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A HIGH-TEMPERATURE DEVICE FOR *IN SITU* MEASUREMENT OF X-RAY ABSORPTION SPECTRA

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Abstract

Description of a high temperature cell designed to record the X-ray absorption spectra of samples heated *in situ* up to 1500 °C under the vacuum (10^{-4} torr) of a synchrotron X-ray beam line. Application to determination of the transition (at ca. 220 °C) from incommensurately-modulated to normal structure in $Ca_2Co[Si_2O_7]$ melilite and the coordination of Ti on K_2O-TiO_2-SiO_2-melts.

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Introduction

X-ray absorption (XAS) spectra yield sensitive information on site geometry, valence, and long-range as well as short-range ordering of atoms in crystalline and amorphous compounds.

For a characterization of materials undergoing unquenchable phase transitions, or for following the kinetics of a phase change or reaction, measurements under *in situ* conditions at elevated temperatures are essential. Moreover, geologically as well as technologically-significant transitions from the solid to the liquid state that cannot be studied by the conventional X-ray diffraction techniques can be studied continuously by X-ray absorption spectroscopy, provided a suitable *in situ* high-temperature cell (HTC) is available.

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We present here the design and first applications of a HTC especially conceived for XAS which has been tested successfully for both XANES and EXAFS measurements at the PULS X-ray line of the synchrotron radiation facility of Frascati.

Design requirements

A high-temperature cell to be used for XAS spectroscopy has to fulfill the following technical requirements:
- homogeneous temperature distribution;
- negligible heating of surrounding parts such as windows, vacuum seals, etc.;
- remote control of sample position;
- operation in vacuum;
- good transparency to X-rays in the pertaining energy region;
- sample holders that minimize the problem of contamination and/or X-ray absorption, but maximize heat transfer;
- accomodation of several samples, or of samples with different thicknesses.

Experimental setup

To achieve these goals, a furnace such as that depicted in Fig. 1 has been constructed. The entire furnace assembly is mounted to a 150 mm vacuum flange containing the feed-throughs for cooling water, heating power (rated to 10 A maximum), and thermocouple, and is then inserted into the experimental vacuum chamber of the X-ray beam line. Vertical movements of the assembly relative to the vacuum chamber are made possible by a motor-driven stainless-steel bellows.
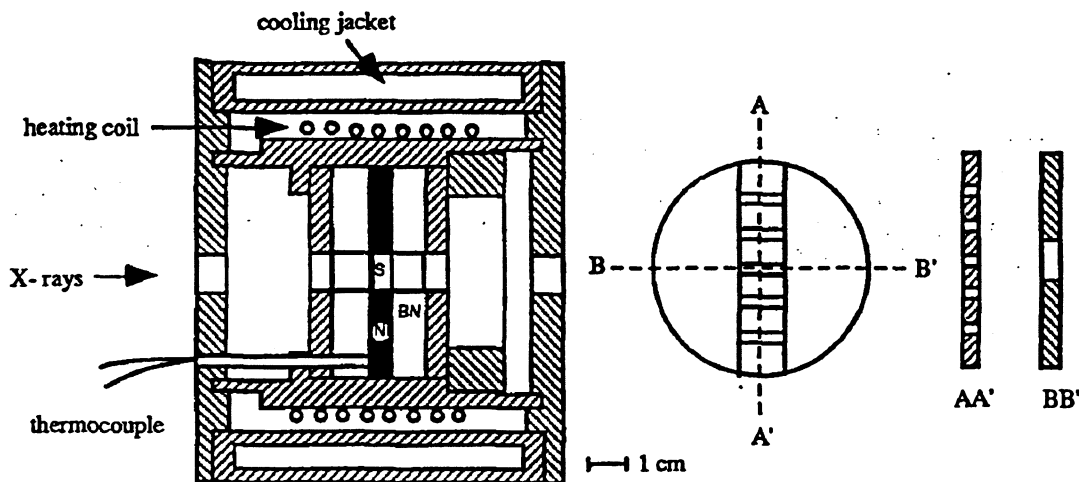

Figure 1: Cross-section through the 800 °C furnace. The symbol S designates the sample compartment, Ni the nickel heating block, BN the boron nitride plates, ruling to the left the stainless-steel caps and jackets, ruling to the right the brass frame of the cell. Right: detail of the nickel block that serves as sample holder. Samples are placed into the five rectangular slits.

