



# MÖSSBAUER SPECTROSCOPY OF GARNETS OF ALMANDINE-PYROPE SERIES

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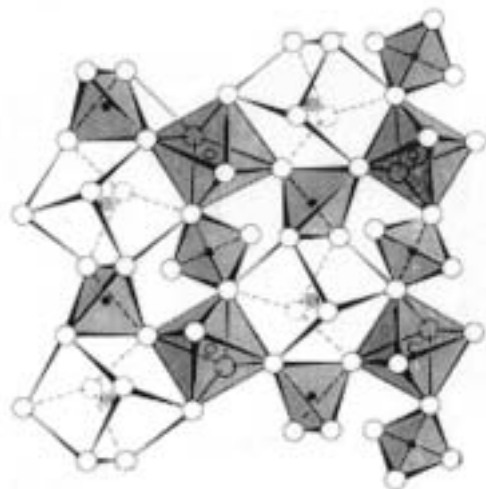
## Abstract

<sup>57</sup>Fe Mössbauer study was performed with eleven powdered samples of different natural garnets of almandine-pyrope series at the room temperature. The direct correlation between the Mg<sup>2+</sup> content in these samples and the asymmetry of spectral lines was found. This correlation allows to select the investigating samples within the framework of almandinepyrope group. The influence of Mg<sup>2+</sup> content on other hyperfine parameters of Mössbauer spectrum (isomer shift, quadrupole splitting) was not found. Electron microprobe analysis and x-ray powder diffraction were used for the determination of the garnet composition.

**Keywords:** Mössbauer spectroscopy, garnets, pyrope

## 1. Introduction

Garnets represent an independent group of orthosilicates with isolated (SiO<sub>4</sub>)<sup>4-</sup> groups. Its general structural formula is X<sub>3</sub>Y<sub>2</sub>Z<sub>3</sub>O<sub>12</sub> (eight formula unit per basic cell). X corresponds to eight-fold (dodecahedral) coordination of metal in 24c position of space group *Ia3d* (X = Ca<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup> or Mn<sup>2+</sup>), Y corresponds to six-fold (octahedral) coordination in 16a position (Y = Al<sup>3+</sup>, Cr<sup>3+</sup> or Fe<sup>3+</sup>) and Z to four-fold



**Figure 1.** Polyhedral model of the garnet structure [1]. The octahedra and tetrahedra are gray.

(tetrahedral) coordination largely Si (in natural garnets only Si) in 24d position (Fig. 1).

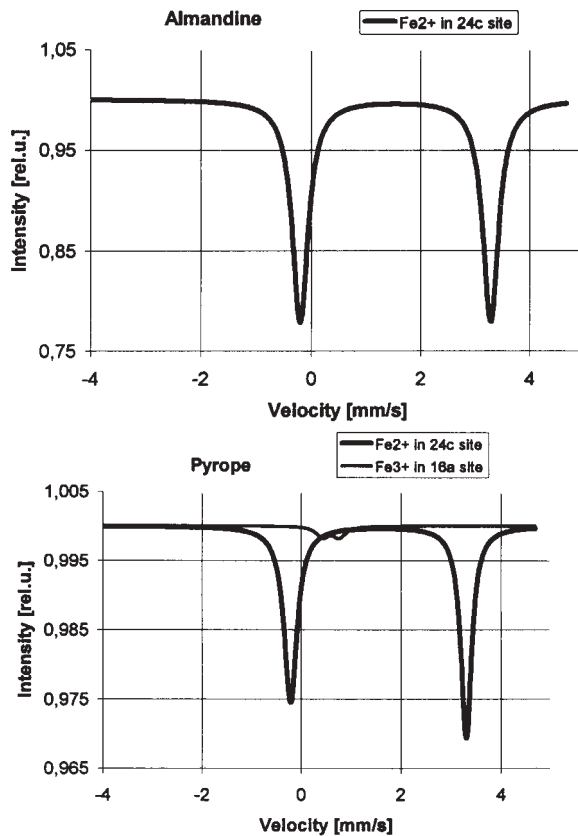
Following the iron distribution in X and Y position, natural garnets are selected into two main groups: almandine-pyrope-spessartine - (Fe<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>)<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> or grossulare-andradite - Ca<sub>3</sub>(A<sup>3+</sup>, Fe<sup>3+</sup>)<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>. In pure almandine (Fe<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>) Fe<sup>2+</sup> ions are located exclusively in 24c positions of the *Ia3d* space group. In pure pyrope (Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>) Mg<sup>2+</sup> ions substitute Fe<sup>2+</sup> completely. Garnets of almandine-pyrope series can be approximated by structural formula (Fe<sup>2+</sup>, Mg<sup>2+</sup>)<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>. However, the minor content of Fe<sup>3+</sup> ions in Y position is usual for natural garnets of almandine-pyrope series.

