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Unique chemical activity in porous YbB_2C_2 ceramics with high porosity and high compressive strength

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High purity layered YbB_2C_2 powder is synthesized by a boro/carbothermic reduction method using YbBO_3 , B_4C and graphite powders as raw materials. Its X-ray diffraction data are presented, and the space group $P4/mbm$ (No. 127) is confirmed. The lattice parameters are $a = b = 5.3389 \text{ \AA}$ and $c = 3.5683 \text{ \AA}$, and the atom positions are Yb (0.0000, 0.0000, 0.0000), B (0.3621, 0.8621, 0.5000), and C (0.1606, 0.6606, 0.5000). Porous YbB_2C_2 ceramics have a high porosity in the range of 69.89–58.11% and a high compressive strength in the range of 19.49–63.44 MPa. Furthermore, the as-produced porous YbB_2C_2 ceramics show unique chemical activity. Porous YbB_2C_2 ceramic with a porosity of 69.89% emits so much heat that it can burn a piece of paper when this ceramic is wetted by water. The rate of reaction between the porous YbB_2C_2 ceramic and water can be simply controlled by adjusting the porosity. The solid reaction products are YbB_6 , C and an unknown amorphous phase.

REB_2C_2 (RE = Y and lanthanides) compounds have a layered crystal structure, which can be described as a stacking of layers, $-\text{RE}-\text{B}_2\text{C}_2-\text{RE}-\text{B}_2\text{C}_2-\text{RE}-$, along the z -direction, with the covalently bonded B-C network consisting of non-regular squares and octagons^{1–4}. The structure of REB_2C_2 is similar to that of $\text{M}_{n+1}\text{AX}_n$ phases (“MAX phases”, where M is an early transition metal, A is an A-group element, X is C or N, and $n = 1–3$)^{5–7}. Two different bonds, namely, the strong metallic-covalent bond of M–X and the weak M–A bond, occur in the MAX phases.

The fabrication methods of REB_2C_2 include arc melting^{8–12}, the two-step method^{13–15}, in situ hot pressing^{16,17} and the boro/carbothermic reduction method derived from the synthesis of transition metal borides^{16,18–20}, as summarized in Table 1. In all REB_2C_2 ceramics, YbB_2C_2 is rather difficult to synthesize^{10,14}. Sakai et al.¹⁴ thought the reason was the high vapor pressure of Yb carbide under high temperature. However, a closer study of Yb shows that there are two other possible reasons. First, the number of 4f valence electrons in Yb is 2, which is different from the 3 of other rare earth metals²¹. Second, the divalent state of 2+ is also reflected in the normalized cell volume $V_n = V/Z$ of the compound, which does not follow the usual lanthanide contraction trend²². In this work, YbBO_3 instead of Yb_2O_3 was employed to fabricate YbB_2C_2 by the boro/carbothermic reduction method. During the process, the possible reaction is shown in Table 1.

To date, most researchers have focused on the magnetic^{14,23,24} or electrical properties^{13,15} of REB_2C_2 . To our knowledge, only a few researchers have recently used first-principles calculations to study the mechanical properties of REB_2C_2 compounds^{25,26}. Regarding experimental work, Zhao et al.^{16,17} successfully synthesized high purity bulk YB_2C_2 and studied its physical and mechanical properties, which showed excellent damage tolerance, easy machinability, high melting point ($2500^\circ\text{C} < T_m < 2600^\circ\text{C}$) and excellent high temperature rigidity (the value of Young’s modulus at 1500°C is still similar to that at room temperature). These features of bulk YB_2C_2 ceramic might endow it with great untapped potential for future ultrahigh temperature applications^{16,17}. Chen et al.²⁷ reported that porous YB_2C_2 ceramics fabricated by a high-temperature reaction/partial sintering process possess high porosity (75.26–57.17%), high compressive strength (9.32–34.78 MPa), and anisotropy in the microstructure and mechanical behavior. These features of porous YB_2C_2 ceramic render it promising as a thermally insulating lightweight component for transpiration cooling systems²⁷.

