# The kinetic pathway of decomposition of $MgSiO_3$ by alkali fusion using sodium hydroxide

*Qian XU*, Min XU， Riqiang LIU , Zirui WANG and Yuchun ZHAI*
*School of Materials Science and Metallurgy, Northeastern University, Shenyang, 110004, PR China*

**Abstract:** The mechanism of decomposition of prepared $MgSiO_3$ by alkali fusion using sodium hydroxide was studied by Raman spectroscopy in situ combining with X-ray diffraction analyses. The results show that alkali fusion $MgSiO_3$ breaks down the bonds between bridging oxygen and silicon (Si-O-Si) within its chain structure. Therefore, the metasilicate with the chain structure is changed to the orthosilicate with the island structure during the fusion process. Sodium ions substitute for Mg ions in magnesium orthosilicate successively, and both $Mg_2SiO_4$ and $Na_2MgSiO_4$ are the reaction intermediates. The $Na_2SiO_4$ and $Mg(OH)_2$ are obtained finally for the alkali fusion process.

**Keywords:** Raman spectroscopy, alkali fusion, $MgSiO_3$, kinetic pathway

## 1. Introduction

Garnierite (Ni, $Mg)_3Si_2O_5(OH)$ is an important constituent in nickel laterite deposits for bearing significant amounts of nickel. In general, silicate rich garnierite ores are amenable to pyrometallurgical processes to produce carbon ferro-nickel alloys, while nickel bound within geothite, clay and saprolite ores are processed hydrometallurgically, such as atmospheric acid leaching and pressure acid leaching. It is due to being more chemically and thermally stable of garnierite compared with the other nickel-bearing ores, and more aggressive reaction conditions for decomposition of garnierite. However, there are several reports recently on the joint processes of alkali-roasting activation and acid leaching for extraction of the valuable components from silicate-bearing laterites [1]. The alkali-activation process is an important operation, which can breakdown the strong binding between the metal and silicon parts within the compound, and destroy the stable structure of the silicate. Therefore, it can leads to high yield of nickel from the activated mass by the subsequent acid leaching process under mild acid conditions. But, there is few reports related to reveal the mechanism of alkali-activation till now, especially for the kinetic pathway of the reactions.

Spectroscopic methods have become a vital investigative tool in determinatively mineralogy conventionally. The Raman scattering measurement can even be used as a fast, non-destructive and reliable method to probe the chemical reaction in situ. Investigation into changes in Raman mode frequencies with the elevated temperatures or pressures can provide the information on the chemical bonding characters and the crystal structures in the reaction mixture [2.3]. Here, we used the synthetic magnesium pyroxene instead of the natural garnierite, and examined binding changes and phase transformations occurring in the alkali-fusion by Raman spectroscopy measurements in situ and X-ray diffraction analyses. The objective of this work is to gain a greater insight into the reaction pathway and kinetics of the alkali-activation process of $MgSiO_3$.

## 2. Experimental methods

$MgSiO_3$ was prepared by the chemical precipitation method from analytical grade $MgCl_2$ and $NaSiO_3$ in the aqueous

solution. The precipitation was dried at 100℃, and then heated to 1200 ℃ for 4 hours. $Mg_2SiO_4$ was synthesized by the solid reaction of the prepared $MgSiO_3$ and MgO at 1200 ℃ All the samples were confirmed by X-ray diffraction examination. The alkali fusion process of prepared $MgSiO_3$ with the various NaOH/ $Na_2SiO_3$ molar ratios was investigated under different operating conditions by Raman spectroscopy in situ. Raman spectra were obtained on Lab RAM HR-800 Raman spectrometer. The cooled alkali fusion clinker with NaOH was washed with tap water at room temperature for several times. After centrifugal separation, the un-dissolved residue was dried at room temperature, and heated up to 600 ℃ for subsequent XRD analyses.

