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Characterisation of prehnite by EPMA, Mössbauer, optical absorption and EPR spectroscopic methods

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Abstract

A sample of prehnite from Rayalaseema zone of Andhra Pradesh, India containing about 2.565 wt.% Fe_2O_3 is used in the present work. The mineral has been characterized by EPMA, optical absorption, EPR, NIR and Mössbauer techniques. Mössbauer studies confirm the presence of iron as an impurity in two sites. An EPR study on powder sample confirm the presence of Fe(III) impurity in the mineral. Optical absorption spectrum also indicates that Fe(III) impurity is present in two sites with octahedral structure. NIR results are due to water fundamentals.

Keywords: Prehnite; Mössbauer studies; Fe(III); Octahedral environment; EPR studies; Optical absorption studies; NIR studies

1. Introduction

The common transition metal ion that occurs in many mineral samples is iron. Prehnite is a rock-forming mineral. It occurs in association with calcite, quartz, zoisite, granites, rocks and minerals. It replaces the primary minerals and also appears in veins and druses [1]. It is transparent to translucent and shows pale apple green or pale-yellow or greyish-white colour. Prehnite is orthorhombic and belongs to the space group $\underline{P}2_{cm}$ with two formula units in each unit cell [2]. The unit cell parameters are $a = 4.646(2)$ Å, $b = 5.49(3)$ Å and $c = 18.52$ Å [3]. Its formula is $[Ca_2(Al, Fe)(AlSi_3O_{10})](OH)_2$. The Al atoms lie in an octahedral environment of two hydroxyl and four oxygen ions. The two hydroxyl groups are at a distance of 1.92 Å and of the four oxygen atoms two are at a distance of 1.93 Å and the rest two are at 1.94 Å from the central Al atom. Further Fe(III) substitutes Al octahedrally to an extent of 17% [3]. This substitution is very small because of ionic radii difference in Fe(III) (0.64 Å) and Al(III) (0.51 Å). It does not show any marked variation in composition. Further Mössbauer studies on prehnite from Greece [4] and other origin [5] with an unusually high $Fe_2O_3 = 8.50$ wt.% was reported. Both they ascribed to Fe(III) substituting for Al at the octahedral site.

Prehnite from Ireland containing FeO = 0.48 wt.% was studied using optical absorption and EPR studies which indicate that iron is in two states, ferric and ferrous [6]. In this study, the authors report the content of iron, the valance state and the site symmetry using EPMA, Mössbauer, EPR and optical absorption spectroscopic features of prehnite sample from India.

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2. Experimental

A light green coloured prehnite originating from Rayalaseema zone of Andhra Pradesh, India, is used in the present work. To know the composition of the mineral electron probe microanalysis has been carried out using CAMBE BAX Micro EPMA. The results of the analysis are presented in Table 1. As seen from Table 1 the sample contains iron as the only transition metal ion. Mössbauer measurements were performed with a conventional constant-acceleration spectrometer in transmission geometry with a source of 50 mCi ^{57}Co in an Rh matrix. All isomer shifts are given relative to that of α-Fe at room temperature. EPR spectra of the sample in powder form are recorded at room temperature (RT) and liquid nitrogen temperature (77 K) on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies (υ = 9.1–9.5 GHz), having a 100 kHz field modulation to obtain a first derivative EPR spectrum. Optical absorption spectrum of the compound is recorded at RT on Carey 5E UV Vis-NIR spectrophotometer in mull form in the range of 200–2000 nm.

3. Results and analysis

3.1. Mössbauer studies

The Mössbauer spectrum of prehnite recorded at 296 K fits well with characteristic pattern of the Zeeman hyperfine splitting of iron sample shown in Fig. 1. The spectrum shows the magnetic ordering of the sample. Therefore the sample does not exhibit any net magnetization (B = 0) and hence it is not ferromagnetic. From the spectrum the Mössbauer constants calculated are given in Table 2. A comparison of these values is also made with the Mössbauer parameters of other iron containing systems of known crystal structures and other origins of prehnite. The values are in good agreement with the present data.

The Mössbauer data suggest that 14% Fe(III) in the D site and 85% in the L site, reveal the presence of Fe(II) and Fe(III) octahedral sites in the mineral [11]. The low IS value of present sample in L site is indicating that Fe(III) is in octahedral site whereas QS = 1.21 and IS = 1.08 confirms the presence of Fe(II) ion in D site in a distorted octahedron.

