups and is suitable for large-scale production and universal application is necessary.

Some researchers have studied the high-temperature thermal stability of MAX phases, such as Ti₃SiC₂ and Ti₃AlC₂, in argon or vacuum [16, 17]. The high-temperature thermal stability of MAX phase materials is closely related to the carbon environment. Reference [17] showed that Ti₃SiC₂ decomposes into TiC_x at 1573 K when graphite crucible is used. A large amount of AlOC whiskers is obtained when Ti₃AlC₂ bulk material is heated at 1523 K–1573 K in a carbon furnace [18]. Reference [19] verified the influence of carbon atmosphere on the thermal stability of Ti₃AlC₂ by using 10% CO–Ar atmosphere. Results showed that Ti₃AlC₂ decomposes when the heating temperature is 1523 K. The thermal stability of MAX phase materials is reduced by the carbon-containing environment. These studies obtained a large number of MX phases (mainly TiC) through MAX phase decomposition. The obtained TiC has large (micron scale) grain size and granular morphology because of its high initial decomposition temperature (above 1523 K).

Molten salt synthesis is a simple method used to prepare ceramic materials [20]. It can be used to prepare anisotropic powders with specific components at low reaction temperature or short reaction time. Molten salt synthesis is suitable for the directional growth of ceramic materials because it easily synthesizes CoB [21] and ZrO₂ [22] nanosheets. Recently, Li et al. [23, 24] found that MAX phases, such as Ti₃ZnC₂ and Ti₂ZnC, have a structural transformation in ZnCl₂ molten salt, that is, the Zn atoms in the A layer of the MAX phases are attacked by Zn²⁺ in the molten salt. Then, they are extracted from A layers. The Cl[−] in the molten salt further enters the A layer, combines with the M_{n+1}X_n sublayer to form the structural units of M_{n+1}X_nCl₂ (Ti₃C₂Cl₂ and Ti₂CCl₂), and dissociates along the interlayer to obtain a new MXene material with all Cl groups. On this basis, they have constructed the Gibbs free energy (*G*) map of redox potential/displacement reaction between cation and A element in a high-temperature molten salt environment and proposed a general strategy for the synthesis of MXene by using the Lewis acid molten salt to etch the MAX phase.

On the basis of previous works, we used carbon black to induce the decomposition of MAX phase materials at low temperature to obtain MX 2D materials. Molten salt was introduced in heat treatment to promote the directional growth of MX materials. As representative materials, TiC MXenes [25, 26] were etched from Ti₂AlC. Carbon black and Ti₂AlC were used as raw materials to prepare TiC MXenes through molten salt heat treatment.

2 Experimental procedure

Carbon black (30 nm on average) was purchased from Daosheng Chemical Co., Ltd. (Shanghai). Ti₂AlC powder (~74 μm, 99.0% purity) was purchased from Laizhou Kai Kai Ceramic Material Co., Ltd. Anhydrous NaCl and KCl (analytical purity) were purchased from Tianjin No. 3 Chemical Plant Co., Ltd.

The formula of raw materials is shown in Table 1. After weighing the raw material powders, they were ground in a grinder for 1 h to make them evenly mixed. These mixed powders were placed in graphite crucibles and covered with a lid. These graphite crucibles were placed in a vacuum carbon tube furnace (Shanghai nichan Vacuum Technology Co., Ltd). Heating system: The heating rate was about 8 K min^{−1}. After the furnace was heated to 973 K in vacuum (~10^{−2} Pa), the vacuum valve was turned off. Then, high-purity argon gas (99.9% purity) was introduced. The powders were heated at 1373 K for 1.5 h and cooled in the furnace. The samples were washed repeatedly with distilled water and alcohol to remove the salt. The products were obtained after drying at 353 K.

The synthesized samples were characterized through X-ray diffraction (XRD, D/MAX-2500PC) and field-emission scanning electron microscopy (SEM, Quanta 250 FEG) combined with energy dispersive X-ray spectroscopy (EDS). The grain size was measured using Image 6.0 software.