The results of Mössbauer studies of natural and synthetic garnets collected in "Mössbauer Mineral Handbook" [2] confirm that Fe<sup>2+</sup> ions are dominantly placed in dodecahedral position (24c), rarely in tetrahedral position (24d) and Fe<sup>3+</sup> ions are placed in octahedral (16a) or tetrahedral (24d) positions (Table 1) [3].

**Table 1.** Hyperfine parameters of <sup>57</sup>Fe Mössbauer spectra of garnets (summary from [3], isomer shift to metal iron)

Oxidation level	Position	Temp [K]	isomer shift (IS) [mm/s]	Quadrupole splitting (QS)[mm/s]
Fe <sup>2+</sup>	24c (dodec.)	298	1,20-1,39	3,47-3,70
		77	1,33-1,44	3,55-3,73
Fe <sup>2+</sup>	24d (tetr.)	298	0,68-0,79	1,53-1,99
		77	0,63	1,62
Fe <sup>3+</sup>	16a (oct.)	298	0,35-0,45	0,29-0,75
		77	0,42-0,52	0,26-0,64
Fe <sup>3+</sup>	24d (tetr.)	298	0,04-0,20	1,05-1,28
		77	0,14-0,29	1,05-1,15

The aim of this study was to determine the dependence of hyperfine parameters of <sup>57</sup>Fe Mössbauer spectra (IS - isomer shift, QS - quadrupole splitting, FWHM - full width at half maximum) of almandine-pyrope series garnets on the Fe and Mg content in X position. The typical Mössbauer spectra of natural almandine (low Mg content) and natural pyrope (low Fe content) are presented on Fig. 2.



**Figure 2.** Room temperature Mössbauer spectra of natural almandine (sample 9, top) and pyrope (sample 10, bottom).

The most intensive doublet with higher IS and QS corresponds to  $\text{Fe}^{2+}$  ions in X position. The low intensive doublet with smaller IS and QS corresponds to  $\text{Fe}^{3+}$  in Y position.

## 2. Materials and Methods

Transmission  $^{57}\text{Fe}$  Mössbauer spectra of eleven samples of natural garnets from different localities were collected at room temperature using a 10 mCi  $^{57}\text{Co}$  rhodium-matrix single-line thin source on a velocity range  $\pm 4$  mm/s with a constant acceleration drive. The samples were pressed from mixture of garnet and synthetic amyl powder. The Fe concentration was less than  $5 \text{ mg/cm}^2$  to avoid of saturation effects. The velocity scale was calibrated with the sodium nitroprusside. The spectra were fitted with one asymmetric doublet (asymmetry of FWHM of doublet peaks) for  $\text{Fe}^{2+}$  X position and one symmetric doublet for  $\text{Fe}^{2+}$  in Y position.

The garnet composition and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio were obtained by means of electron microprobe method and Mössbauer spectroscopy, respectively. The crystallochemical formulas were calculated from the garnet composition. Samples were selected within the framework of almandine-pyrope series by means of X-ray diffraction [4].

## 3. Experimental results and discussion

The chemical formulas and hyperfine parameters of  $^{57}\text{Fe}$  Mössbauer spectra of eleven investigating samples (1÷11) are shown in Tables 2 and 3, respectively. These experimental results are appended by data of six garnets (A÷F) from Amthauer et al. study [3]. It is obvious that isomer