Depending on the temperature range and/or number of samples required, three different designs for the heating element and sample holder have been developed. They all fit the same furnace shell surrounded by water-cooled jacket, and can easily be exchanged.

For the temperature range up to about 800 °C stainless-steel tube is used onto which an Inconel-coated, MgO-insulated heating wire (rated to 1000 °C) is firmly wound and fixed. The interior sample-holder consists of a central nickel block (Ni) sandwiched by sintered boron nitride plates (BN) and steel end-caps. The outer two boron nitride layers serve for the heat transfer to the nickel block and to the samples (S). Temperatures are measured and controlled by a sheated NiCr/Ni thermocouple placed inside the nickel block. Typical power consumption at 800 °C in a 10^{-4} torr vacuum is about 500 W. End plates of the furnace with slits 100 mm wide x 40 mm high (corresponding to the total sample area) prevent excessive thermal radiation to the outside of the furnace.

The central nickel block (Fig. 1, right) contains five slits (3 mm high x 10 mm wide x 4 mm thick) which serve as sample compartments. In the high-energy application (e.g. for the study of Fe or Co K-edges) the appropriate amount of sample (several mg, depending on the type and concentration of the element studied) are intimately mixed with about 50 mg of boron nitride powder to ensure a homogeneous thickness, pressed into the slits of the nickel block, and covered on both sides by thin (1 mm) sheets of boron nitride to hold the sample in place. In the low-energy region (e.g. for studying the Ti K-edge), or if reaction with boron nitride might become a problem, the samples are mounted on a fine metal mesh grids (see below) and attached to the nickel block without the sintered boron nitride cover sheets.

In the temperature ranges up to 1200 °C and 1500 °C Kanthal Al and a Pt90Rh10 (d=0.35 mm, 5 m long) heating wire, respectively is wound directly onto a Al_2O_3 ceramic tube (d_o=25 mm, d_i =20 mm) and fixed by ZrO_2 cement. A radiation shield of Pt foil between the heating tube and the water-jacket minimize thermal losses. Maximum current is 8 A and power consumption is 850 W at 1500 °C. The sample holder, made out of BN or Al_2O_3 machinable ceramic, can accomodate two 3 x 10 mm samples. For these high-temperature applications, the finely powdered samples are pressed into a metal mesh grid (stainless steel, tantalum, or platinum). Even rather fluid melts were found to be held in place on the vertically mounted mesh just by surface tension. This arrangement gives minimal intensity losses (ca. 20%) and contamination.

In the high-temperature set up, temperature controlled is achieved by a Pt90Rh10 thermocouple and ramped (maximum 1500 °C /h) Eurotherm controller operating in phase angle firing mode and power control. Typical temperature stability over extended periods of time (hours) is 1 °C.

Phase transition in melilite

The 800 °C cell has been used for a study of the phase transition in synthetic $Ca_2Co[Si_2O_7]$ melilite by Co K-edge XANES and EXAFS spectroscopy. The high-T structure of this melilite consists of 4-fold coordinated CoO_4 polyhedra linked with Si_2O_7 dimers to form a sheetlike arrangement. Ca atoms occupy the 8-fold coordinated sites between the sheets. It is well known from TEM, Mössbauer, X-ray diffraction, NMR, and DTA studies [1] that many melilite-type compounds, and the $Ca_2Co[Si_2O_7]$ phase in particular, undergo a non-quenchable, hysteresis-free phase transition from the high-temperature normal phase to a low-temperature, incommensurately modulated phase in which the Si_2O_7 dimers are rotated and kinked and the CoO_4 tetrahedra deformed [2]. For $Ca_2Co[Si_2O_7]$, the phase transition temperature is at 210-200 °C [1]. As the phase transition is approached from lower temperatures, the structure changes by a decrease in modulation amplitude and increases in modulation wavelength in the direction towards the high-T normal structure, but nevertheless the final phase transition is sharp and of the lambda type. Local fluctuations of the structure might persist to temperatures above the phase transition.

