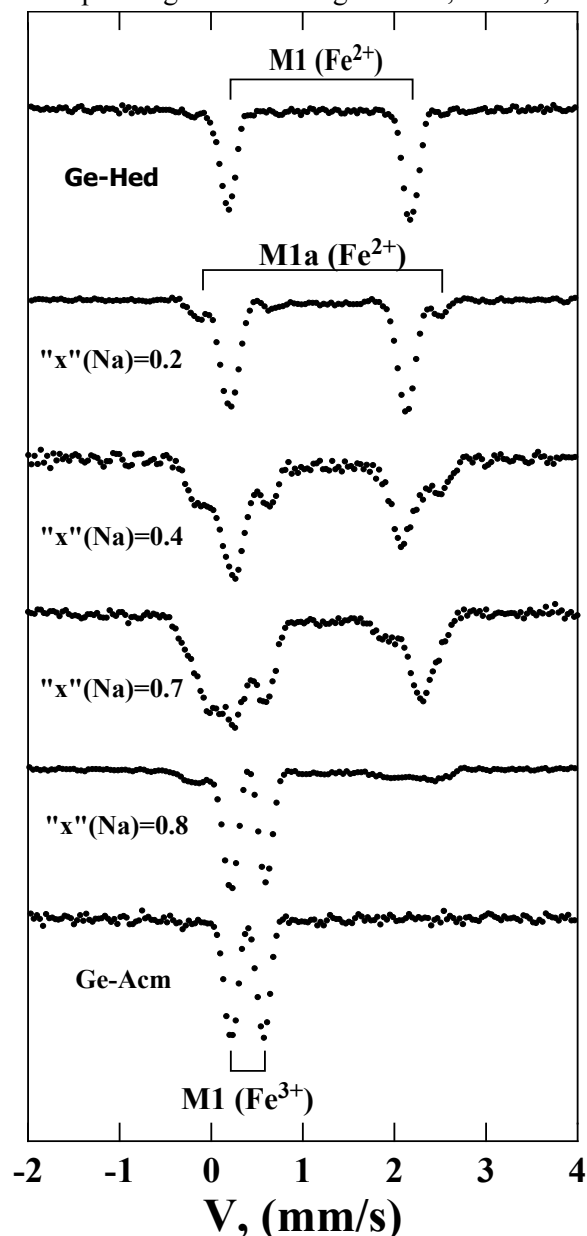


PHASE TRANSITIONS IN GE-CA-NA-FE SOLID SOLUTION WITH PYROXENE STRUCTURE

Novikov G.V. (IEM RAS), Syrovina L.V. (IEM RAS)

novikov@issp.ac.ru; fax: (8-252) 49-687; phone: (8-252) 2-22-80

The solid solutions $\text{Na}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ and $\text{Fe}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ with pyroxene structure are studied by methods X-ray powder diffraction and nuclear gamma-resonance. Synthesis has been carried out by a method of solid state reaction, the size of particles did not exceed ~ 1 micron, that complicated a reliable estimation of compositions of received samples. In the text the nominal composition "x", corresponding to the starting mixture, is used, what is acceptable, if the extra phases are absent in the sample.



sample.

In solid solution $\text{Na}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ ions Fe^{2+} should occupy, at least nominally, only the M1 position. It allows, using the ^{57}Fe gamma-resonance spectroscopy, to study features of their electron structure at gradual substitution of Ca ions by Na ions in other position – M2. Results of such research at $T=300\text{K}$ presented on the fig. 1. To improve the resolution, the original procedure [1] was used, it permitted to resolve some of overlapped components at the cost of signal-to noise ratio, that allows to make a number of important conclusions.

