

Crystal field spectroscopy of Cr³⁺ in glasses: Compositional dependence and thermal site expansion

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Abstract

Optical absorption (=crystal field) spectra of Cr³⁺ 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. Cr³⁺ CFSE ranges between 215 and 234 kJ/mol-Cr³⁺ 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-Cr³⁺ 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 Cr³⁺ absorption bands. CFSE shows a nearly linear negative dependence on temperature, with an overall variation of about 7 kJ/mol-Cr³⁺ 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 $15\text{--}20 \times 10^{-6} \text{ K}^{-1}$ 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 Cr³⁺ 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 Cr³⁺ ions in cationic domains in glasses.

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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 tran-

sition 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, $15\text{--}20 \times 10^{-6} \text{ K}^{-1}$, 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 $\text{H}_2\text{--CO}_2$ gas mixture and was set

Table 1
Chemical composition of the investigated glasses (in wt.%)

Glass #	Di-Glass	NS3	KBS	NBS	#1	#2	#3	#4
SiO ₂	55.49	73	53.2	63	43.6	47.66	60.2	73.71
TiO ₂					2.67			
Al ₂ O ₃		1		1	11.84	11.89	17.5	13.46
MgO	18.61				24.8	26.17	9.9	0.67
CaO	25.90				11.39	11.63	5.92	2.34
Na ₂ O		26		15	4.45	2.2	4.63	4.97
K ₂ O			23.4		1.25	0.45	1.85	4.85
B ₂ O ₃			23.4	21				
Sum	100	100	100	100	100	100	100	100

close to the Ni–NiO buffer. This slightly reducing atmosphere prevented the formation of Cr higher oxidation states. Small Pt capsules, which held about 200 mg of the initial glass powder served as sample containers. Samples were quenched by dropping the crucible into cold H₂O. Glass samples were cut as 1 mm thick plates, and polished to achieve a good optical quality.

Room temperature UV–visible transmission spectra were recorded using a double beam Cary 5 spectrometer. High-temperature UV–visible spectra were recorded in a transmission mode with a homemade diode array spectrometer fitted with a furnace. The spectrometer used a Jobin-Yvon grating system and a photodiode array, in an experimental setting similar to that of a classical diode array spectrometer (see e.g., Janata, 2003). The samples were heated by a homemade heating stage, fitted to the spectrometer by an optical fiber optics. Optical spectra were measured in a transmission mode in the range 350–1000 nm (accuracy 1 nm). As samples were kept at moderate temperatures (up to 800 K), black body emission did not give a significant contribution in the visible range. Spectral data were corrected for Rayleigh scattering using a baseline correction and then fit into Gaussian components.

3. Results and discussion

3.1. Room temperature crystal field spectrum of Cr³⁺ in silicate glasses: spectroscopic parameters and location in the glass structure

Fig. 1 shows the optical absorption spectra of Cr in diopside and NS₃ glasses. They show the major contribution of the two characteristic absorption bands of Cr³⁺. Indeed, the UV absorption arising from chromate groups was limited by the reducing synthesis atmosphere in the former and the presence of As₂O₃ as a reducing agent, in the latter. The crystal field spectrum of Cr³⁺ exhibits two broad, intense bands, which occur

in the visible range and impart the glasses their characteristic green color. In NS₃ glass, a further absorption band occurs near 27 000 cm⁻¹ and may be ascribed to the presence of a low concentration of residual chromate groups arising from an incomplete reaction with the As(V)/As(III) redox couple used to get reducing conditions. The two main absorption bands arise from the spin-allowed *d-d* transitions of octahedral Cr³⁺, ⁴A_{2g}(F) → ⁴T_{2g}(F) and ⁴A_{2g}(F) → ⁴T_{1g}(F), located at about 15 000 cm⁻¹ and 22 500 cm⁻¹ and thereafter referred to as ν₁ and ν₂ bands, respectively (Fig. 1). As in most crystalline and glassy compounds (Rossman, 1988), Cr³⁺ only occurs in octahedral coordination, due to its high crystal field stabilization energy. The ν₁ band has a Gaussian lineshape and we have used a fit with a Gaussian function to define its position and linewidth. The ν₂ band is broader than ν₁, as usually observed in Cr³⁺ crystal field spectra (Calas et al., 1984; Taran et al., 1994). The position of ν₁ and ν₂ is given on Table 2. The width of these absorption bands is larger in the diopside glass than in NS₃, 3400 and 2800 cm⁻¹ for the ν₁ band, respectively; this indicates a larger site distortion in the

