



## A short review on enstatite and pyroxene in L6 chondrites studied by Raman Spectroscopy

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**Abstract:** In this study, Raman spectroscopy analyses obtained from previously published studies on Bursa, Çanakkale, Kamargaon, Château-Renard, Sixiangkou, Braunschweig and Suizhou L6 chondrites were compared. These examples were selected for the presence of enstatite ( $\text{Mg}_2\text{Si}_2\text{O}_6$  or  $\text{MgSiO}_3$ ) and pyroxene to give a brief overview. The aim of this preliminary study is to determine the presence of silicate minerals, which are abundant in the content of L6 chondrites, and to create a future database by collecting the published spectra of silicate minerals.

**Keywords:** Raman spectroscopy; L6 chondrites; Enstatite; Pyroxene.

### 1. Introduction

Meteor fragments that fell on the Earth after survival of atmospheric entry are called meteorites. Mineralogical studies of meteorites provide detailed information about stellar formation, evolution, and the early geologic history of their source bodies. Chondrites are the most abundant type of stony meteorites, and any further data on their chemistry is crucial to understand parent body or asteroidal processes (Norton and Chitwood, 2008). The largest group of chondrites are the ordinary chondrites about 80% of all known meteorite species and more than 90% of chondrites belong to this group. Ordinary chondrites are divided into three different types according to their chemical content and the ratio of metallic iron ( $\text{Fe}^0$ ) to oxidized iron ( $\text{FeO}$ ), H (with high Fe content), L (with low Fe content) and LL (with very low metallic Fe content). (Keil and Fredriksson, 1964; Van Schmus and Wood, 1967; Vernazza et al., 2015; Saikia et al., 2017, 2018; Unsalan and Altunayar-Unsalan, 2020). Mineralogical examination of L6 chondrites gives information about the possible parent body and thermal history of L chondrites. For this reason, it is important to examine in detail silicate minerals such as enstatite, orthopyroxene, clinoenstatite and pyroxene.

More than half of L chondrites, which are rich in silicate minerals such as pyroxene, clinoenstatite, orthopyroxene and olivine are petrologic type 6 and L6 chondrites have been reported that they undergone high degrees of thermal metamorphism. Thermal metamorphism continues increasingly from type 4 to 6. The onset melting temperature of ordinary chondrites of type 4-6, such as L6 stony meteorites, were suggested to be  $\sim 950$  °C. This temperature is an upper limit defined for ordinary chondrites of type 4-6 (Dodd, 1981; Norton and Chitwood, 2008). Other

studies of L chondrites show that L6 chondrites have  $>35$  GPa and approximately  $\geq 850$  °C of thermal metamorphism data (Stöffler et al., 1991; Huss et al., 2006; Jinping, 2016; Fritz et al., 2017). When previous studies on L chondrites are examined, it can be seen that especially L chondrites of petrologic type 4-6 have been studied in order to get more conclusions about their potential source body. Therefore, in this study of L6 chondrites, the aim is to establish a primal Raman spectra-database of silicate minerals such as enstatite found in L6 chondrites.

Silicate minerals, widely distributed throughout the solar system, make up almost 95% of the Earth's upper mantle and crust. Most silicates occur as major components of igneous rocks. In addition, silicates are found in sedimentary and metamorphic varieties. These silicates, such as orthorhombic pyroxenes = orthopyroxene (enstatite, ferrosilite) and monoclinic pyroxenes = clinopyroxene, are important silicate mineral components found in meteorites and most asteroids. Clinopyroxenes are pyroxenes crystallize in the monoclinic system. Typically containing calcium (Ca), magnesium (Mg), and iron (Fe), clinopyroxenes are a group of inosilicate minerals important in the formation of rocks. They are formed under high temperature and/or high-pressure conditions. Pyroxene (Mg, Fe)SiO<sub>3</sub> is one of the most important components in stony meteorites and the upper mantle of the Earth (Chen et al., 2004). Another important pyroxene group is the orthopyroxenes, which crystallize in the orthorhombic system and take its name from it.

