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SYNTHESIS, STABILITY AND CHARACTERISATION OF A SYNTHETIC AMPHIBOLE WITH COMPOSITION $\text{NaNaMgMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$: SOME PRELIMINARY DATA

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Several experiments on amphibole synthesis in the $\text{Na}_2\text{O-MgO-SiO}_2\text{-H}_2\text{O}$ system yielded compositions close to the ${}^{\text{B}}\text{Mg}$ analogue of richterite, $\text{NaNaMgMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ (e.g. Witte et al. 1969). Maresch et al. (1991) described an amphibole composition with three protons per formula unit, $\text{NaNa}_2\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$, related to the former by the NaHMg_{-1} exchange. Four syntheses were carried out in the T range 750-900°C at 50°C intervals at 4 and 5 kbar. Run powders were studied by X-ray diffraction, SEM-EDAX and IR spectroscopy. They are dominant amphibole with very small amounts (< 5%) of quartz. XRPD patterns were indexed in the C2/m space group, and cell dimensions were refined by the Rietveld method. A strong decrease in the *a* and β parameters (and in the cell volume) is observed at increasing *T*, whereas *b* and *c* are virtually constant. This evidence suggests a change either in chemistry or in structural conformation. Infrared spectra for the 750 and 800°C products shows a well-defined doublet with a sharper band centred at 3715 cm^{-1} , and a second broader band centred at 3745 cm^{-1} , which is due to several (possibly three) overlapping components. This band is compatible with the data of Maresch and Langer (1976) and Raudsepp et al. (1991), and can be ascribed to an OH group interacting with Na strongly delocalised at the A-site. Beyond 800°C, an additional band appears at 3674 cm^{-1} , which is assigned to an OH group pointing toward an empty A-site (partial solid-solution toward cummingtonite), indicating that the amphibole formed at higher *T* departs from the nominal stoichiometry. The intensity of this band linearly increases with the temperature of synthesis. Using the curves of Hawthorne et al. (1997) we calculate that the 850°C sample has 5% and the 900°C sample 14% empty A-site.

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THE Na-Li SUBSTITUTION AT THE M4 SITE IN CLINOAMPHIBOLES:

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The B-site occupancy is a key feature in amphibole crystal-chemistry, and is the base of amphibole classification and nomenclature (Leake et al., 1997). The solid solution between ${}^{\text{B}}(\text{Fe}, \text{Mg}, \text{Mn})$ and ${}^{\text{B}}\text{Na}$ amphiboles is restricted in natural samples (Deer et al., 1999), whereas recent work on metasomatic episyenites of the Pedriza Massif (Spain) showed nearly complete solid solution between ${}^{\text{B}}\text{Li}$ and ${}^{\text{B}}\text{Na}$ amphiboles both with A-filled and A-empty sites (Oberti et al., 2000; Caballero et al., 2002). To verify the limits and stability of solid-solution terms, syntheses were done along the ferri-clinoferroholmquistite $\text{Li}_2\text{Fe}^{2+}\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ - riebeckite $\text{Na}_2\text{Fe}^{2+}_2\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ join. Experiments were done at 500°C and 4 kbar in an Internally Heated Pressure Vessel (IHPV), with a Ar-H₂ mixture as pressure medium, a Shaw membrane controlling buffering conditions, but a gold capsule limiting the hydrogen diffusion (Chou, 1987; Iezzi et al., 2001). The run products are amphibole and quartz < 5%. Amphiboles occur as acicular crystals 1 x 1-2 μm in size, thus precluding EMP analysis and single-crystal-refinement. They were analysed by XRPD, SEM-EDAX, FTIR and Mossbauer methods. XRPD patterns were fully indexed in the C2/m space group, and cell dimensions refined by the Rietveld method. Both *a* and β increase as a function of the ${}^{\text{B}}\text{Na}$ content, whereas *b* and *c* are constant over the entire join. The cell volume increases linearly. IR spectra in the OH-stretching region show a single sharp band relative to the ${}^{[\text{M1}]}\text{Fe}{}^{[\text{M1}]}\text{Fe}{}^{[\text{M3}]}\text{Fe-OH-}[\]$ configuration; it is centred at 3614 cm^{-1} for the ${}^{\text{B}}\text{Li}_2$, and linearly shifts to 3618 cm^{-1} for the ${}^{\text{B}}\text{Na}_2$ composition. Mossbauer spectra collected for the ${}^{\text{B}}\text{Li}_2$, ${}^{\text{B}}\text{Na}_2$, and ${}^{\text{B}}\text{LiNa}$ compositions, show Fe^{2+} distributed between M1 and M3, and Fe^{3+} ordered at M2; with a constant $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio of 3:2. These evidences confirm that the products are close to the nominal compositions, and that the ${}^{\text{B}}\text{Na} \rightleftharpoons {}^{\text{B}}\text{Li}$ exchange was complete.