As to be expected for a phase transition in which only subtle changes of the structure occur (e.g. no change in coordination number or valence, but only changes in angular and
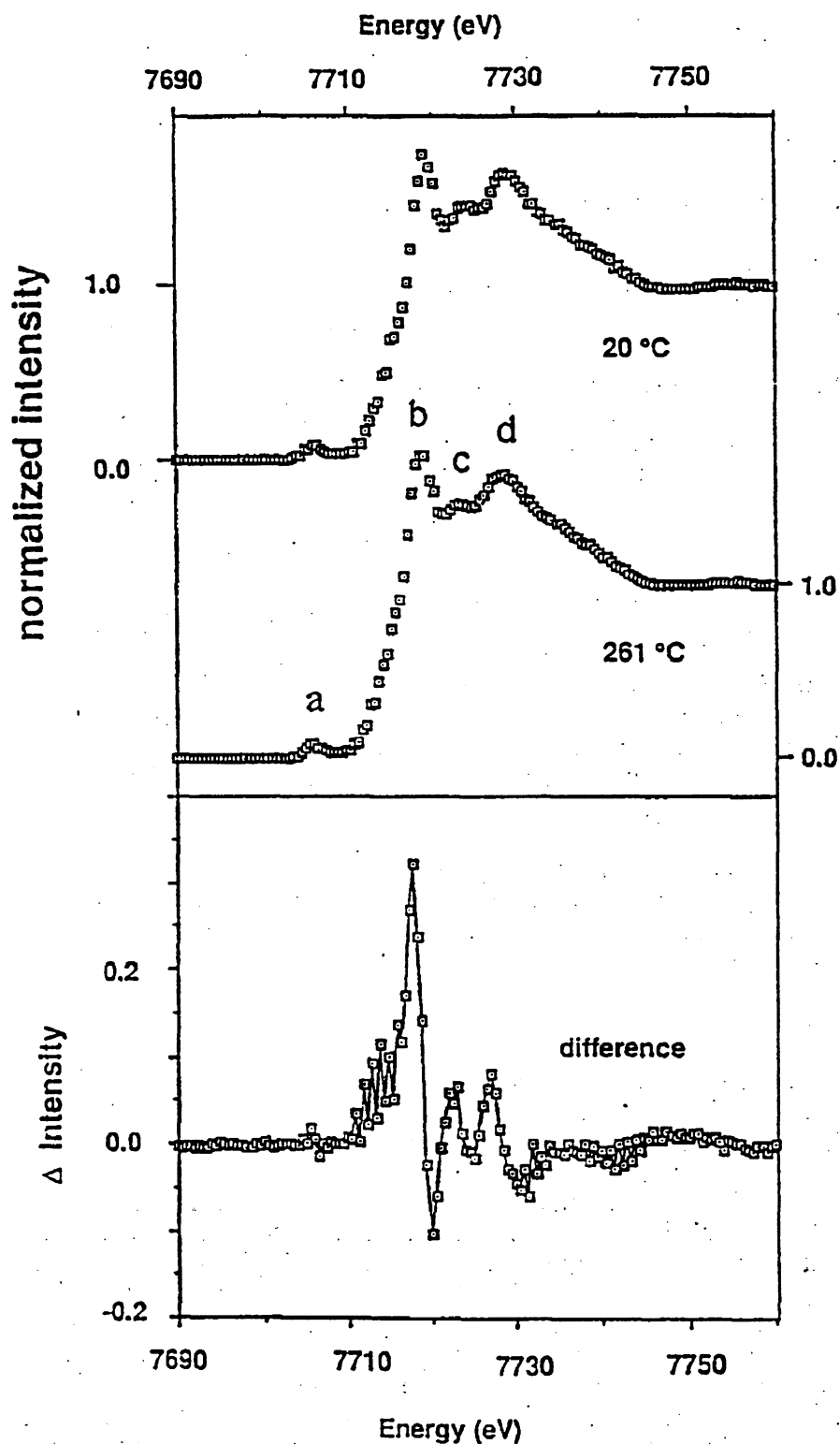
Figure 2: Normalized Co K-edge XANES spectra of $Ca_2Co[Si_2O_7]$ melilite taken at room temperature (top) and at 261°C (middle), and their difference spectrum (bottom).

