

# End-member calcium Tschermak's pyroxene, $\text{CaAlAlSiO}_6$ , from the Allende and Murray meteorites: occurrence, origin and significance

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## ABSTRACT

Calcium Tschermak's pyroxene (CaTs),  $\text{CaAlAlSiO}_6$ , is well known as an important component in pyroxene. It is a member of the Ca clinopyroxene group in which Al dominates in the M1 site. Pyroxenes with more than 80 mol% CaTs were observed previously in Ca-, Al-rich refractory inclusions (CAI) from five carbonaceous chondrites. This study re-investigated the near end-member CaTs in the Allende and Murray chondrites. Electron back scatter diffraction (EBSD) is used to establish that its crystal structure is monoclinic,  $C2/c$ ;  $a = 9.609 \text{ \AA}$ ,  $b = 8.652 \text{ \AA}$ ,  $c = 5.274 \text{ \AA}$ ,  $\beta = 106.06^\circ$ ,  $V = 421.35 \text{ \AA}^3$  and  $Z = 4$ . Its EBSD pattern is an excellent match to that of synthetic  $\text{CaAlAlSiO}_6$  with the  $C2/c$  structure.

MicroRaman is also carried out to confirm the crystal structure. The Allende CaTs, with 46.00 wt%  $\text{Al}_2\text{O}_3$  and 97 mol% Al in the M1 site, has the formula  $\text{Ca}_{1.02}(\text{Al}_{0.97}\text{Fe}_{0.01}\text{Mg}_{0.01})_{\Sigma 0.99}(\text{Si}_{1.00}\text{Al}_{1.00})_{\Sigma 2.00}\text{O}_6$ . It occurs as micro-sized crystals along with melilite, hibonite, perovskite, spinel, corundum,  $\text{Ti}^{3+}$ -rich pyroxene, and grossular in a fluffy Type A CAI. It is probably a secondary phase resulting from the alteration of gehlenitic melilite. The CaTs in Murray, with a formula  $\text{Ca}_{0.98}(\text{Al}_{0.81}\text{Mg}_{0.16}\text{Ti}^{4+}_{0.04})_{\Sigma 1.01}(\text{Si}_{1.11}\text{Al}_{0.89})_{\Sigma 2.00}\text{O}_6$ , occurs with hibonite and Al-rich diopside in a glass-free refractory spherule. This sample formed by solidification of a once-molten droplet early in the history of the solar system.

**Keywords:** Calcium Tschermak's pyroxene, CaTs,  $\text{CaAlAlSiO}_6$ , Al-rich pyroxene, refractory inclusion, Allende meteorite, Murray meteorite.

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## INTRODUCTION

During recent nano-mineralogy investigation of the Allende meteorite, Al-rich pyroxenes have been observed in Ca-, Al-rich refractory inclusions (CAIs). Very Al-rich pyroxenes have been observed previously in the Allende, Murray, Yamato791717, ALH85085, and Acfer182 carbonaceous chondrites (up to 45 wt% Al<sub>2</sub>O<sub>3</sub>) (Kimura et al. 1993; Simon et al. 1998; Krot et al. 1999; Simon et al. 2001; Krot et al. 2007; Kimura et al. 2008) and in terrestrial skarns (up to 24 wt% Al<sub>2</sub>O<sub>3</sub>) (Pascal et al. 2005). In this study, we used electron microprobe, high-resolution SEM, electron backscatter diffraction (EBSD), and microRaman analyses to re-characterize near end-member CaTs pyroxenes (CaAlAlSiO<sub>6</sub>) from Allende (a CV3 carbonaceous chondrite) and Murray (a CM2 carbonaceous chondrite), which were identified by Simon et al. (1998, 2001) based on electron probe microanalysis. An SEM-EBSD combination has recently proven useful for determining crystal structures of new minerals (Ma and Rossman 2006, 2008, 2009). EBSD performed in this study reveals that CaTs pyroxenes from Allende and Murray have the *C2/c* clinopyroxene structure. This letter presents the occurrence and identification of CaTs from Allende and Murray, where the Allende CaTs pyroxene has 46.00 wt% Al<sub>2</sub>O<sub>3</sub> with 97 mol% Al in the M1 site, - the highest CaTs component yet reported in a natural pyroxene.

