

Raman spectra of undoped and uranium doped CaF_2 single crystals

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Raman scattering experiments for nominally pure and uranium doped CaF_2 single crystals were presented. In all crystals, the Raman active T_{2g} vibration mode of CaF_2 was observed, whose frequency shift and full-width at half-maximum (FWHM) broadening correspond well with defects and impurities in CaF_2 lattice. Additional Raman peaks develop in nominally pure CaF_2 with high etch pits density and $\text{U}^{6+}:\text{CaF}_2$ crystals. Part of additional Raman peaks in the experimental results, which are assumed due to vibration modes from F^- interstitials and vacancies, are in well agreement with the theoretical predications by employing the Green-function formulation.

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CaF_2 crystals have been the most important materials both in technical applications and science studies over half century. The cation sublattice of CaF_2 is very stable and the long-range order is maintained while doped with relatively large quantities of impurities. Predominant defect in CaF_2 crystals is the anions Frenkel disorder type in general. Haridasan *et al.*^[1,2] have employed the Green-function formulation to compute the local and resonant modes due to F^- interstitials (F_i^-) and vacancies (V_{F^-}) at the anion sites in CaF_2 crystals. However, there are no experimental data on CaF_2 for a direct comparison with theoretical results, while those of SrF_2 and BaF_2 computed by Nerenberg *et al.*^[3] have been substantiated in Refs. [4] and [5] by Raman spectroscopy. Possible reasons were relatively weak impurity-induced scattering in CaF_2 due to not immediately obvious causes^[6]. In this work, Raman scattering was undergone to present experimental evidence for defect structures of undoped and uranium doped CaF_2 single crystals.

Nominally pure and uranium doped CaF_2 crystals were grown by an improved temperature gradient technique (TGT) as discussed previously^[7]. Pure CaF_2 crystals were grown always with PbF_2 as oxygen scavenger under highly pure Ar gas atmosphere or high vacuum less than 10^{-3} Pa. Uranium doped CaF_2 crystals with 0.05 at.-% uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as raw material were grown always under inert atmosphere in the presence or absence of PbF_2 .

Crystals were cut to slices with (111) end faces orientated by X-ray. The crystal structures and unit cell parameters of $\text{U}:\text{CaF}_2$ crystals were analyzed by model XDC-1000 Guinier-Hägg camera. The sliced plates were polished mechanically for chemical etching and Raman spectrum. The defects presented in CaF_2 crystals were determined through etching freshly polished (111) surfaces in HCl aqueous solution of 4 mol/L in the 40–60 °C for 30–60 minutes, then examined under an optical microscope for calculating the etch pits density (EPD). The Raman scattering experiments were performed with a SPEX 1877 Raman spectrometer in the room temperature. The excitation light source was an argon ion laser with a wavelength of 514.5 nm. A 50× objective lens was

used to focus the beam onto the sample. The scattered radiation was measured at an angle of 180° from the incident laser beam.