As the number of 4f valence electrons in Yb is different from those in other rare earth metals, the YbB_2C_2 ceramic may possess unique properties. In this work, high purity YbB_2C_2 powder was successfully synthesized. The crystal structure and lattice parameters were studied. Then, porous YbB_2C_2 ceramics with high porosity and high compressive strength were prepared. In addition, the as-prepared porous YbB_2C_2 ceramics were found to possess individual chemical activity in wet environments.

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Methods	Starting materials	Routes or reactions
Arc-melting technique ^{8–12}	RE, B and C	(1) $(RE + B + C)_{\text{powder}} \rightarrow (RE + B + C)_{\text{pellet}}$ (2) $(RE + B + C)_{\text{pellet}} \rightarrow (REB_2C_2)_{\text{single crystal}}$ (3) $(REB_2C_2)_{\text{single crystal}} \rightarrow (REB_2C_2)_{\text{sample}}$
Two-step	RE_2O_3 , B and C ^{13,14}	(1) $RE_2O_3 + B \rightarrow REB_6$ (or REB_4) (2) $REB_6 + RE_2O_3 + 9C \rightarrow 3REB_2C_2 + 3CO$ or $2REB_4 + RE_2O_3 + 11C \rightarrow 4REB_2C_2 + 3CO$
	Y, C and B ¹⁵	(1) $Y + 2C \rightarrow YC_2$ (2) $YC_2 + 2B \rightarrow YB_2C_2$
In situ hot pressing ^{16,17}	YH_2 , B_4C and C	$2YH_2 + B_4C + 3C \rightarrow YB_2C_2 + 2H_2$
Boro/carbothermic reduction	RE_2O_3 , B_4C and C ^{16,18–20}	$RE_2O_3 + B_4C + 6C \rightarrow 2REB_2C_2 + 3CO$
	$YbBO_3$, B_4C and C (This work)	$4YbBO_3 + B_4C + 19C \rightarrow 4YbB_2C_2 + 12CO$

Table 1. Comparison of different methods for synthesizing REB_2C_2 .

Experimental

YbB_2C_2 powder and porous YbB_2C_2 ceramics were synthesized by the boro/carbothermic reduction method with a mixture of $YbBO_3$, B_4C (99%, 200 mesh, Jingangzhuan, China), and graphite (99%, 200 mesh, Tianyuan, China) powders. The routes for fabricating YbB_2C_2 powder can be described as follows. First, raw powders with a 4.00:1.28:18.16 molar ratio were milled in a polypropylene jar for 6 h in alcohol to obtain a homogeneous mixture. The powder mixture was then dried in an oven at 60 °C for 24 h. After that, the powder mixture was placed in a graphite crucible heated at a rate of 10 °C/min to 1950 °C and held for 1.0 h under flowing Ar. The route for synthesizing porous YbB_2C_2 ceramics can be generalized as follows: at first, the homogeneous mixture powders of $YbBO_3$, B_4C , and graphite (as above) were uniaxially pressed into columnar compacts by applying different pre-pressures (10, 20, 30, 50, 100, 200 and 300 MPa) with a dwell time of 5 min. Then, these green bodies were placed in a graphite crucible and heated at a rate of 8 °C/min to 1980 °C and held for 1.5 h under flowing Ar.

The phase composition was identified using an X-ray diffractometer with Cu K α radiation (Rigaku D/max-2400, Tokyo, Japan). Rietveld refinement was performed on the XRD results using the GSAS suite with EXPGUI^{28,29}. The morphology was investigated by a SUPRA 35 scanning electron microscope (SEM) (LEO, Oberkochen, Germany) equipped with an energy dispersive spectroscopy (EDS) system. Selected area electron diffraction (SAED) was performed using a Tecnai G2 F20 (FEI, Eindhoven, the Netherlands) instrument equipped with a field emission gun. During the process, a perforated carbon/copper net served as a support for the as-prepared powder.