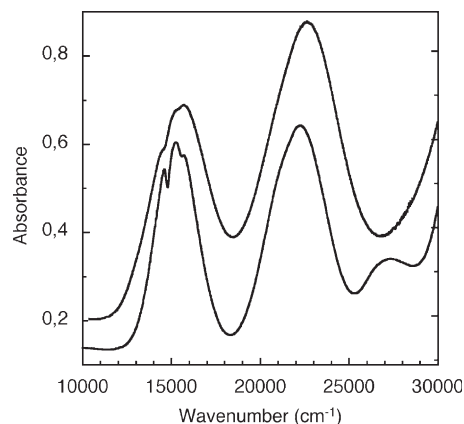


Fig. 1. Optical absorption spectrum of Cr³⁺ in NS₃ glass (bottom) and diopside glass (top). The absorbance scale on the spectrum of the diopside glass has been shifted by 0.1 for clarity purpose.

Table 2

Position of Cr³⁺ absorption bands (ν_1 and ν_2), optical basicity A , CFSE and B parameter values in the investigated glasses

Glass #	Di-Glass	NS3	KBS	NBS	#1	#2	#3	#4
ν_1	15,500	15,265	14,993	15,240	15,700	15,620	15,450	15,150
ν_2	22,730	22,270	21,675	22,285	23,260	22,890	22,625	22,100
A_{glass}	0.618	0.582	0.567	0.512	0.626	0.612	0.568	0.538
CFSE (kJ/mol-Cr ³⁺)	223	219	215	219	225	224	222	218
B (cm ⁻¹)	771	741	706	748	800	774	763	735

former. Crystal field strength, Dq , obtained from the position of the maximum of the ν_1 band, is higher in the diopside glass. Dq and ν_1 linewidth are similar in crystalline (Taran et al., 1994) and glassy diopside, an indication of similar Cr³⁺ sites despite the disorder effects expected in glass structure. The Racah parameter B is used as a measure of Cr–O bond covalence, and is derived from the following relationship

$$B = \frac{1}{3} \frac{(2\nu_1 - \nu_2)(\nu_2 - \nu_1)}{9\nu_1 - 5\nu_2}. \quad (1)$$

B is sensitive to the interelectronic d – d repulsion. The values obtained (Table 2) are consistent with a higher Cr–O bond covalence in NS3 than in the diopside glass, with a reduction by $\sim 30\%$ of the free ion value (1030 cm⁻¹). The value of $Dq/B \sim 2.15$ indicates that Cr³⁺ ions occupy weak-field octahedral sites, and corresponds to the typical range of Dq/B values in silicate glasses (Rasheed et al., 1991).

Additional weak features occur near the maximum of the ν_1 transition, around 14900 and 15700 cm⁻¹. According to the Cr³⁺ 3d-energy level diagram (Burns, 1993), they are assigned to spin forbidden transitions of Cr³⁺ ions in a low crystal field, ${}^4A_{2g}(F) \rightarrow {}^2E_g(G)$ and ${}^4A_{2g}(F) \rightarrow {}^2T_{1g}(G)$, respectively (Fig. 2). As the ${}^4A_{2g}$, 2E_g and ${}^2T_{1g}$ terms result from the same configuration t_{2g}^3 , the bands corresponding to an electron jump between these states are expected to be sharp. In a weak crystal field, the interaction between spin forbidden and spin allowed transitions, which correspond to the localized states 2E_g and ${}^2T_{1g}$ and to the ${}^4A_{2g}$ continuum, respectively, produces dips instead of peaks superimposed over the main transition. This phenomenon has been already described in Cr³⁺ spectra in various glasses and ascribed to Fano antiresonances (Lempicki et al., 1980; Rasheed et al., 1991; Rodriguez-Mendoza et al., 1999) and more recently to spin-orbit coupling (Bussière et al., 2003). The Dq/B value corresponds to the crossing region of the ${}^4T_{2g}(F)$, ${}^2E_g(G)$ and ${}^2T_{1g}(G)$ levels, in agreement with the position of the dips at the maximum of the ν_1 band.

