

Article

A Study on the Raman Spectral Characteristics of Garnet from the Jiama Copper Polymetallic Deposit in Tibet

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Abstract: Raman spectroscopy is an important method to analyze and measure mineral composition and structure, which has the advantages of being non-destructive and rapid. This study considered garnet from the Jiama copper polymetallic deposit in Tibet to carry out micro-Raman spectrum and electron microprobe research to analyze the Raman spectrum characteristics of garnet with different components to reveal its indicative significance for garnet composition and skarn mineralization. The results showed that the Raman peaks T, X, A1, A2, and A3 shift toward lower wavenumber with the increase in andradite (And) content. The variations in T, X, and A2 are more obvious than those of A1 and A3. When And > 50%, the three Raman peaks (T, X, and A2) range are 173–174, 234–239, 513–525 cm^{−1}; when And < 50%, they are 177–178, 240–244, 527–543 cm^{−1}. The Raman peaks also shift with the cation radius and relative atomic mass. Different peaks moved in the low-frequency direction with the increase in the X²⁺ and Y³⁺ radius, and the X²⁺ atomic mass. The Raman spectrum can indicate the composition change in garnet. Raman spectrum analysis of garnet is of great significance for skarn zoning and prospecting.

Keywords: Raman spectroscopy; garnet; Jiama



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1. Introduction

Garnet is a tesseral nesosilicate mineral, and its general chemical formula is X₃Y₂[SiO₄]₃, in which X represents divalent cations, mainly Ca²⁺, Mg²⁺, Fe²⁺, Mn²⁺, etc., and Y represents trivalent cations, mainly Al³⁺, Fe³⁺, and Cr³⁺, and sometimes Ti³⁺, Zr³⁺, V³⁺, Y³⁺, etc. [1]. The garnet group is divided into two series comprising the six more common terms: ugrandite, where X = Ca and Y = Cr, Al, Fe³⁺ (uvarovite Ca₃Cr₂Si₃O₁₂, grossular Ca₃Al₂Si₃O₁₂, andradite Ca₃Fe₂Si₃O₁₂) and pyrope, where Y = Al and X = Mg, Fe²⁺, Mn (pyrope Mg₃Al₂Si₃O₁₂, almandine Fe₃Al₂Si₃O₁₂, spessartine Mn₃Al₂Si₃O₁₂) [2]. Its structural feature is a [YO₆] octahedron with a trivalent cation as the central ion connecting [SiO₄] tetrahedron; a [XO₈] dodecahedral gap is formed between the [SiO₄] tetrahedron and [YO₆] octahedron, which divalent cations occupy [1]. Garnet is an important “indicator” mineral in skarn deposits. In many skarn polymetallic deposits, the color, content, and chemical composition of garnet change significantly in different parts of each contact zone and mineralization zone [3–7], which is one of the important signs indicating skarn zoning and mineralization.

Vibrational spectroscopy is a useful, non-destructive and rapid analysis method for distinguishing between different solid solutions as the spectra change as a function of the garnet composition [8]. Among them, Raman spectroscopy can provide more structural information about various normal vibrational frequencies and related vibrational energy levels inside the molecule. The Raman shift in the spectrum depends on the change in the molecular vibration energy level. At the same time, the change in the Raman shift is reflected in the change in material composition [9–18].

Previous studies on garnet in skarn have mostly focused on composition, and Raman spectroscopy has been rare [19–23]. The few garnet Raman spectroscopy studies are also rarely associated with specific deposits [2,8]. The Jiama copper polymetallic deposit in Tibet is a super large deposit with notable economic value and scientific research significance. Skarn deposits are the most important deposit type, accounting for 65% of the industrial ore reserves [24]. Garnet is a widely distributed main skarn mineral with complex composition changes, and garnet skarn mineralization is good [25–27]. Therefore, this paper undertook an electron probe analysis and Raman spectrum research on Jiama garnet in Tibet, exploring the Raman spectrum characteristics of garnet, analyzing the relationship between garnet composition and Raman shift, that is, the relationship between composition and structure, and discussing the indicative significance of garnet Raman analysis for Jiama skarn mineralization.

2. Geological Background

The Jiama copper polymetallic deposit is located in the eastern part of the Gangdise metallogenic belt in the Tethys tectonic domain, Tibet. The exposed stratum is mainly composed of an Upper Jurassic Duodigou formation (J_3d), lower Cretaceous Linbuzong formation (K_1l), and a small amount of Quaternary (Q) (Figure 1). The Duodigou formation is mainly composed of limestone and marble, which serves as the floor of the skarn; the Linbuzong formation is mainly slate and hornstone, which is the roof of the skarn. The structure of the mining area is mainly nappe, sliding nappe structure, and the resulting interlayer structure, and the interlayer expansion structure is the main occurrence space of the skarn ore body [26]. The structure is generally in the NWW direction, which is consistent with the stratum trend. NEE, NS, and NNW secondary faults control a large number of exposed dikes on the surface [25]. The magmatic activity in the mining area is frequent, there are many magmatic rock types and intrusion periods, and the ore-bearing magmatic rocks are mainly neutral porphyry. Magmatic rocks are mainly produced as vein rocks, among which granite porphyry, granodiorite porphyry, and monzonitic granite porphyry are the most commonly exposed [28]. The main ore body occurs in skarn, and the skarn runs through the whole mining area. The thick skarn can be seen in the No. 24 exploration line. The section of No. 24 exploration line reveals the skarn main ore body, which is large in scale and mostly occurs in a layered, stratoid, or thick plate shape. The overall trend is northwest, extending about 3000 m, leaning toward northeast, and extending about 2600 m (Figure 1b). The mineralization types of the deposit are mainly chalcopyrite, pyrite, bornite, molybdenite and galena, and sphalerite mineralization (Figure 2).