## EXPERIMENTAL METHODS

Backscattered electron (BSE) images were obtained both with a ZEISS 1550VP field emission SEM and a JEOL 8200 electron microprobe using solid-state BSE detectors. Quantitative elemental microanalyses were obtained with a JEOL 8200 electron microprobe operated at 15 kV and 10 nA in a focused beam mode. Standards for the analysis were spinel (AlK $\alpha$ , MgK $\alpha$ ), anorthite (CaK $\alpha$ , SiK $\alpha$ ), TiO<sub>2</sub> (TiK $\alpha$ ), fayalite (FeK $\alpha$ ), and V<sub>2</sub>O<sub>3</sub> (VK $\alpha$ ). Analyses were processed with the CITZAF correction procedure (Armstrong, 1995).

Single-crystal electron backscatter diffraction (EBSD) analyses at a submicrometer scale were performed using an HKL EBSD system on the ZEISS 1550VP scanning electron microscope, operated at 20 kV and 6 nA in a focused beam with a 70° tilted stage. The EBSD system was calibrated using a single-crystal silicon standard. The structure was determined and cell constants were obtained by matching the experimental EBSD pattern with pyroxene structures. The HKL software suggests indexing solutions ranked by the lowest 'mean angular deviation' (MAD) as an index of 'goodness of fit'. MAD numbers less than 1 are considered

desirable for accurate solutions. Each solution selected in this study was the highest ranked solution and exhibited a MAD number  $< 0.40$ .

Raman spectroscopic microanalysis was carried out using a Renishaw M1000 micro-Raman spectrometer system on the pyroxene crystals. Approximately 5 mw of 514.5 nm laser illumination (at the sample) focused with a 100× objective lens provided satisfactory spectra. The spot size was about 1  $\mu\text{m}$ . Peak positions were calibrated against a silicon standard. A dual-wedge polarization scrambler was used in the laser beam for all spectra to minimize the effects of polarization.

## RESULTS

### *OCCURRENCE, PHYSICAL PROPERTIES*

The CaTs pyroxene occurs along with hibonite, perovskite, corundum,  $\text{Ti}^{3+}$ -rich pyroxene, spinel, grossular, anorthite, and nepheline in host melilite within the inner region of an Allende fluffy Type A CAI in section ALH1, as shown in Figure 1. The Allende CaTs appears to be  $\sim 12$  single crystals, 3–9  $\mu\text{m}$  in size, and irregular to subhedral in the section plane. Grossular, anorthite, CaTs, corundum and nepheline appear to be secondary phases, whereas the others are primary phases of the CAI (Simon et al. 2001). The CAI is surrounded by the meteorite matrix consisting of mainly olivine and troilite.

The CaTs from Murray occurs as a primary phase in a Ca-, Al-rich refractory spherule with hibonite and Al-rich diopside (Fig. 2). This spherule is about 75  $\mu\text{m}$  in diameter in section MYSM3. It was described in detail by Simon et al. (1998). The Murray CaTs appears to be  $\sim 10$  grains in different orientations, ranging from  $\sim 1$   $\mu\text{m}$  to 15  $\mu\text{m}$  in size, as indicated by EBSD mapping.

CaTs pyroxenes from both meteorites are transparent, colorless and non-fluorescent under the electron beam. Calculated densities are 3.45 and 3.44  $\text{g}/\text{cm}^3$  (using the empirical formula) for Allende and Murray, respectively. Optical properties were not determined because of the small grain size.

### *CHEMICAL DATA*

Chemical analyses were carried out by means of electron microprobe. The mean analytical results are given in Table 1. The Allende CaTs with 46.00 wt%  $\text{Al}_2\text{O}_3$  yields an empirical formula  $\text{Ca}_{1.017}(\text{Al}_{0.972}\text{Mg}_{0.014}\text{Fe}^{2+}_{0.008}\text{Ti}^{4+}_{0.002}\text{V}^{3+}_{0.001})_{\Sigma 0.997}(\text{Si}_{0.999}\text{Al}_{1.001})_{\Sigma 2.000}\text{O}_6$ , where Al occupies about 97 percent of the M1 sites, the highest proportion of CaTs