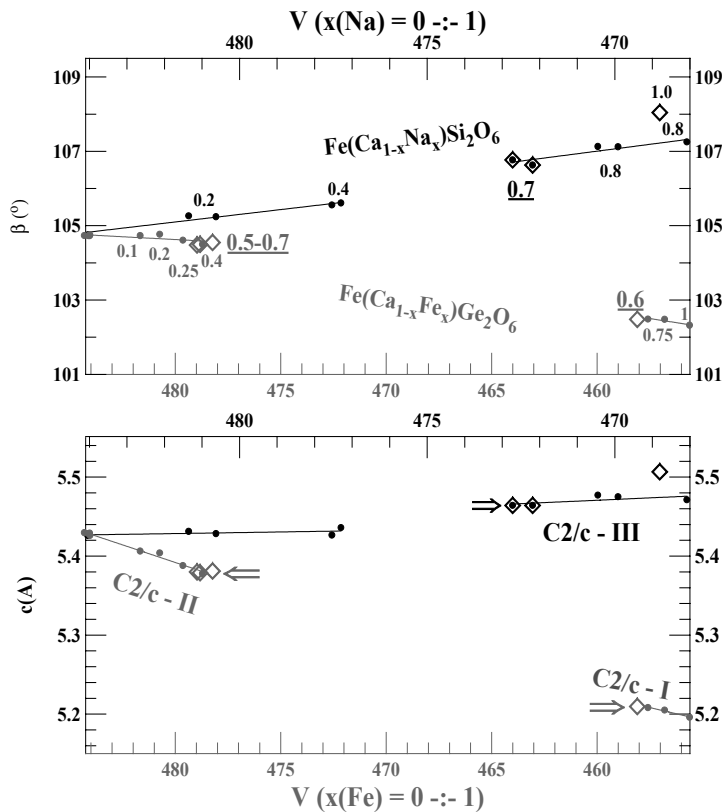
At replacement of Ca ions by Na ions in position M2 while the share of sodium is not higher, than 0.4, the main part of ions Fe^{2+} in position M1 keeps their electronic structure, characteristic for hedenbergite and its Ge-analog. The similar behaviour of main doublet M1 was marked in [2] at detailed studying of Ca-rich members of solid solution $\text{Fe}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ in a temperature range 88 - 300K.

Except for a doublet of the Fe^{2+} ions, dominating in position M1 and keeping their electronic structure, in a spectrum, at substitution $\text{Ca} \rightarrow \text{Na}$ in M2 positions, appears one more doublet (M1a) having greater quadrupole splitting. This phenomenon of splitting of crystallographic position M1 was found at first in [2]. The common type of electronic structure of these two parts of ions Fe^{2+} in these two solid solutions specifies full concurrence not only parameters of doublets M1a, but also character of their temperature dependency. In [2] this doublet has been attributed to the iron ions, occupying position M1, but having the electronic structure which is distinct from one of the "ion – owner", dominating in this position.

Essentially the spectrum of solid solution $\text{Na}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ varies at higher contents of sodium. Dramatic change of parameters of hyperfine structure (HFS) in a spectrum of the main part of ions Fe^{2+} in position M1 at $x(\text{Na})=0.7$ (quadrupole splitting increased to a great extent) proves the essential change of character of interactions of the ion - owner with surrounding oxygen ions. Besides in a spectrum there appears a new Fe^{2+} doublet with broaden components (only right component easily could be determined) with smaller quadrupole splitting, which should be attributed to Fe^{2+} ions, which nearest environment is subject to variations, probably, time-dependent. At last, the most contrast change of a spectrum is observed for solid solution having the content, closer to the end member – Ge-acmite. At $x(\text{Na})=0.8$ relative intensity of doublets of ions Fe^{2+} in a spectrum sharply falls,

halfwidths of their components are very grate. Results of studies of one more sample with the same nominal composition confirms such a contrast change of spectrum at "x" (Na) =0.8. It is worth to mention, that the unit cell parameters determined for these two samples with the same nominal composition essentially differed, forming at the same time for each of parameters - a , b , c and β - the common linear trends with a sample with "x" (Na) =0.7. This interesting feature is connected, obviously, with an opportunity of occurrence structural cation vacancies and/or incomplete end of the ordering processes at synthesis of a solid solution.

