



Reaction pathway led by silicate structure transformation on decomposition of CaSiO_3 in alkali fusion process using NaOH

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Abstract: The mechanism of decomposition of calcium inosilicate (CaSiO_3) synthesized through chemical deposition method using analytical reagent $\text{NaSiO}_3 \cdot 9\text{H}_2\text{O}$ and CaCl_2 during the alkali fusion process using NaOH was investigated by Raman spectroscopy in situ, X-ray diffraction and Fourier transform infrared spectrometer (FTIR). The results show that the tetrahedral silica chains within CaSiO_3 are gradually disrupted and transformed into nesosilicate with the isolated SiO_4 tetrahedra at the beginning of the alkali fusion process. The three intermediates including Ca_2SiO_4 , $\text{Na}_2\text{CaSiO}_4$ and Na_2SiO_3 appear simultaneously in the decomposition of CaSiO_3 , while the final products are Ca(OH)_2 and Na_4SiO_4 . It can be concluded that there exist two reaction pathways in the alkali fusion process of CaSiO_3 : one is ion exchange, the other is in the main form of the framework structure change of silicate. The reaction pathway is led by silicate structure transformation in the alkali fusion process.

Key words: alkali fusion process; CaSiO_3 ; intermediate; reaction pathway

1 Introduction

In recent years, several investigations have focused on the utilization of silicon magnesium laterite nickel ore because of the shortage of high-grade nickel sources [1]. The features of silicon magnesium laterite nickel ore are low nickeliferous grade (1%–2%, mass fraction), abundant in associated ores, contents (mass fraction) of magnesium, silicon and calcium of above 30%, easy to form garnierite ($(\text{Ni}, \text{Mg})\text{SiO}_3 \cdot n\text{H}_2\text{O}$) and calcium silicate ($(\text{Ni}, \text{Ca})\text{SiO}_3 \cdot n\text{H}_2\text{O}$), in which various metal ions are embedded in each other. In general, silicate-rich garnierite ores are amenable to pyrometallurgical processes to produce carbon ferro-nickel alloys, while nickel bound within genthite, clay and saprolite ores is processed hydrometallurgically, such as atmospheric acid-leaching and high pressure acid-leaching [2–4]. However, the stable silicate structure cannot be destroyed to release valuable mineral elements efficiently by the traditional pyrometallurgical and hydrometallurgical processes, which means low

utilization of valuable elements, high energy consumption and negative environmental impact.

Alkali processing of nickel laterite ore has attracted wide concern recently due to its simple process, low energy consumption and low investment [5–7]. A lot of researches were focused on the optimization of the alkali processing conditions, macrokinetics and pre-desilicization [8,9]. The alkali-fusion process is an important operation, during which the strong bonds between the metal and silica part within the compound can be disrupted, then the metal atoms are released from the SiO_4 tetrahedral network. Therefore, it can lead to high yield of nickel from the activated clinker by the subsequent acid-leaching process under moderate conditions. However, there have been few reports on the mechanism of alkali activation for the silicate in detail up to now, especially for the intermediates and kinetic pathway of the reactions, although the initial materials and final products are usually known for the related chemical reactions. It is often difficult, if not impossible, to gather materials which represent reaction intermediates.

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In the current study, Raman spectra in situ during the alkali treatment process were used to identify the presence of the intermediates of the reactions, and reveal the reaction pathway to the alkali treatment process. Furthermore, X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FTIR) analyses were used to identify the changes of mineral phase structure in alkali treatment process. Here, we adopted the synthetic calcium inosilicate (CaSiO_3) instead of the natural garnierite, and examined binding changes and transient phase transformations occurring in the alkali-fusion by Raman spectroscopy in situ and X-ray diffraction analyses. Normally, in garnierite, CaSiO_3 is the major composition, in which minor nickel substitutes calcium. The general formula $(\text{Ca}_{1-x}\text{Ni}_x)\text{SiO}_3$ of their solid solutions are isomorphous. The mechanism of $(\text{Ca},\text{Ni})\text{SiO}_3$ decomposition during the alkali fusion process could be analogous to the formation of CaSiO_3 . The typical Raman spectra with distinct sharp peaks of the colorless CaSiO_3 can be facilely collected, which is another important reason for CaSiO_3 to serve as the subject of investigation in this study instead of the natural dark green garnierite.