The density of the porous YbB_2C_2 ceramics was calculated geometrically, by measuring the volume and weight of five identical samples and averaging the data to ensure accuracy. The porosity (η) of porous YbB_2C_2 ceramics was determined by Eq. (1), where ρ and ρ_0 refer to the sintered density and the theoretical density of YbB_2C_2 ceramics, respectively. The compressive strength was measured using a microcomputer control electron universal testing machine (CMT4204, Shenzhen SANS testing machine Co., Ltd, Shenzhen, China). The tested samples were rectangular bars with dimensions of 5 mm $\times$ 5 mm $\times$ 10 mm. The compressive strengths of the as-prepared porous YbB_2C_2 ceramics were tested in the directions parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the forming direction. For each group, five samples with the same density were used to obtain the average value. The crosshead speed was 0.5 mm/min.

$$\eta = \left(1 - \rho/\rho_0\right) \times 100\% \quad (1)$$

Results and discussion

XRD analysis and Rietveld refinement of YbB_2C_2 . To date, the crystal structure of REB_2C_2 is still controversial. Bauer^{2,30} and Sakai et al.¹⁵ believed that its space group is $P-24c$ (No. 112), but an increasing number of researchers' studies^{4,8,10,31,32} confirmed that its space group is $P4/mbm$ (No. 127). In this work, the $P4/mbm$ space group is used as a starting model for refining the YbB_2C_2 sample, and the initial values of the cell parameters and atom coordinates come from the isostructural compound YB_2C_2 ²⁶. The experimental XRD spectrum (red) and the calculated pattern obtained by Rietveld analysis (black) from $2\theta = 20^\circ$ to 80° are shown in Fig. 1a. Only the YbB_2C_2 phase is detected, which confirms that high purity YbB_2C_2 powder has been successfully synthesized. Considering the difficulty of synthesizing the YbB_2C_2 compound^{10,14}, the as-fabricated YbB_2C_2 powder is remarkable, and the boro/carbothermic reduction method shows more advantages than other methods^{8–17}. It should be noted that the difference between the fabricated molar ratio (4.00:1.28:18.16) and theoretical molar ratio (4.00:1.00:19.00) of the raw powders ($YbBO_3$, B_4C and graphite) may come from their different vapor losses under high temperature.

It is well known that the goodness of fit (GOF) for the peak shape and position, structure and background is measured in terms of profile R (reliability) factors, and that relatively lower values of R_{wp} (the weighted spectrum R factor) and R_p (the spectrum R factor) are considered to indicate good profile refinement³³. R_{wp} and R_p can be written as Eqs. (2) and (3), where W_p , Y_{oi} and Y_{ci} refer to the weight factor based on statistics, diffraction intensity from observation and diffraction intensity from calculation, respectively³⁴. Obviously, the observed and calculated spectra are in good agreement, and low values of R_{wp} (10.37%) and R_p (7.52%) are obtained.

Figure 1. Powder XRD spectra (a) of YbB_2C_2 : observed spectrum (red crosses), Rietveld generated spectrum (black line) and difference between the two (blue line). The green vertical ticks below the pattern represent possible Bragg reflections of YbB_2C_2 . The crystal structure of YbB_2C_2 : unit cell (b) and $2 \times 2 \times 2$ supercell (c).

$$R_{wp} = [W_i(Y_{oi} - Y_{ci})^2 / W_i Y_{oi}^2]^{1/2} \quad (2)$$

$$R_p = \sum |Y_{oi} - Y_{ci}| / \sum Y_{oi} \quad (3)$$

The lattice parameters of YbB_2C_2 calculated from the refinement are $a = b = 5.3389 \text{ \AA}$ and $c = 3.5683 \text{ \AA}$, respectively, and the atom positions are Yb (0.0000, 0.0000, 0.0000), B (0.3621, 0.8621, 0.5000), and C (0.1606, 0.6606, 0.5000). The crystal structure of YbB_2C_2 can be seen in Fig. 1b,c. The results are in accordance with the cell parameters and (or) atom positions of the known REB_2C_2 compound^{4,11,26,32}. The detailed XRD results of the structural refinements are grouped in Table 2. In addition, the theoretical density of the YbB_2C_2 ceramic calculated from the refinement is 7.05 g/cm^3 .