## 3. Results and discussion

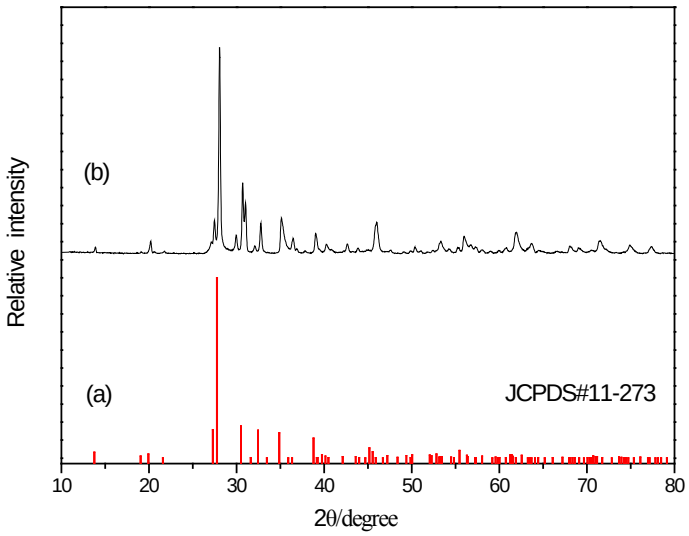


**Fig.1** (a) XRD pattern of prepared $MgSiO_3$ and (b) XRD pattern of protoenstatite (JCPDS No.11-273)

Fig. 1 shows the typical XRD patterns of the prepared $MgSiO_3$ and protoenstatite, respectively, which indicates the prepared $MgSiO_3$ is composed of a single phase of protoenstatite. The Raman spectra of the prepared $MgSiO_3$ at varied temperatures from 35°C to 600°C are shown in Fig.2. Except that all the bands have a minor shift to lower frequencies, Raman spectra of the prepared $MgSiO_3$ are very much alike one another when the temperature changes from 35°C to 600°C. In general, pyroxenes are characterized [4,5] by (1) the Si-O-Si bending vibrations between 400 and 750$cm^{-1}$, (2) the Si-O stretching vibrations between 800 and 1100$cm^{-1}$($Q^n$); and (3) metal-O bending vibrations below 600 $cm^{-1}$. Usually, the frequencies of the stretching modes are related to the degree of polymerization of the $SiO_4$ 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 frequency of Si-O-Si bending vibrations in the prepared $MgSiO_3$ of this study is at around 680$cm^{-1}$, while the frequency of $Q^1$ mode is about 945$cm^{-1}$, and the frequencies of $Q^2$ are 1017 and 1040 $cm^{-1}$ at ambient conditions. The typical Raman spectra of the prepared $MgSiO_3$ confirm that it consists of silica tetrahedral chains which are branched together by magnesium octahedral.