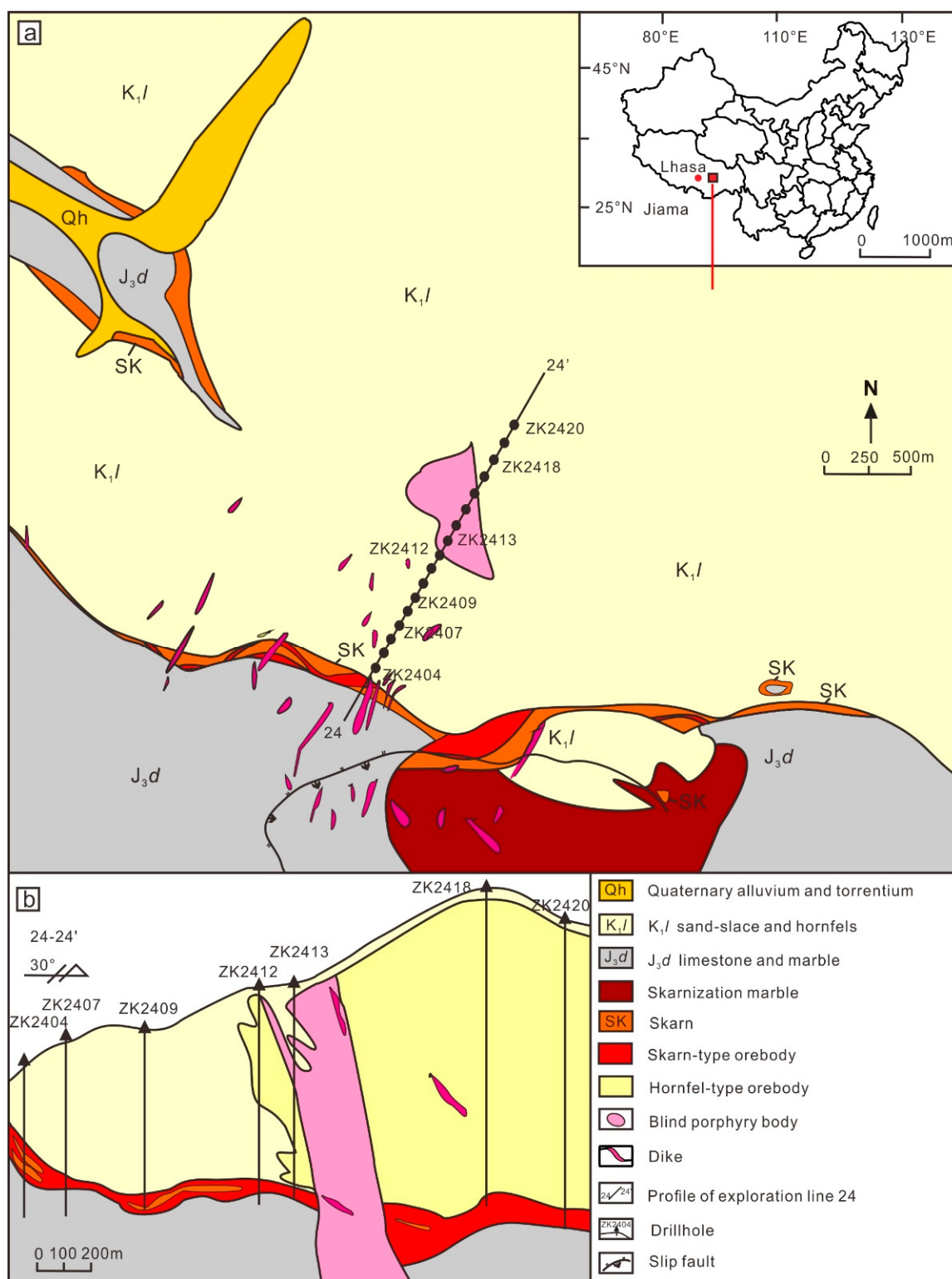


Figure 1. (a) Geological map of the Jiama deposit mining area. (b) Profile of the No.24 exploration line (modified according to [29]).

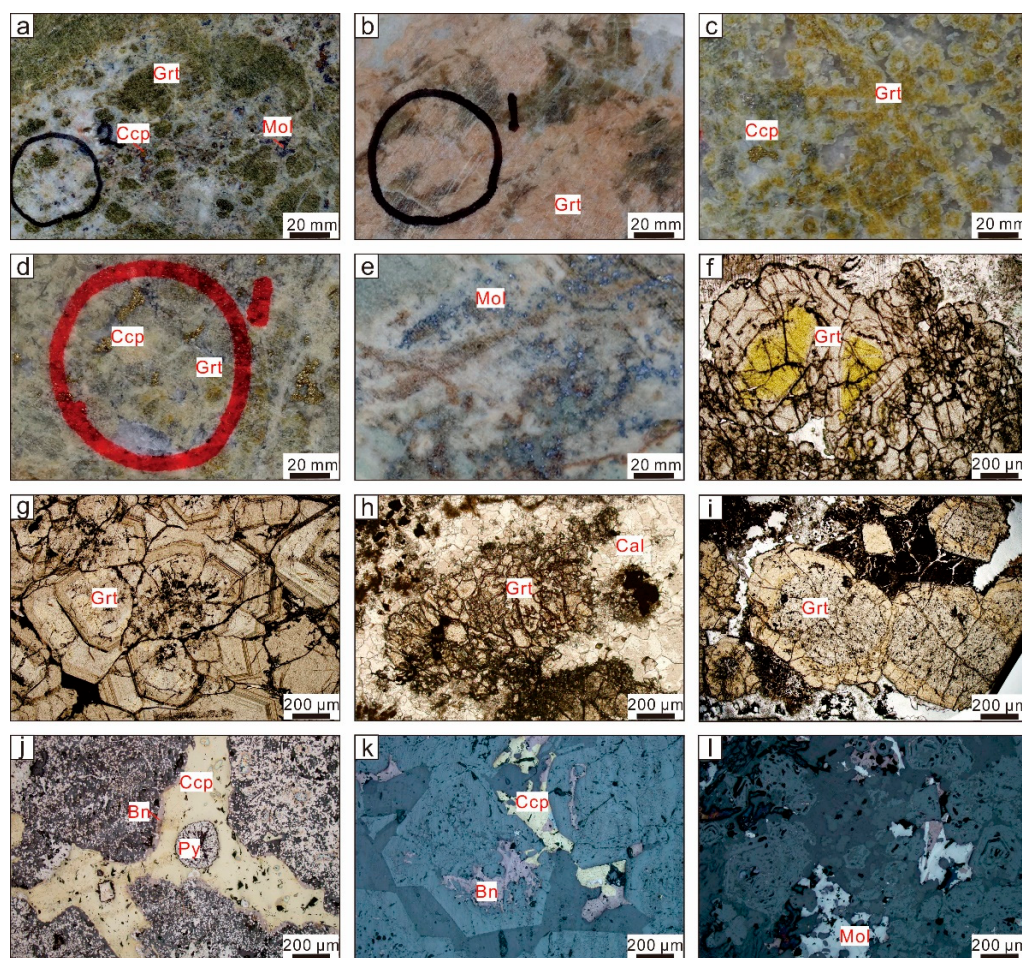


Figure 2. Hand specimen photos and microphotographs from the No. 24 exploration line in Jiama deposit. (a) Green garnet. (b) Red brown garnet. (c) Yellow green garnet. (d) Disseminated chalcopyrite. (e) Vein-shaped molybdenite. (f) Granular garnet. (g) Zoned garnet. (h) Broken garnet. (i) Vein-shaped garnet. (j) Chalcopyrite, bornite, pyrite symbiosis. (k) Chalcopyrite, bornite are filled in the garnet gaps and fissures. (l) Molybdenite filled in garnet gaps. Grt: garnet; Ccp: chalcopyrite; Mol: molybdenite; Cal: calcite; Py: pyrite; Bn: bornite.

