Crystal Structure of GeFe₂O₄

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The brunogeierite $GeFe_2O_4$ is a rare mineral of germanium, with a normal spinel structure and amazing functional properties. Its spectroscopic, optical, magnetic and electronic properties are known. For many years it was left behind, but recently a renewed interest in this oxide has arisen, particularly for its application in the electrochemical field, as anode in Lithium Ion and Sodium Ion Batteries and as electrocatalyst for urea oxidation reaction.

GeFe2O4 Fe2GeO4 brunogeierite

crystal structure

applications

1. Introduction

The natural minerals of Ge, differently from silicon, are few and very rare or even unique to a specific place: the most diffused are sulphides, oxides, sulphates, hydroxides and germanates^[1] In particular, GeFe₂O₄ (GFO), whose mineralogical name is brunogeierite, can be found in large amount in Namibia, in the Tsumeb deposits (**Figure 1**) ^[2].



Figure 1. Image of Brunogeierite crystals from Tsumeb, Namibia, taken from RRuff Database [2].

A curious aspect concerning $GeFe_2O_4$ was the determination of the right oxidation states of the cations, which was rather difficult. Only on the basis of bond-valence calculations, the ideal formula was determined as $Fe^{2+}_2Ge^{4+}O_4$

^[3]. The ferrite spinels, among which brunogeierite could be numbered, are well-known and commonly studied materials with an impressive range of applications extending from millimeter wave integrated circuitry to power handling, simple permanent magnets and magnetic recording, catalysis, sensors, energy, nanomedicine and imaging in magnetic resonance. Some examples of the most commonly studied and applied ferrites are represented by $ZnFe_2O_4$, $CoFe_2O_4$, Fe_3O_4 , $NiFe_2O_4$, $MgFe_2O_4$, and $MnFe_2O_4$ ^{[4][5]}, each of them having peculiar functional properties.

2. Crystal Structure

The crystal structure of brunogeierite (**Figure 2**) was determined by Welch in 2001 on a single crystal from Tsumeb^[6].



Figure 2. Representation of the brunogeierite crystal structure: FeO₆ octahedra (blue) and GeO₄ tetrahedra (red).

In ref. ^[6], however, as in other previous studies, nothing was declared about the valence states of the cations in the brunogeierite. In 2013, on the base of bond-valence calculations, the structure was newly verified and definitively established^[3]. GeFe₂O₄ is a normal cubic spinel with *Fd-3m* space group and a lattice parameter of 8.4127(7) Å. There are eight formula units in the unit cell, as expected for the spinels' structure. The value for the oxygen coordinate in GFO (Ge and Fe ions are located on special sites) is 0.2466(1). Taking into consideration that for an ideal cubic close-packing of oxygens the value is 0.25, brunogeierite has a nearly perfect oxygens framework, in which Fe²⁺ occupies half of the octahedral interstices and Ge⁴⁺ one eighth of the tetrahedral. The Ge-O bond length was 1.771(2) Å, very close to the sum of the ionic radii of the involved ions (0.39Å + 1.38Å = 1.77 Å). The

shorter bond length in GFO can be explained by the presence of some Fe³⁺ on the Ge⁴⁺ site, as suggested by the results of the bond valence calculations^[3]. The Fe-O bond is, instead, 2.132 Å, slightly shorter than the sum of the ionic radii (0.78Å + 1.38Å = 2.16 Å). In this case, some Fe³⁺ could be present on the octahedral sites, influencing the bond length value. The presence of a small amount of Fe³⁺ ions at both tetrahedral and octahedral sites suggested the formation of a solid solution with the magnetite Fe₃O₄ phase. The cubic symmetry of GFO was maintained up to 5 K, without structural distortion, as demonstrated by synchrotron X-ray powder and neutron diffraction measurements^[2]. However, by increasing the pressure, it was suggested that, at about 20–22 GPa, a reduction from cubic (*Fd-3m*) to tetragonal (*I4*₁/amd) symmetry occurred, as determined from the analysis of the band shifts of the Raman spectra and the colour change of crystals^[8]. The same authors suggested, on the base of the pressure of additional bands in the Raman spectra, a partial inversion of the spinel structure, which at ambient pressure and temperature had the normal structure.

As previously discussed, $GeFe_2O_4$ can be found in nature in peculiar locations in the form of single crystals, which were usually employed for crystal structure determination. However, single crystals were also synthesized in laboratory and were used, for example, for high pressure Raman studies and for the determination of optical and electrical properties. For electrochemical and electrocatalytic applications, GFO was used instead in the form of nano-powders, which are more easily synthesized, by using solid state, mechanochemistry, hydrothermal and freeze drying synthetic routes.

GFO single crystals and powders were characterized by many spectroscopic techniques, such as Mössbauer, Xray Photoelectron Spectroscopy (XPS), Infrared Spectroscopy (IR) and Raman, as well as with X-ray diffraction. Mössbauer and XPS spectroscopies allowed to determine the cation oxidation states, that were definitely established as Ge4+ and Fe2+. In some cases, traces of Fe3+ were found, suggesting the formation of solid solutions with Fe3O4. XPS was also useful to characterize the possible carbon coating, particularly for electrochemical applications. The IR spectrum was not conclusively interpreted, diffently from Raman spectra that were collected as a function of pressure to study the structure stability. It was demonstrated that the changes in the collected spectra were not due to sample decomposition (at least below 30 GPa) and/or to polymorphs formation, but possibly to partial spinel inversion. The difference in ionic radii of Fe²⁺ and Ge⁴⁺ ions inhibited the inversion in single crystals but not in nanocrystalline GFO that, when obtained from mechano-synthesis showed an inversion degree of 0.67. The new bands and the band splitting observed in Raman spectra can be due also to structure distortion towards the tetragonal structure $(I4_1/amd)$, the most probable distortion of the cubic spinel containing Fe^{2+} ions. The magnetic properties of GFO were determined in the past and newly measured more recently^[7]. Its behaviour was unusual in non-metallic materials: the reason was attributed to a frustration wave order in GFO derived from exchange interactions between the ordered spin components in a sublattice via the dynamic components of their neighbours in the other. The peculiar magnetic features of GFO were not shared by all the Ge based spinels, because being Ge⁴⁺an inactive ion, they were determined by the B²⁺ sublattice, so a variety of different behaviours could be identified. The positive value of the Hall constant suggested a p-type conduction. Conductivity and Hall effect measurements showed that the acceptor ionization energy was 0.39 eV and that the mobility was low and independent of temperature, probably due to a narrow valence band and/or large polaron

formation. GFO differed, however, with respect to other hopping-type spinels, because its electronic properties were similar to those of NiO at high temperatures^[9].

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