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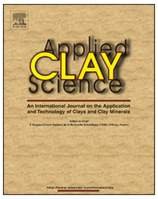

Research paper

In-situ high temperature X-ray diffraction study of dickite

Yu Yan[a,b], Hejing Wang[a,b,*]

[a] School of Earth and Space Sciences, Peking University, Beijing 100871, China
[b] Key Laboratory of Orogenic Belt and Crustal Evolution, Ministry of Education, Beijing 100871, China

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ABSTRACT

Despite abundant thermal studies, the accurate phase-transition temperatures and thermal properties above dickite structure still remain unknown. This article focused on the dickite sample, derived from Fujian province, China, to figure out its phase transition from room temperature (RT) up to 1200 °C and to refine its structures at RT and 550 °C using in-situ high temperature X-ray diffraction (HTXRD) for the first time. The phase transition from dickite to meta-dickite took place within the range of 550–650 °C, and from meta-dickite to mullite happened in the interval of 900–950 °C. The structure parameters of dickite with temperature were refined, and their thermal expansion coefficients were therefore determined. The refined structures at RT and 550 °C indicated thermal expansion affected strongly along *c* axis and the volume expansion was dominantly controlled by the enlarged distortion of the tetrahedral sheet. The relationship between mass percentage and temperature revealed that the formations of meta-dickite and mullite both started at a fast speed and then slowed down later.

1. Introduction

Dickite, $Al_2[Si_2O_5](OH)_4$, classified as a 1:1 dioctahedral phyllosilicate, owns the largest and the most perfect crystals among the kaolin-type clay minerals. The basic structural frame of kaolin-type silicates is made up of unit layers known as kaolin layers, consisting of a sheet of vertex-sharing SiO_4 tetrahedrons and a sheet of edge-sharing Al (O, OH)$_6$ octahedrons, and the silica and alumina sheets linking together by apical oxygen atoms (Pauling, 1930). Bailey (1963) analyzed the polymorphism of the kaolin minerals and differentiated the structures of kaolinite and dickite via the distribution of the vacant cation site in successive octahedral sheet, the consequence of the distribution, the layer distortion and Z-axis periodicity.

The first analysis for dickite structure was carried out by Gruner (1932), and it was further refined to be monoclinic system with the Cc space group, and $a = 5.15$ Å, $b = 8.95$ Å, $c = 14.42$ Å, $\beta = 96°48'$ and Z = 4 respectively (Newnham and Brindley, 1956). The accuracy of structure parameters of dickite was improved soon afterwards and several significant distortions were found in its structure from the geometry of the idealized kaolin layers including deformation and rotation of the SiO_4 tetrahedron (Newnham, 1961).

Although above studies simultaneously attempted to obtain atomic coordinates (Newnham and Brindley, 1956; Newnham, 1961; Bailey, 1963), yet the location of hydrogen atoms in dickite structure still remained obscure and consequently more studies were propelled. Adams and Hewat (1981) used neutron powder diffraction and Joswig and Drits (1986) used single-crystal X-ray diffraction to orientate hydrogen atoms. Bish and Johnston (1993) refined the full structure of dickite at 12 K through time-of-flight neutron powder diffractometer using Rietveld refinement/difference-Fourier method. Dera et al. (2003) complemented structural information using single-crystal X-ray diffraction and diamond-anvil cell techniques. All positions of inner-surface hydroxyl groups are well congruent, but the location of inner hydroxyl groups is still controversial (Fig. 1) (Dera et al., 2003).

Not only the framework of dickite in normal temperature and pressure environment were discussed ardently, but also its structure transformation and rearrangement when exposed to high pressure interested some researchers on account of its great value to fundamental and applied sciences. Dera et al. (2003) explored the displacive structural transformation in dickite, and found out higher pressure drives transformations toward the structure with higher density, smaller volume and significant transitions on stacking sequence and interlayer hydrogen bonding. Meanwhile, structural adjustments of dickite at elevated and declining temperature were also reported. Franco and Ruiz-Cruz (2003, 2006), Ruiz-Cruz and Franco (2000) and Zhong et al. (2017) explored the dehydroxylation process and thermal decomposition of intercalation complex of dickite with hydrazine, dimethyl-sulfoxide and potassium acetate by high-temperature X-ray diffraction, differential thermal and thermogravimetry analysis. Different raw dickite samples around the world have been experimented on

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[*] Corresponding author at: School of Earth and Space Sciences, Peking University, Beijing 100871, China.
E-mail address: hjwang@pku.edu.cn (H. Wang).