3. Measurement Methods

The samples were from different boreholes on the No. 24 exploration line of the Jiama deposit, including ZK2404, ZK2407, ZK2409, ZK2412, ZK2413, ZK2418, and ZK2420. Core samples with strong skarnization were taken. First, mineral composition and structural characteristics were observed under a microscope, and representative garnet sample areas were marked. Then, the electron probe microanalysis (EPMA) measurement and micro-Raman spectroscopy measurement were carried out successively in the same micro-area of garnet to determine the content of major elements and the micro-Raman spectra. Two to three points were selected for each area and the selection of test points shall avoid cracks and unevenness around them as much as possible. Finally, the correlation between the EPMA data and the Raman spectrum was analyzed by using the IBM Statistical Product and Service Solutions (SPSS) Statistics software to verify the close correlation between the composition of garnet and the Raman spectrum. An electron probe test was completed in the Electron Probe Laboratory of the Institute of Mineral Resources, Chinese Academy of Geological Sciences. The experimental instrument model was JXA-8230 (Jeol, Akishima, Japan). The experimental conditions were acceleration voltage 15 kV, excitation current 20 nA, and electron beam diameter 5 μm . A ZAF matrix-correction was applied during data reduction. The following standards and crystals were used for microanalyses: Jadeite

(Si, Na, and Al), forsterite (Mg), orthoclase (K), apatite (P), orthoclase (K), wollastonite (Ca), rutile (Ti), and synthetic oxides (Cr, Mn, Fe, and Ni). The detection limit of most elements is 40×10^{-6} – 200×10^{-6} wt%. The micro-Raman spectroscopy experiment was carried out in the Laboratory of Environmental Mineralogy of Peking University. The test instrument was an inVia Reflex (Renishaw, UK) Raman spectrometer. A solid-state laser was used in the experiment, with an excitation wavelength of 532 nm, laser emission power of 50 mW, and excitation wavelength range of 50–9000 cm^{-1} , each excitation wavelength was equipped with interference filter and two edge Rayleigh filters, and the slit width was 65 μm . In addition, there were 50 times Leica objective lens, numerical aperture of 0.75, and spot diameter of 1 μm and 2400 line grating. The single scanning time of sample was 30 s, the cumulative times was 25, the spectral resolution was 1 cm^{-1} , and the data scanning range was 50–4000 cm^{-1} . The data acquisition range was 50–1300 cm^{-1} , and the application range of data processing in this experiment was 100–1200 cm^{-1} .

4. Results

4.1. Electron Probe Results

The garnet samples from the skarn layer in seven drill holes (ZK2404, ZK2407, ZK2409, ZK2412, ZK2413, ZK2418, and ZK2420) on the No. 24 exploration line are the experimental objects. Table 1 displays the results of some major elements. The total iron content in the sample is calculated using divalent ions because the electron probe cannot measure the valence state of iron. Table 1 showed that the main components were SiO_2 , CaO, FeO, and Al_2O_3 , with the variation range of SiO_2 content being 36.011%–40.148%, CaO being 31.033%–35.505%, and the overall content of SiO_2 and CaO changing little, which was positively correlated. FeO variation ranged from 1.784% to 29.433%, while Al_2O_3 variation ranged from 0% to 21.086%. The overall content of FeO and Al_2O_3 changed greatly, showing a negative correlation. According to Muhling (1991) [30], garnet is mainly composed of andradite (0%–94.17%), followed by grossular (0%–93.15%), and a small amount of almandine (0%–5.45%), belonging to andradite–grossular solid solution series. From ZK2404, ZK2407 to ZK2409, the content of FeO increases, and the proportion of andradite increases; the content of FeO in ZK2412 and ZK2413 decreases relatively, and the content of andradite decreases accordingly; the content of FeO in ZK2418 and ZK2420 increases again, and the garnet is almost mainly andradite.

Table 1. Selected major element contents (wt%) by EPMA, in garnet.

No.	2404-1	2404-2	2404-3	2404-4	2404-5	2407-1	2407-2	2407-3	2407-4	2407-5	2407-6	2407-7
SiO_2	37.691	38.506	38.798	38.545	38.909	39.164	38.393	36.709	38.457	36.675	37.006	37.194
Al_2O_3	0.601	0.394	10.094	12.102	9.115	11.786	12.15	6.919	7.377	0.179	2.316	3.011
FeO	26.818	27.865	14.556	12.867	15.48	13.472	13.03	18.387	17.187	26.281	23.221	22.763
MnO	0.126	0.103	0.362	0.367	0.17	0.371	0.526	0.292	0.412	0.076	0.084	0.095
MgO	0.058	0.079	0.094	0.081	0.021	0.111	0.088	0.072	0.062	0.09	0.108	0.061
CaO	32.234	32.201	33.262	34.848	33.006	33.012	32.984	31.93	32.13	31.572	31.483	31.969
Total	97.528	99.148	97.166	98.81	96.701	97.916	97.171	94.309	95.625	94.873	94.218	95.093
Number of ions on the basis of 12O												
Si	3.145	3.174	3.123	3.032	3.163	3.114	3.07	3.075	3.158	3.153	3.176	3.155
Al	0.059	0.038	0.958	1.122	0.874	1.105	1.146	0.683	0.714	0.018	0.234	0.301
Fe^{2+}	0.046	0.063	0.045	0.014	0.055	0.056	0.044	0.042	0.056	0.041	0.05	0.044
Fe^{3+}	0.164	0.162	0.079	0.082	0.08	0.066	0.069	0.107	0.092	0.162	0.137	0.137
Mn	0.016	0.013	0.043	0.043	0.021	0.044	0.063	0.036	0.05	0.01	0.011	0.012
Mg	0.004	0.006	0.006	0.005	0.001	0.007	0.006	0.005	0.004	0.007	0.008	0.004
Ca	2.882	2.844	2.869	2.937	2.875	2.813	2.826	2.866	2.827	2.909	2.895	2.906
Gro	0	0	43.98	54.36	39.9	49.45	51.96	30.04	31.23	0	8.37	12.16
And	82.26	80.38	38.11	39.05	39.34	31.46	33.15	53.92	45.34	83.85	70.61	69.68

Table 1. Cont.