**Table 2.** Chemical formula, localities and source of garnets

Sample	Crystallochemical formula, locality and source
1	$(\text{Fe}_{1.72}\text{Mg}_{0.71}\text{Mn}_{0.02}\text{Ca}_{0.06})(\text{Al}_{1.85}\text{Fe}_{0.10}\text{Ti}_{0.02})\text{Si}_{3.26}\text{O}_{12}$
	almandine, Ktiš, Czech Republic
2	$(\text{Fe}_{1.7}\text{Mg}_{0.73}\text{Mn}_{0.06}\text{Ca}_{0.10})(\text{Al}_{1.85}\text{Fe}_{0.08}\text{Ti}_{0.10})\text{Si}_{3.17}\text{O}_{12}$
	almandine, Australia
3	$(\text{Fe}_{1.26}\text{Mg}_{0.84}\text{Mn}_{0.04}\text{Ca}_{0.53})(\text{Al}_{1.83}\text{Fe}_{0.07}\text{Ti}_{0.03})\text{Si}_{3.2}\text{O}_{12}$
	almandine, Barton, USA
4	$(\text{Fe}_{0.43}\text{Mg}_{2.15}\text{Mn}_{0.02}\text{Ca}_{0.36})(\text{Al}_{1.68}\text{Fe}_{0.01}\text{Ti}_{0.02})\text{Si}_{3.2}\text{O}_{12}$
	pyrope, Tunduru, Tanzania
5	$(\text{Fe}_{0.38}\text{Mg}_{2.11}\text{Mn}_{0.02}\text{Ca}_{0.30})(\text{Al}_{1.60}\text{Fe}_{0.05}\text{Ti}_{0.02})\text{Si}_{3.34}\text{O}_{12}$
	pyrope, Podsedice, Czech Republic
6	$(\text{Fe}_{0.41}\text{Mg}_{2.16}\text{Mn}_{0.01}\text{Ca}_{0.39})(\text{Al}_{1.99}\text{Fe}_{0.01})\text{Si}_3\text{O}_{12}$
	pyrope, Tunduru, Tanzania
7	$(\text{Fe}_{0.60}\text{Mg}_{1.92}\text{Mn}_{0.01}\text{Ca}_{0.45})(\text{Al}_{1.99}\text{Fe}_{0.01})\text{Si}_3\text{O}_{12}$
	pyrope, Tunduru, Tanzania
8	$(\text{Fe}_{1.53}\text{Mg}_{1.11}\text{Mn}_{0.06}\text{Ca}_{0.30})(\text{Al}_{1.98}\text{Fe}_{0.02})\text{Si}_3\text{O}_{12}$
	almandine-pyrope, Kalalany, Czech Republic
9	$(\text{Fe}_{2.40}\text{Mg}_{0.48}\text{Mn}_{0.04}\text{Ca}_{0.03})\text{Al}_2\text{Si}_3\text{O}_{12}$
	almandine, Indie
10	$(\text{Fe}_{0.84}\text{Mg}_{1.71}\text{Mn}_{0.01}\text{Ca}_{0.42})(\text{Al}_{1.96}\text{Fe}_{0.04})\text{Si}_3\text{O}_{12}$
	pyrope, Tunduru, Tanzania
11	$(\text{Fe}_{2.31}\text{Mg}_{0.18}\text{Mn}_{0.02}\text{Ca}_{0.07})(\text{Al}_{1.96}\text{Fe}_{0.00}\text{Ti}_{0.00})\text{Si}_{3.25}\text{O}_{12}$
	almandine, Zoltye Vody, Ukraine
A	$(\text{Fe}_{1.81}\text{Mg}_{0.57}\text{Mn}_{0.06}\text{Ca}_{0.56})\text{Al}_2\text{Si}_3\text{O}_{12}$
	almandine, charnokite, Varberg, Sweden
B	$(\text{Fe}_{0.56}\text{Mg}_{2.01}\text{Mn}_{0.02}\text{Ca}_{0.41})(\text{Al}_{1.93}\text{Fe}_{0.03}\text{Ti}_{0.01}\text{Cr}_{0.03})(\text{Si}_{2.93}\text{Al}_{1.07})\text{O}_{12}$
	pyrope, kimberlite, Stockdale, USA
C	$(\text{Fe}_{0.44}\text{Mg}_{2.16}\text{Mn}_{0.02}\text{Ca}_{0.38})(\text{Al}_{1.82}\text{Fe}_{0.05}\text{Ti}_{0.05}\text{Cr}_{0.08})\text{Si}_3\text{O}_{12}$
	pyrope, kimberlite, Stockdale, USA
D	$(\text{Fe}_{0.43}\text{Mg}_{2.19}\text{Mn}_{0.05}\text{Ca}_{0.35})(\text{Al}_{1.85}\text{Fe}_{0.02}\text{Cr}_{0.13})\text{Si}_3\text{O}_{12}$
	pyrope, kimberlite, Stockdale, USA
E	$(\text{Fe}_{0.47}\text{Mg}_{2.08}\text{Mn}_{0.03}\text{Ca}_{0.42})(\text{Al}_{1.75}\text{Cr}_{0.25})\text{Si}_3\text{O}_{12}$
	pyrope, peridotite, Sandvik, Norway
F	$(\text{Fe}_{0.45}\text{Mg}_{2.02}\text{Mn}_{0.02}\text{Ca}_{0.51})(\text{Al}_{1.48}\text{Fe}_{0.06}\text{Cr}_{0.49})(\text{Si}_{2.99}\text{Al}_{1.01})\text{O}_{12}$
	Cr pyrope, peridotite, Linhorka T7, Czech Republic