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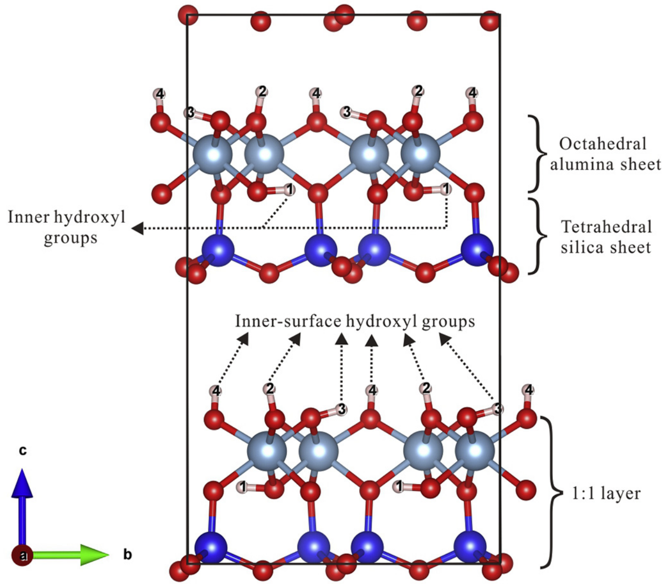

Fig. 1. Ball-and-stick model of dickite, viewed along *a* axis. The aluminum, silicon, oxygen and hydrogen atoms are drawn in light gray, blue, red and light pink respectively. The 1:1 layer, silica and alumina sheets, the inner-surface hydroxyl groups (marked as 2, 3, 4) and inner hydroxyl groups (marked as 1) are labeled respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

differential thermal analyses to determine dehydroxylation process (Schmidt and Heckroodt, 1959; Davis et al., 1970; Brindley and Wan, 1978; Stoch and Waclawska, 1980; Sanchez et al., 1985; Suitch, 1986; Frost and Vassallo, 1996; Lanson et al., 1996; Franco and Ruiz-Cruz, 2006; Stone, 2010; Premovi et al., 2012; Zhong et al., 2017). Generally the intense endothermal peak appears at the range of 650–690 °C preceded by a wide endothermic band within the limits of 500–600 °C, which is explained as a two-stage dehydroxylation progress in dickite. The first dehydroxylation stage is probably attributed to the loss of inner-surface hydroxyl groups through a homogenous mechanism similar to that of kaolinite, whereas, in the second stage an inhomogeneous mechanism takes place on the removal of inner hydroxyl groups (Frost and Vassallo, 1996; Franco and Ruiz-Cruz, 2006). The decreased temperature from 300 K to 10 K was also reported to affect the dickite structure in the stretching frequency, width and intensity of four OH-stretching bands. On this occasion, intra-layer OH-stretching band shifts toward lower frequencies while the inter-layer OH bands toward higher frequencies (Bish and Johnston, 1993; Balan et al., 2010).

It is widely accepted that dickite converts into amorphous phase of meta-dickite firstly and follows by the crystallization of mullite with continuously rising temperature (Shoval et al., 2001). Variation of characteristic bands in micro-Raman and FT-IR spectroscopy also confirms the phase transition of dickite during a heating course from ambient temperature to 1300 °C (Shoval et al., 2002).