The Gibbs free energy change (ΔG) is calculated to determine the change in the heat capacity (ΔC_p) of the reaction from the *C_p* equation of matter and for integration to obtain ΔH_T (Kirchhoff's law). Finally, the Gibbs–Helmholtz equation is used for integration to obtain the ΔG function.

Table 1. Raw material formula.

Sample name	Carbon black (g)	Ti ₂ AlC (g)	NaCl (g)	KCl (g)	Mole ratio of carbon black to Ti ₂ AlC	Weight ratio of flux/powder
A		1.35				
A0	0.12	1.35				
A1	0.12	1.35	1.47	1.47	1:1	2:1
A2	0.12	1.35	2.94	2.94	1:1	4:1
A3	0.12	1.35	5.88	5.88	1:1	8:1
A4	0.06	1.35	2.94	2.94	0.5:1	4:1
A5	0.132	1.35	2.94	2.94	1.1:1	4:1
A6	0.18	1.35	2.94	2.94	1.5:1	4:1

ΔH , T , and ΔC_p are the enthalpy change of reaction, thermodynamic temperature, and difference between the sum of the heat capacities of the products and the sum of the molar heat capacities of the reactants, respectively.

The change in G (ΔG) of the reaction involving Ti₂AlC and Ti₃AlC₂ can be calculated using the above method [27]. Thermodynamic data, such as ΔH , and ΔC_p , of Ti₂AlC and Ti₃AlC₂ can be obtained as previously described [28, 29].

The workload of the above calculation method is large, bringing substantial inconvenience to actual workers. In 1979, Ye introduced the method of the free enthalpy function of matter (Φ) [27]. This method provides a new thermodynamic calculation method with the same calculation results as the above classical algorithm and possesses simple calculation steps. Gibbs free function of matter (Φ_T) can be defined as the following Eq. (1).

$$\Phi_T = -\frac{G_T^0 - H_{298}^0}{T} = -\frac{H_T^0 - H_{298}^0}{T} + S_T^0 \quad (1)$$

The ΔG for the reaction that does not involve Ti₂AlC and Ti₃AlC₂ can be calculated using a previously described equation [27]:

$$\Delta G_T^0 = \Delta H_{T_0}^0 - T\Delta\Phi_T \quad (2)$$

where ΔH , T , and $\Delta\Phi_T$ are the enthalpy change of reaction, thermodynamic temperature, and change in the Φ function of a reaction, respectively.

$$\Delta\Phi_T = \sum (n_i\Phi_{i,T})_{\text{products}} - \sum (n_i\Phi_{i,T})_{\text{reactants}} \quad (3)$$

The ΔH and Φ function data of Al, Al₄C₃, C, TiC, and Al₃Ti can be obtained as described in the literature [27].

Fig. 1. (a) XRD patterns of samples A and A0, FE-SEM images of (b) sample A, and (c) and (d) sample A0.

3 Results and discussion

Figure 1 shows the (a) XRD patterns of samples A and A0, FE-SEM images of (b) sample A sample and (c), (d) sample A0. The XRD patterns of sample A showed that only a small amount of Ti_2AlC was decomposed into TiC in the absence of carbon black. However, Ti_2AlC was completely

Fig. 2. XRD patterns of the synthesized A1, A2 and A3 products under different weight ratio of salt to reactant. The weight ratio of flux/powder were 2:1, 4:1 and 8:1, respectively.

decomposed into TiC, TiAl_3 , Al after adding carbon black. In addition, Al reacted with trace oxygen in the environment to form Al_2O_3 .

As shown in Fig. 1b, typical lath-like Ti_2AlC grains were present in sample A. Figure 1c and d shows SEM images of sample A0. From the lower magnification image (Fig. 1c), the sample was composed of a large number of several micron-sized powder particles. As shown in the higher multiple image (Fig. 1d), these powder particles are aggregates composed of a large number of nanoparticles (60–200 nm) with few lamellar grains.

