PHYSICAL REVIEW B VOLUME 37, NUMBER 8 15 MARCH 1988-I

High-pressure Raman study of CeO_2 to 35 GPa and pressure-induced phase transformation from the fluorite structure

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(Received 17 September 1987)

Cerium dioxide (CeO_2), which crystallizes in the fluorite structure, has been studied by high-pressure Raman spectroscopy with use of a diamond anvil cell, up to 35 GPa. The pressure shift of the first-order fluorite Raman peak (F_{2g}) and the shifts of several second-order features were measured. The Grüneisen parameter for the F_{2g} mode (465 cm^{-1}) is obtained as $\gamma = 1.44$ and for the F_{1u} ($\omega_{LO} = 585$ cm^{-1}) as $\gamma = 1.5$; the latter from the $2\omega_{LO}$ shift in the second-order spectrum. Near 31 GPa, a phase transition occurs and six new Raman peaks appear. By comparison with the high-pressure phases of alkaline-earth difluorides, the high-pressure phase is believed to be of the $PbCl_2$-type structure. The high-pressure phase is found to be metastable over a 20-GPa interval, but completely reverses on releasing pressure.

INTRODUCTION

Pressure-induced phase transitions in fluorite-type compounds have been the subject of some recent studies.[1,2] Pressure-induced postfluorite phases are of geophysical interest, and hence several fluorite-type dioxides have been subjected to high pressure up to 30 GPa, and temperatures around 1000 °C,[3,4] in a laser-heated diamond anvil cell. In materials quenched after high-pressure high-temperature treatment, phase transitions to denser structures have been reported.[3,4] Pressure Raman studies on the alkaline-earth difluorides have shown that CaF_2, SrF_2, and BaF_2 undergo a cubic to orthorhombic phase transition at 8.3, 5.0, and 2.3 GPa, respectively.[1,2,5]

In this study we have investigated CeO_2 up to 35 GPa, in a diamond anvil cell. We find that at room temperature the fluorite phase of CeO_2 undergoes a pressure-induced phase transformation near 31 GPa. The single Raman peak characteristic of the fluorite lattice is observed up to this pressure, above which six new peaks appear in the Raman spectrum of the sample. These new peaks are observed down to 11 GPa, on releasing pressure. We believe that the fluorite phase transforms to the $PbCl_2$-type structure. We have also been able to record some of the features of the second-order Raman spectrum of the fluorite phase of CeO_2 in the diamond cell, which we have followed up to 15 GPa. These results will be presented and discussed in this paper.

EXPERIMENTS

Crystals of CeO_2 were grown from $Li_2W_2O_7$ flux in a platinum crucible.[6] The molten solution (starting materials: CeO_2, Li_2CO_3, WO_3) was held at a temperature of 1280 °C for 6 h, then cooled at a rate of 2.5 °C/h to 1000 °C at which point the crucible was allowed to cool to room temperature in the furnace. The resulting crystals of millimeter size were very clear and colorless.

Pressure was generated using a gasketed diamond anvil cell[7] and measured using the well-known ruby fluorescence technique.[8] The diamond flats were 0.6 mm in diameter. Full-hard tempered stainless steel 301 was used for gasketing. Either a methanol-ethanol mixture in the ratio 4:1, or argon, were employed as pressure media. The two pressure media yielded consistent results.

The Raman spectra were recorded with a Spex double monochromator equipped with a conventional photon counting system. For excitation both the 488-nm and 514.5-nm lines from an Ar^+ laser were used at power levels of 30–40 and 200–300 mW for the first- and second-order Raman spectra, respectively.

RESULTS

In Fig. 1 the first-order Raman spectrum of CeO_2 (sharp peaks) is shown for three pressures. This peak observed at 465 cm^{-1} under ambient conditions[9] shifts to higher frequency with increasing pressure. With the

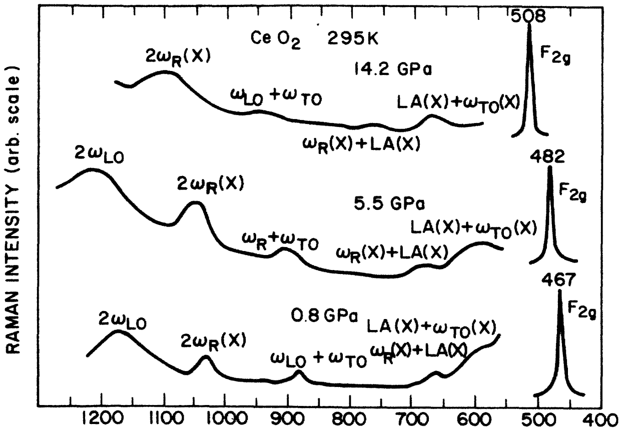

FIG. 1. The first-order (right) and second-order (left) Raman peaks of CeO_2 observed in the diamond cell at three different pressures and at 295 K. Spectra were recorded with the 488-nm Ar^+ laser line at power levels of 40 mW for the first-order and 200 mW for the second-order spectrum.

sample in the diamond cell, we were also able to record a second-order spectrum of the fluorite phase, with four or five peaks in it. The effects of pressure on these peaks are shown in Fig. 1 on the left side. In Fig. 2 the pressure dependencies of the first-order Raman peak of the fluorite phase, and of the second-order features, are plotted.