Table 1
EPMA data of prehnite mineral in wt.%

Oxide	1	2	3	4	Average
SiO_2	41.86	43.81	42.43	42.13	42.558
Al_2O_3	24.19	23.87	24.92	23.62	24.150
Fe_2O_3[a]	2.13	2.92	2.43	2.78	2.565
MnO	0.03	0.01	0.02	0.03	0.023
CaO	25.74	28.13	27.12	27.62	27.153
NiO	–	0.01	–	0.01	0.005
K_2O	0.03	0.04	0.05	0.032	0.038
Total	93.980	98.790	96.970	96.823	96.492

[a] All iron present in the sample has been analysed as Fe_2O_3.

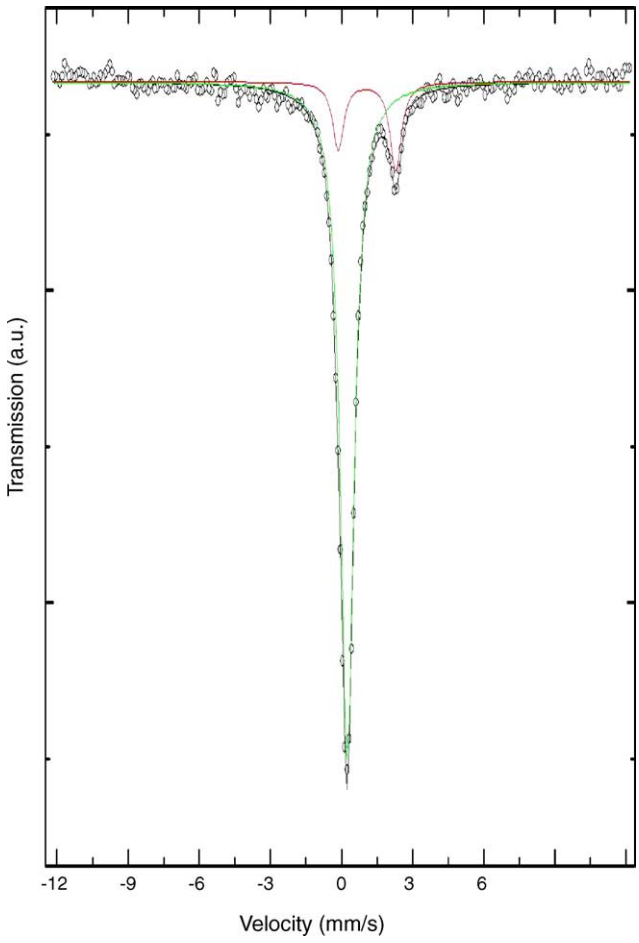

Fig. 1. Mossbauer spectrum of prehnite at room temperature.

3.2. EPR results

A poly crystalline sample of prehnite is made into a fine powder and transferred into a quartz tube for EPR measurements. The EPR spectrum of the sample recorded at room temperature is given in Fig. 2. A set of resonance lines around

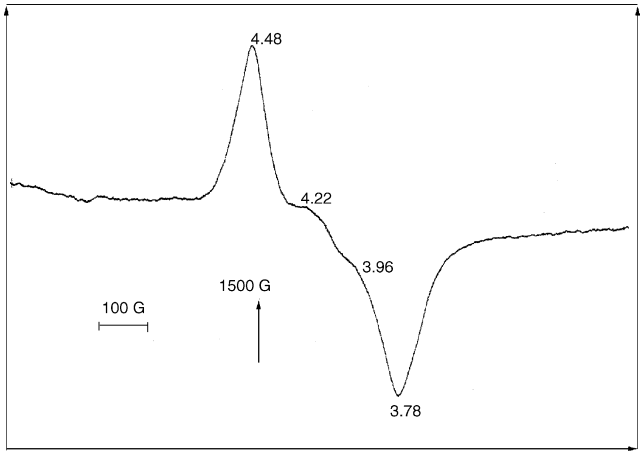

Fig. 2. Powdered EPR spectrum of prehnite at room temperature (υ = 9.39562 GHz).