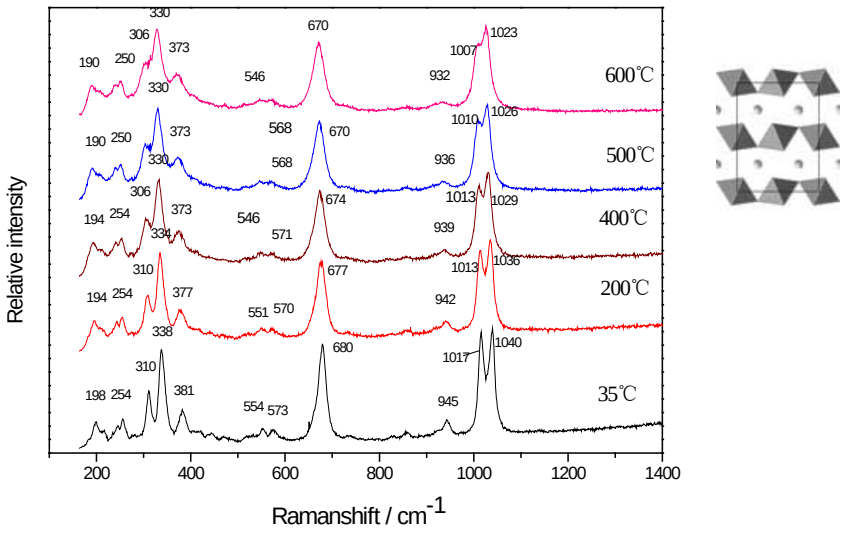


**Fig.2** Raman spectra of prepared $MgSiO_3$ at varied temperatures from 35℃ to 600℃.

In order to obtain details about alkali fusion process of $MgSiO_3$, including the presence of the reaction intemediates, the alkaline fusion of the prepared $MgSiO_3$ using sodium hydroxide was performed under different conditions. The residue after alkali fusion followed by water washing was examined by XRD. Fig.3 shows the typical XRD patterns of the residue for the alkali fusion at 600℃ for 30min with weight ratios of NaOH to $MgSiO_3$ from 5:1 to 16:1. It can be deduced from the XRD patterns that the reaction of alkali fusion of $MgSiO_3$ is completed by 30min at 600℃ when the weight ratio of NaOH to $MgSiO_3$ is 16:1, since MgO is the only one phase detected from the XRD pattern of the residue. The starting materials of NaOH and $MgSiO_3$ can be converted to $Mg(OH)_2$ and sodium silicate as final products of the alkali-fusion process, in which the latter can be dissolved during water-washing and separated from the residue. In this case, MgO is a derivative of $Mg(OH)_2$ after the residue is heated to 600℃ for XRD examination. It also can be found that the higher weight ratio of NaOH to $MgSiO_3$ accelerates the chemical reaction of the alkali-fusion process controlled by the law of mass action. Furthermore, $Na_2MgSiO_4$ can be detected from the XRD patterns for the lower weight ratios of 12:1, 10:1 and 5:1, as one of the reaction intermediates. When the temperature of alkali-fusion process decreases from 600 to 400℃, more details about the reaction intermediates can be found in Fig. 4, which shows the XRD patterns of the residue from $MgSiO_3$ after alkali-fusion at 400 ℃ followed by water-washing. The typical XRD pattern of $MgSiO_4$ can be recognized besides $Na_2MgSiO_4$, as another reaction intermediate. It should be concluded that magnesium enstatite has been converted to Mg and Mg/Na olivine by the alkali-fusion with molten sodium hydroxide, which are un-dissolved in water.

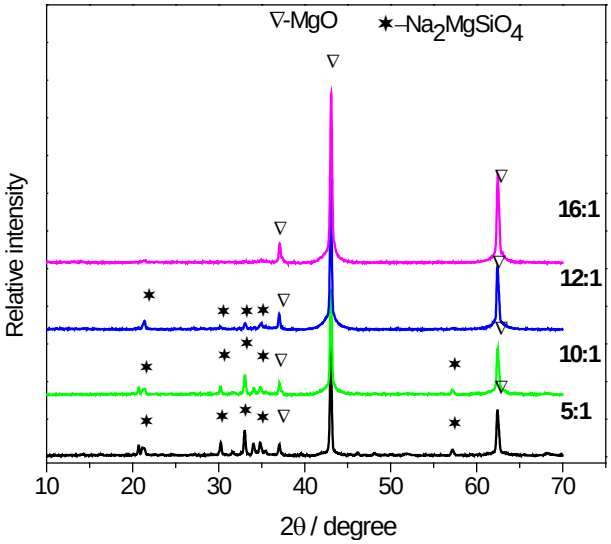


**Fig.3** XRD patterns of the residue from $MgSiO_3$ after alkali fusion followed by water washing at 600℃ for 30 min with different weight ratios of NaOH to $MgSiO_3$.

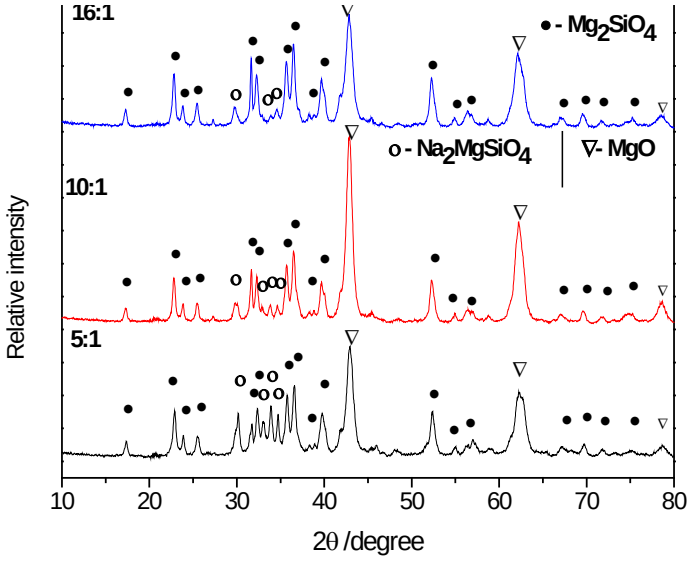


**Fig.4** XRD patterns of the residue from $MgSiO_3$ after alkali fusion followed by water washing at 400℃ for 15 min with different weight ratios of NaOH to $MgSiO_3$.