The experimental results suggest that carbon black may induce Ti_2AlC to decompose completely at low temperature. However, TiC nanosheets were not formed.

The molar ratio (named as X) of carbon black to Ti_2AlC and the weight ratio (named as Y) of salt to reactant (carbon black and Ti_2AlC) are the two key factors in molten salt synthesis. They affect the purity and morphology of the product. In the present study, the effect of weight ratio of salt to reactant on the phase composition and morphology of the products was investigated. Figure 2 shows the XRD patterns of samples A1, A2, and A3 under different weight ratios of salt to reactant. The XRD patterns of these samples were similar, and the phase composition of the products was the same. These products were composed of TiC, TiAl_3 , Al, and Al_2O_3 . The molten salt ratio exerted minimal effect on the phase composition of these products.

Figure 3 shows SEM images of samples A1, A2, and A3. As shown in Fig. 3a, sample A1 was composed of many ag-

Fig. 3. FE-SEM images of (a) and (b) A1, (c) A2, (d) A3 samples, (e) EDS of Fig. 3(b).

glomerated particles with sizes ranging from a few microns to more than 10 microns. As shown in Fig. 3b, their surface consists of many TiC nanosheets, and this finding is confirmed using XRD (Fig. 2) and EDS (Fig. 3e). These nanosheets had a thickness of approximately 10–20 nm and a length of approximately 150–200 nm. Sample A2 was composed of a large number of TiC nanosheets (Fig. 3c). Sam-

Fig. 4. XRD patterns of the synthesized A4, A5 and A6 products under different mole ratio of carbon black to Ti₂AlC. The mole ratio of carbon black to Ti₂AlC were 0.5:1, 1.1:1 and 1.5:1, respectively.

ple A3 was composed of a large number of nano or submicron TiC particles. Low molten salt ratio (2:1 and 4:1) promoted the formation of TiC nanosheets, whereas high molten salt ratio was conducive to the formation of TiC particles.

We used an appropriate weight ratio of salt to reactant ($Y=4$) in the following experiment. Figure 4 shows the XRD patterns of the samples obtained under different molar ratios of carbon black to Ti₂AlC. As shown in Fig. 4, the Ti₂AlC peaks in the A4 product completely disappeared when the carbon black content was the lowest ($X=0.5$). Strong Ti₃AlC₂ and TiC diffraction peaks and weak diffraction peaks of TiAl, TiAl₃, and Al₂O₃ were found. The as-synthesized Ti₃AlC₂ was obtained through the reaction of newly formed TiC to Ti₂AlC. Several studies [30–32] have indicated that Ti₃AlC₂ materials can be efficiently fabricated from TiC and Ti₂AlC mixtures through heat treatment.

The main phase of sample A5 was TiC when the carbon black content was slightly high ($X=1.1$). Few Al, Al₃Ti, and Al₂O₃ were found. Compared with that of A2 ($X=1.0$), the diffraction peak of Al₃Ti was extremely weak. The diffraction peak of Al disappeared when the carbon black content was high ($X=1.5$).

As shown in Fig. 4, carbon black was a reaction material rather than a catalyst. Although Ti₂AlC was completely decomposed, it was not completely transformed into a large amount of TiC when the carbon black content was insufficient. Many impurities, such as Ti₃AlC₂, TiAl, and Al₃Ti, were found in the product. Compared with sample A2, Al

Fig. 5. FE-SEM images of (a) A4, (b) A5, (c) and (d) A6, (e) EDS of lath grains in Fig. 5(a).

and Al₃Ti in the product gradually disappeared with the increase in carbon content in samples A5 and A6. Therefore, the effect of carbon on the synthesis of high TiC content was extremely important. Excess carbon removed the Al and Al₃Ti by-products.