component yet reported in a natural pyroxene. The Murray CaTs with 39.85 wt% Al<sub>2</sub>O<sub>3</sub> has an empirical formula Ca<sub>0.980</sub>(Al<sub>0.807</sub>Mg<sub>0.164</sub>Ti<sup>4+</sup><sub>0.041</sub>Fe<sup>2+</sup><sub>0.002</sub>V<sup>3+</sup><sub>0.002</sub>)<sub>Σ1.016</sub>(Si<sub>1.114</sub>Al<sub>0.886</sub>)<sub>Σ2.000</sub>O<sub>6</sub>; Al occupies about 81 percent of the M1 sites. The end-member formula is CaAlAlSiO<sub>6</sub>, with a composition of CaO 25.71, SiO<sub>2</sub> 27.55, Al<sub>2</sub>O<sub>3</sub> 46.75, total 100.01 wt%.

### *CRYSTALLOGRAPHY*

EBSDF patterns of this phase from Allende and Murray were matched against synthetic CaAlAlSiO<sub>6</sub> (Okamura et al. 1974), Ti-rich clinopyroxene (Dowty and Clark 1973), synthetic CaScAlSiO<sub>6</sub> (Ohashi and Ii 1978), esseneite (Cosca and Peacor 1987), diopside (Redhammer 1998; Prencipe et al. 2000) and orthorhombic pyroxene structures (Molin 1989). The patterns can be indexed only by the monoclinic *C2/c* structure to give a best fit based on unit cell data from synthetic CaAlAlSiO<sub>6</sub> (Okamura et al. 1974) (Fig. 3), showing  $a = 9.609 \text{ \AA}$ ,  $b = 8.652 \text{ \AA}$ ,  $c = 5.274 \text{ \AA}$ ,  $\beta = 106.06^\circ$ ,  $V = 421.35 \text{ \AA}^3$ ,  $Z = 4$ , with the mean angular deviations as low as 0.19.

### *SPECTROSCOPIC PROPERTIES*

The Raman spectra of the CaTs spectra were unusually weak, requiring long scan times and averaging of multiple accumulations. Spectra obtained with both 514 and 783 nm laser illumination consisted of strong fluorescence features and weak pyroxene bands. Particularly at Raman shifts greater than 1200 cm<sup>-1</sup>, fluorescence features, presumably from rare earth elements, dominate the Allende CaTs spectrum. The Raman microanalyses show that the CaTs spectra are generally close to that of synthetic CaAlAlSiO<sub>6</sub> (Sharma et al. 1983) and consistent with other pyroxenes such as diopside, as shown in Figure 4. The spectrum of the synthetic sample displays features (e.g., peaks at 550 and 375 cm<sup>-1</sup>) not associated with pyroxenes which are now recognized to arise from grossular that contaminates the standard sample. Some of the same grossular features can also be seen in the CaTs spectrum from the Allende meteorite, possibly arising from underlying grossular. Raman analysis gave no indication of either H<sub>2</sub>O (or OH) or CO<sub>2</sub>.

## **DISCUSSION**

Calcium Tschermak's pyroxene (CaTs) is a member of the Ca clinopyroxenes (diopside group) with space group *C2/c* (Morimoto et al. 1988), the Al-dominant analog of both esseneite (CaFe<sup>3+</sup>AlSiO<sub>6</sub>), and the newly approved mineral davisite (CaScAlSiO<sub>6</sub>, IMA 2008-030) (Ma and Rossman 2009).

Prior to the formation of the planets, the nascent solar system is thought to have consisted of a disc of hot gas and dust, called the solar nebula, from which condensation of planetary materials subsequently occurred. At the low pressures that existed in the early solar nebula,  $10^{-3} - 10^{-6}$  bar, condensation of solids rather than liquids would occur (Grossman 1972). The first non-metallic condensates from a gas of solar composition are expected to be Ca- and Al-rich, and in carbonaceous chondrite meteorites, we find inclusions that contain the phases predicted from thermodynamic calculations to have formed at high temperatures, such as corundum, hibonite, Mg-Al spinel, melilite and Ti-, Al-rich pyroxene (Grossman 1975). These objects are as old as the solar system. Some inclusions were melted and even remelted, and some underwent alteration events that produced secondary phases. They were eventually incorporated into small, carbonaceous, parent bodies that never underwent internal melting or planetary differentiation and therefore preserved a variety of nebular materials that formed over a wide range of temperatures.

