

21. STRUCTURAL RESULTS FROM METHODS OTHER THAN DIFFRACTION

Recently, we have obtained materials (5) reported to be copolymers with varying comonomer ratios of hydroxybutyrate (HB) to hydroxyvalerate (HV). The ratios of HB to HV run from 98:2 to 53:47 as determined by ^1H NMR. The techniques of x-ray diffraction, NMR spectroscopy (^1H and ^{13}C) and differential scanning calorimetry (DSC) have been used to determine whether these materials are completely random or block copolymers. X-ray diffraction has revealed some interesting peculiarities of the polymer morphology. It appears that for ratios of HB:HV of 4:1 and greater the HV units have little effect on the PHB crystal structure other than to increase the disorder of the crystallites as shown by x-ray diffraction measurements of crystallinity and perfection. At an HB:HV ratio of approximately 1:1 the crystalline structure is the same as that of pure PHV with no indication of any PHB crystallites being present. These results are somewhat unusual in view of the indications from high resolution solution NMR spectroscopy that the copolymers are fully random. It may be that isomorphous replacement of one comonomer by the other occurs in these materials.

References

1. R. Alper, D.G. Lundgren, R.H. Marchessault and W. A. Côté, *Biopolymers*, 1, 545 (1963).
2. M. Yokouchi, Y. Chatani, H. Tadokoro, K. Teranishi and H. Tani, *Polymer*, 14, 267 (1973).
3. M. Yokouchi, Y. Chatani, H. Tadokoro and H. Tani, *Polymer J.*, 6, 248 (1974).
4. J. Cornibert and R.H. Marchessault, *J. Mol. Biol.*, 71, 735 (1972).
5. Materials kindly provided by Dr. Paul Holmes, Agricultural Division, Imperial Chemical Industries, Billingham, U.K.

21.1-6 ELECTRON PARAMAGNETIC RESONANCE OF Ni^{2+} IN FORSTERITE Mg_2SiO_4 . By S. Hosoya, H. Rager and S. S. Hafner, Institute of Mineralogy, University of Marburg, 3550 Marburg, West Germany.

In olivines $(\text{Fe},\text{Mg})\text{SiO}_4$, Ni^{2+} ions may be substituted for Mg and Fe^{2+} at the octahedral sites M1 and M2. According to Rajamani et al. (*Amer. Mineral.* (1975) 60, 292), Bish (*Amer. Mineral.* (1981) 66, 770), and Nord et al. (*Amer. Mineral.* (1982) 67, 1206), Ni^{2+} in synthetic and natural phases with compositions of $1.5 > \text{Ni} > 0.5$, $1.0 > \text{Mg} > 0.3$, and $0.3 > \text{Fe} > 0$ shows strong preference for M1. This is further supported by Annersten et al. (*Amer. Mineral.* (1982) 67, 1212) for synthetic phases $1.8 > \text{Fe} > 0.5$ and $1.5 > \text{Ni} > 0.2$. According to Smyth and Tafto (*Geophys. Res. Lett.* (1982) 9, 1113), exchange kinetics of Ni between M1 and M2 is rapid, exchange being observable in a natural single crystal $\text{Mg}_{1.96}\text{Fe}_{0.18}\text{Ni}_{0.04}\text{SiO}_4$ at temperatures as low as 300°C after heating for 6 days.

We have studied electron paramagnetic resonance of Ni^{2+} at 9.52 and 35 GHz frequencies in a crystal $\text{Mg}_{1.96}\text{Ni}_{0.04}\text{SiO}_4$ grown with the floating zone technique. A strong Ni^{2+} spectrum was observed at 35 GHz which has to be assigned to a position 4a of Pnma because of symmetry reasons. It is, therefore, attributed to M1. The diagonalized terms of the tensor g are $g_x = 2.194$, $g_y = 2.160$, and $g_z = 2.188$. The axial and rhombic fine structure terms are $D = -1186.2$ GHz and $E = -17.37$ GHz, respectively. The value $3D/E = 0.044$ is very small, being indicative of rhombic distortion of M1 in Mg_2SiO_4 by Ni^{2+} .