The silicate minerals are the most important mineral class because they are by far the most abundance rock-forming minerals. Enstatite is an important silicate mineral commonly found in igneous and metamorphic rocks and forming rocks. Enstatite consists of magnesium silicate and is a translucent crystalline mineral. Enstatite mineral, a member of the pyroxene group, also occurs in stony meteorites. Enstatite (Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> or MgSiO<sub>3</sub>) is a silicate mineral crystallizing in the orthorhombic system, belonging to the orthopyroxene subgroup. Clinoenstatite named as the monoclinic polymorph of enstatite, is also a member of the pyroxene group. Previously, characteristic Raman peaks of the enstatite and clinoenstatite were reported to be observed at  $\sim 1000$ ,  $\sim 670$  and  $200\text{-}400$  cm<sup>-1</sup> (Etchepare, 1970; Fabel et al., 1972; Perry et al., 1972; Wang et al., 2001; Unsalan et al., 2012; Saikia et al., 2017; Saikia et al., 2018; Unsalan and Altunayar-Unsalan, 2020).

Here, we reviewed the published results regarding the presence of selected silicate minerals, particularly pyroxene and enstatite, using Raman Spectroscopy of a suite of ordinary chondrites: Bursa, Çanakkale, Kamargaon, Chateau-Renard, Sixiangkou, Braunschweig, and Suizhou L6 chondrites. Raman spectroscopy allows one to obtain detailed information about the minerals and functional groups in the sample in a non-destructive way. Analysis can be done on small sample areas with minimal physical intervention. Raman spectroscopy is preferred when more precise and accurate results have to be obtained because it is very sensitive to distinguish different chemical structures. It also provides the necessary information to distinguish different structural groups and phases of silicate minerals (Lancelot, 2010). Each of the silicate mineral groups has its own representative Raman bands. For this reason, this technique is considered to be ideal for rapid identification and characterization of silicate minerals.

Bursa meteorite (40° 12'N, 29° 14'E) fell in Bursa, Turkey in 1946. With its brecciated chondritic and fine-grained matrix Bursa chondrite was classified as L6. The main mass of the meteorite is 25 kg. In a study by Çağatay and Çopuroğlu (1990), it was shown that about 75% of the polished part of the Bursa chondrite consists of silicates and 20-25% of it consists of metallic minerals. A Raman study on Bursa chondrite by Unsalan and Altunayar-Unsalan (2020) revealed

the presence of enstatite based on its characteristic dominant peaks at 1008, 679, 338 and 223  $\text{cm}^{-1}$  in its Raman spectrum.

Çanakkale meteorite (39° 48'N, 26° 36'E) is another L6 stony meteorite that fell in Çanakkale, Turkey in 1964. The total mass of the largest fragment of meteorite is 4 kg. Presence of pyroxene and enstatite minerals in interior grains (IG) and in the fusion crust (FC) was determined by Unsalan et al. (2012). The authors identified these two minerals from their corresponding Raman peaks at 1005, 680/662 doublet, 336, 234 (IG), 1009, 679/661 doublet, 395, 338, 233 (IG), 1000, 654, 307 (FC) and 997  $\text{cm}^{-1}$ , 669/649 doublet, 395, 323, and 278  $\text{cm}^{-1}$  (FC). It has been stated that the pyroxene peaks obtained in the Raman spectrum have an “orthopyroxene” model (Huang et al., 2000; Wang et al., 2001). Enstatite, on the other hand, from the inner grains (IG) and exterior grains (FC-fusion crust) of the Çanakkale meteorite were identified from the corresponding Raman spectrum peaks (Table 1).