No.	2407-8	2407-9	2409-1	2409-2	2409-3	2409-4	2409-5	2412-1	2412-2	2412-3	2412-4	2412-5
SiO ₂	36.107	37.421	39.4	38.261	38.464	37.703	38.126	38.591	38.056	38.116	39.037	40.148
Al ₂ O ₃	0.031	0.829	5.295	0.132	1.529	2.1	2.548	6.593	0.258	5.797	12.5	16.974
FeO	27.369	26.846	22.049	27.579	26.427	24.927	25.238	20.668	28.462	21.231	12.923	7.929
MnO	0.201	0.046	0.191	0.177	0.127	0.198	0.119	0.43	0.213	0.345	0.314	0.472
MgO	0.038	0.029	0.053	0.052	0.092	0.045	0.091	0	0.005	0.026	0.014	0.015
CaO	31.273	32.129	33.33	32.418	32.6	32.368	32.663	32.742	32.057	32.695	34.725	34.781
Total	95.019	97.3	100.318	98.619	99.239	97.341	98.785	99.024	99.051	98.21	99.513	100.319
Number of ions on the basis of 12O												
Si	3.032	3.134	3.141	3.166	3.148	3.138	3.126	3.1	3.141	3.073	3.049	3.058
Al	0.003	0.082	0.498	0.013	0.148	0.206	0.246	0.624	0.025	0.551	1.151	1.524
Fe ²⁺	0	0.045	0.058	0.052	0.052	0.046	0.048	0.054	0.057	0.056	0.023	0.042
Fe ³⁺	0.19	0.164	0.124	0.166	0.158	0.15	0.151	0.117	0.17	0.12	0.078	0.034
Mn	0.025	0.006	0.023	0.022	0.015	0.025	0.015	0.051	0.026	0.041	0.037	0.054
Mg	0.003	0.002	0.004	0.004	0.006	0.003	0.006	0	0	0.002	0.001	0.001
Ca	2.814	2.883	2.847	2.874	2.859	2.887	2.87	2.818	2.835	2.825	2.906	2.839
Gro	0	0.51	20.04	0	3	6.7	8.03	25.59	0	22.28	54.98	71.52
And	94.17	82.66	59.68	82.48	77.72	75.28	74.63	56.52	84.34	58.25	36.79	15.79
No.	2412-6	2412-7	2412-8	2412-9	2412-10	2412-11	2412-12	2413-1	2413-2	2413-3	2413-4	2413-5
SiO ₂	39.242	39.754	39.322	37.026	38.137	36.011	38.444	37.347	36.907	39.633	39.706	39.863
Al ₂ O ₃	21.086	14.93	8.323	0.202	4.354	0.083	1.954	0.404	0.149	8.487	6.929	8.671
FeO	1.784	10.698	18.573	29.433	22.269	29.327	25.254	27.469	27.474	18.443	19.364	17.922
MnO	0.359	0.342	0.284	0.298	0.132	0.217	0.157	0.077	0.154	0.171	0.171	0.269
MgO	0.211	0.009	0.064	0.036	0.038	0	0.038	0.118	0.144	0.112	0.131	0.144
CaO	35.505	34.158	32.915	31.033	32.554	31.312	32.935	32.398	32.06	33.47	33.411	33.367
Total	98.187	99.891	99.481	98.028	97.484	96.95	98.782	97.813	96.888	100.316	99.712	100.236
Number of ions on the basis of 12O												
Si	3.005	3.068	3.124	3.094	3.144	3.045	3.154	3.119	3.109	3.128	3.167	3.143
Al	1.904	1.358	0.78	0.02	0.423	0.008	0.189	0.04	0.015	0.79	0.652	0.806
Fe ²⁺	0.009	0.049	0.064	0.057	0.051	0.038	0.049	0.039	0.037	0.058	0.06	0.061
Fe ³⁺	0.008	0.05	0.097	0.176	0.129	0.185	0.151	0.172	0.173	0.099	0.105	0.094
Mn	0.041	0.039	0.034	0.037	0.016	0.027	0.019	0.01	0.019	0.02	0.02	0.032
Mg	0.014	0.001	0.004	0.003	0.003	0	0.003	0.008	0.01	0.007	0.009	0.01
Ca	2.914	2.824	2.802	2.779	2.876	2.837	2.895	2.9	2.894	2.831	2.855	2.819
Gro	93.15	62.53	32.73	0	17.11	0	6.15	0	0	33.98	27.84	34.42
And	3.69	23.18	46.57	88.67	64.1	94.14	74.7	86.12	87.52	47.24	50.32	44.62
No.	2418-1	2418-2	2418-3	2418-4	2418-5	2418-6	2418-7	2420-1	2420-2	2420-3	2420-4	2420-5
SiO ₂	37.592	38.447	37.403	37.665	38.478	37.417	36.7	37.71	37.974	38.151	37.78	37.2
Al ₂ O ₃	2.135	11.133	6.528	4.99	10.054	0.518	0.051	0	1.933	1.985	0.064	0.01
FeO	25.709	14.562	20.179	21.606	16.059	27.066	28.267	28.311	26.167	25.577	27.841	28.43
MnO	0.134	0.506	0.361	0.299	0.494	0.206	0.278	0.334	0.175	0.118	0.357	0.315
MgO	0.02	0.069	0.042	0	0.046	0.039	0.022	0.042	0.103	0.074	0.027	0.03
CaO	32.103	34.564	32.579	32.545	34.159	31.792	31.563	31.583	32.375	32.537	31.141	31.24
Total	97.693	99.281	97.092	97.105	99.29	97.038	96.881	97.98	98.727	98.442	97.21	97.225

Table 1. Cont.

Number of ions on the basis of 12O												
Si	3.124	3.009	3.065	3.096	3.029	3.143	3.099	3.149	3.124	3.136	3.177	3.131
Al	0.209	1.027	0.631	0.484	0.933	0.051	0.005	0	0.187	0.192	0.006	0.001
Fe ²⁺	0.051	0.017	0.035	0.041	0.027	0.047	0.044	0.059	0.049	0.042	0.066	0.055
Fe ³⁺	0.153	0.093	0.123	0.13	0.098	0.165	0.175	0.168	0.158	0.157	0.161	0.171
Mn	0.017	0.059	0.044	0.037	0.058	0.026	0.035	0.042	0.021	0.014	0.045	0.04
Mg	0.001	0.005	0.003	0	0.003	0.003	0.002	0.003	0.007	0.005	0.002	0.002
Ca	2.859	2.898	2.861	2.866	2.882	2.861	2.855	2.826	2.854	2.866	2.806	2.817
Gro	5.85	48.77	27.31	20.37	43.36	0	0	0	4.64	5.98	0	0
And	76.73	43.74	60.59	64.34	46.7	83.39	88.92	84.34	77.97	77.53	81.36	86.41

Note: Gro: Grossular; And: Andradite.

4.2. Raman Spectrum Results

There are two main types of Raman spectra of the garnets obtained in the experiment: one is mainly andradite (And > 50%), and the other is mainly grossular (And < 50%), which have essentially similar spectral morphology, which can be divided into three parts: a low-wavenumber part from 100 to 400 cm^{−1}, medium wavenumber part (400–650 cm^{−1}), and high wavenumber part between 800 and 1050 cm^{−1}. The difference between them mainly lies in the range from 800 to 1050 cm^{−1}. The former has three peaks in high wavenumber region of spectra, while the latter has only two peaks (Figure 3). The symmetry of the garnet structure specifies 25 Raman bands: 3A_{1g} + 8E_g + 14F_{2g}, but it is usually impossible to see all 25 bands in one figure [15,31]. For example, the Raman active vibration mode of the X-position cation and [SiO₄] tetrahedron in the garnet structure is shown in Figure 3, and the Y-position cation does not produce a Raman active vibration. The regions 800–1050 cm^{−1} and 400–650 cm^{−1} are related to the Si–O stretching vibrations (ν₁, ν₃) and Si–O bending vibrations (ν₂, ν₄), correspondingly (internal vibration of [SiO₄] tetrahedra), which mainly belong to the A_{1g} mode. These vibrations also exist in the E_g and F_{2g} modes, but the signals in this part of Figure 3 are invisible. The range from 300 to 400 cm^{−1} is associated with the rotation of [SiO₄] tetrahedra, which also belongs to the A_{1g} mode. The peak near 240 cm^{−1} belongs to the F_{2g} mode, and is caused by the translational vibrations of X²⁺ dodecahedral cations. The peak near 175 cm^{−1} belongs to the E_g and F_{2g} modes and is caused by the translation of [SiO₄] tetrahedron [31–33]. According to the degree of variation in Raman activity, structural characteristics and Raman shifts of garnets, the five Raman peaks of T, X, A1, A2, and A3 in Figure 3 were selected for the study. They are shown in Table 2. T and X represent the translation of [SiO₄] tetrahedron and X²⁺ dodecahedral cations, respectively. A1, A2, and A3 represent the rotation vibration, the Si–O bending vibration, and the Si–O stretching vibration of [SiO₄] tetrahedron, respectively.