In order to make reference for distinguishing the reaction intermadiates, Raman spectra of sodium hydroxide, which is one of the other starting materials of alkali-fusion at the different temperatures, are shown in Fig.5. In general, there is no band near to 1000 $cm^{-1}$related to valence vibration of O-H [6] if the NaOH is free of sodium carbonate, while the typical band at approximately 1080 $cm^{-1}$ due to $CO_3^{2-}$ exists in the Raman spectra of sodium carbonate [7]. In this case, Fig.5 shows the intense band at 1076 $cm^{-1}$for Raman spectrum of NaOH at room temperature, the band can shift to the lower frequency with increasing of temperature. It is probably because the NaOH samples contain some sodium carbonate since all the Raman measurements have been carried out at ambient conditions, and sodium hydroxide

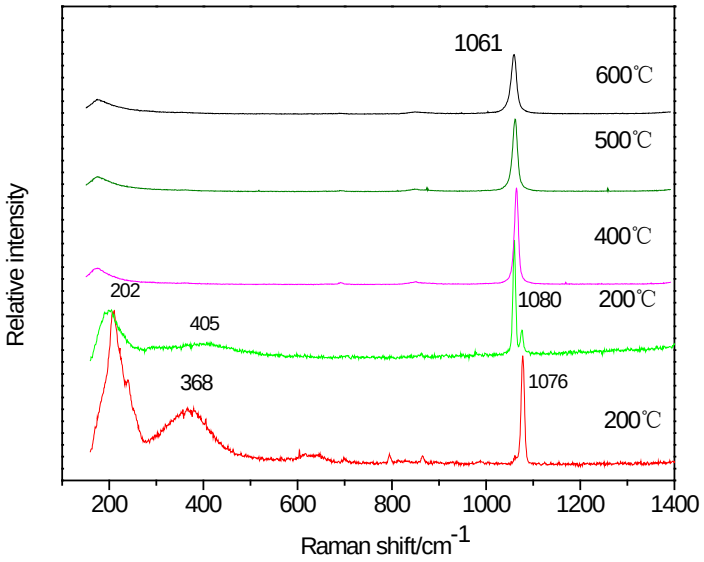


**Fig.5** Raman spectra of anhydrous NaOH at different temperatures.

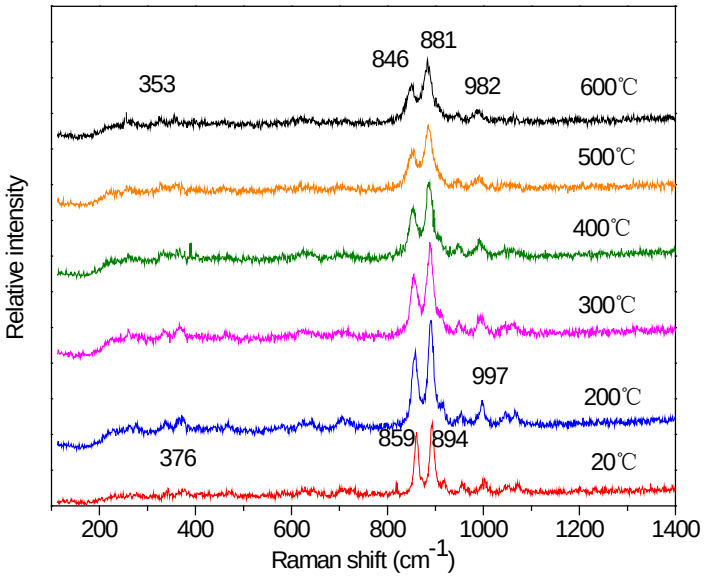


**Fig.6** Raman spectra of the prepared $MgSiO_4$ at different temperatures.

facilely absorbs $CO_2$ in the air and forms sodium carbonate. The Raman spectra of prepared $Mg_2SiO_4$ are shown in Fig6. in which the bands at 859 and 894$cm^{-1}$ at room temperature are attributed to stretching modes of $Q^0$ in forsterite. These bands can small shift to the low frequency as the temperature increase from 20 to 600℃.

The Raman spectra were collected continuously during the alkali fusion process once the reaction mixture was heated up to the different set temperatures, during which the temperature vcincreased at the rate of 10℃/min from the room temperature. Fig.7 displays the Raman spectra of the reaction mixture at different temperatures, in which the mole ratio of NaOH to $MgSiO_3$, as the starting materials, is 2:1.