2 Experimental

2.1 Synthesis of CaSiO_3

The experimental materials including NaOH , $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and CaCl_2 were all analytical reagent and water was distilled water. The CaSiO_3 colloid precursor was synthesized by a chemical precipitation method using the mixed solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and CaCl_2 with uniform molar concentration at room temperature. The colloid precursor was further calcined to form solid CaSiO_3 in a muffle furnace.

2.2 Decomposition of CaSiO_3 by melting NaOH

The decomposition experiments of CaSiO_3 by melting NaOH were carried out in a stainless steel reactor. The reactor was heated with a heating jacket and the reaction temperature was controlled with a KWT type temperature controller. A nickel chromium–nickel silicon thermocouple was used for temperature measurement with a control precision of $\pm 2^\circ\text{C}$. A stirring device and a reflux condenser were on the reactor. The whole reactor was sealed in decomposing CaSiO_3 process by melting NaOH . The device of experimental reactor is shown in Fig. 1. Firstly, the solid NaOH and CaSiO_3 with various $\text{NaOH}/\text{CaSiO}_3$ mole ratios were added into the reactor, and heated to a set of temperatures. After the reaction period, the temperature of the reaction system decreased to room temperature. Then, the leaching was done by adding distilled water into the reactor. The leaching solution containing soluble silicate and leaching residue can be separated through centrifugation method.

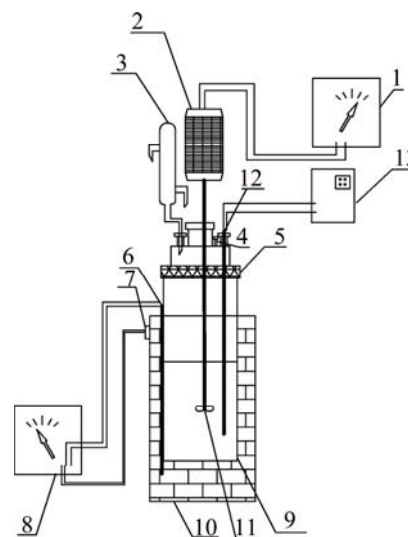


Fig. 1 Experimental apparatus for decomposing CaSiO_3 process by melting NaOH (1—AC adjustable speed controller; 2—Agitator; 3—Reflux condenser; 4—Thief hatch; 5—Nipple; 6—Thermocouple; 7—Set of posts; 8—Temperature controller; 9—Reaction kettle; 10—Heating jacket; 11—Stirrer; 12—Thermocouple; 13—Digital display device)

2.3 In suit Raman spectroscopy analysis

The alkali fusion process of CaSiO_3 with various mole ratios of NaOH to CaSiO_3 was investigated in the homemade micro-furnace under different operating conditions by Raman spectroscopy in situ. Raman spectra were collected on the Raman spectrometer (Jobin Y'von LABRAM HR800). The pulsed exciting light (355 nm) from a Q-switch pulsed THG-Nd: YAG laser was focused by an Olympus BH-2 microscope, and the Raman scattering light from the reactants was collected by a Confocal-len system. The spectral resolution was better than 2 cm^{-1} and the spatial resolution was about $1\text{ }\mu\text{m}$. The Raman spectrometer was equipped with the intensive charge-coupled device (ICCD) to investigate the alkali fusion process.