Table 2. Raman peaks (cm^{−1}) of garnets.

Samples	E _g + F _{2g}	F _{2g}	A _{1g} + E _g + F _{2g}	A _{1g}	A _{1g} + E _g	Samples	E _g + F _{2g}	F _{2g}	A _{1g} + E _g + F _{2g}	A _{1g}	A _{1g} + E _g
	T	X	A1	A2	A3		T	X	A1	A2	A3
2404-1	174	236	370	518	874	2412-6	177	240	370	543	877
2404-2	173	236	369	517	872	2412-7	178	242	372	535	876
2404-3	177	241	372	531	876	2412-8	176	240	372	529	876
2404-4	177	241	373	533	876	2412-9	173	235	369	516	873
2404-5	177	241	371	530	876	2412-10	174	237	370	521	876
2407-1	177	241	372	533	876	2412-11	173	234	365	513	873
2407-2	177	241	372	531	876	2412-12	174	236	371	519	874
2407-3	175	239	371	527	876	2413-1	173	236	367	516	873
2407-4	175	240	372	528	875	2413-2	173	236	371	515	873
2407-3	175	239	371	527	876	2413-1	173	236	367	516	873

Table 2. Cont.

Samples	$E_g + F_{2g}$	F_{2g}	$A_{1g} + E_g + F_{2g}$	A_{1g}	$A_{1g} + E_g$	Samples	$E_g + F_{2g}$	F_{2g}	$A_{1g} + E_g + F_{2g}$	A_{1g}	$A_{1g} + E_g$
	T	X	A1	A2	A3		T	X	A1	A2	A3
2407-4	175	240	372	528	875	2413-2	173	236	371	515	873
2407-5	173	236	369	517	872	2413-3	176	240	372	527	875
2407-6	174	237	370	519	874	2413-4	176	239	371	525	875
2407-7	174	237	371	522	875	2413-5	176	240	372	528	876
2407-8	173	235	369	516	874	2418-1	173	236	369	517	874
2407-9	173	236	371	517	873	2418-2	174	237	369	523	875
2409-1	176	239	371	523	875	2418-3	173	235	369	517	874
2409-2	174	237	371	520	875	2418-4	174	237	370	522	875
2409-3	174	236	371	518	874	2418-5	176	240	367	532	876
2409-4	176	239	371	523	875	2418-6	173	236	370	517	875
2409-5	174	237	371	522	875	2418-7	173	235	369	516	873
2412-1	174	237	369	522	876	2420-1	173	235	369	515	874
2412-2	174	237	370	522	875	2420-2	174	236	371	518	874
2412-3	174	237	370	523	876	2420-3	174	236	371	518	874
2412-4	177	241	372	532	876	2420-4	173	235	369	516	873
2412-5	178	244	373	540	877	2420-5	173	235	369	516	873

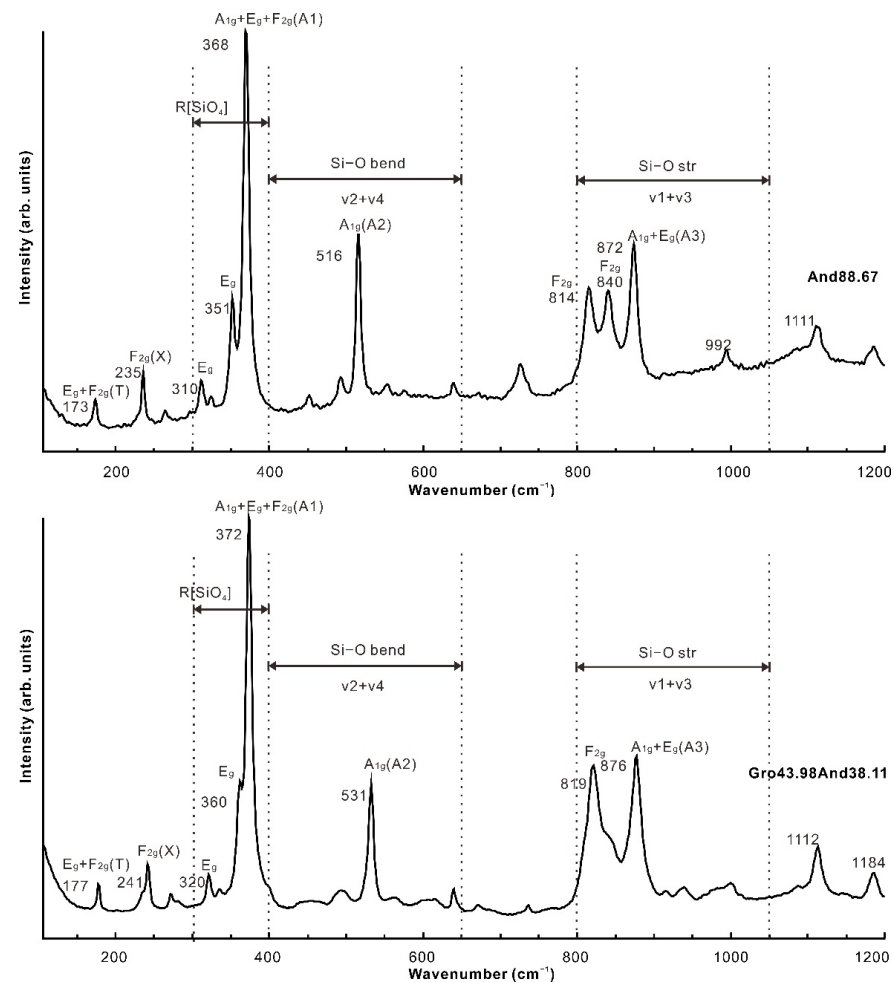


Figure 3. Two typical Raman spectra of the garnets from Jiama. The A_{1g} , E_g , and F_{2g} means the Raman peak is visible in the modes. Many vibration bands of the E_g and F_{2g} modes are not visible. T,

X, A1, A2, and A3 refer to a specific Raman peak, where T and X represent the translation of $[\text{SiO}_4]$ tetrahedron and dodecahedral cations, respectively, A1, A2, and A3 represent the rotation vibration ($R[\text{SiO}_4]$), the Si–O bending vibration (Si–O bend) and the Si–O stretching vibration (Si–O str) of $[\text{SiO}_4]$ tetrahedron, respectively.