A Ni^{2+} spectrum at M2 could not be observed. However, because of the distinct geometrical distortion of M2 compared to M1, a higher frequency than 35 GHz may be needed to observe it. We do, therefore, not conclude that Ni^{2+} at M2 is completely absent.

The same crystal was heated at 300°C for 7.5 days, 600°C for 5.5 days, 900°C for 2.5 days, and 1150°C for 1 day. The crystal was quenched after heating. Although precise, relative intensities could not be measured because of lack of the M2 pattern, it was thought that significant Mg, Ni exchange between M1 and M2 would influence the line intensities of the observed M1 spectrum. Neither occurrence of new Ni^{2+} resonance lines nor a change in the intensities of the M1 spectrum could be detected.

21.1-7 VIBRATIONAL SPECTRA AND STRUCTURAL PROPERTIES OF LiNaCO_3 . By Ernst-Jürgen Zehnder

Inst. f. Anorg. Chem., J.W. Goethe Universität D-6000 Frankfurt-50 and MPI f. Festkörperforschung, D-7000 Stuttgart-80

Isotopic substitution and temperature dependent IR-, FIR- and Ramanspectra are used to get structural information and to discuss anion disorder and structural phase transition in LiNaCO_3 .

An intermolecular vibrational coupling of the carbonate out-of-plane vibration ν_2 is observed in lithium sodium carbonate comparable to those found in carbonates, nitrates and borates with the aragonite structure and in silver carbonate. (E.-J. Zehnder, W. Sterzel, *Spectrosc. Lett.* (1982) 15, 463; E.-J. Zehnder, *J. Mol. Struct.* (1983) 98, 49).

In partially ^{13}C substituted lithium sodium carbonate this coupling results in a fine structure of the infrared active ν_2 band. Our cyclic chain model permits a quantitative description of this fine structure assuming two types of different carbonate ions planar superimposed to form linear chains. The different absorptions can be correlated to single ions, doublets, triplets etc. of one isotopic species in the matrix of the other isotopic ion. The coupling strengths comparable to those in barium carbonate require in chain carbonate-carbonate distances some more than 320pm.

21. STRUCTURAL RESULTS FROM METHODS OTHER THAN DIFFRACTION

The absence of the total symmetric ν_1 vibration in the infrared spectra indicates a site symmetry of (nearly) D_3 (=32) for the carbonate ion. From X-ray powder data (M. Christmann, N. Sadeghi, G. Papin, Rev. Chim. Min. (1978) 15, 312) a monoclinic supercell ($a=43 \times 825$ pm, $b=3 \times 825$ pm, $c=330$ pm, $\beta=91.7^\circ$, room temperature) was found and transitions into two hexagonal phases at 563K and 688K were observed. Thus the carbonate ions may be located parallel (001).

The fivefold splitting of the ν_1 band in the Ramanspectra disappearing with the transformation into the high temperature phases can be explained by the presence of more than two different carbonate ions in the unit cell or by unit cell splitting.

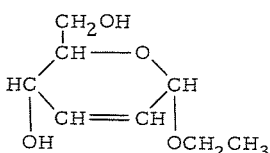
The Li-O lattice vibrations identified by $7\text{Li}/^6\text{Li}$ substitution indicates that several fourfold coordinated Li atoms are present in the unit cell. FIR-spectra between 4K and 300K show an increase of splitting of modes due to carbonate vibrations and carbonate-sodium vibrations at about 250K.

By preliminary experiments a broad anomalous contribution to the lattice heat capacity has been detected in the investigated temperature range of 100K to 300K.

21.1-8 X-RAY AND NMR STUDIES OF TWO FORMS OF AN ENOPYRANOSIDE. By L. M. Wingert and G. A. Jeffrey, Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260 USA.

