

Spectral Evidence of Aluminium Oxyfluorides in Quenched Cryolithic Melts

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The composition of the electrolytic bath is one of the major parameters when trying to optimise the efficiency of the Hall-Heroult electrolysis process. In this context the structure of the bath is crucial, both for an understanding of the electrochemical reactions, and to be able to recognise and predict the properties of the melt.

Although it is well accepted that aluminium oxide exists as oxyfluoride species in the melt,¹ the exact structure of these complexes is obscure. Due to the very high melting point, direct spectroscopic analysis of the melt is very difficult. IR reflectance spectroscopy of the melt has been reported,² although bandwidths are very large. However, some authors have tried to obtain information on the melt indirectly from studies of quenched samples.^{2–4}

In the present work, IR absorption spectrometry and X-ray powder diffraction have been used to examine equimolar mixtures of cryolite and chiolite with alumina added.

Experimental

The samples were prepared from natural cryolite and chiolite, hand-picked at Ivigtut, Greenland. The alumina used was a Merck product (art. 1097, *p.a.*).

The heating of samples was carried out in an open platinum crucible and the samples were quenched by pouring the melt directly into water (0°C). Two other quenching methods were also investigated, viz. pouring onto an aluminium plate (water cooled, 0°C), or into liquid nitrogen.

After quenching, the samples were dried at ca. 120°C for 2 h to remove moisture. Annealing of the samples was carried out by heating them to 700°C, and then allowing them to cool slowly (ca. 3°C min⁻¹).

The IR absorption spectra were recorded using KBr pellets, with a Bruker IFS 113v FTIR spectrometer having nominal resolution of 4 cm⁻¹. X-ray diffraction patterns were recorded with a Philips X-ray diffractometer, using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$).

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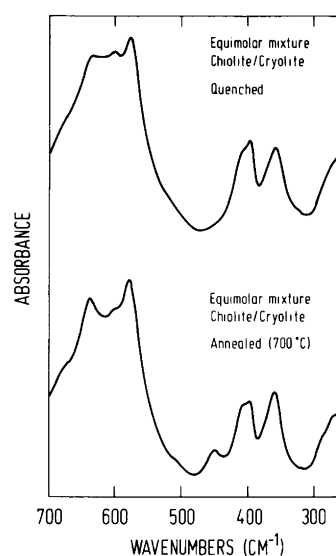


Fig. 1. IR spectra of equimolar mixtures of chiolite and cryolite. Above: Sample quenched in water (0°C) and dried. Below: Same sample annealed at 700°C.

Results and discussion

Fig. 1 shows IR spectra in the range 250–700 cm⁻¹ for an equimolar mixture of cryolite and chiolite, quenched in water, untreated (above), and annealed (below). Fig. 2 shows similar spectra of the same mixture to which 10% (w/w) alumina had been added. Fig. 3 compares the IR spectra in the range 600–1200 cm⁻¹ of the same samples as for Fig. 2.

For the quenched samples, the oxide content can be seen as a broad shoulder at ca. 530 cm⁻¹, and as distinct, but broad bands at ca. 870 and 1170 cm⁻¹. In the annealed samples all these features are removed, but distinct bands with intermediate band-widths are found at 450 and 844 cm⁻¹, together with a shoulder at ca. 509 cm⁻¹. The other bands and shoulders in the spectra are assigned as cryolite and chiolite bands. Variations in the intensity of the bands at 350–430 cm⁻¹ and at 550–660 cm⁻¹ are attributed to variations in the cryolithic ratio.⁵ Except for differences in

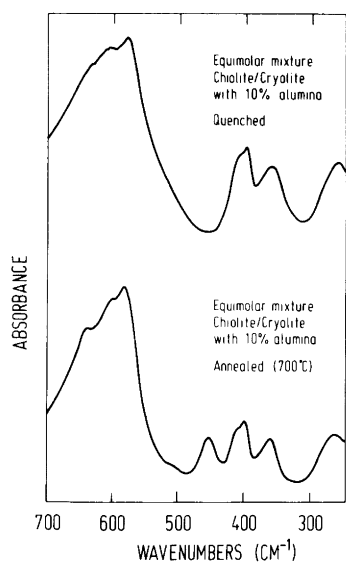


Fig. 2. IR spectra of equimolar mixtures of chiolite and cryolite with 10% alumina added. Above: Sample quenched in water (0°C) and dried. Below: Same sample annealed at 700°C.