It is useful to compare X-trends [3] (dependence "Parameter" – "V") for solid solutions $\text{Fe}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ and $\text{Na}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$, having pyroxene structure. The β - V and c - V trends are presented on fig. 2. The nominal composition of samples "x" is specified, underlining marks compositions of those samples (rhombs), which diffractogram contained reflexes of extra phases. Points of a trend break (arrows) clearly define interval of the "forbidden" volumes, at which solid solution $\text{Fe}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ does not exist.



Samples, which contained except for the main pyroxene phase admixtures, had volume V , practically conterminous to one of boundary (Fe-substituted solid solutions with "x" (Fe) =0.6, and with "x" (Fe) =0.7 and 0.5). Such conclusion accompanying concurrence of values of all parameters of a unit cell proves to be true.

It has allowed to specify borders of area of existence of each of two monoclinic structures (both are characterized by sp. gr. C2/c). The first, "C2/c - I", is characteristic for high pressure ferrosilite [4] and high pressure enstatite [5], the second, "C2/c - II", is characteristic for hedenbergite. Less obvious attributes of break of X-trends for solid solution $\text{Na}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ which research proceeds look. We shall note, however, discrepancy of inclinations of two branches of its trends and specific changes of electronic structure of iron ions in a solid solution with the compositions close to one of Ge-acmite. In aggregate it allows a formal occasion to refer the solid solution having composition close to Ge-acmite to one more structural modification of monoclinic C2/c germanates with pyroxene structure – "C2/c - III" - distinguished from hedenbergite ("C2/c - II"). Let's notice, that for acmite $\text{NaFeSi}_2\text{O}_6$ earlier also it has been established sp. gr. C2/c, but authors do not know about results of similar detailed investigation of a solid solution acmite - hedenbergite.

first, "C2/c - I", is characteristic for high pressure ferrosilite [4] and high pressure enstatite [5], the second, "C2/c - II", is characteristic for hedenbergite. Less obvious attributes of break of X-trends for solid solution $\text{Na}_x\text{Ca}_{1-x}\text{FeGe}_2\text{O}_6$ which research proceeds look. We shall note, however, discrepancy of inclinations of two branches of its trends and specific changes of electronic structure of iron ions in a solid solution with the compositions close to one of Ge-acmite. In aggregate it allows a formal occasion to refer the solid solution having composition close to Ge-acmite to one more structural modification of monoclinic C2/c germanates with pyroxene structure – "C2/c - III" - distinguished from hedenbergite ("C2/c - II"). Let's notice, that for acmite $\text{NaFeSi}_2\text{O}_6$ earlier also it has been established sp. gr. C2/c, but authors do not know about results of similar detailed investigation of a solid solution acmite - hedenbergite.

Financial support of the RFBR, the grant 01-05-64724

References:

1. Novikov G.V., Koshchug D.G. and Rager H. Alternative analysis of room temperature IR spectra of quartz. (1997). Proceedings of the 39-th International Geological Congress, Netherlands. 217-221.
2. Novikov G.V., Sipavina L.V., Sokolov Yu.A. (1998). Local fields and structure features of two Ca-Fe monoclinic chain germanates. 7, 58.
3. Novikov G.V., Sipavina L.V., Sokolov Yu.A. (1999). Comparative crystal chemistry of mantle silicate and their structural analogs. Experiment in Geosciences. 8, 88-90.
4. Hugh-Jones D.A., Woodland A.B., Angel R.J. (1994). The structure of high-pressure C2/c ferrosilite and crystal chemistry of high-pressure of C2/c pyroxenes. Amer. Miner. 79, 1032-1041.
5. Angel R.J., Chopelas A., Ross N.L. (1992). Stability of high-density clinoenstatite at upper-mantle pressure. Nature. 358, 322-324.

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(21) 2003
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2003
URL: http://www.segis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003/mineral-20e.pdf
Published on July 15, 2003

© Department of the Earth Sciences RAS, 1997-2003
All rights reserved