Letter to Editor

Note on the formula of brunogeierite and the first bond-valence parameters for Ge²⁺

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Brunogeierite is a rare Ge-mineral with a spinel-type structure. Inconsistences in the brunogeierite formula suggesting divalent germanium in its structure have occurred since its description. A review of the published data and bond-valence calculations show that the correct ideal end-member formula of brunogeierite is $(Fe^{2+})_2Ge^{4+}O_4$. The mineral is newly classified as a nesogermanate member of the ringwoodite group (Strunz classification 9.AC.15). Formal correction of the brunogeierite formula and classification was approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC) as proposal IMA 11-A. In order to perform bond-valence calculations using divalent germanium, new bond-valence parameters for Ge^{2+}–O (R_0 = 1.778 Å, B = 0.37 Å) and Ge^{2+}–Cl (R_0 = 2.156 Å, B = 0.37 Å) were evaluated.

1. Introduction

Brunogeierite is a rare Ge-mineral with a spinel-type structure. Since its discovery in Tsumeb, Namibia (Otteman and Nuber 1972) it has been described from at least 12 other localities in the French Pyrenees (Aye et al. 1978; Johan et al. 1983; Johan and Oudin 1986). The brunogeierite structure and experimental stability constraints are well known (Otteman and Nuber 1972; Hariya and Wai 1970; Julliot et al. 1987; Welch et al. 2001); however, its formula is ambiguous. In the updated 2011 version of "IMA List of Minerals" and in earlier books and reviews (e.g., Fleischer and Mandarino 1995; Anthony et al. 1997), brunogeierite was listed with the formula $Ge^{2+}(Fe^{3+})_2O_4$ and the respective Strunz classification was 4.BB.05 (Oxides, Spinel Group). The presence of Ge^{2+} in brunogeierite has also been non-critically adopted elsewhere (e.g., Höll et al. 2007). However, the low oxidation state of germanium (Ge^{2+}) along with the high oxidation state of iron (Fe^{3+}) in the same compound is suspicious and, since synthetic compounds with Ge^{2+} are very rare and usually unstable in humid air (e.g., Messer 1978; Thiele et al. 1987), the presence of Ge^{2+} in a natural phase is unlikely.

This study clarifies the inconsistences in the brunogeierite formula and provides new bond-valence parameters for bonds of Ge^{2+} with oxygen and chlorine. A review of published data and bond-valence calculations shows that the correct ideal end-member formula of brunogeierite is $(Fe^{2+})_2Ge^{4+}O_4$. Since the Strunz classification scheme ca-

tegorizes silicates and germanates in the same group, the mineral is newly classified as a nesogermanate, a member of the ringwoodite group (Strunz classification 9.AC.15). Formal correction of the brunogeierite formula and classification was approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC) as proposal IMA 11-A (Williams et al. 2011).

2. Brunogeierite formula

Papers published on brunogeierite have not provided valence states for the cations; the original formula reported by Otteman and Nuber (1972) is $(GeFe_2O_4)_x \cdot (Fe_3O_4)_{1-x}$ with x equal to 0.87 and 0.95 in the two analyzed samples. However, the analytical data were always presented as GeO_2 and FeO (Otteman and Nuber 1972; Johan et al. 1983), although sometimes minor amount of Fe^{3+} (≤0.172 *apfu*) was calculated in order to match the ideal stoichiometry $(Fe^{2+},R^{3+})_2(Ge,Fe^{3+})O_4$ (Johan et al. 1983). Significant inconsistency has occurred especially in subsequent mineral listings and derivative reports, where brunogeierite has been listed either as $(Ge_x, Fe_{1-x})Fe_2O_4$ (Fleischer 1973), $(Ge^{2+},Fe^{2+})(Fe^{3+})_2O_4$ (e.g., Fleischer 1980; Fleischer and Mandarino 1995; Anthony et al. 1997), $Fe_3^{2+}(Ge^{2+}, Fe^{2+})O_4$ (Bernard and Hyršl 2004), $GeFe_2O_4$ (Mandarino and Back 2004) or $(Ge^{2+},Fe)Fe_2O_4$ (Spiridonov and Murashko 2010).

Brunogeierite was referred to as a nesogermanate (Otteman and Nuber 1972) or germanate and an ana-

logue of γ-Fe₂SiO₄ (Welch et al. 2001). Hariya and Wai (1970) studied miscibility of Fe_2SiO_4 and Fe_2GeO_4 with spinel-type structures. In all three publications where brunogeierite chemistry or structure were directly studied (Otteman and Nuber 1972; Johan et al. 1983; Welch et al. 2001), there is no note on the alleged divalent state of germanium or prevailing trivalent state of iron.