**Table 3.** Hyperfine parameters of Mössbauer spectra of garnets

Sample	Fe <sup>2+</sup> in 24c site				Fe <sup>3+</sup> in 16a site			Fe <sup>3+</sup> /Σ Fe
	IS [mm.s <sup>-1</sup> ]	QS [mm.s <sup>-1</sup> ]	FWHM(I) [mm.s <sup>-1</sup> ]	FWHM(h) [mm.s <sup>-1</sup> ]	IS [mm.s <sup>-1</sup> ]	QS [mm.s <sup>-1</sup> ]	FWHM [mm.s <sup>-1</sup> ]	area ratio
1	1.30	3.52	0.36	0.35	-	-	-	0.00
2	1.28	3.47	0.32	0.31	0.40	0.60	0.30	0.05
3	1.28	3.53	0.34	0,33	0.21	0.48	1.09	0.15
4	1.29	3.56	0.32	0.27	0.37	0.57	0.42	0.21
5	1.30	3.58	0.35	0.32	0.33	0.31	0.30	0.12
6	1.29	3.52	0.33	0.28	0.31	0.26	0.30	0.03
7	1.29	3.52	0.37	0.36	0.34	0.41	0.30	0.02
8	1.29	3.52	0.37	0.36	0.34	0.41	0.30	0.01
9	1.29	3.48	0.35	0.35	-	-	-	0.00
10	1.29	3.51	0.28	0.24	0.34	0.39	0.30	0.05
11	1.30	3.55	0.42	0.43	-	-	-	0.00
A	1.29	3.47	0.24	0.22	-	-	-	0.00
B	1.29	3.54	0.29	0.24	-	-	-	0.05
C	1.29	3.53	0.30	0.25	-	-	-	0.11
D	1.29	3.56	0.31	0.25	-	-	-	0.05
E	1.28	3.55	0.32	0.25	-	-	-	0.00
F	1.28	3.56	0.31	0.25	0.36	0.33	0.3	0.13

shifts as well as quadrupole splittings of ferrous iron at the dodecahedral sites are nearly invariable. If the values of isomer shifts belong between 1.28 and 1.30 mm/s, these of quadrupole splittings scatter between 3.47 and 3.58 mm/s. The distinct dependence of isomer shift and quadrupole splitting on the Fe and Mg content in X position can not be recognized. However, the partial substitution of Fe<sup>2+</sup> by Mg<sup>2+</sup> can cause the change of hyperfine parameters of <sup>57</sup>Fe Mössbauer spectra [5]. The IS and QS of Fe<sup>2+</sup> at the dodecahedral sites are large compared to typical Fe<sup>2+</sup> values in other minerals. The large IS and QS values indicate the high spin ferrous iron in a highly ionic state. The invariable IS suggests that the Fe-O distances at the dodecahedral sites are very nearly the same. From the relative near QS values and their relative independence on the Fe and Mg content in dodecahedral site as well as the observed narrow FWHM (less than 0.37 mm/s) there is no reason to assume more than one type of eight-fold coordinated site. From the previous reports and our results it is well known that the peak heights of the Fe<sup>2+</sup> doublet at dodecahedral position in almandine [5] and in almandine-spessartine [6,7] are symmetric. However, the Fe<sup>2+</sup> doublets of magnesium rich garnets show asymmetric peak heights. The low energy peak of the doublet generally exhibits a less intense height and a some broader line width (FWHM(1)>FWHM(h))<sup>1</sup>. The area of the low energy peak is more or less the same as that of the high-energy peak. The maximal differences in the

peak heights and FWHM obtain for Mg-rich pyropes with fairly low content of iron at dodecahedral position. This difference decreases with decreasing magnesium content at dodecahedral site (Fig. 3). Line broadening may be caused by means of three different phenomena [7]:

- texture in the crystal orientation of the polycrystalline sample,
- anisotropic recoilless fraction (Goldanskii-Karyagin effect),
- paramagnetic relaxation.