The x-ray crystal structures of forms I and II of ethyl 2,3-dideoxy- α -D-erythro-hex-2-enopyranoside are compared with their ^{13}C CP/MAS NMR spectra. Both crystal forms are in space group $P2_12_12_1$. In form I ($a=11.220$, $b=18.387$, $c=8.509$ Å, $Z=8$), there are two molecules per asymmetric unit; in form II ($a=9.106$, $b=21.940$, $c=4.762$ Å, $Z=4$), there is one molecule per asymmetric unit. The NMR spectrum of form I shows two peaks for all but one of the eight carbon atoms per molecule; form II shows single peaks. Transition of form II to form I has been observed by NMR. Further NMR studies and comparisons of thermal motion and hydrogen-bonding between molecules in the two crystal forms may lead to assignment of the NMR spectral peaks to carbon atoms of the two symmetry-independent molecules of form I and to an understanding of the nature of the transition between the two crystal forms.

This work is supported by National Institutes of Health Grant No. GM-24526.



21.1-9 IR-SPECTRA OF HYDROXYL S: IMPLICATIONS OF SOME AMPHIBOLE STRUCTURES. By I.L. Lapides, Vinogradovs Institute of Geochemistry, E.K. Vasilyev, Institute of Earth Crust, Siberian Branch, Academy of Science USSR, Irkutsk, 664033, USSR. Amphiboles were studied by IR-, Mössbauer spectroscopy and X-ray powder diffraction: a tremolite, Na-tremolite (1), riebeckite (2) and arfvedsonite with anomalous high sodium contents (3). Isotopic substitution in hydroxyl groups ($\text{OH} \rightarrow \text{OD}$) was carried out by hydrothermal influence of D_2O upon these amphiboles (Pt-ampule, $P=76-110$ MPa, $T=450-470$ C, an exposition 5-7 days), which did not change parameters and metrics of amphibole unit cells.

	Ca	Na	K	Mg	Fe ²⁺	Fe ³⁺
1	1.88	0.82	0.15	4.91	-	0.06
2	0.25	1.81	0.17	0.03	2.54	2.04
3	0.05	2.94	0.39	0.09	2.83	1.34

	Al _{VI}	Ti	Mn	Li	Si	Al _{IV}
1	0.02	0.01	-	-	7.84	0.16
2	0.09	0.09	0.09	0.13	7.83	0.17
3	0.16	0.12	0.22	0.18	8.06	-

The hydroxyl absorption bands (for ν_{OH} and ν_{OD}) being assigned to hydroxyl groups linked to three cations. This was accomplished first time for the Na-tremolite. Computed populationship of M_1 , M_3 octahedra of the amphiboles studied, based on the proposed relationship agree with results of chemical analysis. The complete deuterization of these amphiboles of the kinetics of isotopic exchange to data IR-spectroscopy.

Due to analyses of experimental data it was suggested that in the Na-tremolite and the iron arfvedsonite the sodium partly enters in the octahedric positions. The greatest A-position in Na-tremolite is up to 0.33 populated by sodium, while for arfvedsonite this takes place for 0.5. The parameters of the unit cell do not contradict this hypotese. The data available permit to propose that sodium enters into the M_2 and M_4 sites.

Consequently the crystal chemical formulae should be changed. An increase of the fraction of vacant A-sites is probably stimulated by considerations of compensation of dynamic stresses in the crystal lattice, which arise in the process of the accomodation of actual unit cells with substantially differing emplacement of the octahedra.

Hydroxyl stretching bands in Na-tremolite

ν_{OH} cm ⁻¹	ν_{OD} cm ⁻¹	A M_1 M_3 M_4
3650	2703	□ Mg Mg Fe ³⁺
3675	2717	□ Mg Mg Mg
3687	2728	Na Fe ²⁺ Fe ²⁺ Al
3704	2742	Na (R ²⁺ , R ³⁺)
3710	2760	Na Mg Mg Fe ²⁺