Microstructure of the YbB_2C_2 powder. The morphology of the YbB_2C_2 powder observed by SEM is shown in Fig. 2a,b. The YbB_2C_2 powder consists of typical laminated plates with a size of approximately several microns in thickness and tens of microns in length and width. The laminated plates of YbB_2C_2 reflect the alternate arrangement of the B–C networks and Yb sheets, as shown in Fig. 1c. To clearly observe the morphology of the YbB_2C_2 powder, TEM was used as well. Figure 2c shows the bright field image (BFI) of YbB_2C_2 . The as-prepared YbB_2C_2 possesses a typical laminar microstructure. Figure 2d,e show the diffraction results along the [001] and [010] zone axes. All maxima can be indexed on the basis of a tetragonal cell, with parameters $a = 5.2835 \text{ \AA}$ and $c = 3.4920 \text{ \AA}$; both values are in good agreement with those measured results from the XRD spectra. In addition, Fig. 2d,e and Table 2 show that the reciprocal space spots were not extinct as long as they met “ $0kl$: $k = 2n$, $h00$: $h = 2n$ or hkl : $h + k = 2n$ ”. According to the *International Tables of Crystallography*³⁵, the reflection conditions are compatible with the space group $P4/mbm$ (No. 127), which confirms the previous choice for Rietveld refinement.

Porous YbB_2C_2 ceramics. Advanced porous ceramics (also called ceramic foams) usually have low density, high porosity, large specific surface area, thermal shock resistance, corrosion and wear resistance, and high chemical stability^{36–38}. SEM images of the as-prepared porous YbB_2C_2 samples with porosities of 69.89%, 61.58% and 58.11% are shown in Fig. 3. The microstructure can be described as an incompact stacking of uniform lamellae with a size of approximately one or two microns in thickness and tens of microns in length and width. It should be noted that the microstructure of porous YbB_2C_2 is slightly different from that of porous YB_2C_2 .

Reflection (<i>hkl</i>)	$2\theta_{\text{Obs}}$ (°)	$2\theta_{\text{Calc}}$ (°)	d_{Obs} (Å)	d_{Calc} (Å)	$I/I_{0\text{Obs}}$ (%)	$I/I_{0\text{Calc}}$ (%)
110	23.60	23.55	3.775	3.785	65.74	63.50
001	24.96	24.93	3.568	3.593	30.46	28.28
200	33.60	33.54	2.669	2.677	29.22	26.48
111	34.60	34.56	2.593	2.606	100.00	100.00
201	42.29	42.24	2.138	2.146	52.63	48.91
220	48.22	48.17	1.888	1.893	14.57	11.78
002	51.21	51.16	1.784	1.797	15.76	12.44
310	54.32	54.29	1.688	1.693	23.38	21.03
221	55.04	54.99	1.669	1.674	19.20	16.17
112	57.07	57.05	1.613	1.623	21.36	19.26
311	60.65	60.63	1.526	1.531	21.91	20.55
202	62.61	62.57	1.483	1.492	14.48	13.63
400	70.53	70.49	1.335	1.338	3.59	3.20
222	72.92	72.89	1.297	1.303	9.62	9.31
330	75.51	75.48	1.258	1.262	2.93	2.78
401	76.11	76.07	1.250	1.254	8.41	7.86
312	77.86	77.83	1.226	1.232	15.78	15.64
411	78.50	78.52	1.217	1.221	0.85	0.80

Table 2. Reflections, 2θ positions, d (interplanar spacing) and intensity data of YbB_2C_2 powder from observation (Obs.) and calculation (Calc.).

Figure 2. SEM images of the YbB_2C_2 powder: low magnification (a) and high magnification (b). TEM image of the YbB_2C_2 powder (c). SAED patterns corresponding to the YbB_2C_2 : [001] (d) and [010] (e) zone axes.

Figure 3. SEM images of the as-prepared porous YbB_2C_2 samples with different porosities. Top surface perpendicular to the forming direction (a) and cross section parallel to the forming direction (b) of the as-prepared sample ($\eta=69.89\%$). Top surface (c) and cross section (d) of the sample ($\eta=61.58\%$). Top surface (e) and cross section (f) of the sample ($\eta=58.11\%$).

This difference in microstructure comes from the different kinds of raw materials employed. For porous YB_2C_2 ceramics, Y_2O_3 , BN and C were used as raw materials, and small grains and large lamellar grains were obtained due to the in situ reaction process and inheritance from graphite, respectively²⁷. In the porous YbB_2C_2 ceramics, the lamellas are oriented to a certain degree, more or less, in the plane perpendicular to the forming direction; this may be due to the raw material of graphite, which has a typical lamellar structure. The anisotropic microstructure of the porous YbB_2C_2 becomes more obvious with decreasing porosity.