5. Discussion

5.1. Raman Spectra of End Member Garnet

Figure 4 shows the Raman spectra and Raman peaks positions of five end member garnets (andradite, grossular, spessartine, almandine, and pyrope) [14,19,34]. As can be seen from the figure, there are variations in the Raman spectral characteristics of different end member garnets, including spectral morphology, peak intensity, peak positions, etc. [35]. The main difference lies in the number of peaks ranging from 800 to 1050 cm^{-1} , of which only andradite has three peaks. The other end groups, including grossular, spessartine, almandine, and pyrope, have two peaks with a large difference in peak intensity between the two peaks. It should be noted that the peak intensity of one of the two peaks of almandine and spessartine is relatively small, sometimes showing only one peak. In addition, the spectral morphology of the other regions is basically the same, but there are differences between peak positions.

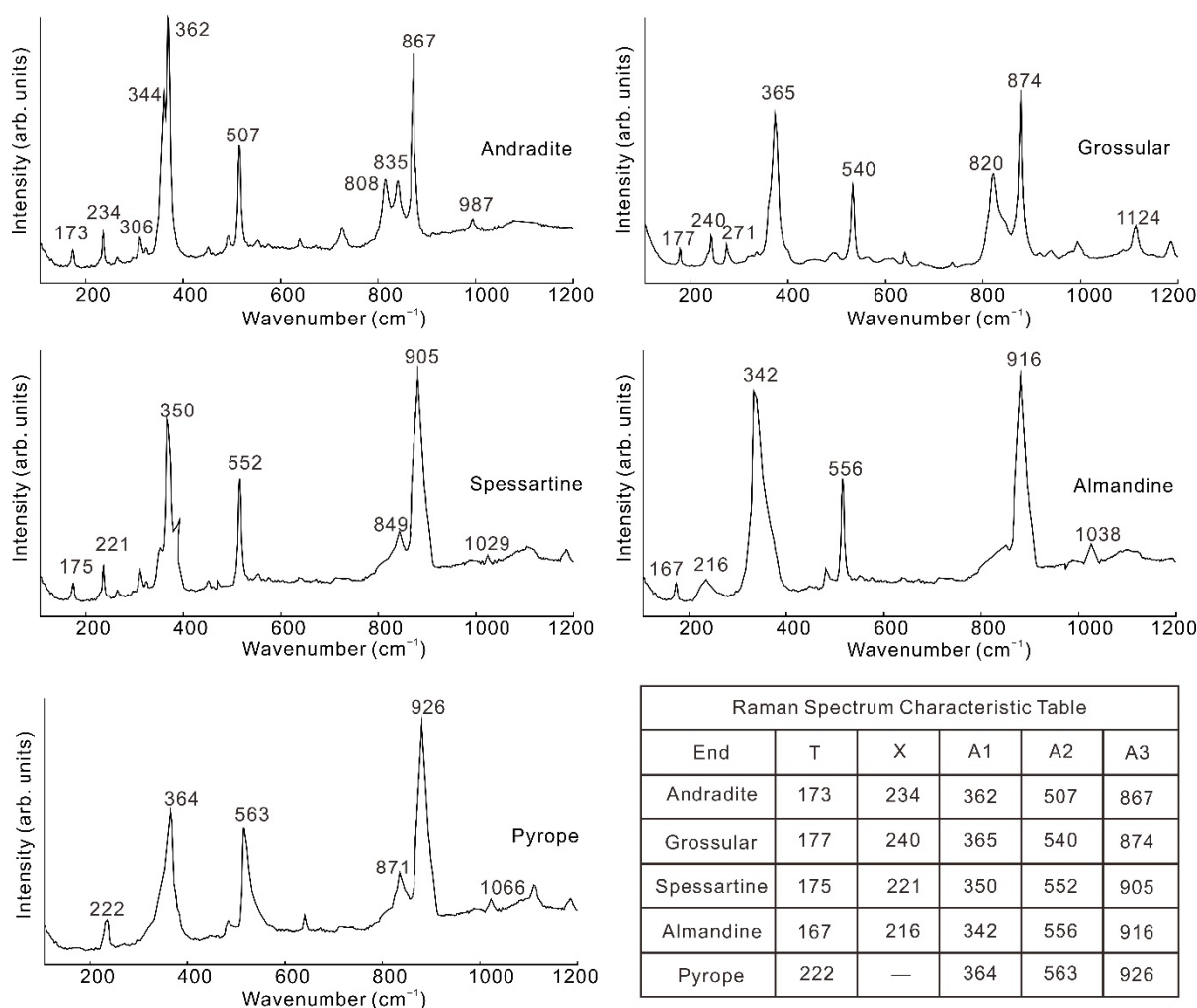


Figure 4. Raman spectra of end member garnet (modified according to [14,19,34]).

The variation in the peak positions of end member garnets is closely related to the composition and structure of the garnets. For the same X^{2+} and different Y^{3+} in the chemical

formula of garnet (andradite and grossular), it was found that as the Y^{3+} radius increases ($Fe^{3+} > Al^{3+}$), the size of the $[YO_6]$ octahedron increases, leading to a decrease in the bond energy of the Si–O bond to which it is attached [18], so that all the Raman peaks are shifted toward lower wavenumber. When X^{2+} is different and Y^{3+} is the same in the chemical formula of garnet (grossular, spessartine, almandine, and pyrope), there are two cases: (1) With the atomic mass of X^{2+} increasing ($Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$), the Raman peaks (T, X, A1) shift to lower frequency, indicated by almandine (167, 216, 342 cm^{-1}), spessartine (175, 221, 350 cm^{-1}), grossular (177, 240, 365 cm^{-1}), and pyrope (222, –, 364 cm^{-1}). Pyrope has some particularity because it shows only two Raman peaks, T and A1. The X Raman peak is in the lowest F_{2g} mode, corresponding to the “translation” of the cation in the $[SiO_4]$ tetrahedra cage in silicates. Due to the small size of the Mg^{2+} ion vibrating in its large dodecahedral cage, it cannot be measured and only the T Raman peak is displayed [36]. These peaks (T, X, A1) move to a higher wavenumber with the increase in X^{2+} atomic mass because the energy generated by the vibration itself (X) decreases, and because the $[SiO_4]$ tetrahedron vibration obstacle increases due to the increased dodecahedron mass, so the $[SiO_4]$ tetrahedron translation (T) and rotational vibration (A1) decrease in energy. Assuming that, the total energy promoting the vibration of functional groups is certain, the results are also consistent with the vibration energy model of A. M. Hofmeister (1991) [11]. The greater the energy, the greater the peak intensity, and the greater the frequency. (2) As the X^{2+} radius increases ($Ca^{2+} > Mn^{2+} > Fe^{2+} > Mg^{2+}$), the Raman peaks A2 and A3 shift to lower wavenumber, which is manifested as grossular (540, 874 cm^{-1}), spessartine (552, 905 cm^{-1}), almandine (556, 916 cm^{-1}), and pyrope (563, 926 cm^{-1}). The larger the X^{2+} radius, the larger the $[XO_8]$ dodecahedron, so the Si–O bond energy connected to it is relatively low, and the Raman shifts of A2 and A3 move in the low-frequency direction [11,18,19].

