Autocorrelation infrared analysis of mineralogical samples: The influence of user controllable experimental parameters

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Abstract

Autocorrelation infrared (ACIR) analysis is based upon the application of the autocorrelation function $\text{corr}(\alpha, \omega') = \int_{-\infty}^{\infty} \alpha(\omega + \omega')\alpha(\omega)\,d\omega$ to standard Fourier transform infrared (FTIR) transmission spectra. We present a rigorous examination of the effect of experimental parameters such as dilution ratio, spectral resolution, grinding time and pressing conditions upon the ACIR analysis of haematite. Results were found to vary by less than 4.5% irrespective of sample preparation, instrumental and data collection parameters. For a series of perovskite samples, the relationship between the measured effective linewidth and material composition appears to be reproducible, even though the absolute magnitudes of Δcorr values do not. Our results further indicate that the ACIR technique is indeed valid for comparative analysis of synthetic sample sequences that vary slightly in composition or structural state, provided that primary spectra are all recorded by the same instrument.
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1. Introduction

An infrared transmission spectrum may be used to determine the constituents of a sample, both qualitatively and quantitatively. However, this becomes challenging for the analysis of complex spectra, such as those obtained from minerals or mixtures of pure substances, as broad phonon bands in their vibrational spectra tend to overlap [1]. Consequently scientists at Cambridge University developed the autocorrelation infrared (ACIR) technique [2,3] for the quantification of linewidth variations in powder absorption spectra from mineralogical samples. ACIR analysis relies on the application of the autocorrelation function $\text{corr}(\alpha, \omega') = \int_{-\infty}^{\infty} \alpha(\omega + \omega')\alpha(\omega)\,d\omega$ to primary infrared (IR) absorption spectra, where $\alpha(\omega)$ is the primary IR spectrum itself and $\alpha(\omega + \omega')$ is the primary spectrum offset in frequency by ω' [3,4]. This function serves to parameterise the effective linewidths (Δcorr) of individual absorption bands or groups of bands within a spectrum, without the need for any

peak fitting to the primary spectrum itself [3–6]. The width of the autocorrelation spectrum offers a statistical measurement that is proportional to the average linewidth of absorbance bands in the region of the spectrum under investigation [5]. Accordingly, ACIR is applicable to samples with varying composition, degree of cation order or structural state, and to complex IR spectra containing broad overlapping peaks [3,4,7]. Applications include the analysis of garnets [7,8], feldspars [3,5,9], perovskites [4,10] and a broad range of other solid solutions such as alumino-silicates and Mg–Fe bearing silicate solutions [11–16]. An advantage of the autocorrelation analysis is that it directly measures peak linewidth without requiring any direct peak fitting to the primary spectrum (which is susceptible to ambiguity when the background near an absorption peak changes sharply). Hence, the autocorrelation method provides a more dependable measure of slight changes in linewidth between samples (or across a series of complex spectra) than that which can be achieved using conventional methods [5,6]. A comprehensive description of the autocorrelation method, derivation of values, and theory behind its application toward the measurement of effective linewidths of primary IR absorption spectra was reported by Salje et al. [3].

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At present, doubts remain about the sensitivity of line width parameters obtained by the ACIR method to sample preparation and instrumental parameters. In this article, we report a thorough examination of the sensitivity of the technique to experimental parameters, and an investigation of reproducibility through comparison of new results with previously published data from independent research.

2. Experimental

2.1. Sample preparation

Reagents were all of analytical grade unless otherwise specified. Synthetic haematite (Fe_2O_3, calcined, 97%, BDH Chemicals Ltd., England) was ground using an agate mortar and pestle for 5–15 min. A known quantity of this sample was subsequently diluted in a known mass of either potassium bromide (KBr, Uvasol®, Merck, Germany) or caesium iodide (CsI, Suprapur®, Merck, Germany) and ground for a further 3–5 min. A known amount (150–300 mg) of the mixed powder is then transferred to a hydraulic die press where a pressure of 10 t is applied for 5 or 7 min whilst under vacuum. Synthetic perovskite samples $(Ba_{1-x}La_x)_2In_2O_{5+x}$ $(0 < x < 0.6)$ were obtained from the South Australian Museum and prepared as described previously by Tenailleau et al. [4].