The differences observed between the relative intensity of these dips in the diopside and NS3 glasses arise from a different coupling between the spectroscopic states corresponding to the spin-allowed (${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$) and spin-forbidden (${}^4A_{2g}(F) \rightarrow {}^2E_g$ and ${}^4A_{2g}(F) \rightarrow {}^2T_{1g}$) optical transitions. The better resolution of these dips in the NS3 glass indicates a stronger coupling than in the diopside glass. This may be related to the presence of Cr in less distorted octahedra in the NS3 glass, which favors the electron–phonon coupling at the origin of these dips. By contrast, the weak intensity of these features in the diopside glass is an indication of more distorted Cr-bearing octahedral sites, which is consistent with a larger line width.

3.2. Chemical dependence of crystal field spectra of Cr³⁺ in silicate glasses

Crystal field spectra show that Cr³⁺ is in octahedral coordination in the Fe-free glasses simulating magma compositions ranging between basanitic and granitic

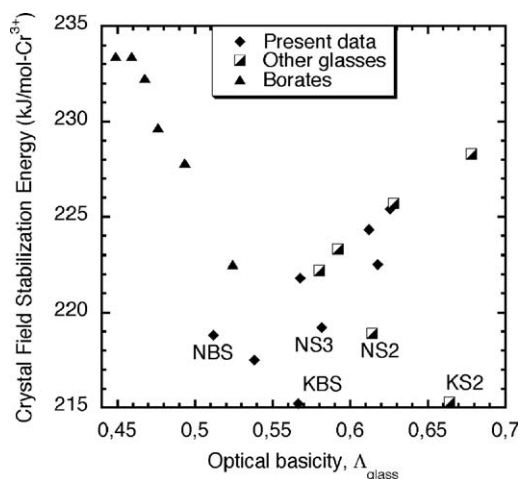


Fig. 2. Variation of crystal field stabilization energy among various oxide glasses. Filled diamonds: present data (A_{glass} , CFSE and B values are reported in Table 2); half-filled squares: silicate and aluminosilicate glasses (after Rasheed et al., 1991; Rodriguez-Mendoza et al., 1999); filled triangles: alkali borate glasses (after Paul and Upreti, 1975).

compositions. This is consistent with the solution behavior of chromium in basaltic melts (Murck and Campbell, 1986). The position of the absorption bands of Cr^{3+} depends on glass composition. The crystal field intensity has been directly derived from the position of the ν_1 absorption band, evaluated from the maximum of its Gaussian envelope with an uncertainty of 80 cm^{-1} . Crystal field splitting increases with glass basicity, from 218 to 225 kJ/mol- Cr^{3+} in the glasses representing simplified magmatic compositions (Table 2; experimental uncertainty of 1 kJ/mol- Cr^{3+}). The similar evolution of CFSE and B with glass composition is not consistent with a variation of Cr–O distances, $d(\text{Cr–O})$. Indeed, an increase of $d(\text{Cr–O})$ will cause at the same time a decrease of CFSE and an increase of B, as bond covalence is expected to decrease with increasing cation–oxygen distance. Our spectroscopic data rather indicate a decrease of the effective charge of the oxygen ligands with increasing glass polymerization. A similar behavior of the variation of crystal field parameters has been observed in the same glasses for transition elements such as Cu^{2+} and V^{4+} (Calas and Petiau, 1983). Similarly, the main absorption band of Fe^{2+} shifts from $10\,400 \text{ cm}^{-1}$ down to 9500 and 8550 cm^{-1} , in basaltic, rhyolitic and sodium silicate glasses, respectively (Combes et al., 1995). If this trend of a compositional dependence of CFSE is retained in the corresponding silicate melts, the higher mineral/liquid partition coefficients in silica-rich than in silica-poor systems (Bédard, 2005) may be related to a decrease of CFSE with increasing silica content.

At room temperature, the optical spectrum of Cr^{3+} in KBS is similar to that in potassic silicate glasses, with the same crystal field energy and the presence of dips superimposed at the same position on the crystal field absorption band. By contrast, the Dq values of Cr^{3+} , determined by Paul and Upreti (1975) in alkali borate glasses, are higher than the values in borosilicate glasses and the dips are almost absent from the absorption spectra. Spectroscopic data are then consistent with a preferential location of Cr^{3+} in sites linked to a silicate rather to a borate surrounding, despite the absence of segregation of borate and silicate units in borosilicate glasses (Wang and Stebbins, 1999).