5.2. Raman Spectral Characteristics of Jiama Garnet and Its Relationship with Composition

Jiama garnet belongs to the andradite–grossular solid solution series. Nine groups of Raman spectra were selected and sorted according to the order of increasing andradite content (Figure 5). It can be seen from the figure that the position of the Raman peaks shifts to lower frequency with the increase in andradite content, which is consistent with the above discussion. Since the Raman peaks of andradite are concentrated in the low-frequency part, the increase in andradite content means an increase in the proportion of low-frequency Raman peaks of andradite–grossular solid solution, which is shown as a Raman shift to lower frequency.

In Figure 5, it can be seen that the Raman peaks T, X, A1, A2, and A3 vary with the content of andradite. The variation in the T, X and A2 Raman peaks is more obvious than that of A1 and A3, as evidenced by the electron probe data and Raman peak positions of the nine groups extracted in Table 3. To find out why the T, X, and A2 Raman peaks can better reflect the characteristics of garnet, the correlation between the five Raman peaks, and the principal component content and andradite content was analyzed by SPSS. The results are shown in Table 4. The results showed that the five Raman peaks significantly correlated with the principal component content of garnet, but the significant correlations of T, X, and A2 were greater than those of A1 and A3. Thus, the T, X, and A2 Raman peaks show more pronounced changes in the figure. Among them, SiO_2 , CaO , Al_2O_3 , and FeO were significantly correlated with the Raman peaks. Al_2O_3 was significantly positively correlated with the Raman peaks, while FeO was significantly negatively correlated. Similarly, the content of andradite was also significantly negatively correlated with the Raman peaks, that is, the frequency of Raman peaks decreases with the increase in andradite content. In addition, there is essentially no correlation between MnO , MgO , TiO_2 , and the Raman peaks, but MnO has a certain degree of correlation with X and A2, which confirms the special situation of pyrope in the above discussion. Combined with the vibration mechanism represented by X and A2, it is speculated that Mn^{2+} partially replaces Ca^{2+} , which is also consistent with Wu’s findings (2015) [18]. In the crystal structure of garnet, there

are two oxygen in the $[\text{SiO}_4]$ tetrahedron contributions to the divalent cations forming dodecahedron, so the divalent cations affect the vibration of the $[\text{SiO}_4]$ tetrahedron. The Raman peaks T, X, and A2 with the best correlation were taken and a linear fitting result with the andradite content was produced (Figure 6). It is found that the fitting result is very good. It can also be seen that the three Raman peaks are positively correlated, which shows that the change in the garnet Raman peaks is overall and the difference lies in the magnitude of the variation.

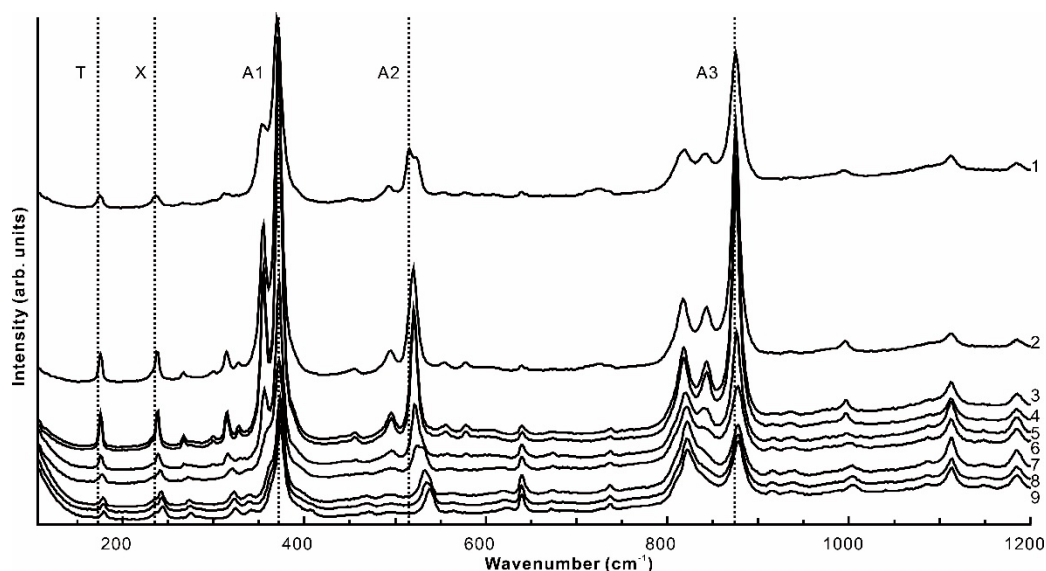


Figure 5. Relationship between the content of andradite and the Raman peaks: (1) 2412-11 (And94.14Gro0); (2) 2412-2 (And84.34Gro0); (3) 2412-12 (And74.70Gro6.15); (4) 2412-10 (And64.10Gro17.11); (5) 2412-1 (And56.52Gro25.59); (6) 2412-8 (And46.57Gro32.73); (7) 2412-4 (And36.79Gro54.98); (8) 2412-7 (And23.18Gro62.53); (9) 2412-5 (And15.79Gro71.52).

Table 3. EPMA data (wt%) and Raman peaks (cm^{-1}) of nine groups of garnets.

No.	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Gro	And	T	X	A1	A2	A3
1	36.011	0.038	0.083	29.327	0.217	0	31.312	0	94.14%	173	234	365	513	873
2	38.056	0.023	0.258	28.462	0.213	0.005	32.057	0	84.34%	174	237	370	522	875
3	38.444	0.03	1.954	25.254	0.157	0.038	32.935	6.15%	74.70%	174	236	371	519	874
4	38.137	0	4.354	22.269	0.132	0.038	32.554	17.11%	64.10%	174	237	370	521	876
5	38.591	0.187	6.593	20.668	0.43	0	32.742	25.59%	56.52%	174	237	369	522	876
6	39.322	0.163	8.323	18.573	0.284	0.064	32.915	32.73%	46.57%	176	240	372	529	876
7	39.037	0.041	12.5	12.923	0.314	0.014	34.725	54.98%	36.79%	177	241	372	532	876
8	39.754	0.228	14.93	10.698	0.342	0.009	34.158	62.53%	23.18%	178	242	372	535	876
9	40.148	0.176	16.974	7.929	0.472	0.015	34.781	71.52%	15.79%	178	244	373	540	877

Table 4. Correlation results.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Gro	And
T	0.856 **	0.621	0.958 **	−0.953 **	0.625	0.065	0.915 **	0.959 **	−0.948 **
X	0.903 **	0.616	0.954 **	−0.953 **	0.674 *	0.097	0.909 **	0.952 **	−0.959 **
A1	0.948 **	0.385	0.725 *	−0.757 *	0.355	0.420	0.832 **	0.715 *	−0.796 *
A2	0.912 **	0.626	0.951 **	−0.950 **	0.686 *	0.074	0.911 **	0.949 **	−0.958 **
A3	0.856 **	0.542	0.788 *	−0.803 **	0.619	0.166	0.728*	0.776 *	−0.843 **

** When the confidence level is 0.01, the correlation is significant; * when the confidence level is 0.05, the correlation is significant.