Raman spectra at room temperature for nominally pure CaF_2 single crystals grown by TGT under inert atmosphere (CaF_2 -I) and high vacuum (CaF_2 -II) are shown in Fig. 1. For the former, there is one single line located at 328 cm^{-1} from the Raman active T_{2g} vibration mode of pure CaF_2 . The position of this peak is in good agreement with observation of Denham *et al.*^[8] and Tu *et al.*^[9]. Dramatic changes happened in the Raman spectrum of CaF_2 crystal grown under high vacuum (CaF_2 -II). First, the frequency of the allowed T_{2g} mode shifts to lower level from 328 to 322 cm^{-1} , while the full wave at half maximum (FWHM) of the peak obviously broadens. The results fit with that obtained by Tu *et al.*^[9] in lanthanum doped CaF_2 , which was interpreted as defect-induced scattering due to anion vacancies and interstitials. On the other hand, the peak position at 322 cm^{-1} is consistent with the data reported by Russell^[10] and Levenson *et al.*^[11]. Second, several additional peaks appear in the Raman spectrum of CaF_2 -II in the frequency range from 50 to 800 cm^{-1} , whose central frequencies are listed in Table 1, for comparing with theoretical results of the vibration modes due to F^- interstitials (F_i^-) and vacancies (V_{F^-}) in CaF_2 crystal^[12]. These extra peaks are surprisingly coincident with computed results for both F_i^- and V_{F^-} within very little errors. The volatilization of CaF_2 under high vacuum is very severe, even creating color centers because of fluorine loss. Chemical etching experiments provided us direct evidence that EPD of CaF_2 -II is much higher than that of CaF_2 -I, which indicates high concentrations of disorder in crystal lattice to a certain extent. It should be noted that F_i^- and V_{F^-} coexist in pure CaF_2 as anion Frenkel pairs, and the mode frequencies of V_{F^-} are essentially overlapped with those of F_i^- since the FWHMs of Raman peaks induced by the defects are very large. Last, the low frequency spectra of the two CaF_2 crystals are very different. That of the CaF_2 -II is very flat even low to 50 cm^{-1} , while the other rapidly increases with

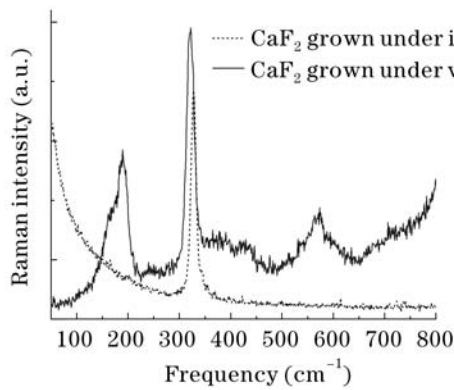


Fig. 1. Raman spectra at room temperature of CaF₂ single crystals grown by TGT under inert atmosphere and high vacuum.

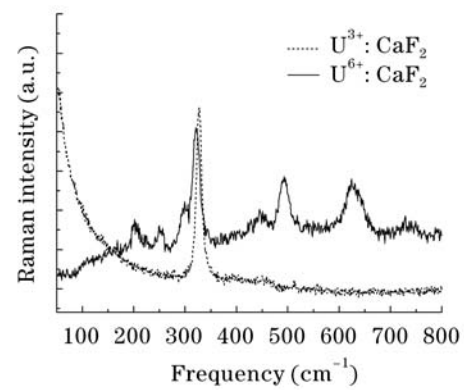


Fig. 2. Raman spectra at room temperature of U³⁺ and U⁶⁺ doped CaF₂ single crystals grown by TGT under inert atmosphere.

Table 1. Frequencies of the Peaks in Raman Spectra of Undoped and Uranium Doped CaF₂ at Room Temperature in the Range of 50—500 cm⁻¹ along with Theoretical Results on F⁻ Interstitials (F_i⁻) and Vacancies (V_F⁻)

Experimental Data (cm ⁻¹)		Theoretical Results (cm ⁻¹)	
CaF ₂ -II	U ⁶⁺ :CaF ₂	F _i ⁻ [1]	V _F ⁻ [2]
165	202	170	167
190	249	290	200
370	298	310	204
429	448	380	288
	493		307
			363
			428

frequency decreasing from 200 to 50 cm⁻¹ due to elastic Rayleigh scattering. The definite interpretation might need further determinations. But we want to note that the trace impurity contents in CaF₂-I are higher than those in CaF₂-II, because the inert atmosphere is disadvantageous to elimination of volatile impurities.

