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Rapid identification of steatite–enstatite polymorphs at various temperatures

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Abstract

The mechanical properties of steatite ceramics after high-temperature processing depend on inversion of high-temperature $Mg_2Si_2O_6$ protoenstatite polymorph to low clino- or ortho-enstatite, which are characterized by Raman spectroscopy. The Raman spectrum of a pure $Mg_2Si_2O_6$ protoenstatite is sufficiently distinct from those of low clino- and ortho-enstatite to allow rapid identification in a bulk sample both at ambient and high temperatures. With its high-lateral resolution (about 2 μm), speed, and ease of application on rough materials, Raman spectroscopy can be used to map transformation sequences of enstatite in quenched materials or at high temperature during the fabrication of the steatite-type ceramics, and their relationship with microstructural defects such as voids and cracks.

Keywords: Silicate; Spectroscopy; Optical microscopy; Microstructure

1. Introduction

Steatite, $Mg_2Si_2O_6$, is a major compound of steatite ceramics that is used for its mechanical and electrical properties.[1] The natural form of this material is the mineral enstatite, which is an important silicate mineral of the Earth's mantle and of meteorites. The mechanical properties of this phase depend strongly on the temperature cycling during a given synthesis procedure, in large part because enstatite undergoes a complex series of polymorphic transitions. The three commonly observed polymorphs at ambient pressure are low-clinoenstatite (l-CEn, *P2₁/c*), ortho-enstatite (OEn, *Pbca*) and protoenstatite (PEn, *Pbcn*). Experiments show that PEn actually forms at high temperature from OEn.[2] PEn can be quenched from high temperature if the crystal size is small, and can invert to either l-CEn or OEn.[1] In order to stabilize the high-temperature form to low temperatures, PEn can be stabilized by additives like Li and Sc.[3] Phase equilibrium experiments suggest that l-CEn has a restricted stability field below 566 °C,[4] with OEn an intermediate temperature form. However, some authors consider l-CEn as a metastable low-temperature low-pressure phase that is stabilized by non-hydrostatic stresses and strain associated with transformation.[5] l-CEn is also formed during decompression of a high-pressure form of *C2/c* symmetry often called high clinoenstatite.[5–7] Finally, using high-temperature transmission electron microscopy, l-CEn has been observed to transform to a high-temperature *C2/c* polymorph that is distinct from the high-pressure form.[8] In nature, OEn is the dominant polymorph, and l-CEn is seldom observed in meteorites and terrestrial rocks.

In the high-temperature processing of steatite or, more generally, Mg–Si–O-based ceramics, PEn is the stable form but the recovered materials can contain l-CEn and OEn from the inversion of PEn.[1] The back-transformation of PEn on cooling or ageing is undesirable because the associated strains cause cracks that decrease the mechanical performance. Polymorphic transformations of enstatite in ceramics have thus far characterized using bulk techniques such as X-ray diffraction or NMR.[9] X-ray diffraction can also be performed in situ at high temperature to determine transformation kinetics.[10] However, such techniques do not allow or microscopic determination of the transformation at the grain-size scale, although grain size is a major factor

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on the quenching of the desired PEn phase.[9] In addition, these techniques are time consuming and do not lend themselves easily to rapid examination of bulk samples with a minimum of sample preparation. Here we demonstrate the use of Raman spectroscopy as a relatively quick and convenient method for characterizing the steatite–enstatite polymorphs, both at ambient and high temperatures.

2. Materials and methods

The l-CEn sample was synthesized in the multianvil press at the Bayerisches Geoinstitut (Bayreuth, Germany) from synthetic $Mg_2Si_2O_6$. OEn was sealed in Au capsules and held at 9 GPa and 1100 °C for 4.5 h where it transformed to the *C2/c* polymorph.[11] Upon decompression, the *C2/c* phase transformed to the $P2_1/c$ phase. Large OEn crystals (0.1–2 mm) were synthesized using a flux.[12] Pure $Mg_2Si_2O_6$ PEn crystals were synthesized from a melt of enstatite composition by quenching in water, forming dendritic crystals small enough to maintain the metastable high-temperature *Pbcn* structure at ambient temperature. These are abbreviated as q-PEn in the remainder of the text. A large stabilized PEn crystal of composition $Mg_{1.6}Li_{0.2}Sc_{0.2}Si_2O_6$[13] was also used for comparison to check the effect of stabilizers on the Raman spectra of PEn.[14] This is abbreviated as s-PEn in the remainder of the text.

Raman spectra were recorded with a LabRam HR800 Jobin-Yvon™ microspectrometer equipped with 1800 g/mm gratings and using the 514.53 nm line of an Ar laser for excitation. High-temperature spectra were obtained in a Leitz1350 heating stage. Temperature was measured with a Pt–Pt/Rh10% thermocouple calibrated against known melting point compounds to an accuracy of 5 K. Typical recording times were 10–100 s at high temperature.