The chemical dependence of glass and melt properties is often represented as a function of the ratio of non-bridging oxygen to tetrahedrally coordinated cations NBO/T (Mysen, 1983). This parameter has been used to rationalize the mineral/melt Cr-partition coefficients (Hanson and Jones, 1998). However, the influence of the nature of the cations present in the glass on Cr^{3+} spectroscopic properties (see below) shows that such

simplified parameters may be inadequate. We have rationalized the evolution of CFSE as a function of glass composition with the concept of optical basicity, Λ (see e.g., Duffy, 1993; Duffy and Ingram, 2002). These authors have shown that a theoretical optical basicity of a glass may be derived from its chemical composition, using the optical basicity values of the individual component oxides, according to the relationship:

$$\Lambda_{\text{glass}} = X_{\text{AO}_{a/2}}\Lambda(\text{AO}_{a/2}) + X_{\text{BO}_{b/2}}\Lambda(\text{BO}_{b/2}) + \dots \quad (2)$$

in which $\Lambda(\text{AO}_{a/2})$, $\Lambda(\text{BO}_{b/2})\dots$ are the optical basicities of the oxides $\text{AO}_{a/2}$, $\text{BO}_{b/2}\dots$; and $X_{\text{AO}_{a/2}}$, $X_{\text{BO}_{b/2}}\dots$ are the proportions of oxygen atoms contributed by each of the oxides, that is their equivalent fractions.

The basicity dependence of CFSE of Cr^{3+} in glasses is shown on Fig. 2, which compares the present results with CFSE values calculated from spectroscopic data from the literature (Rodríguez-Mendoza et al., 1999; Rasheed et al., 1991). There is a general trend of increasing CFSE with theoretical optical basicity in most silicate and aluminosilicate glasses, but two kinds of glasses exhibit a different behavior, alkali silicates and borates, which would be briefly discussed below. The positive trend observed for most glasses arises from the sensitivity of crystal field splitting to the effective charge of oxygen ligands (Platonov et al., 1996). Increasing basicity results in a larger average negative charge borne by the oxygen ligands and then in the crystal field values at the Cr site. At the same time, the higher charge of these ligands causes a stronger covalence of the Cr–O bond at higher basicity.

The CFSE values of Cr^{3+} in alkali silicate glasses calculated from the data of Rodríguez-Mendoza et al. (1999) show that the nature of the cations coexisting with Cr^{3+} in the glass is an important parameter: CFSE changes from 216 to 220 kJ/mol- Cr^{3+} between K- and Li-disilicate glasses, despite the fact that the optical basicity of K_2O is higher than that of Li_2O , 1.4 and 1.0, respectively. A similar negative variation of CFSE with theoretical glass basicity is observed in alkali borates. However, Na- and K-borosilicate glasses show the same CFSE as Na- and K-silicate glasses, although the optical basicity may change significantly among these glasses. These observations show that basicity is not the only parameter to affect CFSE. They also indicate that chromium does not probe the average glass structure, as other transition elements, which are preferentially located in cationic domains (Greaves, 1989; Galoisy et al., 2000; Cormier et al., 2001).

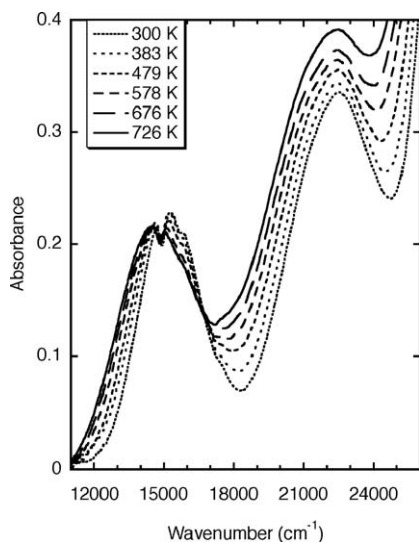


Fig. 3. Optical absorption spectra of Cr^{3+} in the KBS glass at ambient and high temperature.