A natural sample of monolithic haematite that was obtained from the Iron Monarch Mine, Iron Knob, South Australia (S. Aust. Museum G9851) was used in this study. The iron oxide appeared as sheaves of bladed crystals with a silvery metallic lustre. When scraped, the haematite crystals fractured parallel to the basal plane. This yielded small plates and grains of silvery haematite. The haematite crystals were ground for 30 min with aliquots of the material removed at 5 min intervals. IR pellets were prepared at a 1:150 sample to KBr matrix ratio (by mass), with 5 min mixing and 5 min press at 10 t of applied pressure in the hydraulic vacuum press.

2.2. IR spectroscopy

IR spectra were recorded on a Nicolet Nexus 870 (Thermo Electron Corporation) FTIR spectrometer. For synthetic haematite, mid-IR region spectra were acquired using a data point spacing of $0.482\,cm^{-1}$ with 64 scans per spectrum, using an Ever-Glo® IR source, KBr beamsplitter and a DTGS detector over a range of $2000–400\,cm^{-1}$. Perovskite spectra that were acquired in the far-IR region were obtained using a solid substrate beamsplitter and DTGS-PE (polyethylene window) detector, 512 scans per spectrum over the region $700–50\,cm^{-1}$, an aperture setting of 60 and with other settings held constant. In all cases Happ-Genzel apodization and Mertz phase correction were implemented, whilst a blank disc of either KBr or CsI was used for background correction. For the perovskites, sample discs were held in the chamber at an angle of approximately 27° to the incident IR beam using a modified sample mounting stage to eliminate interference fringing effects.

2.3. Autocorrelation analysis

All work involving the autocorrelation and fitting of IR spectra presented here was performed using IGOR Pro (Version 4.0) software (WaveMetrics, Inc., Oregon, USA) in accordance with the method described by Salje et al. [3].

3. Results and discussion

3.1. Preliminary experiments

Preliminary experiments were focussed on obtaining primary infrared spectra for synthetic haematite and determining the appropriate regions for application of autocorrelation analysis. As can be seen in Fig. 1, the infrared spectrum of an haematite pellet prepared at a sample to KBr ratio of 1:250 (w/w) exhibits two prominent peaks centred at ~470 and $~550\,cm^{-1}$ and a broad peak at $~1000\,cm^{-1}$. There were no significant spectral features observed above $1200\,cm^{-1}$. Consequently the region of $422–675\,cm^{-1}$, which gave intense peaks (related to lattice modes within the haematite [17,18]), was chosen for all autocorrelation of haematite. Experiments were then performed to investigate the influence of sample preparation parameters on the primary infrared spectrum and hence on the autocorrelation spectrum.

3.2. The influence of dilution

Pellets of synthetic haematite at different sample to matrix ratios (1:200, 1:250 and 1:300 by mass) were prepared by directly mixing with KBr for 5 min, followed by pressing 200 mg of the resultant powder for 5 min at 10 t. Primary IR spectra for these samples are given in Fig. 2, whilst their associated autocorrelation spectra are shown in Fig. 3. Autocorrelation analysis of the primary spectra resulted in an effective linewidth (Δcorr) of $57.8 \pm 0.5\,cm^{-1}$ at 95% confidence (calculated using the Student's *t* test) with individual values within $0.4\,cm^{-1}$ of each other and a relative standard deviation of 0.34%. Evidently, despite the difference in the intensities of the primary spectra, the peak
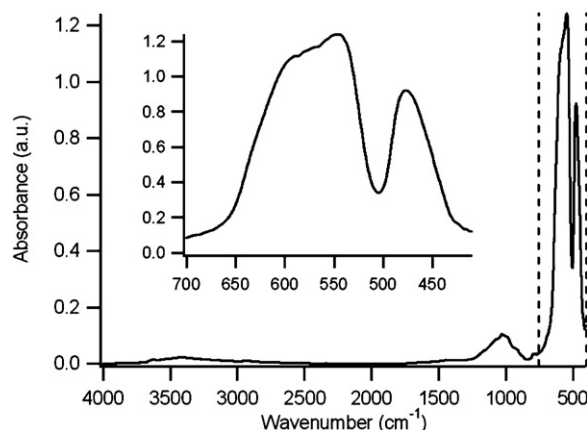

Fig. 1. IR spectra for synthetic haematite (1:250 by mass in KBr) showing the peaks that were used for autocorrelation. Inset: the analysis region.