Kamargaon meteorite (26° 37' 57"N, 93° 46' 11"E) fell on Bali-Chapori village near Kamargaon town in Golaghat District, Assam, India on 13 November 2015. The meteorite was a single fall and weighs 12.095 kg (Ray et al., 2017). In the first of two different Raman studies, the presence of pyroxene (enstatite) in Kamargaon chondrite was defined by 337.12, 680.45 and 1006.13  $\text{cm}^{-1}$  peaks in the Raman spectrum (Saikia et al., 2017). In the latter study, it was shown as an indicator of orthopyroxene (opx) according to its peak values at 1008, 680, and 334  $\text{cm}^{-1}$  in the Raman spectrum. In addition, Raman peaks observed at 1012, 579, 427 and 323  $\text{cm}^{-1}$  were assigned as clinoenstatite (Saikia et al., 2018). However, in addition to previous work by Saikia et al. (2017) on the Kamargaon meteorite, Raman peaks of pyroxene, orthopyroxene and clinoenstatite were found. These peak values are as follows: 746, 680, 548, 411, 387, 337, 293, and 224  $\text{cm}^{-1}$  for pyroxene, 1025, 1008, 938, 690, 680, 660, 405, 337, 334, 301, and 234  $\text{cm}^{-1}$  for orthopyroxene and 1048, 1012, 752, 668, 579, 427, 323, and 254  $\text{cm}^{-1}$  for clinoenstatite (Saikia et al., 2018).

The Château-Renard meteorite (47° 56'N, 2° 55'E) is an L6 chondrite that fell in France on June 12, 1841. The total mass of the Château-Renard meteorite is estimated to be 30 kg. In the Raman spectrum based on the previous Raman study on Château-Renard (L6) chondrite, ~662/680  $\text{cm}^{-1}$  doublet and ~1016  $\text{cm}^{-1}$  enstatite peaks have been shown to be typical for orthopyroxene (Baziotis et al., 2018).

Sixiangkou meteorite (32° 26'N, 119° 52'E) fell on Sixiangkou town of Taizhou city, Jiangsu Province, China on August 15, 1989. The total mass of the meteorite is 630 g. In the study based on the Raman analysis of the Sixiangkou chondrite by Zhang et al. (2006), 337, 661 and 667  $\text{cm}^{-1}$  doublet and 1007  $\text{cm}^{-1}$  peaks were found in the Raman spectrum and these peaks were attributed to enstatite.

The Braunschweig meteorite (52° 13' 33"N, 10° 31' 12"E) fell on April 23, 2013 at 02:05 in the city of Braunschweig in the state of Niedersachsen, Germany. The total mass of the meteorite is 1.3 kg. The meteorite was classified as L6 chondrite by R. Bartoschewitz. Based on the Raman study of Hochleitner et al. (2015), the presence of pyroxene (as opx) in Braunschweig chondrite was identified from 1009.8  $\text{cm}^{-1}$ , 658.6, 376.2, 341.9, 307.5 and 125.0  $\text{cm}^{-1}$ .

The Suizhou meteorite (31° 37'N, 113° 28'E) fell on the city of Suizhou, Hubei province of China, on April 15, 1986. A meteorite with a mass of 270 kg was recovered. In a Raman study by Xie et al. (2001) on the Suizhou (L6) chondrite, the presence of pyroxene was revealed by its distinctive peaks at 1011, 664, 554, 511, 390, 322, and 191  $\text{cm}^{-1}$  in Raman spectrum.

This preliminary study we performed here over seven different L6 chondrites that are rich in silicate minerals was carried out on pyroxenes. The presence of silicate minerals and their Raman signals were investigated by examining previously published data of the aforementioned L6 stony meteorites. Detailed investigation of abundant silicate minerals in chondrites will also enable us to extract further information and to interpret the thermal metamorphism history and possible source body(ies) of L type chondrites. Therefore, in this preliminary study on L6 chondrites, the aim is to create a future database by collecting/gathering the Raman spectra of silicate minerals such as pyroxene, clinoenstatite, enstatite and orthopyroxene obtained from Raman analyses and to contribute to future research in Meteoritics.

