Crystal chemical properties of synthetic lazulite–scorzalite solid-solution series

Abstract Members of the lazulite–scorzalite (MgAl2-(PO4)2(OH)2-FeAl2(PO4)2(OH)2) solid-solution series were synthesized in compositional steps of 12.5 mol% at $T = 485^\circ$C and $P = 0.3$ GPa under hydrothermal conditions and controlled oxygen fugacities of the Ni/NiO-buffer. X-ray powder diffraction and $^{57}$Fe-Mössbauer studies show that under these conditions a complete solid-solution series is formed which is characterized by the substitution of Mg$^{2+}$ and Fe$^{2+}$ on the octahedral $\text{Me}^{2+}$ site. The $^{57}$Fe-Mössbauer spectra which reveal the presence of both ferrous and ferric iron and the compositional data were interpreted in terms of a defect model with a distribution of the ferric ions over both the $\text{Me}^{2+}$ and the $\text{Al}^{3+}$ positions and vacancies on the $\text{Me}^{2+}$ site. The $^{57}$Fe-Mössbauer parameters of the synthetic compounds correspond to those of natural lazulites except for the total absorption ratio of the ferric iron $A(\text{Fe}^{3+})/(A(\text{Fe}^{3+})+A(\text{Fe}^{2+}))$, which is significantly higher in natural lazulites of the same composition. The total absorption ratio of the ferric iron increases from 4% in pure scorzalite to 15% in a Mg-rich solid-solution with $x_{\text{Fe}} = 12(1)\%$

Key words Phosphate minerals · Lazulite · Scorzalite · Solid-solution · $^{57}$Fe-Mössbauer spectroscopy

Introduction

Natural lazulites are Mg-rich members of a solid-solution series between lazulite, MgAl$_2$(OH)$_2$(PO$_4$)$_2$ and scorzalite, FeAl$_2$(OH)$_2$(PO$_4$)$_2$. They occur as accessory phases in a variety of geological environments such as metamorphic and pegmatitic rocks, alluvial and colluvial sediments (Pecora and Fahey 1950), as well as in Alpine fissures (e.g. Menzel 1976). Wet chemical analysis suggested for natural lazulite–scorzalite samples a complete solid-solution series between the end-members (Abernathy and Blanchard 1982). Contrasting results have exclusively been reported by Duggan et al. (1990) who proposed a miscibility gap between $>35$ and $>75$ mol% scorzalite based on microprobe data of coexisting iron-lazulites and magnesio-scorzalites in hydrothermally altered triassic andesites from Mt. Perry (Queensland, Australia) and the Victory Mine pegmatite (South Dakota, USA).

The characteristic blue colour of natural and synthetic lazulites is a result of an optically induced intervalence charge transfer between Fe$^{2+}$ and Fe$^{3+}$ ions in neighbouring face-sharing octahedra (Lehmann 1978; Amthauer and Rossman 1984). The intensity of the blue colour depends on the occurrence of Fe$^{2+}$-Fe$^{3+}$ couples and increases generally with increasing iron content. A contrasting example was reported by Morteani and Ackermand (1996) from lazulites in metaqueartzites of the Pfitscher Joch (Hohe Tauern). The rims of these crystals were more intensively coloured than the cores although the latter were richer in iron.

The subject of this study is to investigate the crystal chemical properties of the lazulite–scorzalite solid-solution series and their defect chemistry under controlled oxygen fugacities.

Previous work

Lazulite is the name-giving member of the lazulite group to which the isotypic minerals lazulite, scorzalite, barb-
osalite (Lindberg and Christ 1959; Giuseppetti and Tadini 1983) and hentschelite (Sieber et al. 1987) belong. They crystallize in space group \( P2_1/c \). As shown in Fig. 1 the octahedra populated by divalent and trivalent cations share common faces and form infinite chains in the [110] and [110] direction. These chains are interconnected via common hydroxyl ions and \( \text{PO}_4 \) tetrahedra. According to the sequence \( \square\text{-Me}^{3+}\text{-Me}^{2+}\text{-Me}^{3+}\square \), the occupied octahedral positions alternate with an empty octahedron (Fig. 1) forming trimers of occupied polyhedra and common hydroxyl ions and \( \text{PO}_4 \) tetrahedra. The symmetrically equivalent chains run into the [110] and [110] direction (space group \( P2_1/c \)). The cations occupy three adjacent octahedra forming a trimer denoted as \( h \)-cluster by Moore (1970).