the intensities of the bands attributed to the oxides, and changes due to variations in chiolite/cryolite ratio, no principal difference between the spectra of the samples with and without added alumina was found. IR spectra of samples with 5% alumina added are not given here, but they show characteristics intermediate between those of samples with and without 10% alumina added.

Except for the numerous lines attributable to chiolite and cryolite, only one line was found in the X-ray pattern of the quenched samples, i.e. at $d = 5.7\text{\AA}$. This line probably arises from the presence of small amounts of basic aluminium fluorides with composition $\text{Al}(\text{F},\text{OH})_3 \cdot x\text{H}_2\text{O}$.⁶ For samples with and without added alumina, the intensity of this line was about 1% and 2%, respectively, of the intensity of the line at $d = 2.743\text{\AA}$ due to cryolite. When the samples were heated to 400°C this line was removed, although no other changes were observed in the IR spectrum or the X-ray pattern. In the X-ray patterns of the samples annealed at 700°C all main α -alumina lines were detected. No lines other than those belonging to cryolite, chiolite and α -alumina were detected.

The samples quenched by the alternative methods, i.e. on aluminium plates or in liquid nitrogen, showed narrower X-ray diffraction lines, significantly lower intensity of the line at $d = 5.7\text{\AA}$, and lower oxide content as seen from the IR spectra. No other differences were observed.

Holm⁷ has explained the changes in the X-ray diffraction pattern upon annealing by proposing the existence of extremely microcrystalline or amorphous alumina in the quenched sample. Upon heating, the microcrystallites grow to crystallites detectable by X-ray diffraction measurements.

The IR spectra indicate that this explanation is only a part of the story. The significant change in the IR spectra

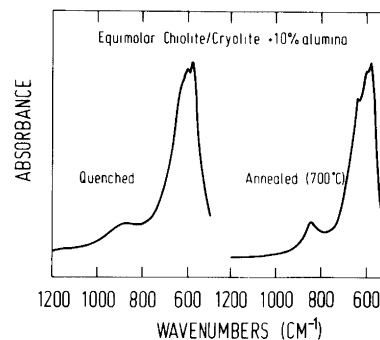


Fig. 3. IR spectra in the range 600–1200 cm^{-1} of equimolar mixtures of chiolite and cryolite with 10% alumina added (same samples as for Fig. 2). Left: Quenched sample. Right: Annealed sample.

upon annealing seems to be difficult to explain on the basis of structural changes alone. A more pronounced change in the chemical environment of the oxides also seems to take place. The most probable change in the chemical environment for the oxides that can provide such a different spectrum is a transformation of oxyfluorides into oxides. Such a reaction should liberate fluorides, and hence slightly increase the chiolite/cryolite ratio. In fact an increase in the chiolite/cryolite ratio was observed, to an extent roughly in agreement with that expected. The increase is, however, not conclusive, as inhomogeneity may result in a significant statistical variation in composition for each of the samples.

The IR spectra therefore indicate that aluminium oxide does not exist as alumina in the quenched samples, but as oxyfluorides. Such an assumption is in accordance with the accepted structure of the solvated oxide species in the fluoride melt. There is probably no single oxyfluoride species in the quenched samples; we would rather expect a mixture of several different more or less complex entities to be formed, as indicated by the broad shoulders present in the IR spectra of quenched cryolite samples.

However, it should be stressed that this conclusion is preliminary. Some structural changes, especially if changes in coordination numbers are involved, may give rise to significant changes in the IR spectrum. Although the very marked changes in the IR spectrum observed upon annealing make this alternative conclusion less likely, it cannot at present be ruled out.

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