Churbakov et al. (1964) reported synthesis of magnetite containing Ge^{2+} under nitrogen atmosphere using rather unclear synthesis procedure from Fe-sulphate and $GeCl_2$ in alkaline solution. However, the reported powder X-ray diffraction patterns of the precipitates heated at 400 °C in a stream of CO_2 strongly resemble those for mixtures of magnetite, GeO_2 and hematite; therefore, the synthesis products do not seem to be sufficiently characterized.

3. Crystal chemistry of ionic Ge²⁺-compounds

Compounds containing Ge^{2+} have been synthesized in the past but are never observed in nature. Germanium with formal valence 2+ is stable especially in covalent bonds with S, Se, Te, As, P and N; ionic bonds with halogenides and oxygen are less frequent. Ratios of ionic/covalent bond components are disputable (e.g. Höll et al. 2007); covalent bonding becomes more important for bromides and iodides but it is significant for bonds with anions of high electronegativity (O, F, Cl). Ionic bonding in Ge^{2+} compounds is more significant than in Ge^{4+} compounds due to lower electronegativity (cf. Li and Xue 2006).

Only three of 31 ionic structures with Ge^{2+} in the ICSD database (Fachinformationszentrum Karlsruhe 2011) contain Ge^{2+}–O bonds. Synthesis of ionic compounds of Ge^{2+} always requires strong reducing agents (the most commonly used is hypophosphorous acid H_3PO_2; Everest 1953) and an inert atmosphere (Everest 1953; Lee and Weng 2008). In ionic compounds with halogens or O^{2-}, divalent germanium typically occurs in triangular pyramidal coordination, with a stereochemically active lone

electron pair oriented opposite to the triangle of anions. Bond lengths between Ge^{2+} and O^{2-} range from 1.86 to 1.95 Å (Weakley and Watt 1979; Lee and Weng 2008).

For the purpose of demonstration of bond-valence sums (Brown 2002) of Ge in brunogeierite, we examined the three compounds with Ge–O bonds (Tab. 1). Because no bond-valence parameters for Ge^{2+}–O have been published to date, we used the structures of $GeCl(H_2PO_2)$ and $Na[Ge_4(PO_4)_3]$ for their calculation; the quality of the $Ge_2(H_2PO_2)_6$ structure model was insufficient for the calculation because of the unresolved positional disorder of the Ge^{2+} site reported by Weakley (1983). In the case of the $GeCl(H_2PO_2)$ structure, Ge^{2+} is bonded to one chlorine and two oxygen atoms; since the calculation required bond-valence (BV) parameters for Ge^{2+}–Cl as well, we calculated them using four other compounds where Ge^{2+} is bonded to chlorine atoms only (Tab. 1). Bond valence parameters R_0 were obtained according to Brown (2002) as an average of R_{0i} values for all Ge^{2+}-polyhedra. R_{0i} is defined as:

$$R_{0i} = B \times \ln\left(V_i / \sum exp^{-\frac{R_{ij}}{B}}\right)$$

where B is a bond-valence parameter (B = 0.37 Å), V_i the formal valence of the cation (V = 2), and R_{ij} the bond length between atoms i and j. Advanced least-squares fitting of R_0 and B constants (e.g. Krivovichev 2012, and references therein) was not possible due to the lack of structural data.

The calculated bond-valence parameters may be influenced by interactions of the free electron pair with adjacent atoms. In $GeCl(H_2PO_2)$, the distance between Ge and P is 4.17 Å, and in $Na[Ge_4(PO_4)_3]$ the two neighboring Ge atoms are 3.94 Å apart; these distances are too long for significant covalent interactions. This is in agreement with Wang and Liebau (1996) who showed correlation between the <φ–Sb^{3+}–φ> bond angles and free electron pair interaction for Sb^{3+} in triangular pyramidal coordination. All compounds used for the calculation of BV parameters feature O–Ge–O angles between 90 and 100° (Tab. 1), suggesting only very weak interactions.

Tab. 1 Calculation of bond-valence parameters for Ge^{2+}–Cl and Ge^{2+}–O

Compound (reference)	<Ge–φ> [Å]	R_{0i} [Å]	< φ–Ge–φ>
N(CH₃)₄GeCl₃ (Depmeier et al. 1980)	2.294	2.143	95.2°
RbGeCl₃ (Messer 1978)	2.311	2.161	94.5°
CsGeCl₃ (Christensen and Rasmussen 1965)	2.272	2.122	93.5°
CsGeCl₃ (Thiele et al. 1987)	2.348	2.198	94.2°
	R_0 (Ge^{2+}–Cl) = 2.156		
Na[Ge₄(PO₄)₃]	<Ge1–O>: 1.908	1.758	88.9°
(Lee and Weng 2008)	<Ge2–O>: 1.905	1.753	88.0°
GeCl(H₂PO₂)	<Ge–Cl>: 2.351	–	90.2°
(Weakley and Watt 1979)	<Ge–O>: 1.953	1.824	
	R_0 (Ge^{2+}–O) = 1.778		