Figure 5 shows SEM images of (a) A4, (b) A5, and (c) (d) A6. As shown in Fig. 5a, Ti₃AlC₂ lath grains (confirmed by XRD and EDS (Fig. 5e) were present in sample A4. Similar to samples A1 and A2, samples A5 and A6 were composed of a large number of TiC nanosheets.

The ratio of raw materials (or excess carbon content) exerted a key influence on the synthesis of high TiC content. The best TiC sample was A6 after optimizing the above process.

TiC nanosheets were synthesized by molten salt treatment of carbon and Ti₂AlC. Compared with common acid etching technology, such as HF etching [2] and LiF–HCl [10], TiC nanosheets without surface functional groups can be prepared using molten salt synthesis. In addition, the production cost is low and easy to mass produce.

This process has easy batch production and is simple, which is helpful to promote the application of MXene materials.

The reaction mechanism of the carbon induced decomposition of Ti₂AlC to synthesize TiC nanosheets is discussed as follows.

The decomposition reaction [17–19] of MAX phases, such as Ti₃SiC₂ and Ti₃AlC₂, in carbon-containing atmosphere can be expressed as Eq. (4):

Combined with the XRD results of Fig. 2b, the thermal decomposition reaction of Ti₂AlC induced by carbon black can be expressed as Eq. (5):

Fig. 6. XRD patterns of the samples obtained by molten salt treatment of Al–Ti₂AlC and Al–Ti₃AlC₂ equimolar mixtures with a weight ratio of flux/powder of 2:1 at 1373 K.

Ti₂AlC reacted with the newly formed TiC (generated in Eq. (5)) to form Ti₃AlC₂.

The diffraction peaks of Ti₃AlC₂ were not observed when the carbon/Ti₂AlC ratio was normal ($X = 1$) or higher. Ti₃AlC₂ can be easily reduced by carbon to form TiC and Al, which can be expressed as Eq.(6):

When studying the Al/Ti₂AlC [33] and Al/Ti₃AlC₂ [34] composites, the reaction equations of Al with Ti₂AlC or Ti₃AlC₂ can be obtained as follows:

Molten salt heat treatment experiments of Al–Ti₂AlC and Al–Ti₃AlC₂ powders were conducted to verify Reactions (7) and (8). Figure 6 shows the XRD patterns of the samples obtained through the molten salt treatment of Al–Ti₂AlC and Al–Ti₃AlC₂ equimolar mixtures with a weight ratio of flux/powder of 2:1 at 1373 K. As shown in Fig. 6, the molten salt products of Al–Ti₃AlC₂ mixtures were Al₃Ti, TiC, and Al₂O₃. The molten salt products of Al–Ti₂AlC mixtures were Ti₂AlC, Ti₃AlC₂, Al₃Ti, TiC, and Al₂O₃. The XRD results were in good agreement with Eqs. (7) and (8).

The content of Al₃Ti decreased gradually when the carbon content in the raw material increased gradually. The possible reaction formula of carbon black to Al₃Ti is expressed as follows:

In terms of kinetics, Al and C react easily to form Al₄C₃. However, Al₄C₃ is unstable at high temperatures. Previous studies on the Al–Ti₂AlC [33] and Al–Ti₃AlC₂ [34] systems

Fig. 7. Change of Gibbs free energy (ΔG) as function of temperature for Reactions (5)–(11).

indicated that Al₄C₃ can form at low temperatures. However, Al₄C₃ reacts with TiAl₃ to form TiC and Al at temperatures exceeding 1173 K.

Figure 7 shows the change in Gibbs free energy (ΔG) as a function of temperature for Reactions (5)–(11). As shown in Fig. 7, Reactions (5)–(11) occurred spontaneously in the experimental temperature range because their ΔG val-

Fig. 8. Isothermal section at 1573 K of the Ti–Al–C phase diagram.