The CaTs-bearing sample from Murray is an unaltered spherule that was likely a molten droplet formed by the melting of Al-rich precursor grains (Simon et al 1998). In contrast, inclusion ALH1 was altered before incorporation into the Allende parent body. It contains many secondary phases, such as grossular, corundum, nepheline and CaTs, formed by alteration of primary, gehlenitic melilite, which is very abundant in this inclusion (Simon et al. 2001).

Although synthetic  $\text{CaAlAlSiO}_6$  pyroxene is a high-pressure phase (Okamura et al. 1974), natural  $\text{CaAlAlSiO}_6$  pyroxene, found in refractory inclusions in carbonaceous chondrites, apparently did not form in high pressure environments.

### **ACKNOWLEDGMENTS**

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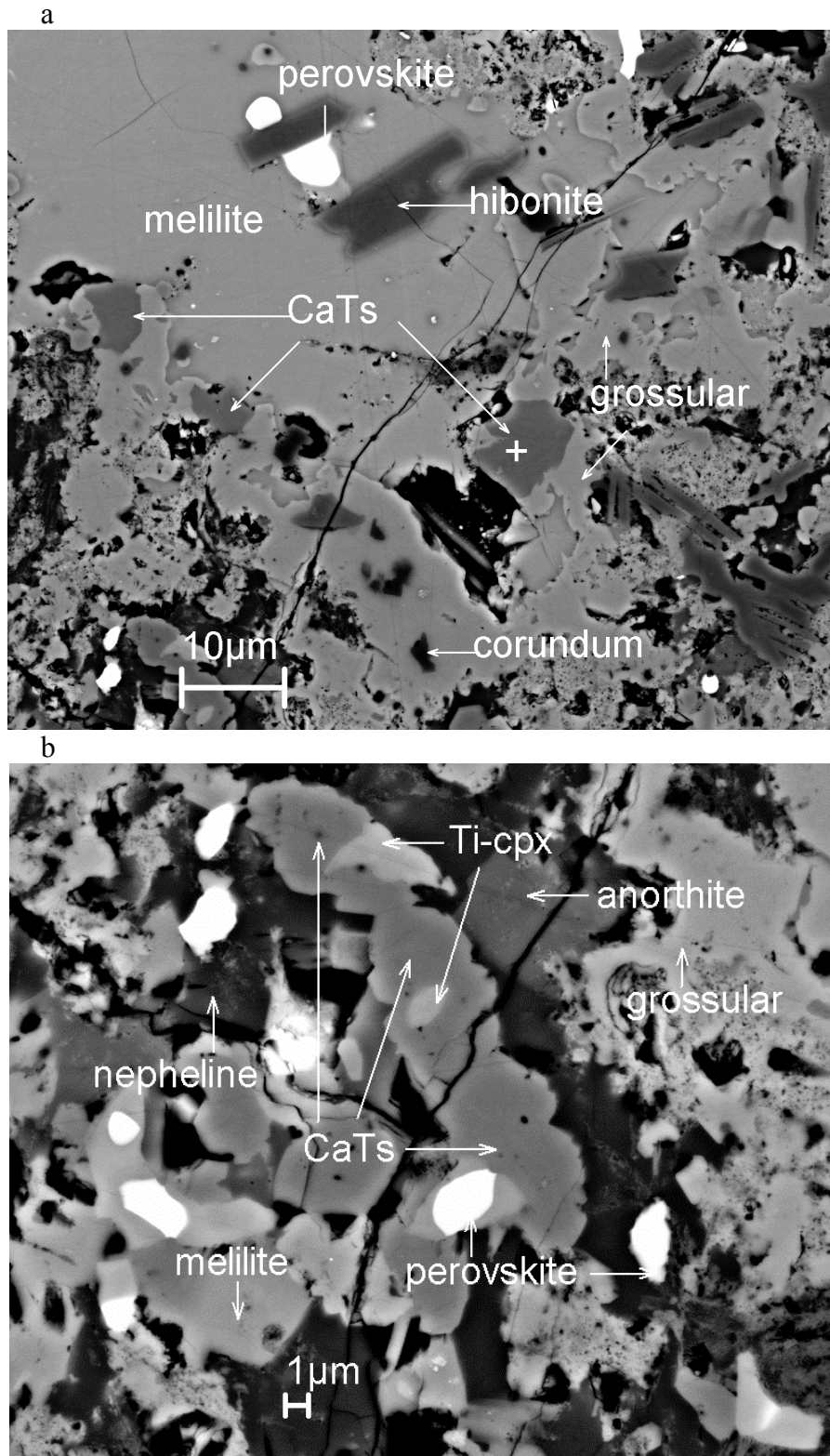
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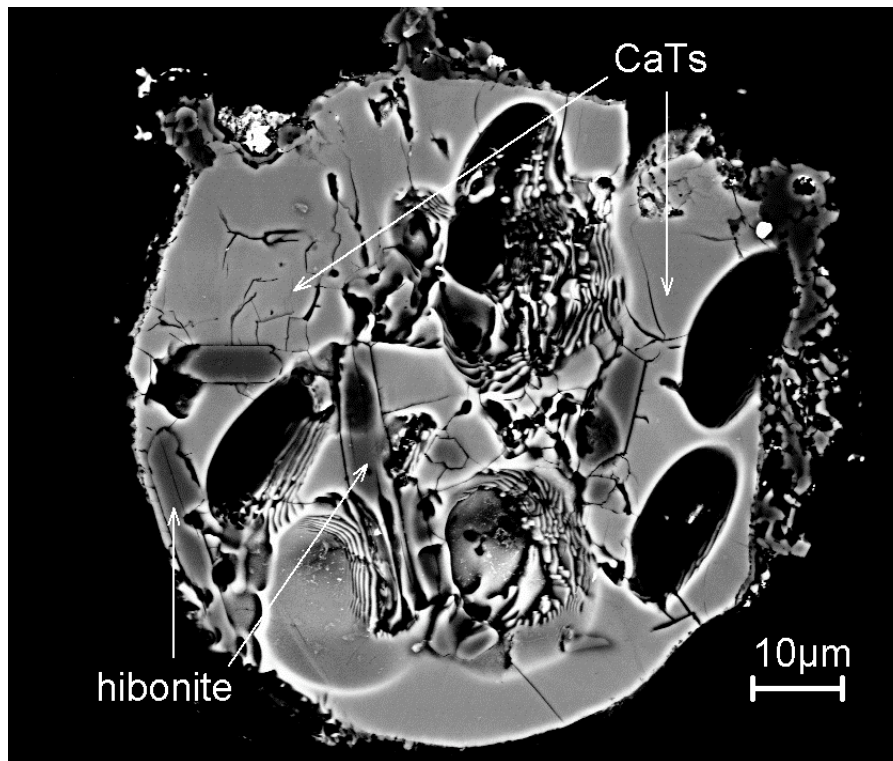
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**Table 1.** The mean electron probe analyses of CaTs pyroxenes.