bond-length distortion), the changes in XANES and EXAFS spectra as a function of temperature are only slight. Fig. 2 gives the normalized 261 °C Co K- XANES spectrum (i.e. above the phase transition, in the field of the normal melilite structure) and the room-temperature spectrum (in the stability field of the modulated phase).
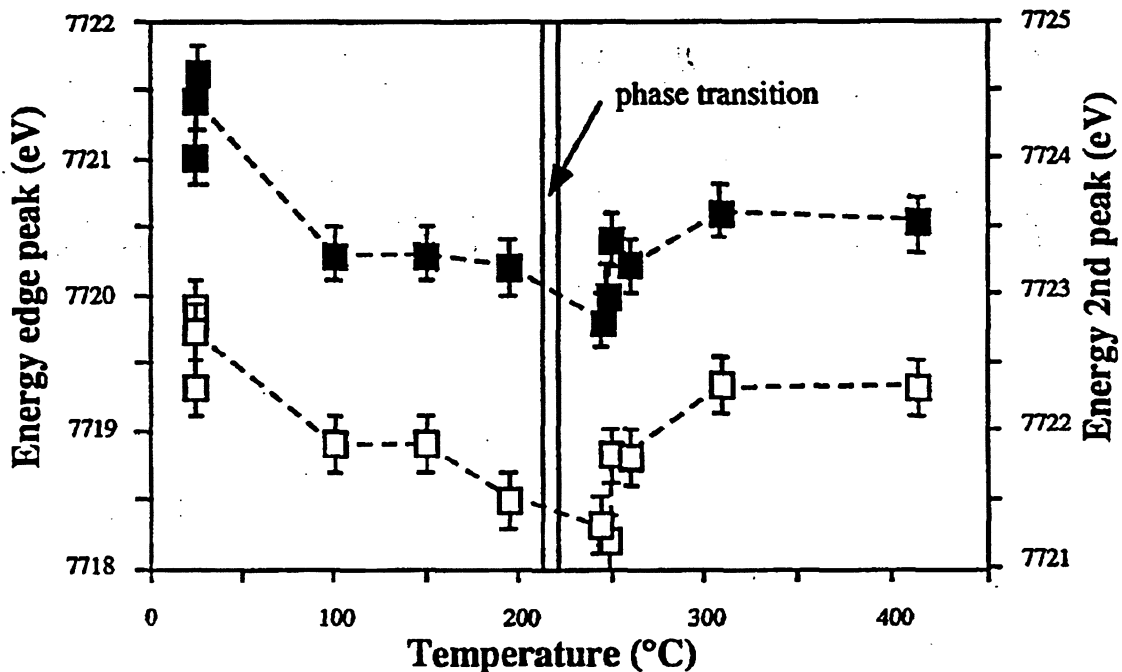

Figure 3: Energy positions of the Co K-edge peak b (bottom) and of the peak d (above) of melilite $Ca_2Co[Si_2O_7]$ as a function of temperature. The vertical bars indicate the experimental uncertainty in energy. Temperature uncertainty is less than the width of the plotted square.

Energy changes of the XANES features are related to changes in the structural environment around the absorbing atom [3]. In $Ca_2Co[Si_2O_7]$ melilite, first attempts to evaluate the peak positions (Fig. 3) indicate minor but rather systematic trends for the strong first peak (b) and the weaker second peak (d), but no changes for the pre-edge peak (a), and just weak changes for the third peak (c). For both peaks b and d, the energy reaches minima close to the phase transition, near 220 °C.

For a final assessment, the recording of the spectra with higher energy resolution and the fitting of the spectral envelope to sums of Lorentzians will be required. However, the trends observed so far can tentatively be referred to the anomalous thermal expansion of the structure near the phase transition [4].

TiO_2 coordination in silicate melts and glasses

TiO_2 is a crucial component of terrestrial and lunar magmas, high temperature slags and modern melt-based ceramic materials. The growth of high-purity TiO_2 crystals from the melts is also of industrial importance. The concentration of TiO_2 in natural melts ranges up to 16% and ceramic materials can even be richer in TiO_2. Thus, the effects of this major component on transport properties as well as its partial molar properties are important input for the modeling on crystal-melt interaction.

The coordination of Ti^{4+} in silicate glasses has been little investigated to date, but the existing data point to features which can be interpreted as a mixture 4, 5, and 6-coordinated Ti^{4+}. Among the clearest distinctions between, for example, 4- and 6-coordination is the

presence of a strong pre-peak for the 4-fold coordination as opposed to a weaker one for the 6-fold coordination [5]. XAS studies on quenched silicate glasses [6] indicate the presence of either 4-, 5- or 6-coordinated Ti^{4+}, or a mixture of 4- and 6-fold coordination. These results suggest that Ti coordination is very sensitive to chemical or physical parameters and that, at a given composition, Ti might behave differently in a melt compared to a glass.