2.4 XRD and FTIR analysis

The cooled clinker of products of the alkali fusion process was washed with tap water at room temperature several times. The undissolved residue was centrifugally separated from the solution and dried at room temperature for subsequent XRD and FTIR analyses. Phase analyses of all the samples were carried out with a D/Max-2500PC X-ray diffractometer with $\text{Cu K}\alpha$ radiation and a Nicolet 380 FTIR spectrometer.

3 Results and discussion

3.1 Structure of synthetic CaSiO_3

The XRD patterns of the CaSiO_3 colloid precursor calcined at 900, 1000 and 1100 $^\circ\text{C}$ for 3 h are shown in

Fig. 2. The characteristic diffraction peak intensity of the products is enhanced with increasing the calcination temperature. It is demonstrated that the characteristic diffraction peak of the calcination product at 1100 °C is very sharp and has less impurity peaks, which shows that the calcined product is in a good crystalline state. The calcined product phase is found to be CaSiO_3 (JCPDS No.42–547). The SEM image of CaSiO_3 particles including cube and schistose is shown in Fig. 3.

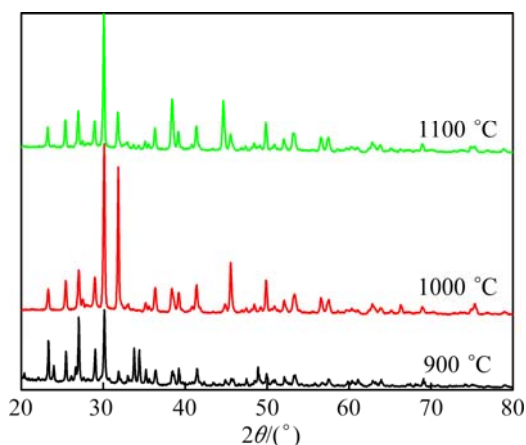


Fig. 2 XRD patterns of CaSiO_3 precursor calcined at different reaction temperatures

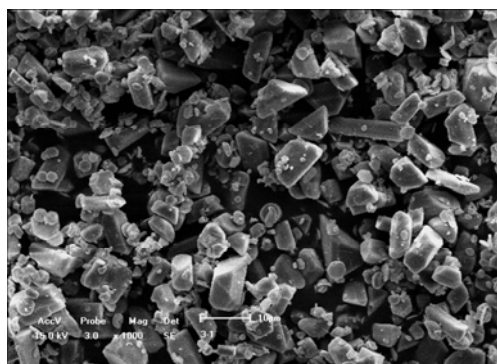


Fig. 3 SEM image of CaSiO_3 precursor calcined at 1100 °C for 3 h

Figure 4 shows the FTIR pattern of CaSiO_3 calcined at 1100 °C for 3 h. Previous theory analysis indicated that there exist four major infra vibration modes for the CaSiO_3 lattice structure: symmetric stretching mode of Si—O—Si (725 and 693 cm^{-1}) [10,11], antisymmetric stretching mode of Si—O—Si (1012 and 936 cm^{-1}) [12,13], symmetric stretching mode of Si—O_{nb} (872 cm^{-1}) and bending of Si—O_{nb} mode (555 and 436 cm^{-1}) [14,15].

Figure 5 shows the Raman spectra of CaSiO_3 prepared at different temperatures from 20 to 500 °C. All the bands show a minor shift to lower wavenumber with temperature increasing from 20 to 500 °C because of the increase of bond distance between Ca^{2+} and SiO_4^{4-}

