

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.

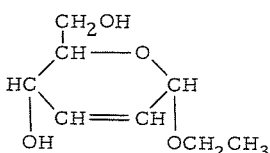
The Li-O lattice vibrations identified by $7\text{Li}/^6\text{Li}$ substitution indicates that several fourfold coordinated Li atoms are present in the unit cell. FIR-spectra between 4K and 300K show an increase of splitting of modes due to carbonate vibrations and carbonate-sodium vibrations at about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

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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 _{IV}	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⁺