The first and second possibilities can be excluded because the cubic lattice symmetry is due to silicate garnets. Also, the asymmetry of the lines does not change in the spectra taken at different orientations of the absorber to the incident gamma rays. The similar areas of the two resonant lines also show that the asymmetry cannot result from a Goldanski-Karyagin effect. The commonly observed asymmetry in quadrupole doublets in the room temperature spectra was already explained as arising out of paramagnetic relaxation of Fe<sup>2+</sup> in the dodecahedral position [3, 8]. However, no dependence of this asymmetry on garnet composition has been noted within the pyrope-almandine series. The dependence of differences in the peak heights on the chromium content in octahedral position has been found for magnesium-rich pyropes with fairly low content of iron [3]. Two main types of relaxation process are possible [9]. The spin-lattice relaxation decreased with decreasing

<sup>1</sup> FWHM(1) and FWHM(h) are FWHM for low and high energy peaks, respectively.

temperature causes the increase of the asymmetry of paramagnetic doublet resonant lines with decreasing temperature. No decrease has been verified in low and high temperature measurements. The results from these measurements show that the asymmetry is approximately constant with temperature and simultaneously depends on  $Mg^{2+}$  ( $Fe^{2+}$ ) content in dodecahedral site (Fig. 3). This is characterised for spin-spin relaxation. It obvious, that the asymmetry of  $Fe^{2+}$  doublet in almandine-pyrope samples is induced by spin-spin paramagnetic relaxation.

#### 4. Conclusions

The asymmetry of resonant lines of  $Fe^{2+}$  dodecahedral site Mössbauer spectrum was found in spectra of almandine-pyrope garnets. This asymmetry depends on  $Mg^{2+}$  content in dodecahedral sites and is induced by spin-spin paramagnetic relaxation of ions in dodecahedral sites.

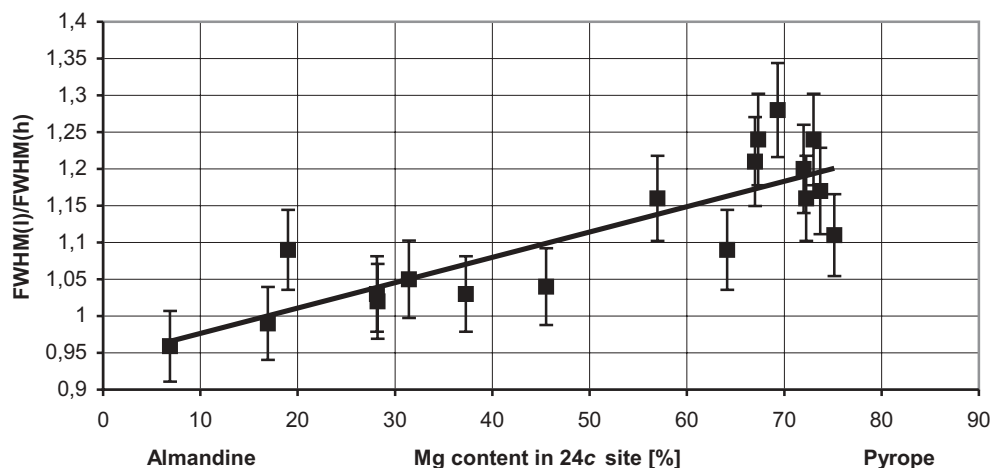
The dependence of resonant lines asymmetry on  $Mg^{2+}$  content in dodecahedral positions allows to select the garnet samples within the framework of almandine-pyrope series.

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**Figure 3.** The dependence of FWHM(l)/FWHM(h) ratio of  $Fe^{2+}$  in dodecahedral site quadrupole doublet on  $Mg^{2+}$  content in this site.