Fig. 9. Schematic illustration of the fabrication of 2D TiC MXenes via an effective carbon induced decomposition approach.

ues were below zero. The ΔG of Al₄C₃ rapidly increased at approximately 800 K and approached zero. The ΔG of Reactions (9) and (11) intersected with that of Reaction (10) at 800 K and decreased rapidly. Al₄C₃ was unstable at 800 K and higher temperatures. The XRD results (Figs. 1 and 3) confirmed that Al₄C₃ does not exist in the product. The results of previous experiments and thermodynamic calculations of the Al–Ti–C system [33–35] showed that Al₃Ti, Al₄C₃, and TiC can be formed at temperatures below 1100 K. At higher temperatures, Al₃Ti and Al₄C₃ gradually changed into TiC. Therefore, the most stable compound in the Al–Ti–C system was TiC. In fact, Al₃Ti, Al₄C₃, and other compounds existed in a certain stage of the reaction as intermediate products, which disappeared and were replaced by TiC.

The calculation results of ΔG of standard Reactions (9) and (11) showed that the decrease rate of ΔG was accelerated after 900 K. Obviously, at higher temperatures, Al₃Ti and Al₄C₃ exhibited stronger tendencies to form TiC spontaneously. The experimental results and thermodynamic calculation results are in good agreement with the previous work [33–35].

Therefore, the most stable compound in the reaction system of C–Ti₂AlC was TiC. Ti₂AlC, TiAl, TiAl₃, and Al₄C₃ were transformed into TiC and Al.

Figure 8 shows the isothermal section at 1300 °C of the Ti–Al–C phase diagram. As shown in Fig. 8, when the carbon content was increased significantly, Ti₂AlC was easily induced to decompose into TiC and Al.

The above dynamics and thermodynamics study suggested Ti₂AlC was decomposed into TiC through carbon induced decomposition. Under the action of molten salt, TiC grains grew directionally and developed into nanosheets. On the basis of the above experimental results and analysis, we propose a reaction mechanism of carbon black-induced Ti₂AlC decomposition to form TiC nanosheets in molten salt environment. As shown in Fig. 9a, carbon black was first adsorbed on the Ti₂AlC surface (Fig. 9a). Carbon black then induces Ti₂AlC decomposition to form TiC(I) and Al (Fig. 9b). Then, the newly generated Al reacts with Ti₂AlC to form Ti₃AlC₂ and Al₃Ti (Fig. 9c). Ti₃AlC₂ is decomposed into TiC (II) and Al by carbon black. Al₃Ti reacts with carbon black to form TiC(III). Under the action of molten salt, these TiC nanocrystals develop into nanosheets (Fig. 9d). Al reacts with trace O₂ in the system to form Al₂O₃.

4 Conclusion

In this study, TiC nanosheets were synthesized through molten salt synthesis in NaCl–KCl at 1373 K. Carbon black significantly induced the decomposition of Ti₂AlC into Al and TiC. Salt content exerted minimal effect on the phase composition of the products. The molar ratio of carbon/Ti₂AlC was the key factor in the synthesis of high TiC content. High carbon/Ti₂AlC molar ratio contributed to eliminating the Al and Al₃Ti by-products. The sample with the highest TiC content was obtained with a molar ratio of car-

bon/Ti₂AlC = 1.5:1. The single-phase TiC was obtained after pickling and ultrasonic treatment. Two-dimensional TiC nanosheets had a thickness of 10–20 nm and a length of 150–200 nm.

Funding: This project was sponsored by the National Natural Science Foundation of China (51864028, 51973246, 51805557), Key scientific research projects of colleges and universities in Henan Province (18A430033), Innovation and entrepreneurship training plan for Provincial College Students in Henan Province (S202010465023), Program for Interdisciplinary Direction Team in Zhongyuan University of Technology, Program for Science and Technology Innovation Talents in Universities of Henan Province (19HASTIT024), Natural Science Foundation of Henan (2023000410513).