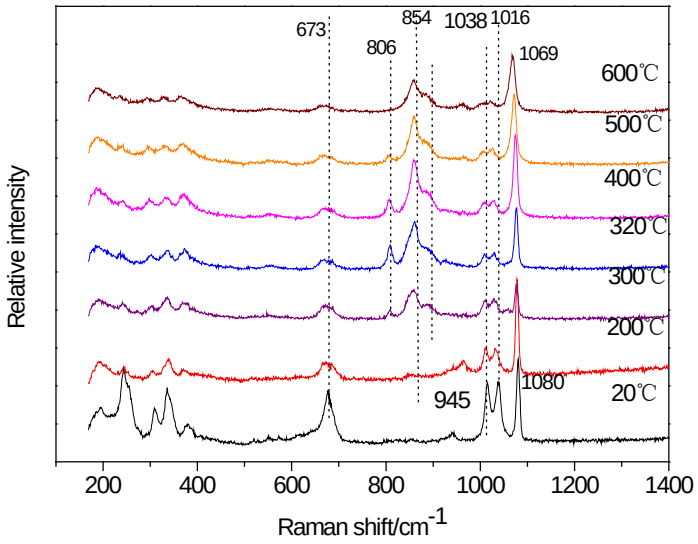


**Fig.7** Raman spectra of prepared $MgSiO_3$ during alkali fusion process as a function of the elevated temperature at mole ratio of NaOH to $MgSiO_3$ of 2:1.

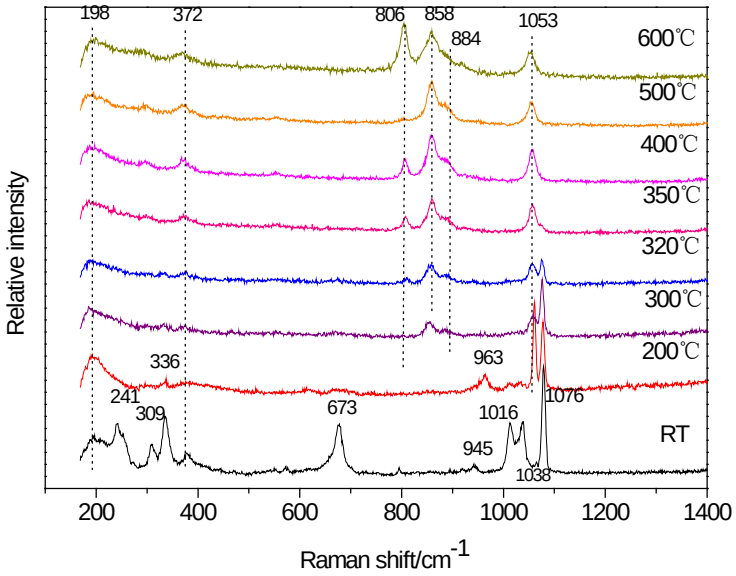


**Fig.8** Raman spectra of prepared $MgSiO_3$ during alkali fusion process as a function of the elevated temperature at mole ratio of NaOH to $MgSiO_3$ of 5:1

Upon temperature increasing, the intensity of the bands for $Q^2$ bending mode at 673 $cm^{-1}$ and stretching mode at 1016 and 1038 $cm^{-1}$ decreases distinctly as the reaction progress, while the appearance of the bands at ~858 and 805$cm^{-1}$ characterizes for stretching mode of $Q^0$. It is well known that the bands around 858 $cm^{-1}$can be attributed to non-bridging Si-O stretching mode in forsterite($Mg_2SiO_4$) [8] as shown in Fig.6. The band around 805 $cm^{-1}$ should be attributed to Si-O stretching mode in sodium silicate ($Na_4SiO_4$), since magnesium is heavier than sodium, and the vibration of Si-O stretching should be appear at lower frequencies when Na acts as a network modifier instead of Mg [9]. It can be found that the chains of silica tetrahedra are broken down gradually during the alkali fusion, which leads to diminishing of number of $Q^2$, and increasing of number of $Q^0$. The variations observed on Raman spectra for the

alkali fusion are related with tetrahedral network reorganization. Consequently, it can be deduced that $Mg_2SiO_4$ is one of the reaction intermediates, which is good agreement with results with XRD analyses above. However, the bands at around 850 and 881 $cm^{-1}$ are incorporated to a broad bump, not like the sharply separated two peaks for the pure $Mg_2SiO_4$. Probably, the bands for stretching mode of $Q^0$ in $Na_2Mg_2SiO_4$ overlap with those of $Mg_2SiO_4$ since $Na_2Mg_2SiO_4$ is the other one of reaction intermediates which is found in the former XRD analyses. Hence, it can be concluded that $Na_4SiO_4$ should be one of the final products besides $Mg(OH)_2$ for the alkali fusion process.