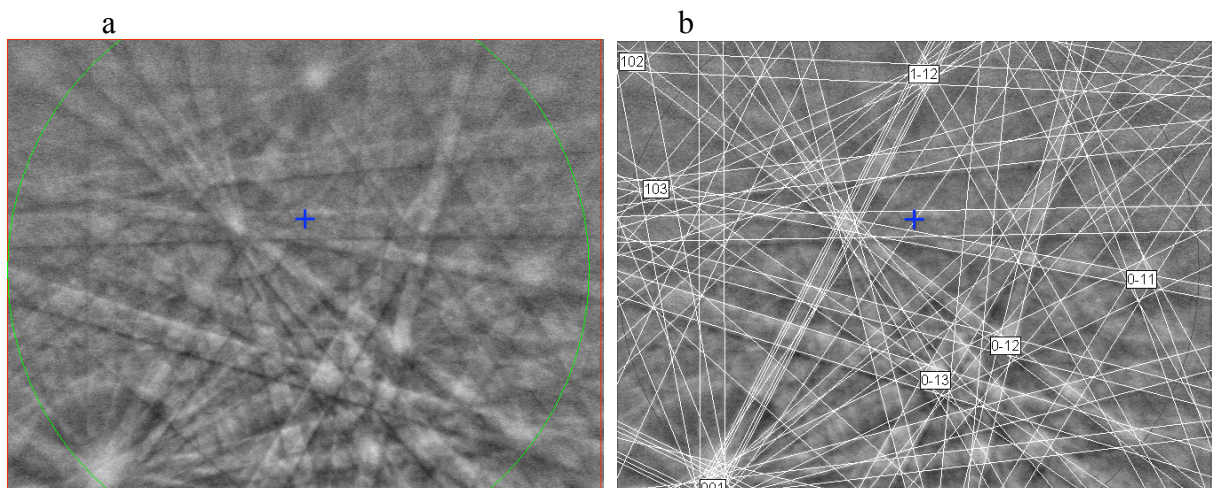
	Allende	n=6	Murray	n=5
Oxide	wt%	Stand. Dev.	wt%	Stand. Dev.
SiO <sub>2</sub>	27.44	0.60	30.92	0.73
Al <sub>2</sub> O <sub>3</sub>	46.00	0.35	39.85	0.76
MgO	0.26	0.16	3.06	0.20
FeO	0.26	0.19	0.06	0.07
TiO <sub>2</sub>	0.05	0.03	1.52	0.53
V <sub>2</sub> O <sub>3</sub>	0.02	0.01	0.06	0.04
CaO	26.09	0.25	25.37	0.61
Total	100.12		100.84	
Formula based on 6 O				
Si <sup>IV</sup>	0.999		1.114	
Al <sup>IV</sup>	1.001		0.886	
Al <sup>VI</sup>	0.972		0.807	
Mg	0.014		0.164	
Fe <sup>2+</sup>	0.008		0.002	
Ti <sup>4+</sup>	0.002		0.041	
V <sup>3+</sup>	0.001		0.002	
Ca	1.017		0.980	