3.3. High-temperature crystal field spectra

The modification of the crystal field spectra in the KBS glass as a function of temperature is depicted in Fig. 3. The major changes observed are an increase in the UV absorbance and a shift of the Cr^{3+} absorption bands to lower wavenumbers. Some enhancement of the UV absorption may arise from a stronger O to Cr^{3+} charge transfer with increasing temperature, as observed on high-temperature spectra of Cr-bearing minerals (Taran et al., 1994). However, the contribution of low concentrations of chromate groups may also increase with temperature, as a result of a shift of the redox interaction between the Cr(VI)–Cr(III) and As(V)–As(III) couples. The modification of the Cr^{3+} absorption bands is related to the modification of the Cr^{3+} sites at high temperatures, which will be discussed below. All these modifications are correlated between themselves, as shown by the presence of an isosbestic point near $17\,000\text{ cm}^{-1}$. The shift of the transmission window from $18\,300\text{ cm}^{-1}$ down to about $17\,000\text{ cm}^{-1}$ causes a thermochromic effect with a color change from green to yellow.

The most important modifications of the ν_1 band with temperature are a shift towards lower wavenumbers (red shift), a modification of the line shape and a decreasing intensity. The red shift is directly related to the influence of thermal site expansion on the crystal field splitting of Cr^{3+} ions. The modification of the line shape is mostly visible through a significant broadening. A similar shift is observed in the other investigated glasses and has been described in soda lime glasses (Tilquin et al., 1998; Gödeke et al., 2001). High-temperature spectra of Cr^{3+} in minerals show a

similar broadening related to a higher temperature-induced local disorder (both radial and angular).

By contrast, the shift of the ν_2 band remains modest, but the shape of this band is modified in the same way as that of ν_1 , with a decreasing relative intensity and a broadening at increasing temperatures. By comparison with the optical absorption spectra of Cr^{3+} in minerals, the absence of enhancement of the absorption coefficient of ν_1 and ν_2 with temperature indicates a distortion of the Cr^{3+} sites in glasses. Indeed, the intensity of crystal field transitions of Cr^{3+} located in high symmetry sites is enhanced at high temperature (Taran et al., 1994). The intensity of the dips decreases with increasing temperature. This is consistent with an increasing local disorder with temperature, at the origin of the broadening of the optical transitions. The position of these features remains almost independent of the temperature and the red shift modifies the shape of the ν_1 band at high temperature.

3.4. Variation of spectroscopic parameters as a function of temperature

As for the room temperature spectra, the position of the ν_1 transition has been taken at the maximum of the Gaussian envelope of the ν_1 band, in order to avoid the perturbation of the dips. The red shift of the ν_1 band with increasing temperature is noticeable since the first heating step and it reaches 490 cm^{-1} at 726 K, with increasing temperature. This red shift is well correlated with temperature and causes a steady linear decrease (within experimental uncertainty) of the CFSE with increasing temperature (Fig. 4).

The overall variation of CFSE is similar in the investigated glasses, 7–8 kJ/mol- Cr^{3+} in a 500 K range,

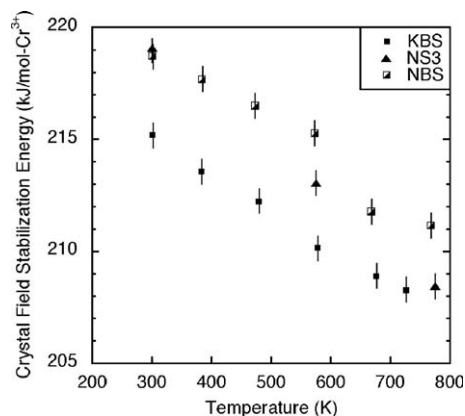


Fig. 4. Variation of crystal field stabilization energy as a function of temperature in silicate and borosilicate glasses (uncertainty bars are indicated).

a value similar to that characterizing the CFSE chemical dependence. This provides a direct spectroscopic evidence of the thermal expansion of Cr^{3+} sites in glasses. A similar influence of thermal expansion on the spectroscopic properties of Cr^{3+} has been observed in various Cr-bearing minerals (Taran et al., 1994).

The Racah parameter B increases with temperature (Fig. 5). At high temperatures, the Dq/B ratio decreases down to 2.03, a significant difference with the room temperature value, 2.15. This large modification of the Dq/B ratio is due to the opposite variation of Dq and B with temperature. The Cr–O bond ionicity may be rationalized using an ionicity factor β defined by the relation

$$\beta = \frac{B}{B_0} \quad (3)$$

where B_0 is the free ion value.