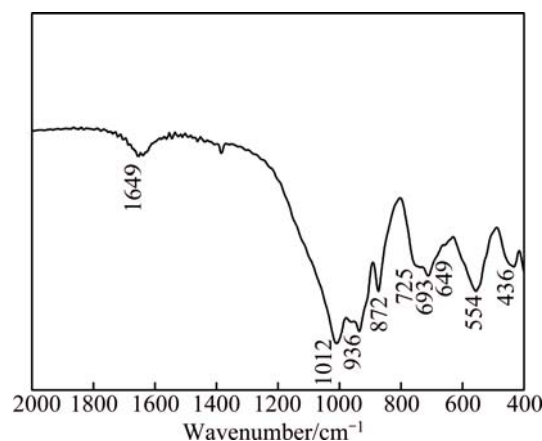


Fig. 4 FTIR pattern of CaSiO_3 precursor calcined at 1100 °C for 3 h

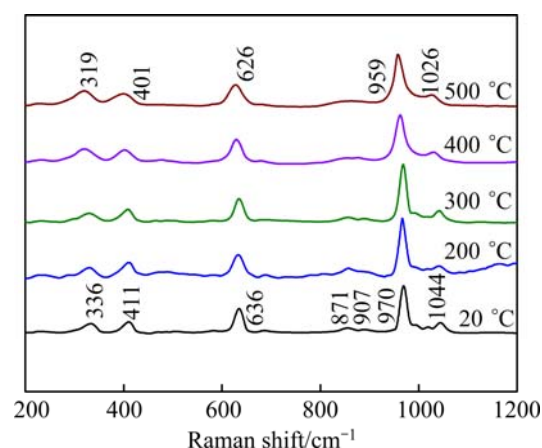


Fig. 5 Raman spectra of CaSiO_3 at prepared temperatures from 20 to 500 °C

tetrahedra. In general, the inosilicates are characterized by the Si—O—Si bending vibration bands between 400 and 750 cm^{-1} , the Si—O stretching vibration bands (Q_n) between 800 and 1100 cm^{-1} and metal—O bending vibration bands below 600 cm^{-1} . The characteristic peaks of Raman vibration spectrum of CaSiO_3 are all located in the wavenumber range of 200–1200 cm^{-1} , among which 970 cm^{-1} belongs to a symmetric stretching vibration peak of SiO_4^{4-} , 1044 cm^{-1} belongs to an antisymmetric stretching vibration band of SiO_4^{4-} , 411 and 636 cm^{-1} belong to bending vibration mode of Si—O—Si [16,17]. The frequencies of the stretching modes are related to the degree of polymerization of the SiO_4^{4-} tetrahedral network: the tetrahedra with zero (Q_0), one (Q_1), two (Q_2) and three (Q_3) bridging oxygen atoms are associated with the modes at 850, 900, 950–1000 and 1050–1100 cm^{-1} , respectively. The wavenumbers of Si—O—Si bending vibration of the prepared CaSiO_3 in current study are at around 411 and 636 cm^{-1} , while the wavenumbers of Q_2 are 970 and 1044 cm^{-1} under ambient conditions. The vibration band below 400 cm^{-1} is caused by the large

frame vibration with the participation of the cation. The typical Raman spectrum of the prepared CaSiO_3 confirms that it has silica tetrahedra (Q_2), which is branched together by calcium octahedra.

3.2 Silicate structure transformation in alkali fusion process

The alkaline fusion process of the prepared CaSiO_3 using NaOH under different operating conditions was carried out to obtain the details about the alkali fusion process of CaSiO_3 , including the presence of the reaction intermediates. The residues from the alkali fusion process followed by water washing were examined by XRD analysis. Figure 6 shows XRD patterns of water-leaching residues from CaSiO_3 after alkali fusion process at 500°C for 1 h with mole ratios of NaOH to CaSiO_3 being 4:1, 6:1 and 8:1. It can be deduced from the XRD patterns that the structure of CaSiO_3 is decomposed into the nesosilicate (Q_0) Ca_2SiO_4 and $\text{Na}_2\text{CaSiO}_4$ and a small quantity of chains (Q_2) Na_2SiO_3 , since the phases including Ca_2SiO_4 , $\text{Na}_2\text{CaSiO}_4$, Na_2SiO_3 and $\text{Ca}(\text{OH})_2$ were detected from the XRD pattern of the residue at a mole ratio of NaOH to CaSiO_3 being 4:1. Excess NaOH could keep reacting with Na_2SiO_3 and Ca_2SiO_4 to form the nesosilicate (Q_0) Na_4SiO_4 and $\text{Na}_2\text{CaSiO}_4$ except for the decomposition of CaSiO_3 . Furthermore, Ca^{2+} released from the silicate structure and then combined with OH^- to form $\text{Ca}(\text{OH})_2$ because the reaction between NaOH and Ca_2SiO_4 or $\text{Na}_2\text{CaSiO}_4$ was promoted with the increase of mole ratio of NaOH to CaSiO_3 . Thus, the probable reactions between CaSiO_3 and melting NaOH are as follows:

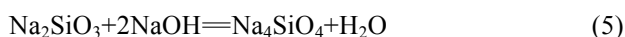
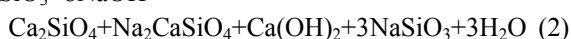
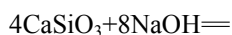
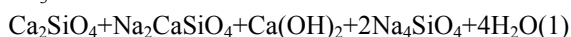
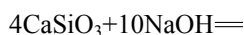


Figure 7 shows the FTIR patterns of water-leaching residues from CaSiO_3 after alkali fusion process at 500°C for 1 h with mole ratios of NaOH to CaSiO_3 being 4:1, 6:1 and 8:1. In the FTIR patterns of reaction mixture, the peaks at $1610\text{--}1649\text{ cm}^{-1}$ are attributed to the bending vibration mode of H—O—H in combined water, while the peaks at $1428\text{--}1446\text{ cm}^{-1}$ are attributed to the stretching vibration mode of C—O in CO_3^{2-} [18]. This indicates that part of molten NaOH can react with CO_2 in ambient air to produce Na_2CO_3 .

With increasing the mole ratio of NaOH to CaSiO_3 , the peaks at 725 and 693 cm^{-1} belonging to Si—O—Si symmetric stretching mode disappear [19]. In the mean

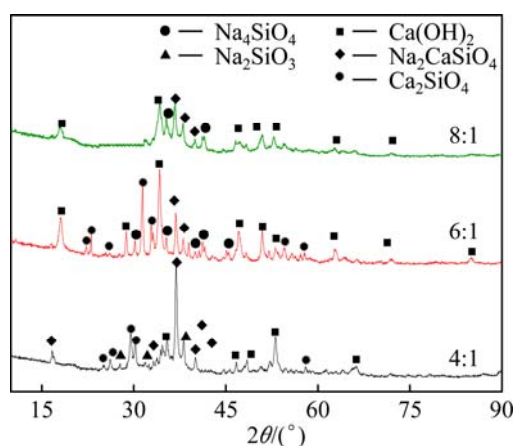


Fig. 6 XRD patterns of water-leaching residues from CaSiO_3 after alkali fusion process at 500°C for 1 h with mole ratios of NaOH to CaSiO_3 being 4:1, 6:1 and 8:1

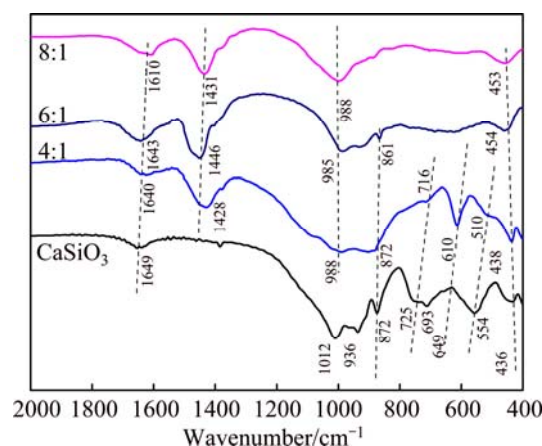


Fig. 7 FTIR patterns of water-leaching residues from CaSiO_3 after alkali fusion process at 500°C for 1 h with mole ratios of NaOH to CaSiO_3 being 4:1, 6:1 and 8:1

