Structural relaxation in tetrahedrally coordinated Co\textsuperscript{2+} along the gahnite-Co-aluminate spinel solid solution

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ABSTRACT

The structural relaxation around the Co\textsuperscript{2+} ion along the gahnite (ZnAl\textsubscript{2}O\textsubscript{4})-Co-aluminate (CoAl\textsubscript{2}O\textsubscript{4}) join was investigated by a combined X-ray diffraction (XRD) and electronic absorption spectroscopy (EAS) approach. Monophasic spinel samples (Zn\textsubscript{1-y}Co\textsubscript{y}Al\textsubscript{2}O\textsubscript{4} with y = 0, 0.25, 0.5, 0.75, and 1 apfu) were obtained through solid-state reaction (1300 °C with slow cooling). The cobalt incorporation induces a linear increase of the unit-cell parameter (a) accompanied by an increasing inversion parameter (up to 0.07) so that the Co\textsuperscript{2+} for Al\textsuperscript{3+} substitution in the octahedral site is, at a first approximation, the cause of the lattice expansion. However, a careful consideration of T-O distances highlights the role played by an enhanced covalence degree of Zn-O bonds. The optical spectra are characterized by the occurrence of electronic transitions of Co\textsuperscript{2+} in tetrahedral coordination affected by a strong spin-orbit coupling, causing a threefold splitting of spin-allowed bands. Further complications stem from mixing of quadruplet and doublet states (leading to a consistent intensity gain of spin-forbidden bands) and vibronic effects (producing intense sidebands). Crystal field strength goes from 4187 to 4131 cm\textsuperscript{-1} with increasing cobalt amount, while the Racah B parameter is in the 744–751 cm\textsuperscript{-1} range (C ∼3375 cm\textsuperscript{-1}). To achieve a reliable estimation of the local Co-O distance, the tetrahedral distance evolution was recast to eliminate the effects of the inversion degree. By this way, a relaxation coefficient as low as ε = 0.47 was obtained, i.e., significantly smaller than literature data for other spinel systems. The gahnite-Co-aluminate join seems to be constrained by the strong preference of Zn\textsuperscript{2+} for the tetrahedral site in which its enhanced covalency can be exerted, limiting the cation exchange between tetrahedral and octahedral sites as well as the lattice flexibility.

Keywords: Gahnite, Co-aluminate, spinel structure, X-ray powder diffraction, Rietveld refinement, electronic absorption spectroscopy, structural relaxation

INTRODUCTION

In the last decades, several studies have demonstrated that the stability of isomorphous solid solutions, at the atomic scale, is affected by a structural relaxation around substituting cations (e.g., Galoisy 1996; Langer 2001; Langer et al. 2004; Taran et al. 2004; Andrut et al. 2004). Along a binary join, the average structure obtained by diffraction methods does not give any indication on the local mean distances between the central ion and its surrounding oxygen-based polyhedron. The lack of this information may be overcome by the use of spectroscopic methods. As proposed by Urusov (1992), the deviation from the Vegard’s rule can be quantified, on a geometrical basis, through the relaxation coefficient (ε), as:

\[ \varepsilon = \frac{1}{\langle B-O \rangle_{\text{end}} - \langle A-O \rangle} \times \frac{1}{\langle B-O \rangle - \langle A-O \rangle} \]  \hspace{1cm} (1)

where, for a hypothetic \textit{A}→\textit{B} O solid solution, \langle A-O \rangle and \langle B-O \rangle are the mean polyhedral distances for the two end-members (measured for instance by XRD), and \langle B-O \rangle_{\text{end}} is the local mean distance for \textit{A}→\textit{B} O, with y→0 (estimated by spectroscopy). The behavior of exchanging cations in a solid solution falls between two extreme cases deriving from the Equation 1. The case of full relaxation, i.e., the situation implied by the hard sphere (HS) model, \( \varepsilon = 1 \), means that the interatomic (\textit{B}-\textit{O})→\textit{A} distance will not change with composition: \( \langle B-O \rangle_{\text{end}} = \langle B-O \rangle \). In absence of relaxation, on the other side, \( \varepsilon = 0 \) (corresponding to the Vegard’s additivity rule predicted by the virtual crystal approximation, \( VCA \), model), therefore \( \langle B-O \rangle_{\text{end}} = \langle A-O \rangle \) (Wildner et al. 2004; Andrut et al. 2004). It follows that the accurate determination of the local structure around substituting ions is fundamental to provide detailed information on their incorporation and on physical properties; for instance, the presence of transition metal ions as impurities is one of the most important and studied causes of color in minerals and synthetic analogs (e.g. Gaudry et al. 2006; Juvin et al. 2007, 2008; Cruciani et al. 2009; Hälenius et al. 2010). Although evidences of a large deviation from the Vegard’s rule in tetrahedral site were already reported for simple binary solid solutions (e.g., Levelut et al. 1991), the above mentioned structural relaxation studies about silicate and oxide solid solutions of geological interest are mainly focused on cation substitution in octahedral coordination sites. The only exception is represented by the work of Hälenius et al. (2011) where the effects of the tetrahedral Mn\textsuperscript{2+}-Mg substitution were assessed along the MgAl\textsubscript{2}O\textsubscript{4}-MnAl\textsubscript{2}O\textsubscript{4} spinel join.

Minerals belonging to the spinels group are ternary oxides