β rises from 68% to 70% from room temperature to 700 K, indicating that Cr–O bond ionicity slightly increases with T . This modification of the Cr–O bonding arises from thermal expansion of the chemical bond, which increases d -electron localization. However, the thermal dependence of the B -Racah parameter is significantly lower in glasses than in crystals, in which the (Cr–O) bond ionicity rises by up to 8% between room temperature and 800 K.

3.5. Quantification of the thermal expansion of Cr^{3+} sites in glasses

Using a point charge model, the temperature-induced variation of the Cr–O distances may be derived from crystal field theory (Burns, 1993):

$$10Dq = \frac{5q\langle r^4 \rangle}{R^5} \quad (4)$$

where q is the effective charge in the ligands, r the d -

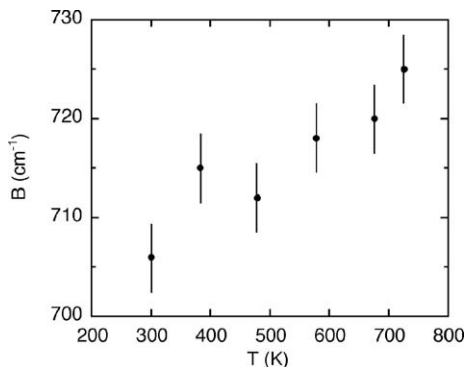


Fig. 5. Variation of the B Racah parameter as a function of temperature in the KBS glass (uncertainty bars are indicated).

electron-core distance and \bar{R} the mean Cr–O distance. As q and r do not change within a reasonable range of temperature for a given site, it is possible to use relation (4) to get R . The local linear thermal expansion coefficient α_{loc} is defined as a function of the Cr–O distance R (Hazen and Finger, 1982):

$$\alpha_{\text{loc}} = \frac{1}{R} \frac{\partial R}{\partial T}. \quad (5)$$

The α_{loc} -values derived from high-temperature Cr^{3+} crystal field spectra are similar in all investigated glasses, $16\text{--}20 \times 10^{-6} \text{ K}^{-1}$. These values explain the difficulty of directly determining local thermal expansion in glasses using methods such as EXAFS or X-ray scattering, with typical bond length uncertainties of the order of 0.01 Å (Brown et al., 1995). The R^5 dependence of CFSE makes optical spectroscopy an interesting approach.

The α_{loc} -values determined in glasses are also similar to the values derived from high-temperature Cr^{3+} crystal field spectra of crystalline silicates, such as Ca- and Mg-garnets and diopside ($18\text{--}15\text{--}16 \times 10^{-6} \text{ K}^{-1}$, respectively: Taran et al., 1994), which confirms the local character of thermal site expansion in silicates, and the validity of a polyhedral approach (Hazen and Finger, 1982) in silicate glasses. Oxides, such as corundum and spinel present smaller α_{loc} -values, $11\text{--}12 \times 10^{-6} \text{ K}^{-1}$, respectively (Taran et al., 1994).

α_{loc} is larger than α , which lies typically in the range $0.7\text{--}10 \times 10^{-6} \text{ K}^{-1}$ in glasses. This is expected, as cations are involved in ionic bonds, which expand more easily than the rigid covalent bonds of the glassy network. In the glasses investigated, bulk α -values of borosilicate and silicate glasses are different, typically 3 and $9 \times 10^{-6} \text{ K}^{-1}$, respectively. However, α_{loc} -values remain similar. This lack of sensitivity of α_{loc} on glass composition demonstrates the decoupling between local and bulk thermal expansion. This independence on the nature of the polymeric network may indicate the preferential location of Cr^{3+} ions in cationic domains. Recent structural models of glasses favor a non-homogeneous distribution of cations, in domains, the size of which extends up to 10 Å (Cormier et al., 2001).

4. Conclusion

Chromium is a sensitive probe of the evolution of glass structure as a function of composition or temperature. Glass polymerization causes a decrease of crystal field intensity with an overall variation of Cr^{3+} CFSE of 7 kJ/mol- Cr^{3+} in glasses representing simplified magmatic compositions. The chemical dependence

of Cr^{3+} spectroscopic properties may be rationalized using the concept of glass basicity. Alkali-bearing glasses represent a noticeable exception, in which spectroscopic parameters only depend on the nature of the alkali and not on its concentration. In these glasses, Cr^{3+} is not sensitive to the average glass structure, an indication of the heterogeneous structure of silicate glasses at the atomic scale.