time, the peaks of Si—O_{nb} antisymmetric stretching and bending mode appear at about 985 and 610 cm^{-1} , respectively, which prove that the structure of silicate transforms from Q_2 to Q_0 [20]. XRD analysis shows that the main products of reaction are Ca_2SiO_4 and $\text{Na}_2\text{CaSiO}_4$ when mole ratio of NaOH to CaSiO_3 is 4:1. The new antisymmetric stretching mode of Si—O—Si at 716 cm^{-1} indicates part silica chain units still remain in reaction mixture while the structure of silicate network varies with the development of reaction. XRD analysis shows that Ca^{2+} is replaced by Na^+ in Q_2 silicate species when the mole ratio of NaOH to CaSiO_3 is 4:1.

As the NaOH content rises furthermore, the peak of Si—O_{nb} stretching mode appears at about 870 cm^{-1} while one of Si—O—Si antisymmetric stretching modes disappears gradually [21]. This indicates that the remaining Si—O—Si bonds in Na_2SiO_3 lattice are decomposed by NaOH . XRD analysis shows that Na_4SiO_4 (a kind of Q_0 silicate species) appears when the

mole ratio of NaOH and CaSiO₃ rises up to 8:1.

The Raman spectra were collected continuously during the alkali fusion process to make references for distinguishing the reaction intermediates by Raman spectroscopy in situ, once the reactants were heated up to different setting temperatures, which rose at the rate of 10 °C/min from room temperature. Figures 8 and 9 display the Raman spectra of the reaction mixture at different temperatures, in which the mole ratios of NaOH to CaSiO₃ are 4:1 and 8:1, respectively.

The intensity of Raman spectrum of the sample diminishes intensely when temperature is 300 °C. Similar phenomena are observed at the Raman spectra of ceria doped by rare-earth cations. In these systems, the distribution of defects in the lattice causes the disappearance of the Raman spectra. This suggests that in a similar way, the ordered defects such as polysynthetic twins happen in the reaction of silicate with NaOH.

The variations in Raman vibration mode of CaSiO₃ decomposed by alkali with temperature rising are shown in Figs. 8 and 9. In the present work, Raman bands below 400 cm⁻¹ are assigned to vibrations of the M—O (M=Ca or other metals) bonds and the long-range

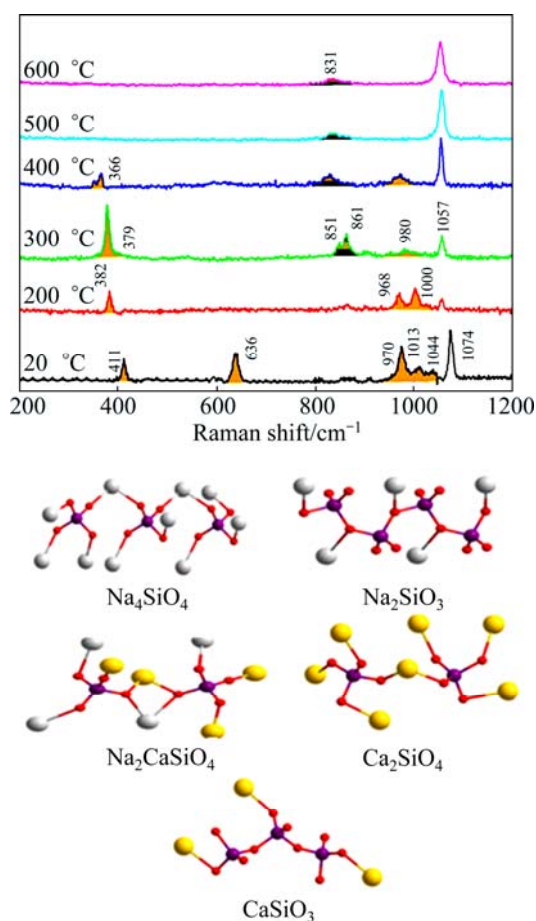


Fig. 8 Raman spectra of prepared CaSiO₃ during alkali fusion process as function of elevated temperature at mole ratio of NaOH to CaSiO₃ being 4:1