## 2. Materials and methods

The low-iron chemical group of ordinary chondrites is called L chondrites. L chondrites, located between the H and LL group ordinary chondrites, are distinguished by their oxygen isotope composition, relatively low siderophilic element content, and medium-sized chondrules about 0.7 mm in size. L chondrite meteorites with petrologic type 6 metamorphosed under adequate conditions. All mineral compositions are almost homogenized, all low Ca pyroxene is converted to orthopyroxenes, secondary phases (such as feldspar) are coarsened to sizes about  $\geq 50$   $\mu\text{m}$ , obliterating many chondrule outlines thermal metamorphism progresses due to decay of the short-lived radionuclides. L6 chondrites, are composed of chondrules, which are almost spherical in structure and rich in silicate particles.

Data on selected meteorites presented here were mainly retrieved from the Meteoritical Bulletin Database. SAO/NASA Astrophysics Data System, Web of Science and Mendeley were used to search the literature based on Raman studies of L6 chondrites. It was seen that there is a diverse data regarding both enstatite and pyroxene minerals. Thus, we decided to collect Raman data over the literature to give a better picture on published Raman spectra as a sort of a brief review. Raman analysis was reported on a polished section of the Bursa chondrite sample (Unsalan and Altunayar-Unsalan, 2020). Authors reported the usage of Renishaw InVia Raman spectrometer to determine mineral phases in Bursa chondrite. According to the authors of that study (Unsalan and Altunayar-Unsalan, 2020), the enstatite peaks in the Raman spectrum of the Bursa meteorite were compared and verified with the RRUFF database. The Raman study by Unsalan et al. (2012) used approximately 6 g of Çanakkale meteorite sample for measurements and analysis on this meteorite fragment. In the analysis, micro-Raman spectra of the samples obtained from the meteorite were recorded by a Thermo Scientific DX-R micro-Raman spectrometer.

The Kamargaon meteorite sample was ground for Raman analysis and Raman spectra were collected in powder form with the Jobin-Yvon Horiba LabRam-HR Micro Raman spectrometer (Saikia et al., 2017). In another Raman study by Saikia et al. (2018), ~20 mg of the Kamargaon meteorite powder sample was used for Raman analysis. Raman spectra were collected from the meteorite sample with a Jobin-Yvon Horiba LabRam-HR Micro Raman spectrometer. The peak positions of the pyroxene obtained from the spectrum were defined using the RRUFF database.

A polished thin section of the Château-Renard (L6) meteorite was used in the Raman study by Baziotis et al. (2018) and the spectra were collected using the Renishaw inVia Reflex spectrometer. Identification of the enstatite mineral was made by comparison with data published from the RRUFF database and the Handbook of Raman Spectra. A thin section prepared from the Sixiangkou meteorite sample was used in the analysis of the Raman study by Zhang et al. (2006). Raman spectra of the meteorite thin section were recorded with a Renishaw RM2000 micro-Raman

spectrometer. In the Raman study by Hochleitner et al. (2015) on the Braunschweig (L6) meteorite, surface areas that do not require sample preparation procedure were selected and Raman spectroscopy analysis was performed on a large meteorite sample. Horiba Xplora Integrated confocal LASER micro-Raman system was used for analysis. In the Raman study by Xie et al. (2001) on the Suizhou (L6) meteorite, a polished thin section of the meteorite sample was used. Raman spectra were recorded on a Renishaw RM-1000 laser Raman microscope.