\[ \text{MgAl}_2(\text{OH})_2(\text{PO}_4)_2 \] (lazulite) \( \Rightarrow \) \( \text{MgAl(PO}_4^\text{)}\text{O} + \text{AlPO}_4^\text{\text{(berlinite)}} + \text{H}_2\text{O} \) (1)

\[ \text{FeAl}_2(\text{OH})_2(\text{PO}_4)_2 \] (scorzalite) \( \Rightarrow \) \( \text{FeAl(PO}_4^\text{)}\text{O} + \text{AlPO}_4^\text{\text{(berlinite)}} + \text{H}_2\text{O} \) (2)

The isotypic compounds \( \beta^\prime\text{-MgAl(PO}_4^\text{)}\text{O} \) and \( \text{FeAl(PO}_4^\text{)}\text{O} \) which have not been found as minerals were identified in the run products together with berlinite. The former phases are not isotypic to the mineral stanékite, \( (\text{Mn,Fe}^{2+},\text{Mg})\text{Fe}^{3+}\text{(PO}_4^\text{)}\text{O} \), recently described by Kellner et al. (1997). At \( P = 0.2 \text{ GPa} \) lazulite decomposes at \( T = 660 \text{ °C} \) and scorzalite at \( T = 525 \text{ °C} \) under the oxygen fugacity of the Ni/NiO buffer. Hence, scorzalite was found to be thermally less stable than lazulite.

**Experimental procedure**

**Synthesis**

Members of the lazulite–scorzalite solid-solution series were synthesized hydrothermally in compositional steps of 12.5 mol% under controlled oxygen fugacities of the Ni/NiO buffer. Mixtures of MgAl(PO_4)O, FeAl(PO_4)O and berlinite (\( \alpha\text{-AlPO}_4 \)) were used as starting materials. MgAl(PO_4)O and FeAl(PO_4)O were prepared from pelletized mixtures of MgO (Merck 5865 p.a.) and \( \alpha\text{-AlPO}_4 \) for MgAl(PO_4)O and Fe (Merck 519 p.a.), FeO (Merck 3924) and \( \alpha\text{-AlPO}_4 \) for FeAl(PO_4)O. MgAl(PO_4)O was synthesized at 1150 °C for four days in air. FeAl(PO_4)O was synthesized at 900 °C for three days in closed silica ampoules together with an iron pellet to keep the oxygen fugacity low. \( \alpha\text{-AlPO}_4 \) was prepared from \( \gamma\text{-Al}_2\text{O}_3 \) and \( \text{H}_3\text{PO}_4 \) (Merck 573 p.a.) with a small excess of orthophosphoric acid at 0.3 GPa and 500 °C for 3 days. \( \gamma\text{-Al}_2\text{O}_3 \), which was used instead of the less reactive \( \alpha\text{-Al}_2\text{O}_3 \) (corundum), was synthesized by dissolving Al-ribbon (Merck 1057 p.a.) in HCl and by heating the precipitate at temperatures slightly below 1000 °C for 10 min.

For the synthesis of the lazulite–scorzalite solid-solution series, 50 to 100 mg of the homogenized starting mixtures were sealed into Ag/Pd tubes together with 20 μl of distilled water. These Ag/Pd tubes were then placed, together with 200 mg of powdered Ni/NiO or hematite/magnetite buffer, and 30 μl of distilled water into outer Au capsules, which were then sealed. The syntheses were carried out in conventional hydrothermal apparatus with horizontally arranged Tuttle-type cold-seal bombs at \( T = 485 \text{ °C} \) and \( P = 0.3 \text{ GPa} \). Temperatures were controlled using Ni-CrNi thermocouples. The overall uncertainty in temperature was estimated to be less than \( +/−3 \text{ °C} \). The pressure was measured with a Heise gauge with an uncertainty of \( +/−2.5 \text{ MPa} \). An experiment was ended by switching off the power and the autoclaves were cooled in a cold-air stream; room temperature was attained within 1/2 of an hour. The experiment durations were 3 days.

**Analytical methods**

Powder diffractograms for phase characterization were recorded using a SIEMENS D5000 powder diffractometer with Cu-K\(_\alpha\) radi-