Note: all structures at ambient temperature (20–25 °C). B = 0.37 Å for both R_0 (Ge^{2+}–Cl) and R_0 (Ge^{2+}–O)

Tab. 2 Brunogeierite bond-valence formula models

	(1)			(2)			(3)		
Formula	$Ge^{2+}(Fe^{3+})_2O_4$			$(Fe^{2+})_2(Ge^{4+})O_4$			BV-optimized formula		
Site occ.	Fe^{3+}	Ge^{2+}	O^{2-}	Fe^{2+}	Ge^{4+}	O^{2-}	$Fe^{2+}_{0.904}Fe^{3+}_{0.096}$	$Ge^{4+}_{0.808}Fe^{3+}_{0.192}$	O^{2-}
Avg. cat. charge	3	2	–2	2	4	–2	2.096	3.808	–2
$\sum$ BV	2.19	4.07	–2.11	2.05	3.75	–1.96	2.059	3.772	–1.972
Δ	**0.81**	**–2.07**	–0.11	–0.05	**0.25**	–0.04	0.037	0.036	–0.028

(1) model with Ge^{2+} and formula $Ge^{2+}(Fe^{3+})_2O_4$;
(2) model with Ge^{4+} and formula $(Fe^{2+})_2(Ge^{4+})O_4$;
(3) model with Ge^{4+} and disordered bond-valence optimized formula;
Δ = difference between the average cation charge and the bond-valence sum.

4. Bond-valence calculations in brunogeierite

The bond-valence model (Brown and Altermatt 1985; Brown 2002) is frequently used in verification and modeling of inorganic crystal structures using empirical relationships between bond length and bond valence. The bond valence is related to the bond length using the equation:

$$S_{ij} = exp^{\frac{R_0 - R_{ij}}{B}}$$

where R_{ij} represents the bond length from atom i to atom j, S_{ij} the corresponding bond valence, and R_0 and B are empirical parameters. The sum of all experimental bond valences S_{ij} around the atom i is equal to its formal valence V_i (Brown and Altermatt 1985; Brown 2002).

The bond-valence model was employed to calculate the valence states of Fe and Ge in three individual cases: 1) all Ge as Ge^{2+} and all Fe as Fe^{3+}, 2) all Ge as Ge^{4+} and all Fe as Fe^{2+}, and 3) bond-valence optimized formula with minor Fe^{3+} disordered between tetrahedral and octahedral sites. The brunogeierite structure and bond lengths reported by Welch et al. (2001) were used. Bond-valence calculations results for brunogeierite are listed in Tab. 2.

The unsuitable character of the Ge^{2+}-bearing model is proven by the disagreement between the formal average cation charges and calculated bond-valence sums of tetrahedral and octahedral sites in brunogeierite (Tab. 2, model 1). On the other hand, the slightly lower bond-valence sums in the model with structural sites fully occupied by one cation species (model 2) suggest minor substitutions of Fe^{3+} at both sites. The bond-valence optimized formula of brunogeierite, with Fe^{3+} employed (model 3), is $(Fe^{2+}_{0.904}Fe^{3+}_{0.096})_2(Ge^{4+}_{0.808}Fe^{3+}_{0.192})O_4$.

5. Discussion and summary

The literature review shows that previous studies have never reported the presence of Ge^{2+} or prevalence of Fe^{3+} in the brunogeierite formula. The error regarding the valence state of Fe and Ge probably started in Fleischer (1980) and could be due to the title of the original paper (Otteman and Nuber 1972) where the term "Germanium-Ferritspinell" is used ("Ferrit" is a common chemical term for Fe-spinel). This might have caused the subsequent confusion of terms (*"Ferrit"* vs. *"ferric"*?) and valence states.

Brunogeierite has a spinel-type structure, with fully ordered Ge and Fe atoms at tetrahedral and octahedral sites, respectively (normal spinel structure; Welch et al. 2001). The bond length <Ge–O> =1.771(2) Å for Ge at the tetrahedral site in brunogeierite is slightly shorter than those reported for the synthetic germanate spinels Mg_2GeO_4, Co_2GeO_4 and Ni_2GeO_4 (1.775–1.801 Å). The shorter bond length in brunogeierite can be explained as an effect of minor Fe^{3+} present at the Ge^{4+} site, as indicated by the results of the bond valence calculations.

The ideal end-member formula is therefore $(Fe^{2+})_2Ge^{4+}O_4$. Small amounts of Fe^{3+} occurring at the tetrahedral and octahedral sites suggest minor solid solution with a magnetite component. Since the Strunz classification scheme categorizes silicates and germanates in the same group, the mineral should be classified as a nesogermanate member of the ringwoodite group (Strunz classification 9.AC.15).

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