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SYNTHESIS OF $(Na_{1-x}Li_x)MnFe^{3+}_2(PO_4)_3$ (WITH x=0 TO 1) COMPOUNDS WITH THE ALLUAUDITE STRUCTURE TYPE: THE CRYSTALLOCHEMICAL ROLE OF LITHIUM

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Alluaudite occurs as a mineral in numerous granitic pegmatites. In the Buranga mine, Rwanda, its chemical composition is ideally close to NaMnFe³⁺₂(PO₄)₃ (Fransolet, 1980).

A compound with the same composition and exhibiting the alluaudite structure has been synthesized by solid state reaction in air and at 950°C, corresponding to its congruent fusion temperature. Similarly, compounds of the $(Na_{1x}Li_x)MnFe^{3t}_2(PO_4)_3$ series were prepared with different x values: 0.25, 0.5, and 0.75. These compounds appear to be pure according to their diffraction patterns. For x = 0.8 and 1, the material is not pure any more: the alluaudite-like phase is mixed with $Li_3Fe^{3t}_2(PO_4)_3$ (Winand et al., 1990). For all the synthesized compounds the unit-cell dimensions were calculated and the infrared spectra were recorded.

Additionally, for $(Na_{0.55}Li_{0.45})MnFe^{3+}_{2}(PO_{4})_{3}$ obtained as crystals and wet chemically analyzed, the crystal structure has been solved in the space group C2/c, with the cell parameters: a 11.988(2), b 12.500(3), c 6.392(1) Å and β 114.67(3)°. According to Moore (1971), M(1) is occupied by Mn and M(2) by Fe³⁺; X(2) is empty whereas 0.5 Na occurs in X(1). Li and a small amount of Na reside in a site with a (4 + 4) coordination polyhedra, different of X(2).

References

Fransolet, A.-M. (1980): *Mineral. Mag.* 43, 1015-1023. Moore, P.B. (1971): *Amer. Mineral.* 56, 1955-1975. Winand, J.-M., Rulmont, A. & Tarte, P. (1990): *J. Solid State Chem.* 87, 83-94.

Keywords

CRYSTALCHEMISTRY PHOSPHATE

ALLUAUDITE LITHIUM

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LARGE-ANGLE CONVERGENT BEAM ELECTRON DIFFRACTION: MICROSCOPIC STRAIN DETERMINATION IN TETRAGONAL GARNET

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Large Angle Convergent Beam Electron Diffraction (LABCED) provides a powerful method of recording crystal rocking curves. In contrast to X-ray rocking curves, electron rocking curves are not restricted to low order reflections and have the resolution of the transmission electron microscope. LABCED has the advantage of combining both real space and reciprocal space information. LABCED patterns are obtained by using an incident electron beam with a very high convergence (typically 3°) which is focused below or above the specimen.

LABCED has now been used to measure the microscopic spontaneous strain in tetragonal garnet. The ferroelastic macroscopic spontaneous strain is expressed as the macroscopically measured relative change of the low symmetry lattice constants to the extrapolated high symmetry lattice constant at the same temperature and pressure. In the case of the high temperature high pressure phase

transition of majorite-pyrope garnets the cubic lattice constants for the extrapolation are not accessible at high temperatures and high pressures. In LACBED determination of the microscopic strain this extrapolation is not necessary.

Cubic $Ca_3Mn_2Ge_3O_{12}$ transforms at ca. 250°C to a tetragonal garnet structure. $Ca_3Mn_2Ge_3O_{12}$ garnet shows the same symmetry change as tetragonal majorite-pyrope garnets. At the ferroelastic phase transition ferroelastic twins develop. Across the ferroelastic domain walls {011} the tetragonal plane (001) is rotated into the tetragonal plane (100) due to the tetragonal spontaneous strain. The microscopic spontaneous rotation ρ of this rotation is proportional to the spontaneous strain across the twin wall. The spontaneous rotation produces the shift of the Bragg contour [008]* relative to the Bragg contour [800]* in LACBED patterns. At room temperature the spontaneous rotation is $\rho=0.22$ rad and the tetragonal spontaneous microscopic strain is $^{1}/_{3}$ ρ .

Kevwords

LACBED

tetragonal garnet

microscopic strain domain boundary

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INTERCRYSTALLINE EXCHANGE OF AI AND Fe³⁺ BETWEEN GRANDITE AND EPIDOTE SOLID SOLUTIONS: A REVERSAL OF PREFERENCE

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The intercrystalline distribution of Al and Fe³ between grossularandradite and clinozoisite-epidote solid solution series were determined experimentally within the temperature range of 500 -650°C at 0.3 GPa, HM-buffer.

The Al-Fe exchange reaction exhibits a remarkable dependence with composition and temperature, due to the existance of two intermediate solvi along the join clinozoisite-epidote. The solvi project in the range of $X_{Fe}^{epi} = 0.54-0.76$ and $X_{Fe}^{epi} = 0.24-0.50$ at 500°C/0.3 GPa, HM buffer, respectively. Both miscibility gaps are separated by a narrow range of single-phase epidote at about $X_{Fe}^{epi} = 0.52$.

According to the intercrystalline partition data a reversal in preference of Al and Fe³⁺ occurs at $X_{\rm Fe}^{\rm grt} = 0.41 / X_{\rm Fe}^{\rm epi} = 0.90$. The azeotropic behaviour is caused by the nonideal thermodynamic mixing properties of grandites and epidotes.

The application of the distribution curves on grandite/epidote pairs on skarn and calcsilicate rocks demonstrates that the intercrystalline Al-Fe exchange reaction between grandite and epidote can be used as a geothermometer with regard to the composition of the equilibrated epidote phases.

Keywords

grossular - andradite

clinozoisite - epidote

Al-Fe exchange

geothermometer