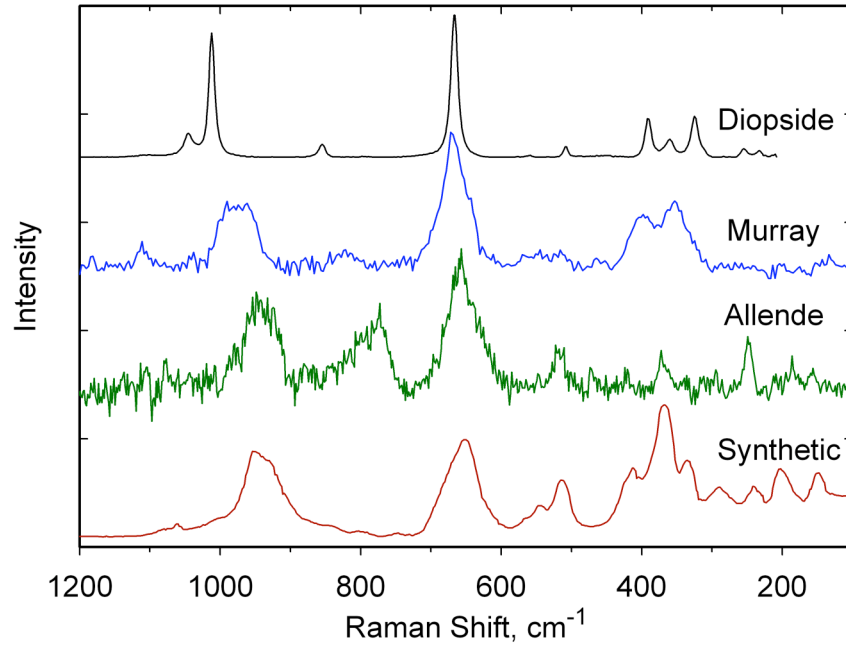
**Figure 1.** Backscattered electron images showing the CaTs pyroxene along with other phases in the inner region of an Allende CAI in section ALH1. The cross in Fig. 1a marks where the EBSD pattern (shown in Fig. 3) was collected from an Allende CaTs crystal.



**Figure 2.** BSE image showing the CaTs pyroxene - hibonite spherule in section MYSM3 of the Murray meteorite, surrounded by epoxy. The pits were caused by previous ion probe analyses.



**Figure 3.** (a) EBSD pattern of the labelled Allende CaTs crystal (marked with a cross) in Fig. 1a; (b) the pattern indexed with the  $C2/c$  synthetic  $\text{CaAlAlSiO}_6$  structure.



**Figure 4.** Raman spectra of CaTs from Allende and Murray, synthetic  $\text{CaAlAlSiO}_6$  (Sharma et al. 1983), and diopside  $\text{CaMgSi}_2\text{O}_6$  (from Rajasthan, India), corrected for baseline. The spectra were scaled to equivalent intensities and offset vertically for clarity.