### 3. Results and discussion

Based on the data we covered, we gathered diverse data on the identified selected silicate minerals (enstatite and pyroxene) in those meteorites. The result of previous Raman studies on Bursa, Çanakkale, Kamargaon, Château-Renard, Sixiangkou, Braunschweig and Suizhou L6 chondrites by the above authors showed the presence of silicate minerals (enstatite, pyroxene, orthopyroxene and clinoenstatite) in L6 type stony meteorites. In this paper, previous Raman studies of seven different L6 chondrites by the aforementioned authors were examined and these studies were compared to each other. As a result of the comparisons, the composition of silicate minerals in meteorites and the Raman peak positions of these minerals were summarized and the results were presented in Table 1.

In the Raman study by Unsalan and Altunayar-Unsalan (2020), the Raman peaks of the enstatite mineral from the Raman peaks collected at 532 nm wavelength for Bursa chondrite were given in Table 1. Saikia et al. 2017 and 2018 described that the Raman peaks of the enstatite mineral from the Raman spectra collected at 532 nm wavelength in Kamargaon chondrite are 1006.13, 680.45, and 337.12  $\text{cm}^{-1}$ . Raman peaks of pyroxene are 680, 746, 548, 411, 387, 337, 293, and 224  $\text{cm}^{-1}$ . Raman peaks of orthopyroxene are 1025, 1008, 938, 690, 680, 660, 405, 337, 334, 301, and 234  $\text{cm}^{-1}$ . Additionally, Raman peaks of clinoenstatite were observed at 1048, 1012, 752, 668, 579, 427, 323, and 254  $\text{cm}^{-1}$ .

Baziotis et al. (2018) reported the Raman peaks of the enstatite mineral observed by 514 nm wavelength excitation in Château-Renard chondrite are approximately 1016, 680, and 662  $\text{cm}^{-1}$ . In the Raman study based on by Hochleitner et al., (2015), Raman peaks of orthopyroxene from the Raman spectra collected at 532 nm wavelength in Braunschweig chondrite are 1009.8, 658.6, 376.2, 341.9, 307.5, and 125  $\text{cm}^{-1}$ .

Raman investigation performed by Zhang et al. (2006), Raman peaks belonging to the enstatite mineral were assigned as 1007, 667, 661, and 337  $\text{cm}^{-1}$  from the Raman spectra collected at 514 nm wavelength in Sixiangkou chondrite. In the Raman study by Xie et al. (2001), Raman peaks of pyroxene from the Raman spectra collected at 514.5 nm wavelength in Suizhou chondrite were defined as 1011, 664, 554, 511, 390, 322, and 191  $\text{cm}^{-1}$ .

The presence of silicate minerals abundantly in L6 chondrites provides us with information about the possible parent body of L chondrites. For this reason, it is crucial to investigate these chondrites and the silicate minerals they contain in detail. Consequently, this study of L6 chondrites, the presence of silicate minerals in seven L6 chondrites, which were selected based on previous studies and summarized in detail above, were investigated and it was observed that silicate minerals such as enstatite, orthopyroxene, clinoenstatite and pyroxene were abundant in these meteorites. A summary table of the aforementioned Raman peaks based on previous Raman studies of seven L6 chondrites were presented in Table 1.

**Table 1.** Raman peak positions ( $\text{cm}^{-1}$ ) of selected minerals for Bursa, Çanakkale, Kamargaon, Château-Renard, Braunschweig Sixiangkou and Suizhou L6 chondrites, respectively (En: enstatite, Px: pyroxene, Opx: orthopyroxene, CEn: clinoenstatite).