For porous ceramics, the compressive strength is an important parameter. To confirm the anisotropic mechanical properties of porous YbB_2C_2 samples, a compression test was carried out in two directions: $\sigma_{//}$ (the loading direction parallel to the forming direction) and $\sigma_{\perp}$ (the loading direction perpendicular to the forming direction), as shown in Fig. 4a and Table 3. The $\sigma_{//}$ strengths of the as-prepared porous YbB_2C_2 samples with porosities of 69.89–58.11% are in the range of 19.49–63.44 MPa. It is obvious that the $\sigma_{//}$ strength decreases with increasing porosity. Different from the trend of the $\sigma_{//}$ strength, the maximum $\sigma_{\perp}$ strength occurs at a porosity of 61.58% (62.40 MPa). The $\sigma_{\perp}$ strengths are higher than the corresponding $\sigma_{//}$ strengths for samples with porosities of 69.89–61.58%, while the former are lower than the latter for samples with porosities of 58.98–58.11%. Two factors determine the $\sigma_{\perp}$ strengths, namely, the porosity and anisotropic microstructure. With increasing porosity, the $\sigma_{\perp}$ strength decreases as well, which is similar to the trend of the $\sigma_{//}$ strength. The anisotropic microstructure, i.e., the YbB_2C_2 lamellas are oriented in the plane perpendicular to the forming direction has an adverse effect on the $\sigma_{\perp}$ strength. This may be due to the weak adhesion between the YbB_2C_2 laminates. The influence of the anisotropic microstructure of the porous YbB_2C_2 samples on their compressive strengths can be understood by a model, as shown in Fig. 4b,c. On one hand, when lamellas of porous YbB_2C_2 samples are oriented to a small

Figure 4. Compressive strengths vs porosities of porous YbB₂C₂ samples (a). Model of the influence of the anisotropic microstructure of porous YbB₂C₂ samples on their compressive strengths: the lamellas of the porous YbB₂C₂ samples are oriented to a small degree in the plane perpendicular to the forming direction (b) and the lamellas of the porous YbB₂C₂ samples are oriented ideally in the plane perpendicular to the forming direction (c).

Sample	Pre-pressure (MPa)	Sintered density (g/cm ³)	Porosity (%)	Compressive strength (MPa)	
				$\sigma_{//}$	$\sigma_{\perp}$
1	10	2.12	69.89	19.49	21.38
2	20	2.38	66.35	22.70	28.88
3	30	2.51	64.26	28.00	33.75
4	50	2.61	62.96	33.86	47.93
5	100	2.71	61.58	43.95	62.40
6	200	2.89	58.98	53.10	41.70
7	300	2.95	58.11	63.44	44.59

Table 3. Pre-pressure, sintered density, porosity and compressive strength of the as-prepared porous YbB₂C₂ samples.

degree in the plane perpendicular to the forming direction (Fig. 4b), some lamellas act as diagonal bracings that enhance the $\sigma_{\perp}$ strength (samples with porosity of 69.89–61.58%, $\sigma_{//} < \sigma_{\perp}$). On the other hand, when the lamellas of the porous YbB₂C₂ samples are oriented ideally in the plane perpendicular to the forming direction (Fig. 4c), the oriented lamellas easily disintegrate because of the weak adhesion between them, which weakens the $\sigma_{\perp}$ strength (samples with porosities of 58.98–58.11%, $\sigma_{//} > \sigma_{\perp}$). For the porous YbB₂C₂ sample with a porosity of 61.58%, the porosity is not high enough and the lamellas are oriented to an appropriate degree. These two factors work together and ultimately enhance the $\sigma_{\perp}$ strength (a maximum of 62.40 MPa). According to Chen et al.²⁷, porous YB₂C₂ ceramics also exhibit anisotropy in their mechanical properties: samples with porosities of 75.26–57.17% possess $\sigma_{//}$ strengths of 9.32–34.78 MPa, samples with porosities of 72.40–54.02% possess $\sigma_{\perp}$ strengths of 17.47–98.57 MPa. However, the mechanism of the anisotropic properties in porous YbB₂C₂ ceramics

Figure 5. Photographs of the as-prepared porous YbB₂C₂ sample ($\eta = 69.89\%$) and its reaction with water (a–d). SEM micrograph of the as-prepared porous YbB₂C₂ sample ($\eta = 69.89\%$) (e). SEM micrograph of the solid reaction products of the YbB₂C₂ sample ($\eta = 69.89\%$) with water for 3 h (f).

is different from that in porous Yb₂C₂ ceramics. For the latter, the mechanism can be described as follows: the failure of $\sigma_{//}$ is caused by accumulated damage^{27,39}, and the failure of $\sigma_{\perp}$ is caused by permanent damage^{27,40}.

