INFRARED SPECTRA OF AMORPHOUS OXIDES

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SUMMARY

Amorphous oxides of Cr^{3+} , V^{5+} , Mn and Pb^{4+} have been prepared and chracterized by X-ray diffraction, thermal analysis and other methods. The infrared spectra are compared to those from crystal modifications.

INTRODUCTION

In several fields of materials research infrared (IR) spectra are studied in order to discriminate between the amorphous state and the crystal modifications of solid phases. We once investigated amorphous phosphor-nitrogen compounds (ref.1). All polymer scientists know about the presence of crystalline and amorphous portions in polyethylene and how these determine, e. g., the pattern of CH_{2} rocking vibrations in the IR spectrum around 720 cm⁻¹. The amorphous material has no unit cell and no correlated vibrations and therefore just one IR rocking absorption also known from the melt (ref. 2). We note as the specific feature of the amorphous state that a splitting of bands which has its cause in crystal structure is absent.

Amorphous metal oxides have a practical importance as surface species and in galvanic energy sources (ref.3). For a definition of their amorphous state it is important that they do not show X-ray diffraction lines, but rather a continous refraction (example: fig. 1). Furthermore, an enthalpy of crystallization should be observed in differential thermal analysis (DTA).

PREPARATION OF AMORPHOUS NETAL OXIDES

 $a-Cr_2O_3$ was prepared by heating ammonium dichromate in vacuo to 488 K. A mixture of brown and green spherules results. They are sorted manually. The green ones are highly crystalline, the brown ones amorphous (fig. 1). Enthalpy of crystallyzation is observed at 678 K, cf. to ref 4.

Fig. 1. X-ray diffraction, goniometer measurements 10 to 80 degrees, Cu Ka. Both samples from decomposition of ammonium dichromate. Above: green particles, highly crystalline, below: brown particles, amorphous.



 $a-V_2O_5$ is obtained from hydrolytic decomposition of vanadyl trichloride. This was dissolved in benzene and left to the reaction with atmospheric humidity. The product did not show the pure orange-yellow, but some greenish-brown discoloration. Some reduction had occured, as was investigated by X-ray absorption and ESCA together with K. H. Hallmeier, Leipzig. Crystallization occures around 630 K

 $a-MnO_2$: Manganese nitrate in aqueous solution was heated. By the addition of polyvinyl alcohol, e.g. 0.45g of the polymer to 24 ml of water, $a-MnO_2$ is stabilized. After washing by water and acetone, some organic matter remains in the sample.

a-PbO₂ was obtained by hydrolysis of the tetra-acetate of lead.

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a-Cro03

A comparison of the IR-spectra of the corundum type and the amorphous structure of the oxid discloses slight impurities in the latter: adsorbed water (ca. 1600 cm⁻¹), traces of dichromate (1400 cm⁻¹), and CrOH groups (928 cm⁻¹). IR spectroscopy achieves much lower detection limits than X-ray diffraction with such inorganic groups.

Main result is, that five different CrO-vibrations (ref.5) of the corundum structure are replaced by one broad and rather symmetric band. A slight inflection in the flank of the broad absorption region at wavenumbers around 300 (visible in the FT-IR spectrum) may indicate that the Cr-Cr vibrations conserve their nature. $a-V_2O_5$

The structure of vanadium pentoxide is not so simple as the corundum structure. Each V-atom exhibits a V=O-bond directed to the apex of the tetragonal pyramid which forms its coordination polyhedron. This is really a double bond, as its wavenumber shows (fig.3). The bases of the pyramids form a dense girder since O-atoms share three pyramids. But one O-atom of each V is situated in a bridge of remarkable length to the next of the girders that

traverse the structure. The V=O-bonds preserve their identity in the amorphous material with negligible broadening. With the VOVbridges, lowering of the wavenumbers and broadening occurs, apparently because of longer VOV-distances and loss of uniformity in bond angles. Amalgamation occurs just for two bands: The crystal shows absorption at 605 cm⁻¹ and 472 cm⁻¹ from vibrations parallel axis a and axis b, respectively, within the V0 planes of the girders. In the amorphous material there are no longer such axes.

A separate band followes at 378 cm^{-1} . It represents the bending vibration belonging to V=0. Definition of an angle requires one further atom at least. Non-uniformity of angles in the a-phase causes a broadening which contrasts to the sharpness of V=0 stret-ching. (The assignments of bands in vanadium pentoxide are well established, ref. 6.)