Fig.8 shows Raman spectra of the reaction mixture at different temperatures, in which the mole ratio of NaOH to $MgSiO_3$, as the starting materials, is 5:1. Comparing with the Raman spectra for the reaction mixture with the ratio of 2:1 at the same temperature in Fig.7, the intensity of the bands due to Si-O-Si vibration is much weaker in Fig.8. Furthermore, the intensity of band due to $Q^0$ in $Na_4SiO_4$ increases more distinctly with the temperature when the ratio is bigger, even though there exists discrepancy with the spectrum at 500°C probably because of inhomogeneity of the reaction mixture. These results confirm that more amount of NaOH in the alkali fusion process can enhance rate of breaking down the chains of silica tetrahedral and of reorganizing island structure of $Na_4SiO_4$

## 4. Conclusions

Combining the XRD analyses with Raman spectroscopy in situ can give the kinetic pathway of decomposition of $MgSiO_3$ by alkali fusion using sodium hydroxide.

The silica tetrahedral chains within enstatite $MgSiO_3$ can be broken down gradually during the alkali fusion process. Within the $SiO_4$ tetrahedral network, the tetrahedral with two bridging oxygens transfers the tetrahedral with zero bridging oxygens. Therefore, the metasilicate with the chain structure is changed to the orthosilicate with the island structure after the alkali fusion process with sodium hydroxide.

$Mg_2SiO_4$ and $Na_2MgSiO_4$ are the two intermediates for decomposition of $MgSiO_3$ by alkali fusion, and the substitution of sodium for magnesium in Mg-olivine occurs successively. Thereafter, $Na_2SiO_4$ and $Mg(OH)_2$ are gained finally. The increase of the amount of NaOH can enhance the alkali fusion process obviously, and make Mg release easier from silicate netwoks.

## Acknowledgement

The authors gratefully acknowledge the financial support from National Program on Key Basic Research Project of China (Grant No.2007CB613603) and the open research program of Shanghai Key Lab of metallurgy and materials processing in Shanghai University (2009-02). The authors are very thankful to Professor Jinglin You of Shanghai University for helpful discussion.

## References

[1] Q. Guo, J. Qu, T. Qi, G. Wei, B. Han. Activation pretreatment of limonitic laterite ores by alkali-roasting method using sodium carbonate. *Minerals Engineering*, 2011, 24, p825-832.

[2] P. Novak, A. Kisic, T. Hrenar, T. Jednacak. Journal of Pharmaceutical and Biomedical Analysis, 2011,54, p660-666.

[3] D. Reed, D. Book. Recent application of Raman spectroscopy to the study of complex hydrides for hydrogen storage.

*Current Opinion in Solid State and Materials Science*, 2011,15, p62-67.

[4] E. Huang, C.H. Chen, T. Huang, E.H. Lin, J. Xu. Raman spectroscopy characteristic of Ma-Fe-Ca pyroxene. *Amenrican Mineralogist*, 2000, 85, p473-479.

[5] S. Sim, K. Catalli. Compositional dependence of structural transition pressures in amorphous phases with mantle-related compositions. *Earth and Planetary Science Letters*, 2009, 283, p174-180.

[6] I.D. Zakiriyanova, V.A. Khokhlov, V.A. Kochedykov. Raman spectra and microdynamics of the hydroxide-ion in molten NaOH and NaCl-NaOH mixtures. *Journal of Molecular Liquids*, 1999,83, p153-162.

[7] H. Meekes, T. Rasing, P. Wyder, A. Janner, T.Janssen. Raman and infrared spetra of the incommensurate crystal $Na_2CO_3$. *Physical Review B*, 1986, 34(6), p4240-4254.

[8] B.A. Kolesov, J.V. Tanskaya. Raman spectra and cation distribution in the lattice of olivines. *Materials Research Bulletin*, 1996, 31(8), P1035-1044.

[9] N. Trcera, S. Rossano, M. Tarrida. Structural study of Mg-bearing sodosilicate glasses by Raman spectroscopy. *Journal of Raman spectroscopy*, 2011, 42, p765-772.