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CRYSTAL-CHEMICAL APPROACH TO DESIGN OF NOVEL ACTINIDE WASTE FORMS

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Searching for host phases for long-lived actinides immobilization is a very actual problem. Promising host for actinide wastes are garnet-structure phases of general formula (AVIII)₃(BVI)₂[XO₄]₃. It was found that incorporation of Ce⁴⁺, U⁴⁺, and Pu⁴⁺ into REE - Al - Ga garnets was restricted by 4 - 6 wt.% only (1). In order to select the garnet-type compounds with higher solubility in respect of tetravalent actinides a structural-chemical research has been carried out. These elements can be inserted into the [A]VIII-sites of the structure if low charge and large cations occupy the [X]IV and [B]VI sites. The largest ion, which can occupy both IV- and VI-coordinated sites of the garnet structure, is Fe³⁺ (rIV = 0.049 nm, rVI = 0.065 nm). Its radii are larger than those of Al³⁺ (rIV = 0.039 nm, rVI = 0.054 nm) or Ga³⁺ (0.047 nm, 0.062 nm). Hence, from crystal-chemical point of view, it can be expected that ferrite garnets have the highest loading capacity relatively to actinides. For confirmation of this conclusion about thirty ceramics were fabricated. The runs were performed by cold pressing mixtures composed of CaO, Fe₂O₃, Al₂O₃, SiO₂, ZrO₂, Gd₂O₃, UO₂, ThO₂ or PuO₂ and their sintering in air at 1400 - 1500°C for 1 - 2 hours. Initial batch compositions were prepared taking into account ideal garnet stoichiometry A₃B₂[XO₄]₃ with various possible schemes of the three structural sites occupation. The samples were studied using XRD, SEM/EDS, and TEM. Maximal solubility of actinides reached up to 30 wt.% Th, 20% U, and at least 15% Pu was observed in the ferrite garnets (Ca,An,Gd)₃(Zr,An,Fe)₂Fe₃O₁₂, An = U, Th, or Pu.

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FINE STRUCTURE OF INFRARED OH-STRETCHING BANDS IN NATURAL AND HEAT-TREATED AMPHIBOLES OF THE TREMOLITE-FERRO-ACTINOLITE SERIES

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Fine structure in the principal OH-stretching bands of amphiboles of the tremolite-ferroactinolite series have been examined. In samples with partly filled A-sites, a broad (composite) band is observed at 3725~3680 cm⁻¹ and is assigned to mainly two types of configurations: (M1 M1 M3)-OH^{-A}(Na,K):^{T1}Si^{T1}Al in which Al occurs at the T1 site, and (M1 M1 M3)-OH^{-A}(Na,K)-^{O3}(O²⁻,F⁻,Cl⁻); the component of (M1 M1 M3)-OH^{-A}(Na,K):^{T1}Si^{T1}Si configuration is small, because Na and K at the A site are locally associated with Al at an adjacent T1 site. In tremolite, manganoan tremolite and Fe²⁺-poor actinolite, a weak shoulder on the principal A band at

~3669 cm⁻¹ is assigned to the configuration M⁴C a^{M4}(Mg, Fe²⁺, Mn²⁺, Na): (MgMgMg) - OH^{-AV}:^{T1}Si^{T1}Si(V=vacancy). Fine structure in the principal bands B (B' and B'') and C (C' and C'') are also observed: the higher frequency band B'' is assigned to ^{M1}Fe²⁺ ^{M1}Mg ^{M3}Mg-OH^{-AV}, and the lower frequency band B' to ^{M1}Mg^{M1}Mg^{M3}Fe²⁺-OH^{-AV}; the higher frequency band C' is assigned to ^{M1}Fe²⁺^{M1}Fe²⁺^{M3}Mg-OH^{-AV} and the lower frequency band C'' to ^{M1}Mg^{M1}Fe²⁺^{M3}Fe²⁺-OH^{-AV}. Supposing a random distribution of Mg and Fe²⁺ at the M1 and M3 sites, the band intensity for B'' is twice that of B' and that for C'' is twice that C', respectively. Some broad OH-stretching bands attributed to (M1 M1 M3)-OH^{-AV}:^{T1}Si ^{T1}Al are observed at 3640 ~ 3580 cm⁻¹. In amphiboles of the tremolite-ferroactinolite series which show substantial B=(MgMgFe²⁺)-OH stretching band, a new OH-stretching band at around 3641 cm⁻¹, E, appear near the principal C band at around 3643 cm⁻¹ on heat treatment. The shape of this band E is similar to that of the original band B, and is assigned to (MgMgFe³⁺)-OH stretching and its local configuration is O²⁻-(MgMgFe³⁺)-OH. A weak and broad band A** appear at ~3690 cm⁻¹ in some Na-bearing actinolites, and is ascribed to the (MgMgMg)-OH^{-A}Na-O²⁻ configuration.

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FINE-STRUCTURE IN THE INFRARED OH-STRETCHING BANDS IN ANTHOPHYLLITE

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The principal infrared OH-stretching bands in anthophyllites show fine structure due to the occurrence of two symmetrically distinct OH groups in the crystal structure. There are two distinct tetrahedral double-chains in the orthorhombic amphibole structure, the A-chain and the B-chain. The B-chain is much more rotated than the A-chain, and the stereochemistry around each of the OH sites suggests that the hydrogen bond to the bridging anion(s) of the B-chain is stronger than the hydrogen bond to the bridging anion(s) of the A-chain. This difference is sufficient to shift the frequency of the principal OH₂ stretching band(s) ~ 5 cm⁻¹ downward and allow resolution of the two bands in the infrared spectrum. This distinction could allow detection of possible OH-F ordering between the two distinct monovalent-anion sites in the orthorhombic amphibole structure.