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov: *Science* 306 (2004) 666. PMID:15499015; DOI:10.1126/science.1102896
- [2] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J.J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M.W. Barsoum: *Adv. Mater.* 23 (2011) 4248. PMID:21861270; DOI:10.1002/adma.201102306
- [3] M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M.W. Barsoum: *ACS Nano* 6 (2012) 1322. PMID:22279971; DOI:10.1021/nn204153h
- [4] M.W. Barsoum: *Prog. Solid. State. Chem.* 28 (2000) 201. DOI:10.1016/S0079-6786(00)00006-6
- [5] Z.M. Sun: *Int. Mater. Rev.* 56 (2011) 143. DOI:10.1179/1743280410Y
- [6] Q.M. Peng, J.X. Guo, Q.R.N. Zhang, J.Y. Xiang, B.Z. Liu, A.G. Zhou, R.P. Liu, Y.J. Tian: *J. Am. Chem. Soc.* 136 (2014) 4113. PMID:24588686; DOI:10.1021/ja500506k
- [7] Y. Luo, G.F. Chen, L. Ding, X.Z. Chen, L.X. Ding, H.H. Wang: *Joule* 3 (2019) 279. DOI:10.1016/j.joule.2018.09.011
- [8] Z.Y. Yao, H.J. Sun, H.T. Sui, X.F. Liu: *Nanoscale. Res. Lett.* 15 (2020) 78. DOI:10.1186/s11671-020-03314-z
- [9] R. Li, L. Zhang, L. Shi, P. Wang: *Acs. Nano* 11 (2017) 3752. PMID:28339184; DOI:10.1021/acsnano.6b08415
- [10] M. Ghidui, M.R. Lukatskaya, M.Q. Zhao, Y. Gogotsi, M.W. Barsoum: *Nature* 516 (2014) 78. PMID:25470044; DOI:10.1038/nature13970
- [11] A.H. Feng, Y. Yu, F. Jiang, Y. Wang, L. Mi, Y. Yu, L.X. Song: *Ceram. Int.* 43 (2017) 6322. DOI:10.1016/j.ceramint.2017.02.039
- [12] T.F. Li, L.L. Yao, Q.L. Liu, J.J. Gu, R.C. Luo, J.H. Li, X.D. Yan, W.Q. Wang, P. Liu, B. Chen, W. Zhang, W. Abbas, R. Naz, D. Zhang: *Angew. Chem. Int. Ed.* 57 (2018) 6115. PMID:29633442; DOI:10.1002/anie.201800887
- [13] W.M. Sun, S. Shah, Y.X. Chen, Z.Y. Tan, H.L. Gao, T. Habib, M. Radovic, M. Green: *J. Mater. Chem. A* 5 (2017) 21663. DOI:10.1039/C7TA05574A
- [14] M. Naguib, V. Presser, D. Tallman, J. Lu, L. Hultman, Y. Gogotsi, M.W. Barsoum: *J. Am. Ceram. Soc.* 94 (2011) 4556. DOI:10.1111/j.1551-2916.2011.04896.x
- [15] S.Y. Pang, Y.T. Wong, S.G. Yuan, Y. Liu, M.K. Tsang, Z.B. Yang, H. Huang, W.T. Wong, J.H. Hao: *J. Am. Chem. Soc.* 141 (2019) 9610. PMID:31117483; DOI:10.1021/jacs.9b02578
- [16] C. Racault, F. Langlais, R. Naslain: *J. Mater. Sci.* 29 (1994) 3384. DOI:10.1007/BF00352037
- [17] X.H. Wang, Y.C. Zhou: *Chem. Mater.* 15 (2003) 3716. DOI:10.1021/cm030022v
- [18] J.L. Gai, J.X. Chen, H. Zhang, M.S. Li: *Mat. Lett.* 167 (2016) 73–76. DOI:10.1016/j.matlet.2015.12.166
- [19] J.L. Gai, J.X. Chen, H. Zhang, M.S. Li: *J. Eur. Ceram. Soc.* 36 (2016) 2837–2841. DOI:10.1016/j.matlet.2015.12.166