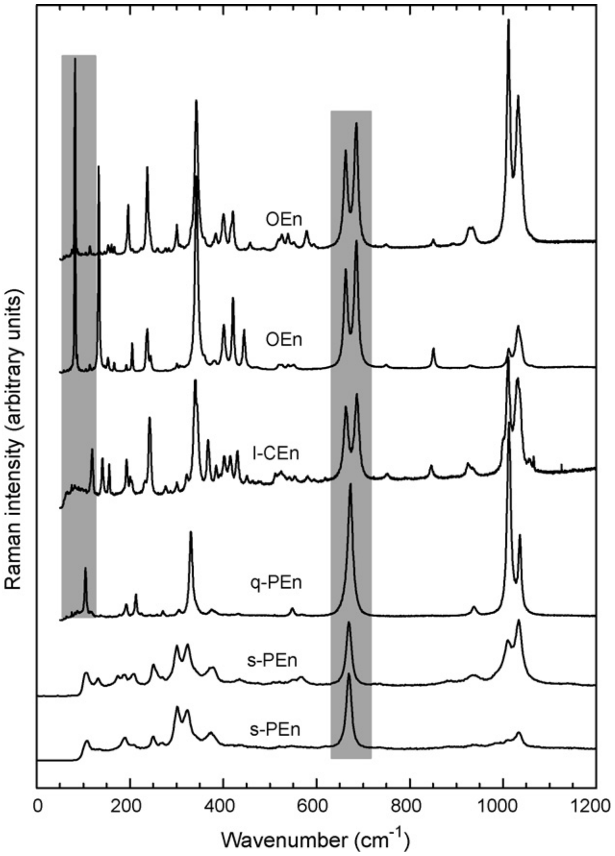

Fig. 1. Ambient temperature unpolarized Raman spectra of the enstatite polymorphs. The shaded areas indicate the spectral regions useful for quick identification. The symmetric Si—O—Si bending doublet at 663–685 cm^{-1} in l-CEn and OEn is reduced to a single peak at 673 in PEn. l-CEn and OEn can be distinguished easily by the position of the lowest lying mode at 82 cm^{-1} in OEn and 118 cm^{-1} in l-CEn. Two spectra are shown for two different orientations of OEn and s-PEn large crystals. They show that the intensities of the diagnostic peaks in the 660–690 cm^{-1} range are not very sensitive to orientation, whereas other peak intensities (e.g. stretching Si–O vibrations above 1000 cm^{-1}) are.

3. Ambient temperature spectra

Unpolarized spectra of the polymorphs display significantly different features that allow a quick determination of each polymorph (Fig. 1). The spectrum of pure $Mg_2Si_2O_6$ protoenstatite (q-PEn) at ambient temperature was found to be similar to that of the stabilized samples (s-PEn this study[14]), but the peaks are sharper and better defined than in the stabilized sample where line broadening occurs due lattice strain induced by the substitution of Li and Sc for Mg.[14,15] PEn spectrum shows a smaller number of peaks than the l-CEn and OEn spectra. This is consistent with the number of Raman active modes in PEn being reduced by a factor of 2 with respect to l-CEn and OEn.[14,16] A significant example of the reduction of mode number is the transformation of the strong doublet at 663–685 cm^{-1} for OEn and CEn, which is attributed to a bending vibration of Si–O–Si bridges in the silicate chains, into a single peak at 673 cm^{-1} in PEn (Fig. 1). It is similar to the diagnostic used for the high-pressure transformation of l-CEn to C2/c h-CEn,[11] during which a reduction of the unit cell by a factor of 2 also occurs. Because these peaks are intense whatever the orientation of the crystal, the 673 cm^{-1} peak is a useful tool for distinguishing PEn from any of the two other polymorphs l-CEn and OEn. This is of particular importance because the back-transformation of PEn to any of the OEn or l-CEn polymorphs will result in stress and cracks that alter the mechanical properties of ceramics. Spectra can be recorded within seconds that allow unambiguous determination; this is fast enough to perform Raman mapping of enstatite polymorphs with a few micrometer resolution over a millimeter area. It can thus allow one to determine the spatial relationships between the phases present, undesired microstructures such as cracks, and texture observed by microscopy. Also, the similarity of the spectra of pure and significantly doped PEn demonstrates that the identification method will not be affected by the use of stabilizers. Further identification can be performed using more subtle variations, especially in the low frequency (400–450 cm^{-1}) range. Of particular significance is the position of the lowest lying intense mode of Ag symmetry. It occurs at 105 cm^{-1} in q-PEn, 118 cm^{-1} in l-CEn and 82 cm^{-1} in OEn. This provides a secondary diagnostic for of identifying OEn versus l-CEn.