The XANES spectrum of a melt of $K_2Si_4TiO_{11}$ composition, obtained at 1300 °C following heat treatment in the HTC at temperatures up to 1450 °C is compared with the room temperature of the glass in Fig. 4. The broad features of the spectra are similar but details differ. The relative intensity of the pre-peak remains high in the high-temperature liquids, consistent with the coordination number intermediate between 4 and 6 for Ti^{4+} in the liquid as in the glass.

These examples testify the broad application field of *in-situ* high-temperature XAS analysis. Expecially regarding the study of melts, of geological as well as technological relevance, this device will allow to obtain structural information not suitable to be obtained by other methods.
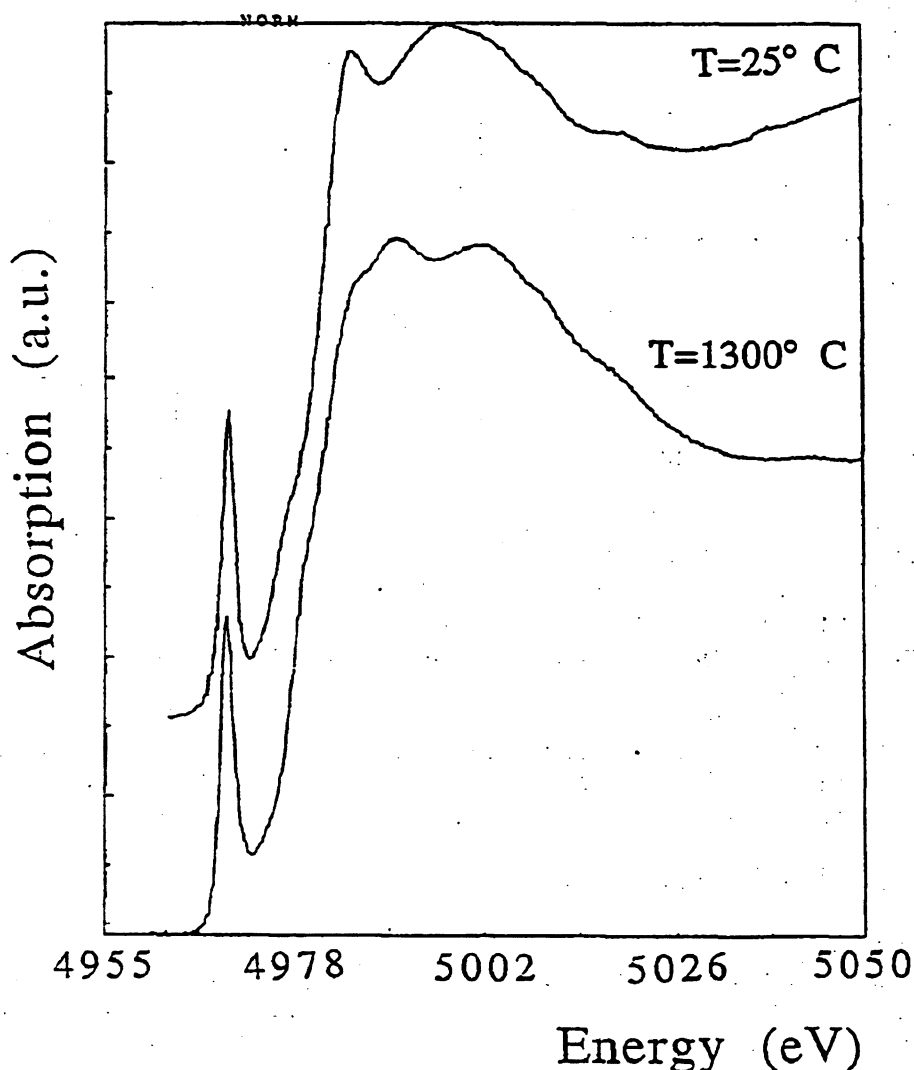

Figure 4: XANES spectra of a $K_2Si_4TiO_{11}$ composition as quenched glass at room temperature (top) and as liquid at 1300 °C. (bottom).

Acknowledgements

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