Local thermal expansion may be treated in glasses using the polyhedral approach, which has been used to describe the thermal evolution of mineral structures (Hazen and Finger, 1982). The values derived from high-temperature crystal field spectra of Cr^{3+} in silicate glasses, $16\text{--}20 \times 10^{-6} \text{ K}^{-1}$, are similar to those determined in silicate minerals. The determination of these local thermal expansion coefficients sheds light on the processes, which control at the atomic scale the evolution of the specific volume of glasses at high temperatures. It is interesting to point out that Cr site thermal expansion does not change much with glass composition by contrast to the bulk thermal expansion of glasses. If such a behavior acts in silicate melts, the important variations of Cr^{3+} CFSE observed among the glass compositions of geological interest will be retained. The CFSE values obtained in this study may then help in a better description of the chemical dependence of mineral/melt partition coefficients. Complementary studies at higher temperatures will be needed to get a better understanding of the complex Cr speciation in natural magmas (Colson et al., 2000).

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References

- Bamford, C.R., 1977. *Colour Generation and Control in Glasses*. Elsevier, Amsterdam.
- Bédard, J.H., 2005. Partitioning coefficients between olivine and silicate melts. *Lithos* 83, 394–419.
- Biggar, G.M., O'Hara, M.J., 1969. A comparison of gel and glass starting materials for phase equilibrium studies. *Min. Mag.* 36, 198–205.
- Blundy, J., Wood, B., 2003. Partitioning of trace elements between crystals and melts. *Earth Planet. Sci. Lett.* 210, 383–397.
- Brown Jr., G.E., Farges, F., Calas, G., 1995. X-ray scattering and X-ray spectroscopy studies of silicate melts. *Rev. Mineral.* 32, 317–410.
- Burns, R.G., 1993. *Mineralogical Applications of Crystal Field Theory*, 2nd ed. Cambridge University Press, Cambridge. 574 pp.
- Bussière, G., Reber, C., Neuhauser, D., Walter, D.A., Zink, J.I., 2003. Molecular properties obtained by analysis of electronic spectra containing interference dips. Comparisons of analytical equations and exact models based on coupled potential energy surfaces. *J. Phys. Chem., A* 107, 1258–1267.
- Calas, G., Petiau, J., 1983. Structure of oxide glasses: spectroscopy studies of local order and crystallochemistry. *Geochemical implications. Bull. Minéral.* 106, 33–55.
- Calas, G., Manceau, A., Novikoff, A., Boukili, H., 1984. Comportement du chrome dans les minéraux d'altération du gisement de Campo-Formoso (Bahia, Brésil). *Bull. Minéral.* 107, 755–766.
- Colson, R.O., Colson, M.C., Nermoe, M.K.B., Floden, A.M., Hendrickson, T.R., 2000. Effects of aluminum on Cr dimerization in silicate melts and implications for Cr partitioning and redox equilibria. *Geochim. Cosmochim. Acta* 64, 527–543.
- Combes, J.M., Creux, S., Calas, G., 1995. Influence of field strength parameters on the optical spectra of iron-containing silicate glasses. *Proc. XVI Int. Congr. Glass, Pekin*, pp. 90–94.
- Cormier, L., Calas, G., Gaskell, P.H., 2001. Cationic environment in glasses studied by neutron diffraction with isotopic substitution. *Chem. Geol.* 174, 349–363.
- Dalba, G., Fornasini, P., Rocca, F., Monti, F., 2001. EXAFS studies of local thermal expansion in borate glasses. *J. Non-Cryst. Solids* 293–295, 93–99.
- Duffy, J.A., 1993. A review of optical basicity and its applications to oxydic systems. *Geochim. Cosmochim. Acta* 57, 3961–3970.
- Duffy, J.A., Ingram, M.D., 2002. Solvent properties of glass melts: resemblance to aqueous solutions. *C. R., Chim.* 5, 797–804.
- Galoisy, L., Cormier, L., Rossano, S., Calas, G., Gaskell, P.H., 2000. Cationic ordering in oxide glasses: the example of transition elements. *Mineral. Mag.* 64, 409–424.
- Gödeke, D., Müller, M., Rüssel, C., 2001. High-temperature UV–VIS–NIR spectroscopy of chromium-doped glasses. *Glasstech. Ber. Glass Sci. Technol.* 74, 177–182.
- Greaves, G.N., 1989. EXAFS, glass structure and diffusion. *Philos. Mag. B* 60, 793–800.
- Hanson, B., Jones, J.H., 1998. The systematics of Cr^{3+} and Cr^{2+} partitioning between olivine and liquid in the presence of spinel. *Am. Mineral.* 83, 669–684.
- Hazen, R.M., Finger, L.W., 1982. *Comparative Crystal Chemistry: Temperature, Pressure, Composition and the Variation of Crystal Structure*. John Wiley & Sons, New York.
- Irving, A.G., 1978. A review of experimental studies of crystal/liquid trace element partitioning. *Geochim. Cosmochim. Acta* 42, 743–770.
- Janata, E., 2003. Instrumentation of kinetic spectroscopy-17. The use of a diode array multichannel detector in kinetic experiments. *Radiat. Phys. Chem.* 66, 145–148.
- Kepler, H., 1992. Crystal field spectra and geochemistry of transition metals ions in silicate melts and glasses. *Am. Mineral.* 77, 62–75.
- Lempicki, A., Andrews, L., Nettel, S.J., McCollum, B.C., Solomon, E. I., 1980. Spectroscopy of Cr^{3+} in glasses: fano antiresonances and vibronic Lamb shift. *Phys. Rev. Lett.* 44, 1234–1237.
- Murck, B.W., Campbell, I.H., 1986. The effect of temperature, oxygen fugacity and melt composition of the behavior of chromium in basic and ultrabasic melts. *Geochim. Cosmochim. Acta* 50, 1871–1887.
- Mysen, B.O., 1983. The structure of silicate melts. *Annu. Rev. Earth Planet. Sci.* 11, 75–97.