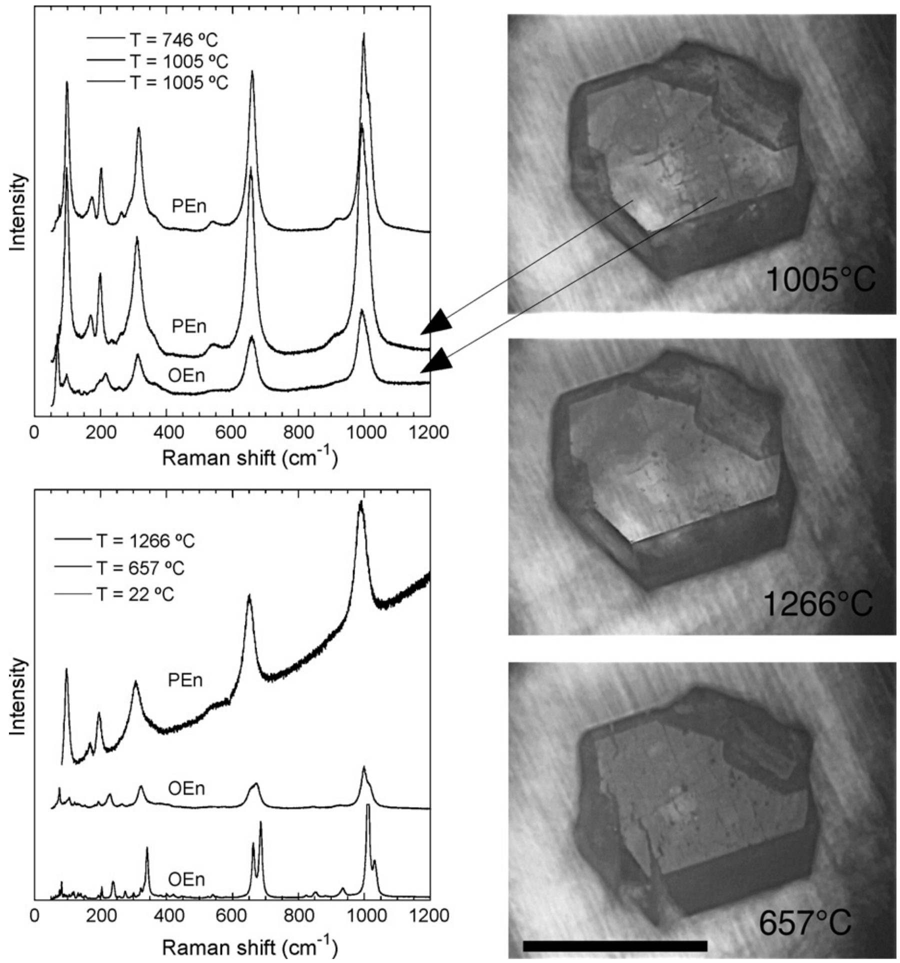

Fig. 2. High-temperature Raman spectra of enstatite across the PEn–OEn transition. Above 1200 °C, a PEn single-crystal formed from a large OEn crystal is clear and devoid of defects. On cooling, cracks are formed at the transition at about 1000 °C due to associated strain (top micrograph). OEn is identified along the cracks with the lowest lying intense Ag mode in the 60–70 cm^{-1} range, while PEn is still observed in clear untransformed areas with its lowest lying intense Ag mode occurs near 95–100 cm^{-1} in this temperature range. Heating up back into the PEn stability field from 1005 °C heals the cracks (middle photograph). PEn domains were preserved metastably down to 746 °C in this crystal. At 657 °C, the back-transformation is complete and the original single-crystal has been shattered as the transition proceeded to completion. It is quenched as OEn at 22 °C. Scale bar is 1 mm.

4. High-temperature spectra

Unpolarized spectra were recorded at temperatures up to 1266 °C using the large OEn crystals as a starting material. Upon heating, transformation to PEn is observed above 1200 °C for this sample. The exact temperature of the transition is dependent on the sample (crystal shape and size, impurity concentration, etc.) and a strong hysteresis is observed, with temperatures of the back-transformation on cooling between about 1000 °C (first appearance of OEn) and 750 °C (disappearance of PEn) at the timescale of the experiment (temperature steps of about 25 °C lasting about 10 min for recording a spectrum). This hysteresis loop is larger than formerly determined by Raman spectroscopy[15] because the recording time has been drastically reduced with the improvements of optics. Raman spectroscopy can thus allow following high-temperature transformation with spatial and temporal resolution of micrometers and seconds, respectively, as illustrated in Fig. 2 with typical spectra across the transition and corresponding micrographs of the sample. The identification of OEn with respect to PEn is more difficult at high temperature than at ambient conditions because the typical doublet at 660–690 cm^{-1} in OEn is almost reduced to a single peak due to pre-transitional effects.[17] Unambiguous identification of the polymorphs is provided by the position of the lowest lying intense Ag mode. This occurs in the 60–70 cm^{-1} range for OEn and in the 95–100 cm^{-1} range for PEn, in agreement with former study.[15] Identification of transformed zones in a partially transformed crystal can be performed with the micrometer spatial resolution of Raman micro-spectroscopy, and their relationship to cracks associated with the strain at the phase transition is illustrated in Fig. 2.

5. Conclusions

Raman spectroscopy provides easy and rapid identification of enstatite polymorphs at ambient conditions and at high temperature. Raman mapping of steatite-type ceramics can thus be performed to identify enstatite polymorphs, or to investigate in situ the transformation kinetics and localization at high temperature. It can be performed either on polished section or on rough sections and compared with optical or scanning electron microscopic images in order to relate transformations to microstructures (e.g. cracks, porosity).

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