As reported earlier^[7], valence of uranium ions in uranium doped CaF₂ crystals with concentration of 0.05 at.-% in the melt grown by TGT under inert atmosphere is +3 in the presence of PbF₂ as oxygen scavenger. Raman spectrum of U³⁺:CaF₂ single crystal is shown in Fig. 2, where only one line at 326 cm⁻¹ from the Raman active T_{2g} vibration mode of CaF₂ host lattice appears. Contrasting with pure CaF₂-I, the T_{2g} mode has a slight shift to lower frequency partly due to F_i⁻, which are presented in certain numbers because of the excess positive charge of U³⁺ ions substituting Ca²⁺^[9]. Heavier uranium ions replacing Ca²⁺ also influence the T_{2g} mode in which the anion sublattice vibrates in antiphase and the cations are stationary. That no any extra lines in the Raman spectrum might indicate that the concentrations of defects in 0.05 at.-% doped U³⁺:CaF₂ would not be enough large.

In the absence of PbF₂, green U:CaF₂ was produced, with optical absorption spectrum identical to that of

U⁶⁺:CaF₂ by McLaughlin^[12]. Raman spectrum of the U⁶⁺:CaF₂ crystal is also displayed in Fig. 2. Compared to U³⁺:CaF₂, the frequency of T_{2g} mode in U⁶⁺:CaF₂ shifts to 321 cm⁻¹ with FWHM slightly broadening. Moreover, quite a few additional peaks develop in the range of 50—800 cm⁻¹, five of which were listed in Table 1 in the range of 50—500 cm⁻¹. A distinct shoulder peak at 298 cm⁻¹ locates at the lower frequency of T_{2g} mode, which is similar to that in lanthanum doped BaF₂. It is interesting that the additional peak in La³⁺:BaF₂ locates at higher energy of T_{2g} mode in BaF₂^[5]. According to Haridasan *et al.*^[1] resonant modes because of F_i⁻ are anticipated to have excitation frequencies at 290 and 310 cm⁻¹, which are very close to the central frequency of the broad shoulder band. At the same time, another band at 202 cm⁻¹ corresponds with the computed mode frequencies of V_F⁻ at 200 and 204 cm⁻¹^[2]. So, part of the additional Raman peaks in U⁶⁺:CaF₂ crystal can be associated with the anion Frenkel defect pairs, which had not been observed in rare-earth doped CaF₂ crystals. Since the crystal was grown in the absence of PbF₂, oxygen could not be avoided to enter the lattice of CaF₂ as charge compensation for excess positive charge induced by U⁶⁺ ions substituting Ca²⁺. Other extra Raman peaks not assigned should be associated with oxygen impurity and local lattice distortion around U⁶⁺ ions with very smaller radius than Ca²⁺ resulting in complicated charge compensation mechanisms. It should be noted that X-ray analyses with Model XDC-1000 Guinier-Hägg camera indicates the U⁶⁺:CaF₂ crystal still keeps the cubic symmetry structure of CaF₂.

In the last, we must point out that the number of anion defects in U⁶⁺:CaF₂ must be several times more than that in U³⁺:CaF₂ because excess positive charge produced by U⁶⁺ is four times of that by U³⁺. So, additional Raman peaks in U⁶⁺:CaF₂ do not develop in U³⁺:CaF₂ with equal uranium doping concentrations. Otherwise, the frequencies of additional Raman peaks because of F_i⁻ and V_F⁻ in U⁶⁺:CaF₂ and nominally pure CaF₂-II have evident differences because the F_i⁻ and V_F⁻ in the former are associated with uranium ions.

In conclusion, including the Raman active T_{2g} vibration mode of CaF₂, additional Raman peaks were observed in nominally pure CaF₂ with high EPD and

$U^{6+}:\text{CaF}_2$ crystals. The frequency shift and FWHM broadening of T_{2g} mode provide the evidence for defects and impurity in CaF_2 lattice. Part of additional Raman peaks in the experimental results, which are assumed due to vibration modes from F^- interstitials and vacancies, are in well agreement with the theoretical predications by Haridasan *et al.*^[1,2] employing the Green-function. Since some Raman peaks are not yet assigned, further details about the defect structure in $U^{6+}:\text{CaF}_2$ crystal will be obtained from combined Raman and far infrared absorption spectra as well as X-ray analyses.

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