To sum up, the dehydroxylation process and thermal phase transformation of dickite have been identified clearly, but the accurate transition temperature and high-temperature structure still remains a riddle. In addition, the variation of structure parameters with rising temperature and thermal expansion coefficients of dickite also need to be solved, which would make a great sense to industrial application probably. Hence, this article tries to use in-situ high temperature X-ray diffraction (HTXRD) at the first attempt to simultaneously record the phase transition of dickite sample from RT to 1200 °C, and to figure out the structure parameters of dickite varying with elevated temperature and its thermal expansion coefficients, and to refine its structures at ambient temperature and high temperature before phase transition. The refined structure of dickite at room temperature would be compared with the heated one, and to conclude the influence of temperature on the layered structure of dickite. IR, FESEM and EDS analyses in this article are entirely used for supporting the obtained conclusion.

2. Materials and methods

The pale yellow dickite sample presented as dense aggregates was collected from the paddy field in Shoushan village, Fujian province. It contains dickite as the essential mineral at a purity of about 99%. The high purity sample was ground into powder < 200 mesh with an agate grinding bowl for IR and in-situ HTXRD analyses.

The morphology and composition analysis were executed with field emission scanning microscopy (FESEM) equipped with EDS accessory. FESEM measurement was carried out with a QUANTA-650FEG microscope operating at 15 kV, beam spot diameter 4.0 μm. The vibration of groups in dickite were detected by Fourier Transform Infrared (FTIR) spectroscopy performed with a PE-983G infrared spectroscope. The test conditions of FTIR were in an absorption mode with a 0.09 cm^{-1} highest resolution and in the scanning range of 400 to 4000 cm^{-1}. The powder sample was mixed with KBr powder in a proportion of 1:100 and pressed into tablet before testing. All X-ray experiments were operated with an X'pert Pro MPD diffractometer installed with an X'Celerator detector and an Anton Paar HTK-1200 N oven system. The measuring conditions of in-situ high temperature XRD were Cu Kα radiation ($\lambda = 1.54056$ Å), 45 kV by 40 mA, 5 to 90° (2θ) scanning range, 0.017° (2θ) step size and 20 s per step. The temperature was controlled by a TCU 1000 N temperature controller, Eurotherm 2604 with S type thermo couple and the maximum temperature deviation is ± 2 °C. Dickite sample was heated from ambient temperature (27 °C) up to 1200 °C in 50 °C interval with a rate of 5 °C/min and 2 min waiting time for thermal equilibration before collecting data.

The non-hydrogen structure of dickite was refined in space group Cc using powder diffraction data and Rietveld refinement method. Program X'Pert Highscore Plus (version 4.6) was used for Rietveld structural refinement. The structure parameters of dickite were refined by both X'Pert Highscore Plus (version 4.6) and Unitcell – a least squares refinement program retrieves unit cell constants from powder diffraction data (Holland and Redfern, 1997). Mass percentage of meta-dickite and mullite was calculated by intensity ratio of characteristic reflection of meta-dickite or mullite to total intensity of the whole XRD curve. The volume of polyhedron was calculated on the tetrahedral volume formula (Cho, 1995).

3. Results

3.1. Dickite characterization

The micrograph observation of dickite sample is presented in Fig. 2 (a and b) in which large dickite particles exist as pseudo-hexagonal tablets and in size of roughly 8 μm × 5 μm. Compared with the reports by Sanchez et al. (1985), Keller (1988), Lanson et al. (1996) and Allard et al. (2003), our dickite sample seems slightly poorer in crystal form.

The EDS data shown in Table 1 suggest that our dickite sample is mainly composed of elements Al, Si, O and H. It leads to a structural formula $Al_{1.88}Si_2O_{4.63}(OH)_{4.37}$ (average on 13 measured spots, and calculated on the basis of $Si_2(O, OH)_9$), which is basically close to the ideal formula $Al_2Si_2O_5(OH)_4$.

XRD pattern indicates dickite is the sole detectable phase in powder sample at RT as shown in Fig. 3. The concise and intense reflections supplement its high purity as well.

Table 2 summarizes IR absorption bands of dickite and their assignments, and IR spectra are shown in Fig. 4. Although there exists no water molecule in dickite structure, the absorbed water from ambient environment could still be detected whose characteristic bands are centered at 1635 and 3440 cm^{-1}. Dickite has absorption bands between