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Crystal field spectroscopy of Cr^{3+} in glasses: Compositional dependence and thermal site expansion

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Abstract

Optical absorption (=crystal field) spectra of Cr^{3+} in silicate glasses have been investigated as a function of chemical composition and temperature. In a large range of glass compositions, most spectra show a variation of Crystal Field Stabilization Energy (CFSE) as a function of glass chemistry. Cr^{3+} CFSE ranges between 215 and 234 kJ/mol-Cr^{3+} and it increases with the theoretical glass basicity. Alkali-bearing glasses make a noticeable exception, as CFSE only varies with the nature of the alkali and not with its concentration. In glasses representing simplified magmatic compositions, CFSE varies by 7 kJ/mol-Cr^{3+} and the lowest CFSE values are observed in silica-rich compositions. This CFSE variation may contribute to the compositional dependence of mineral/liquid Cr-partition coefficients. Near UV–visible absorption spectra have been recorded up to 800 K, using a homemade diode array spectrometer fitted with a furnace. The modification of the optical spectra at high-temperature is characterized by a red shift of the Cr^{3+} absorption bands. CFSE shows a nearly linear negative dependence on temperature, with an overall variation of about 7 kJ/mol-Cr^{3+} over 500 K, a value similar to that characterizing the CFSE chemical dependence. This systematic red shift is related to the local thermal expansion of the Cr site and may be treated in glasses using a polyhedral approach. The Cr–O linear thermal expansion coefficient is $15–20 \times 10^{-6}\ K^{-1}$ in alkali-bearing silicate and borosilicate glasses and is similar to those determined in silicate minerals. The local thermal expansion coefficient exhibits a weak compositional dependence and is larger than the bulk thermal expansion coefficient of the glasses. The compositional and thermal dependence of the Cr^{3+} crystal field spectra shows that this ion is a sensitive probe of the evolution of glass structure as a function of composition or temperature. These data are consistent with the location of Cr^{3+} ions in cationic domains in glasses.

Keywords: Glasses; Transition elements; Chromium; Glass structure; Thermal expansion, Visible spectroscopy

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1. Introduction

Trace element geochemistry has long been used to constrain the formation conditions of magmatic systems, including their source, degree of melting and subsequent fractional crystallization (Irving, 1978; Blundy and Wood, 2003). This approach has been quantified by an extensive set of mineral/melt partition coefficients, which have been determined over a large range of mineral and melt compositions through numerous experimental studies and extensive observations in natural systems (Irving, 1978; Bédard, 2005). Chromium is a trace element compatible in several minerals that crystallize from basaltic magmas. Under the oxidation conditions of terrestrial magmas, it occurs

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predominantly in the trivalent state and its fractionation is governed primarily by its entry as an essential constituent into spinels and as a trace element in major phases, such as pyroxenes and olivines. This property has been interpreted as a direct consequence of Crystal Field Stabilization Energy (CFSE), which favors site preference of octahedral Cr^{3+} for minerals, with a fast depletion in mafic liquids as magmatic differentiation proceeds (Burns, 1993). There is evidence that liquid composition influences mineral/liquid partitioning of Cr^{3+} (Hanson and Jones, 1998; Petermann and Hirschmann, 2002; Bédard, 2005). Though Cr is an element of great geochemical interest, few spectroscopic studies on Cr-bearing silicate glasses of geological interest have been published (Keppler, 1992). The direct determination of Cr^{3+} CFSE in minerals and glasses, using UV–visible spectroscopy, gives a possibility of establishing a link between Cr^{3+} crystal chemistry and glass composition. We show that a significant variation of CFSE occurs as a function of glass chemistry. It increases with the theoretical glass basicity, with the noticeable exception of alkali-bearing glasses, in which crystal field strength only varies with the nature of the alkali and not with its concentration. In Fe-free glasses ranging between basanitic and granitic compositions, CFSE decreases with increasing silica content. This variation may contribute to the compositional dependence of olivine/liquid and clinopyroxene/liquid Cr-partition coefficients (Hanson and Jones, 1998; Petermann and Hirschmann, 2002; Bédard, 2005).

Thermal expansion directly derives from the temperature dependence of the specific volume V. However, despite the importance of V for modeling glass properties, the microscopic origin of glass thermal expansion is largely unknown. This is due to the lack of high-temperature structural data describing, at the atomic scale, the structural evolution of a glass with temperature. Because of the asymmetry of the potential well, the average interatomic distances are expected to increase with temperature due to thermal vibrations of atomic bonds. Recent high-temperature EXAFS spectroscopic measurements are among the few data, which exist on the influence of temperature on inter-atomic distances in glasses (Dalba et al., 2001). As crystal field strength is a sensitive measurement of the surrounding of transition elements, UV–visible spectroscopy may be used to probe the temperature- or pressure-induced modification of the local environment of transition elements in minerals (Burns, 1993; Taran et al., 1994), silicate glasses and melts (Tilquin et al., 1998; Nowack et al., 2001). This approach opens the possibility to quantify these modifications around transition elements present in low concentrations in minerals (Taran et al., 1994). Indeed, the high sensitivity of crystal field to cation-oxygen distances gives a direct access to site thermal expansion in glasses. This approach opens also the possibility of a direct determination of CFSE. Previous high-temperature UV–visible spectroscopy studies of Cr-bearing glasses have shown significant modifications of these spectra with increasing temperature (Tilquin et al., 1998; Gödeke et al., 2001). These temperature-induced changes concern as well the O–Cr charge transfer in chromate groups as the position and relative intensity of the Cr^{3+} absorption bands. The present study investigates the temperature dependence of crystal field spectra of Cr^{3+} in glasses up to 800 K. The variation of the crystal field strength, Dq, and of the Racah parameter, B, gives a good description of site thermal expansion of Cr^{3+}. Using crystal field theory, it is possible to quantify the modification of the Cr–O distances as a function of temperature. We find that the Cr–O thermal expansion coefficient is higher than the bulk thermal expansion coefficient of the glasses investigated. The similarity of Cr–O thermal expansion coefficients in all glasses, including low thermal expansion borosilicate glasses, $15–20 \times 10^{-6}$ K^{-1}, is an additional evidence of the location of Cr^{3+} in specific cationic domains of silicate glasses.

2. Experimental

Two kinds of samples were prepared, model silicate and borosilicate glasses and glasses with a composition simulating Fe-free magmatic rocks, including basanitic, basaltic, andesitic and rhyolitic compositions. The compositions of the base glasses are given in Table 1. The silicate synthesized by melting reagent grade materials, Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, B_2O_3, Al_2O_3 and SiO_2, in a platinum crucible at 1400 °C. The base glasses were finely ground together with 1 wt.% Cr_2O_3, molten at 1400 °C for 2 h and then cast in a graphite mould and slowly cooled to room temperature. The concentration of Cr higher oxidation states was buffered by adding As_2O_3, a reducing oxide, which does not modify the spectroscopic properties of the glass (Bamford, 1977). The diopside glass and the glasses simulating Fe-free rock compositions were prepared from gel precursors prepared following a co-precipitation method (Biggar and O'Hara, 1969). After sintering at temperatures ranging between 500 and 900 °C, the mixtures were molten at 1420 °C in a 1 atm, high-temperature gas mixing furnace. The sample atmosphere was controlled by a H_2–CO_2 gas mixture and was set