- [20] A. Selloni, P. Carnevali, R. Car, M. Parrinello: *Phys. Rev. Lett.* 59 (1987) 823. PMID:10035880; DOI:10.1103/PhysRevLett.59.823
- [21] J.L. Ma, N. Li, Q. Zhang: *Energ. Environ. Sci.* 11 (2018) 2833. DOI:10.1039/C8EE01472H
- [22] X.F. Liu, T. Wang, J.M. Liu, F. Jiang, H.D. Tang, G. Feng, W.H. Jiang: *Ceram. Int.* 46 (2020) 4864. DOI:10.1016/j.ceramint.2019.10.222
- [23] Y. Li, H. Shao, Z. Lin, J. Lu, Q. Huang: *Nat Mater* 19 (2020) 894. DOI:10.1038/s41563-020-0657-0
- [24] M. Li, J. Lu, K. Luo, Y. Li, K. Chang, K. Chen, J. Zhou, J. Rosen, L. Hultman, P. Eklund: *J. Am. Chem. Soc.* 141 (2019) 4730. DOI:10.1021/jacs.9b00574
- [25] M. Xu, J. Yang, L.H. Liu: *Phys. Biol.* 560 (2019) 146. DOI:10.1016/j.physb.2019.02.025
- [26] A. Heidarpour, H. Aghamohammadi, S. Ghasemi: *Synthetic Met.* 267 (2020). DOI:10.1016/j.synthmet.2020.116478
- [27] D.L. Ye, J.H. Hu: *Practical inorganic thermodynamic data book*. Second Ed, Metallurgical industry press, Beijing (2002).
- [28] M. Stumpf, T. Fey, P. Greil: *J. Ceram. Sci. Technol.* 7 (2016) 223–227 DOI:10.4416/JCST2016–00029.
- [29] Y. Chen, M.Y. Chu, L.J. Wang, X.H. Bao, Y. Lin, J.Y. Shen: *Phys. Status Solidi A* 208 (2011) 1879. DOI:10.1002/pssa.201127020
- [30] A.G. Zhou, C.A. Wang, Y. Huang: *Mater. Sci. Eng. A* 352 (2003) 333–339. DOI:10.1016/S0921-5093(02)00937-1
- [31] C.L. Yeh, Y.G. Shen: *J. Alloy Compd.* 466 (2008) 308. DOI:10.1016/j.jallcom.2007.11.037
- [32] A.M. Liu, Q.Y. Yang, X.F. Ren, F.N. Meng, L.H. Gao, M.F. Gao, Y.A. Yang, T.L. Ma, G. Wu: *Ceram. Int.* 46 (2020) 6934. DOI:10.1016/j.ceramint.2019.11.008
- [33] M. Stumpf, X.M. Fan, J. Biggemann, P. Greil, T. Fey: *J. Eur. Ceram. Soc.* 39 (2019) 2003. DOI:10.1016/j.jeurceramsoc.2019.01.047
- [34] W. Wang, V. Gauthier-Brunet, G. Bei, G. Laplanche, J. Bonnevillie, A. Joulain, S. Dubois: *Mater. Sci. Eng. A* 530 (2011) 168. DOI:10.1016/j.msea.2011.09.068
- [35] V.T. Witusiewicz, B. Hallstedt, A.A. Bondar, U. Hecht, S.V. Sleptsov, T.Y. Velikanova: *J. Alloys Compd.* 623 (2015) 480. DOI:10.1016/j.jallcom.2014.10.119

(Received January 29, 2021; accepted July 28, 2021)

Correspondence address

Dr. Baoyan Liang
Zhongyuan University of Technology
Materials & Chemical Engineering school
Zhengzhou
P.R.China, 450007
Tel.: +86 371 69975740
Fax: +86 371 69975740
E-mail: baoyanl@126.com

Bibliography

DOI 10.1515/ijmr-2021-8225
Int. J. Mater. Res. 112 (2021) 11; page 852–859
© 2021 Walter de Gruyter GmbH, Berlin/Boston, Germany
ISSN 1862-5282 · e-ISSN 2195-8556