	Experiment title:	Experiment number:
ESRF	**kinetics of crystallisation and phase transformations in Mg, Fe, Na, K doped $CaO \cdot SiO_2$ system**	08-02-189
Beamline: BM-8	**Date of experiment**: from: 09/10/99 at 7:00 to: 11/10/99 at 7:00	**Date of report**: 22/10/01
Shifts: 6	**Local contact(s)**: Meneghini Carlo	*Received at ESRF:*

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Report:

Introduction

The wollastonite system $CaO\text{-}SiO_2$ is one of the minerals-systems involved in the glass-ceramics industry.

Our aims are the more accurate determination of the kinetic parameters, the identification of the phases and polytypes formed during the thermal treatment of the samples. During the study of polytypism and kinetics (of the formation of the polytypes and of the transformation of one polytype to the other) we are also interested in the role of dopant elements. These information are as well very important for any application on industrial scale in order to optimise and set the temperature treatment.

Wollastonite ($CaSiO_3$) is a single chain silicate, with a chain repeat unit of three tetrahedra (pyroxenoid). The chains are linked to Ca-octahedral columns. The chains are organised in pair. Each pair is constituted by inversion-related chains and represents one basic slab of the structure. Polytypism in wollastonite pyroxenoids is generated by different stacking sequence of the slabs along the a-axis. The more common polytypes are the 1 slab triclinic wollastonite-1T and the 2 slabs monoclinic wollastonite-2M, there are other polytypes with more complex periodicity or partially disordered. Only in the last year the kinetic study of this system consider the role of the polytypism [1,2]. Wollastonite is the main component of Ca-rich glass ceramics, Ca-based glazes and other ceramics.

Previous works [1,2] have shown that the polytypism is very complex and depends on the reactivity of the samples (i.e. depends on the particle size of the powder of the starting glass matrix). Such a characteristics requires the short collecting times allowed by X-ray diffraction by synchrotron radiation and the full angular information obtained by the use of translating Image Plate.

Experimental aspects

The experimantal setup [3,4] consists of a micro reaction chamber, a hot air heater, a Translating Imaging Plate (TIP) camera for collecting time resolved powder diffraction data and 0.5-1.0 mm quartz glass capillaries in air. The experiments consist in four steps. The first step is the calibration of with experimantal set with one-shot X-ray powder diffraction of standard powder of LaB_6. The next step is the collection of one

temperature ramp of standard powder of Si in the working temperature range (RT-1000 °C). The third step is the collection of the teperature ramps on the samples in the same range as the Si. The last step is the real kinetics experiment and consists in isothermal experiment at the selected temperatures: 950, 960, 970, 980, 990 °C (Two examples in Fig.1,2). The temperatures choice depends on the phases studied, here we are interested in the crystallisation of intermediate phases (disorder polytypes) and in the crystallisation of the final stable 2M-wollastonite. The time required by isothermal experiments is too long for a complete kinetic study and more isothermal runs should be done.

Results

The results are affected by some experimental problems, related to the characteristics of the sample and/or the experimental setup. One is the higher temperature limit that is too low for achieved the crystallisation of 2M-wollastonite, only in the temperature ramp experiment we can see the early stage of this process. The second problem is related to the experimental setup. The discovered of such a problem is possible only during the mathematical treatment of the data. In fact the lattice parameters obtained from the refinement of the Si standard spectra in the temperature ramp experiment are without sense. Moreover they depends on wich portion of the spectra is refined. Such a effect prevents a fully crystallographics study of the phases involved in the experiments and permits only a qualitative analyses. Moreover this problem prevents also a good calibration of the temperature for the kinetic study. This effect could be the coupling of different disalignement of the Image Plate.

Another problem is the multiple phase transitions from different disordered polytypes. In fact, diffraction peaks belong to different disordered polytypes appears and then disappears at different times of same run. This behaviour seems a continuos rearrangement of the wollasonite structure through different disordered schemes and results in a sort of dynamic disorder[5]. This problem make the unambiguous attribution of the peaks more difficult and then also the determination of the kinetic parameters is more difficult.

Fig.1 Isothermal run at 950 °C

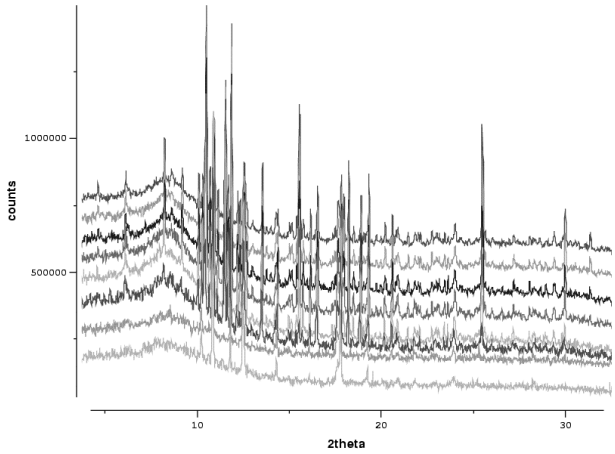
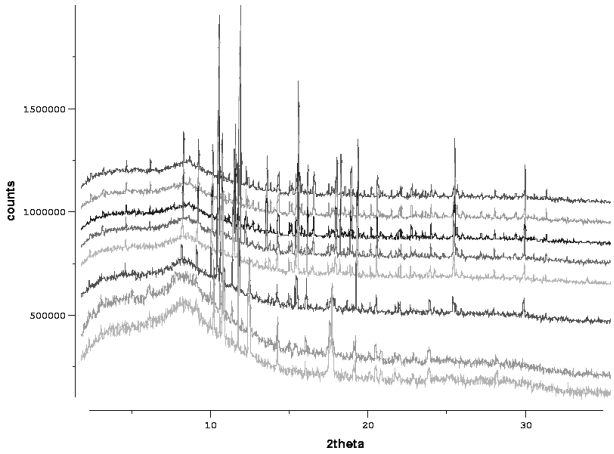


Fig.2 Isothermal run at 990 °C



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