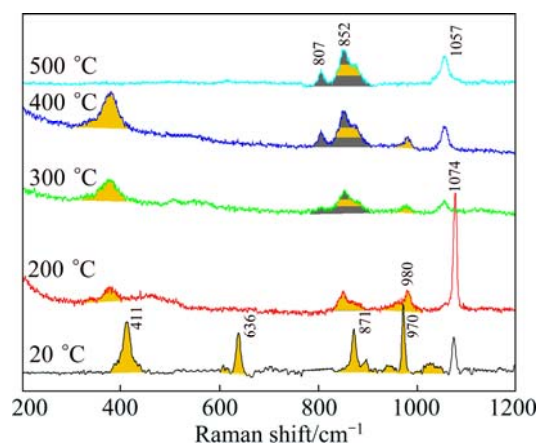


Fig. 9 Raman spectra of prepared CaSiO₃ during alkali fusion process as function of elevated temperature at mole ratio of NaOH to CaSiO₃ being 8:1

ordering of the silicate network [22]. The highest wavenumber bands at about 1074 cm⁻¹ is due to OH⁻ in NaOH. With the temperature rising, the bending vibration band of CaSiO₃ at 411 cm⁻¹ shifts to low wavenumber. Previous studies on temperature dependent Raman spectra of inorganic crystals and melts assign similar red shifts to the weakening of the central atom ligand bonding due to volume expansion with temperature rising and the degree of crystal defect in natural materials. This may imply that crystal defect and structural disorders appear in CaSiO₃ lattice in molten alkali at high temperature as the radiation or metamictization does in natural silicate material.

When the mole ratio of NaOH to CaSiO₃ is 4:1, the bands at 970, 1010 and 1039 cm⁻¹ assigned to Si—O—Si bond of CaSiO₃ diminish at above 300 °C. With the increase of NaOH content, the bands of CaSiO₃ disappear at lower temperature, which indicates that higher OH⁻ content accelerates the decomposition of CaSiO₃. The vibration bands at 850 cm⁻¹ attributed to Si—O_{nb} bonds appear after the bands of CaSiO₃ diminish. These features indicate the chain silicate structure of CaSiO₃ is disrupted by NaOH and isolated silicate species is obtained during the alkali fusion reaction process. With the increase of NaOH content, the vibration band at 850 cm⁻¹ shifts to 830 cm⁻¹. This behavior reflects that a lot of cations which bond to SiO₄⁴⁻ tetrahedron in Q-species diminish with the loading of NaOH. The XRD analysis proves that Ca₂SiO₄ as an intermediate transforms to Na₂CaSiO₄ during NaOH fusion reaction process.

The appearance of bands at 980 cm⁻¹ assigned to enstatine phase (Na₂SiO₃) proves that part of SiO₄ tetrahedra polymerize to Q₂ silicate species at the initial stage of reaction [23]. With the increase of temperature, the vibration bands at 807 cm⁻¹ assigned to the

asymmetric stretching vibration of Q_0 in Na_4SiO_4 show that Si—O—Si bonds in Na_2SiO_3 lattice are disrupted by NaOH again. Only the bands assigned to the symmetric stretching vibration can be observed when temperature rises up to 500 °C, which proves that Ca atoms are replaced by Na atoms completely. So, Na_4SiO_4 is obtained as final products.

