

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

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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

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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.