IR transmission spectra. Trace crystalline, amorphous. Powders pressed in KBr. Spectrometer CZ M80.

DTA shows that enthalpy of crystalliztion is released from 573 K to a maximum at 629 K etc. According to the IR spectrum of a sample treated at 573 K one may obtain at this temperatur crystal-like VOV-bridges. At 648 K crystal-like V=O-bending developes, but the sample is still amorphos in regard to the order within the denser

regions in the unit cell. The example shows how IR spectroscopy may track down disorder to certain elements of structure. a-MnO₂

Both the IR spectra (fig.4) contain bands from impurities since natural pyrolusite is shown in order to represent the crystal. Organic matter from the stabilizer of the amorphous state is visible at 1560 cm⁻¹ and at 1400 cm⁻¹ together with nitrate. Thermogravimetry and differential thermal analysis were important in establishing these interpretations. MnOH appears between 1000 and 1110 cm⁻¹.

Fig. 4. IR transmission spectra of manganese dioxides. Trace _____ crystalline (pyrolusite), amorphous. Conditions as in fig. 2 and 3.



The two intense absorptions of the crystal correspond to unisonant vibration of the oxygen lattice against the manganes lattice parallel and normal to the tetragonal axis. This is meaningless for the a-phase. One broad band appears. It is not symmetric: at lower wavenumbers, the second degenerate vibration keeps its identity. This band arises from one half of the O-atoms moving in opposite direction to the other half. A low IR intensity is expected, and this must be taken as the proof for the assignment, since single crystals of manganes dioxide which would allow reliable measurements with reflected polarized radiation have not been found or prepared (ref.7). From the behaviour of the second degenerate vibration when going to the amorphous state we learn that phase relations may retain their part in defining certain vibrations in an a-phase.

Thermogravimetry and DTA indicate various changes. According to IR spectra taken from samples after treatment at 429 K the contents of water and organic matter are reduced, but still present. Oxydation of the carbon compounds apparently occured by reduction of manganese ions to 3+, since the sharp nitrate absorption at 1400 wavenumbers appeares undiminished, and a short-wave shoulder to the broad MnO-absorption has formed, which we attribute to the 3+-Ions joined by oxygene vacations. At 488 K a strong exothermic effect sets in, and IR-spectra taken afterwards show disappearance of the organic matter and separation of the broad MnO-band into the two components charactristic of the crystallized modifications. By the difficulties introduced by the organic stabilizers it was only the combination of observations that could reveal the temperatur of 488 K as connected with the crystallization process.

In the course of former investgations into the series of manganese dioxide modifications epsilon-forms had been defined. The IR spectra are dominated by the uniform broad region of MnO-absorption (ref. 8,9) which now is confirmed to be characteristic of the amorphous state. When special X-ray patterns had been ascribed to such preparations (ref. 8), one has to assume that these did contain crystallized impurities which caused the weak but various diffraction lines while the main portion of the sample produced diffuse scattering which was not recognized.

a-Pb02

in fig. 2 and 3.

This compound was of much concern to us since a vibrational



spectrum of PbO₂ was not known. Electroconductivity and therefore

the absorption of the freely moving electrons obscures any vibrational bands. The formation of conduction bands is a lattice property should be reduced in amorphous material. Figure 6 shows the and conductivity continuum, best known from graphite. But in the spectrum of our partially amorphous material some minor impurities appear and especially a broad band with an absorption maximum at 500 wavenumbers. This should belong to PbO-vibrations. Lead dioxide and manganese dioxide (in its tetragonal modification) are isostructural. In such cases there is a crystallographic parameter by which solids may be put into a row so that wavenumbers of their lattice vibrations form a systematic series: volum density ρ , defined as volume of the ions taken as spheres with their ionic radii, divided by volume of the unit cell (ref.10). This comparison $\rho = 0.86 \ \mu Mn0 = 560 \ cm^{-1}$ a-MnO, here gives:

 $a-Pb0_{2} \quad \rho = 0.61 \quad rPb0 = 500 \text{ cm}^{-1}.$

In a more densely packed unit cell the elastic forces are evidently stronger.

CONCLUSIONS

IR spectroscopy appears as a powerful method for the characterization of amorphous solids. It seems that the principles by which the differences between the spectra of crystalline and amorphous modifications can be understood become well apparent from the examples of amorphous metal oxides.

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