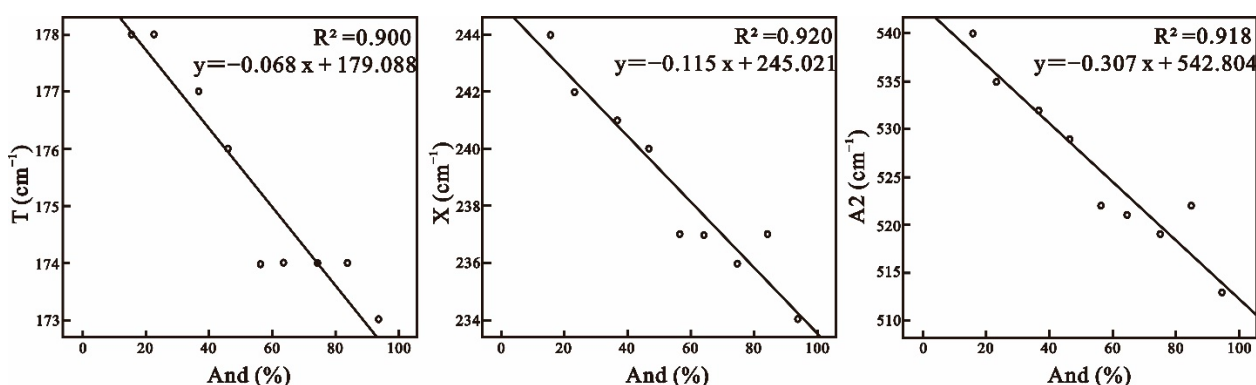


Figure 6. The linear fitting results between andradite content and Raman peaks (T, X, and A2).

Table 5 shows the relationship between the garnet end member content and Raman peaks: when And > 50%, the five Raman peaks (T, X, A1, A2, and A3) ranges are 173–174, 234–239, 365–371, 513–525, and 872–876 cm^{-1} ; when And < 50%, they are 177–178, 240–244, 368–373, 527–543, and 875–878 cm^{-1} . The range of Raman peak positions corresponding to A1 and A3 are overlapped with respect to T, X, and A2, which also proves that the latter three are indeed more correlated than the former two and that the end composition of garnets can be determined based on specific Raman peaks.

Table 5. The relationship between the garnet end member content and Raman peaks (cm^{-1}).

		T	X	A1	A2	A3
Andradite	And > 50%	173–174	234–239	365–371	513–525	872–876
Grossular	And < 50%	177–178	240–244	368–373	527–543	875–878

Note: data are listed in the Table S1 and Data S1. And: Andradite.

5.3. Relationship between Garnet and Mineralization

Referring to Figure 1 and Table 1, from the proximal skarn ZK2404, ZK2407, and ZK2409 which are close to the wall rock, and to the distal skarn ZK2420 which is far from the wall rock, the content of andradite increases and the Raman peaks shift to the lower wavenumber, and the mineralization type changes from chalcopyrite and bornite to molybdenum mineralization, indicating that the distal andradite-rich garnets have Raman peaks with a small wavenumber, generally 173–174 cm^{-1} , 234–239 cm^{-1} , 365–371 cm^{-1} , 513–525 cm^{-1} , and 872–876 cm^{-1} , which are easily mineralized with copper; the proximal grossular-rich garnets have large wavenumber Raman peaks, usually 177–178 cm^{-1} , 240–244 cm^{-1} , 368–373 cm^{-1} , 527–543 cm^{-1} , and 875–878 cm^{-1} , which are easily mineralize molybdenum. Compared with the three proximal boreholes, andradite content is lower in ZK2412 and ZK2413 and developing pyrite. It is speculated that the formation of porphyry at the bottom promoted the consumption of iron.

Previous results [37–39] showed that grossular forms mainly in a weakly oxidizing–weakly reducing environment of 550–700 °C, medium-acid solution, and low oxygen fugacity ($\log f_{\text{O}_2} = -28.637 \sim -16.514$, $E_h = -1.15 \sim -0.27$ V, [39]), and andradite is generally formed at 450–600 °C, pH = 4.0–11.0, in an oxidizing–weakly oxidizing environment with high oxygen fugacity ($\log f_{\text{O}_2} = -21.763 \sim -11.066$, $E_h = 0.13 \sim 0.97$ V, [39]). Garnets with high grossular composition form under more reducing and acidic conditions than those with high andradite composition. Relatively speaking, the formation of andradite under alkaline conditions is common; that is, alkaline conditions are conducive to iron mineralization. Grossular is best formed in an acidic medium, while lead–zinc mineralization and molybdenum mineralization are also formed in relatively acidic environments. Andradite are formed in almost the same amount as grossular under neutral conditions conducive to copper mineralization. The garnets in the Jiama deposit are similar to those in many skarn deposits in China; they are mainly composed of andradite–grossular series, such as

Shizhuyuan in Hunan, Daye in Hubei, and Tiantang in Guangdong copper polymetallic deposits, which are formed in a relatively oxidized or weakly oxidized environment [40,41]. From the center of the rock mass to the far end, the garnets in the Jiama deposit are mainly grossular to andradite, reflecting the transformation from acidic to alkaline metallogenic solution, from weak oxidation–weak reduction to oxidation–weak oxidation metallogenic environment, and from copper to lead–zinc and molybdenum mineralization type.

6. Conclusions

(1) The Raman peaks of garnet in the Jiama deposit are negatively correlated with the content of andradite. The peaks shift toward a lower wavenumber with the andradite content increasing. This is also closely related to the cation radius and relative atomic mass. When X^{2+} is the same and Y^{3+} is different, all the Raman peaks (T, X, A1, A2, and A3) move in the low-frequency direction with the increase in the Y^{3+} radius. When X^{2+} is different and Y^{3+} is the same, some peaks (T, X, and A1) move in the low-frequency direction as the X^{2+} radius increases, while some peaks (A2 and A3) move in the low-frequency direction with the increase in the X^{2+} atomic mass.

(2) The correlations of T, X, and A2 are greater than those of A1 and A3. We can judge that garnet belongs to andradite (And > 50%) or grossular (And < 50%) by the former three Raman peaks when the garnet Raman spectrum is determined. When And > 50%, the three Raman peaks (T, X, and A2) range are 173–174, 234–239, 513–525 cm^{-1} ; when And < 50%, they are 177–178, 240–244, and 527–543 cm^{-1} .

(3) Grossular is mostly formed in an acidic, weakly oxidizing–weakly reducing environment, while andradite is generally formed in an alkaline, oxidizing–weakly oxidizing environment. The change in garnet composition reflects the variation in the metallogenic environment, and the Raman spectrum can indicate the change in garnet composition. The Raman spectrum analysis of garnet can be used to study skarn mineralization, which is of great significance for deposit exploration.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min12121578/s1>, Table S1: EPMA results, garnet end member content and Raman peak position; Data S1: the Raman spectral files in the format.txt.

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