In addition, the as-prepared porous YbB₂C₂ ceramics were found to produce a large amount of heat when they were wetted by water. One typical example is the reaction between a porous YbB₂C₂ sample ($\Phi 10 \times 3$ mm) with a porosity of 69.89% and water, as shown in Fig. 5a–d. The sample was first immersed in deionized water for 1 min (Fig. 5a), then the soaked sample was wrapped by a piece of A4 paper (Fig. 5b), and the paper was completely burned up after about approximately 3 h (Fig. 5c,d). It is clear that a large amount of heat was emitted during the reaction process. This result implies that porous YbB₂C₂ ceramics possess individual chemical activity in wet environments, which is different from the chemical inertness of other porous ceramics^{37,38}. It was also found that the reaction between porous YbB₂C₂ ceramic and water became slow and non-obvious with decreasing porosity. For example, when the porous YbB₂C₂ ceramic's porosity was reduced to 58.11%, the paper could not be burned up by reaction heat. Obviously, the chemical activity of the porous YbB₂C₂ ceramics can be controlled by adjusting their porosity, which can be understood by a sponge model (Fig. 6). During the reaction process, the porous YbB₂C₂ ceramic acts as a sponge that can easily soak up water at the beginning. The soaked water can keep the reaction going, while a large amount of heat begins to accumulate. Finally, the wrapped paper was burned up by the accumulated heat.

Figure 5e,f show the microstructures of the as-prepared porous YbB₂C₂ sample and its solid reaction products with water for 3 h. The laminated plates of the porous YbB₂C₂ sample are smooth (Fig. 5e), while the plates of its products with water are rough and look like floccules (Fig. 5f). The XRD spectrum of the solid reaction products of the as-prepared porous YbB₂C₂ sample with water for 3 h is shown in Fig. 7a. Obviously, apart from the residual YbB₂C₂, the solid products consist of YbB₆, C and an unknown amorphous phase. The amorphous phase

Figure 6. Sponge-like structure of the porous YbB_2C_2 sample (a). The structure of the water-absorbed YbB_2C_2 sample (b).

Figure 7. XRD spectrum (a) and SEM images (b) of solid reaction products of the as-prepared porous YbB_2C_2 sample ($\eta = 69.89\%$) with water for 3 h.

can be converted into YbBO_3 by annealing (800 °C for 1 h under argon flow). Figure 7b shows the morphologies of the solid products. According to the EDS analysis, the lamellas are residual YbB_2C_2 , the small particles are amorphous phases, the white plates are YbB_6 , and the black plates are graphite.

Conclusions

High purity YbB_2C_2 powder was successfully synthesized by the boro/carbothermic reduction method. The space group $P4/mbm$ (No. 127) of YbB_2C_2 was confirmed. Its X-ray diffraction data, lattice parameters and atom positions were obtained as well. The as-prepared YbB_2C_2 powder possesses the typical feature of a layered microstructure. The porous YbB_2C_2 ceramics possess a high porosity of 69.89–58.11% and a high compressive strength of 19.49–63.44 MPa, and show unique chemical activity in wet environments. The reaction between the porous YbB_2C_2 ceramic and water can be controlled by changing the porosity. The solid reaction products of the as-prepared porous YbB_2C_2 sample with water consist of YbB_6 , C and an unknown amorphous phase. The amorphous phase can be converted into YbBO_3 by annealing.

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Author contributions

Z.L. and J.C. wrote the main manuscript. Z.L., J.C., H.Z. and Y.Z. synthesized the YbB_2C_2 sample and performed the SEM analysis. Z.L., L.S. and M.L. carried out the Rietveld refinement. J.Y., M.H. and Z.Z. performed the TEM analysis. All authors discussed the results and contributed to the preparation and critical revision of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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