- Nowack, N., Okretic, S., Pfeifer, F., Zebger, I., 2001. Ultraviolet-visible spectroscopy of molten slags and glasses (up to 1600 °C). *J. Non-Cryst. Solids* 282, 30–40.
- Paul, A., Upreti, G.C., 1975. EPR and optical absorption of Cr³⁺ in binary Na₂O-B₂O₃ glasses. *J. Mater. Chem.* 10, 1149–1153.
- Petermann, M., Hirschmann, M.H., 2002. Trace-element partitioning between vacancy-rich eclogitic clinopyroxene and silicate melt. *Am. Mineral.* 87, 1365–1376.
- Platonov, A.N., Langer, K., Andrut, M., Calas, G., 1996. Cr³⁺ in phyllosilicates: influence of the nature of coordinating ligands and their next cationic neighbors on the crystal field parameters. In: Dyar, M.D., McCammon, C., Schaefer, M.W. (Eds.), *Mineral Spectroscopy: A Tribute to Roger G. Burns*. Special Publication-Geochemical Society, vol. 5, pp. 41–48.
- Rasheed, F., O'Donnell, K.P., Henderson, B., Hollis, D.B., 1991. Disorder and the optical spectroscopy of Cr³⁺-doped glasses: I. Silicate glasses. *J. Phys., Condens. Matter* 3, 1915–1930.
- Rodriguez-Mendoza, U.R., Rodriguez, V.D., Lavin, V., Martin, I.R., Nuñez, P., 1999. Fano anriresonances of Cr³⁺ in alkaline disilicate glasses. *Spectrochim. Acta, A* 55, 1319–1322.
- Rossmann, G.R., 1988. Optical spectroscopy. In: Hawthorne, F.C. (Ed.), *Spectroscopic Methods in Mineralogy and Geology*. *Rev. Mineral.*, vol. 18, pp. 207–254.
- Taran, M.N., Langer, K., Platonov, A.N., Indutny, V.V., 1994. Optical absorption investigation of Cr³⁺ ion-bearing minerals in the temperature range 77–797 K. *Phys. Chem. Miner.* 21, 360–372.
- Tilquin, J.Y., Duveiller, P., Glibert, P., Claes, P., 1998. Comparison between high-temperature UV–visible spectroscopy and electrochemistry for the in situ study of redox equilibria in glass-forming melts. *J. Non-Cryst. Solids* 224, 216–224.
- Wang, S., Stebbins, J.F., 1999. Multiple-quantum magic-angle spinning 17O NMR studies of borate, borosilicate, and boroaluminate glasses. *J. Am. Ceram. Soc.* 82, 1519–1528.