Minerals	<sup>a</sup> Bursa (532 nm)		<sup>b</sup> Çanakkale (532 nm)			<sup>c</sup> Kamargaon (532 nm)		<sup>d</sup> Château- Renard (514 nm)	<sup>e</sup> Braunschweig (532 nm)	<sup>f</sup> Sixiangkou (514 nm)	<sup>g</sup> Suizhou (514.5 nm)
	Interior Grains (IG)			Fusion Crust (FC)							
Enstatite	233	---	232	233	233	---	---	---	---	---	---
	338	336	337	337	338	--	337.12	---	---	337	---
	679	662	661	662	661	--	---	~662	---	661, 667	---
	---	680	679	681	679	--	680.45	~680	---	---	---
	---	851	860	---	---	--	---	---	---	---	---
	1008	1005	1007	1005	1009	--	1006.13	~1016	---	1007	---
Pyroxene	---	234	233	---	---		278	224,293	---	---	191
	---	336	338	---	---	307	323,395	337,387	---	---	322,390
	---	662	661	---	---	654	649	411,548	---	---	511,554
	---	680	679	---	---	---	669	680,746	---	---	664
	---	1005	1009	---	---	1000	997	---	---	---	1011
Orthopyroxene	---	---	---	---	---	---	---	234	---	125	---
	---	---	---	---	---	---	---	301	---	307.5	---
	---	---	---	---	---	---	---	334,337	---	341.9	---
	---	---	---	---	---	---	---	405	---	376.2	---
	---	---	---	---	---	---	---	660	---	658.6	---
	---	---	---	---	---	---	---	680	---	---	---
	---	---	---	---	---	---	---	690	---	---	---
	---	---	---	---	---	---	---	938	---	---	---
---	---	---	---	---	---	---	1008	---	1009.8	---	
Clinoenstatite	---	---	---	---	---	---	---	1025	---	---	---
	---	---	---	---	---	---	---	254	---	---	---
	---	---	---	---	---	---	---	323	---	---	---
	---	---	---	---	---	---	---	427	---	---	---
	---	---	---	---	---	---	---	579	---	---	---
	---	---	---	---	---	---	---	668	---	---	---
	---	---	---	---	---	---	---	752	---	---	---
---	---	---	---	---	---	---	1012	---	---	---	
---	---	---	---	---	---	---	1048	---	---	---	

<sup>a</sup>Unsalan and Altunayar-Unsalan, 2020, <sup>b</sup>Unsalan et al., 2012, <sup>c</sup>Saikia et al., 2017; Saikia et al., 2018, <sup>d</sup>Baziotis et al., 2018, <sup>e</sup>Hochleitner et al., 2015, <sup>f</sup>Zhang et al., 2006, <sup>g</sup>Xie et al., 2001.

#### 4. Conclusion

Here, we give a brief review of previous Raman spectroscopic investigations the selected silicate minerals (enstatite and pyroxene) in L6 chondrites. To the best of our knowledge, no such work has been performed particularly focuses on enstatite and pyroxene minerals. In addition, this study provides detailed information about the peak location and composition of silicate minerals in an organized manner for the case of L6 type stony chondrites. Based on studies on selective silicate minerals, we can conclude that there is still an urgent need on compilation of the published spectra in an organized manner. Thus, we believe that the readers in this field will eventually benefit such gathered data on such minerals in terms of a database approach. Considering the literature review of the L6 chondrites in this work, it is worth noticing that based on Raman study, Sixiangkou is akin to L6 (Zhang et al., (2006)) rather than recommended L5 class for this meteorite in Meteoritical Bulletin (Meteoritical Bulletin Database, 2021). In short, it is obvious that more investigations and reviews, data gathering is required for an all-inclusive view. We believe that our preliminary effort, could serve as a beginning point in constructing a database of silicate minerals found in L6 stony

chondrites. Examination of the presence of silicate minerals in these chondrites by Raman spectroscopy in detail allows one to learn more about the possible source bodies of L chondrites and the history of their thermal metamorphism they experienced. Therefore, researchers in this field would eventually benefit from the collected and compiled published spectra of silicate minerals such as enstatite, orthopyroxene, clinoenstatite and pyroxene in selected L6 chondrite samples presented here.

### Conflict of interest

Authors declare no conflict of interest

### CRedit Author Statement

**Ceren Kamil:** Validation, Investigation, Resources, Data Curation, Writing - Original Draft. **Ozan Unsalan:** Conceptualization, Methodology, Validation, Formal analysis, Review&Editing.

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