3.3 Reaction pathway

There exist two reaction pathways in the calcium silicate alkali fusion process: one is ion exchange, the other is in the main form of the framework structure change of silicate. According to the silicate structure transformation in alkali fusion process, the reaction pathway and lattice structure variation of silicate in reaction system are shown in Fig. 10. After the two pathways of parallel structure transformation, $CaSiO_3$ is changed to the final product Na_4SiO_4 . According to the above experimental analysis results of Raman, FTIR and XRD, there exist three intermediate products in the two pathways. They are Ca_2SiO_4 , Na_2CaSiO_3 and Na_2SiO_3 , respectively. The two pathways are $CaSiO_3 \rightarrow Ca_2SiO_4 \rightarrow Na_2CaSiO_3 \rightarrow Na_4SiO_4$ and $CaSiO_3 \rightarrow Na_2SiO_3 \rightarrow Na_4SiO_4$, respectively, which take place simultaneously in alkali fusion process. Based on this finding, it can provide reference to the optimization of NaOH addition by alkaline method in the silicate–laterite–nickel ore process.

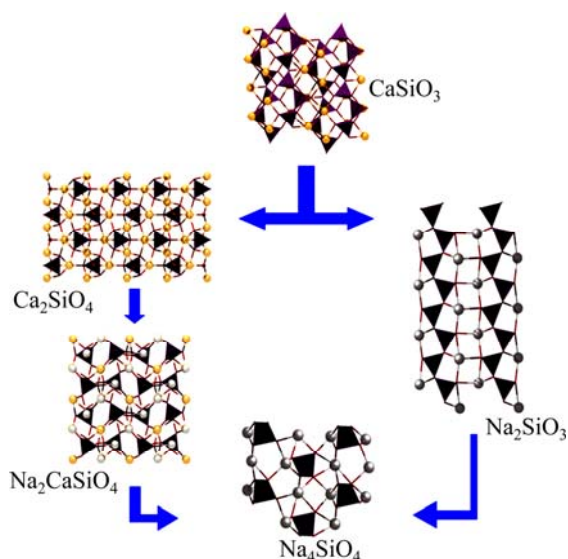


Fig. 10 Reaction pathway and structure evolution of silicate

4 Conclusions

1) Combining Raman spectroscopy in situ with the XRD and FTIR analyses can give the decomposition pathway of $CaSiO_3$ during the alkali fusion process using NaOH.

2) The silica tetrahedral chains within calcium

inosilicate ($CaSiO_3$) are gradually disrupted, and nesosilicates with the isolated tetrahedra are reorganized at the beginning of the alkali fusion process.

3) Ca_2SiO_4 , Na_2CaSiO_3 and Na_2SiO_3 are the three intermediates appearing in the decomposition process, however, the final products are $Ca(OH)_2$ and Na_2SiO_4 .

4) There exist two reaction pathways in the calcium silicate alkali fusion process: one is ion exchange, the other is in the main form of the framework structure change of silicate.

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NaOH 碱熔分解 CaSiO_3 过程中 导致硅酸盐结构转变的反应路径

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摘 要: 以 $\text{NaSiO}_3 \cdot 9\text{H}_2\text{O}$ 和 CaCl_2 为原料, 通过化学沉积法合成链状硅酸盐(CaSiO_3)。采用拉曼光谱、X 射线衍射和红外光谱研究其在 NaOH 碱熔过程中的分解机制。结果表明, CaSiO_3 在碱熔过程中链状结构的硅氧四面体结构逐渐断裂、转变生成岛状结构的硅氧四面体。 CaSiO_3 分解过程中同时生成 3 种中间体: Ca_2SiO_4 , $\text{Na}_2\text{CaSiO}_4$ 和 Na_2SiO_3 , 最终产物是 $\text{Ca}(\text{OH})_2$ 和 Na_4SiO_4 。因此, CaSiO_3 在 NaOH 碱熔反应过程中存在两条反应途径, 分别以离子交换和硅酸盐骨架结构改变为主要形式, 碱熔过程中硅酸盐结构的变化贯穿于整个反应过程。

关键词: 碱熔过程; CaSiO_3 ; 中间体; 反应路径

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