In Fig. 3 the effect of pressure on the first-order Raman spectrum of CeO_2 is shown for increasing (open circles) as well as for decreasing pressure (solid circles). For increasing pressure, only the first-order fluorite Raman peak is observed up to 32 GPa. At this pressure a few additional weak Raman features begin to appear, and they become stronger with time and application of higher pressure. This is due to a first-order phase transition to a lower symmetry structure. On decreasing pressure the Raman peaks of the high-pressure phase continue to be present down to 12 GPa and then suddenly disappear. Below 12 GPa, only the fluorite Raman peak is observed. Thus the high-pressure phase exhibits a large region of metastability. The critical pressure for the phase transition on the increasing pressure cycle is marked by the dashed line in the figure. The Raman spectra of the high-pressure phase recorded at 33.4, 22.6, and 13.4 GPa are presented in Fig. 4; the latter two spectra were obtained on the decreasing pressure cycle. The spectrum of the high-pressure phase appears to become stronger as pressure is released, which is evident from the spectra at 22.6 and 13.4 GPa (see Fig. 4). The fluorite Raman peaks recorded at 1 atm. and at 28.5 GPa are presented on top of the figure.

DISCUSSION

Cerium dioxide CeO_2 crystallizes in the cubic fluorite-type lattice and belongs to the space group O_h^5 ($Fm3m$). Group theory predicts one triply degenerate Raman-active optical phonon of Γ_{25} symmetry (F_{2g}) and two infrared-active phonons of Γ_{15} symmetry (F_{1u}), corresponding to the LO and TO modes. Therefore the first-order Raman spectrum of CeO_2 is very simple and consists of only one Raman line. In the second-order Raman spectrum, overtones of this and of the zone-boundary phonons, as well as combinations and difference frequencies at each wave vector q are allowed. With nine phonon branches there are 45 two-phonon modes possible. The one-phonon dispersion curves are needed to identify the second-order features and these have been calculated[10] for CeO_2 using the rigid-ion model and the known elastic constants and the frequencies ω_R, ω_{LO}, and ω_{TO}. Assuming that most of the critical points are at the high-symmetry points of the Brillouin zone, the two-phonon dispersion curves of CeO_2 have been calculated.[10] The ω_{LO} frequency of 750 cm^{-1} assumed for the calculation appears to be much higher than the value of 585 cm^{-1}

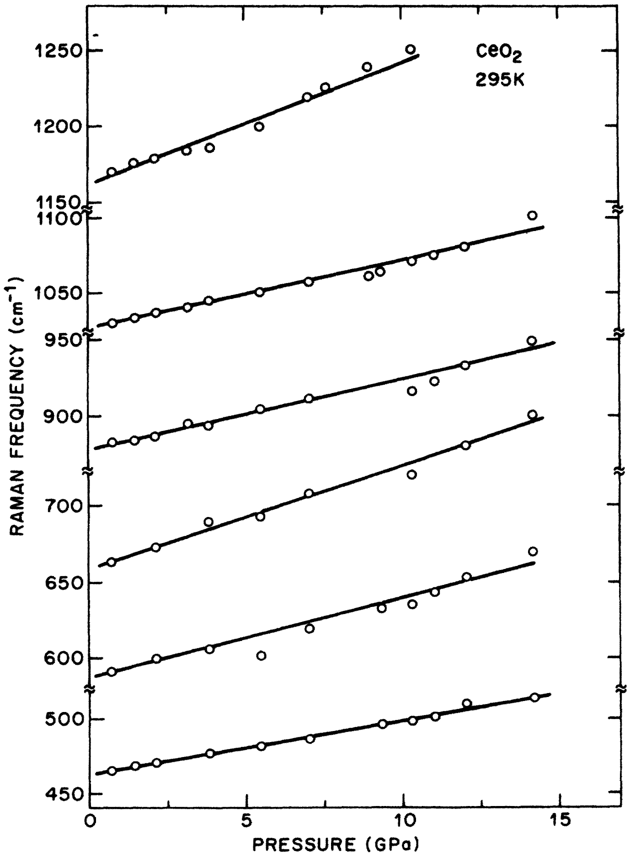

FIG. 2. The pressure dependence of the first-order Raman peak (bottommost) and the second-order peaks, all in the fluorite phase.

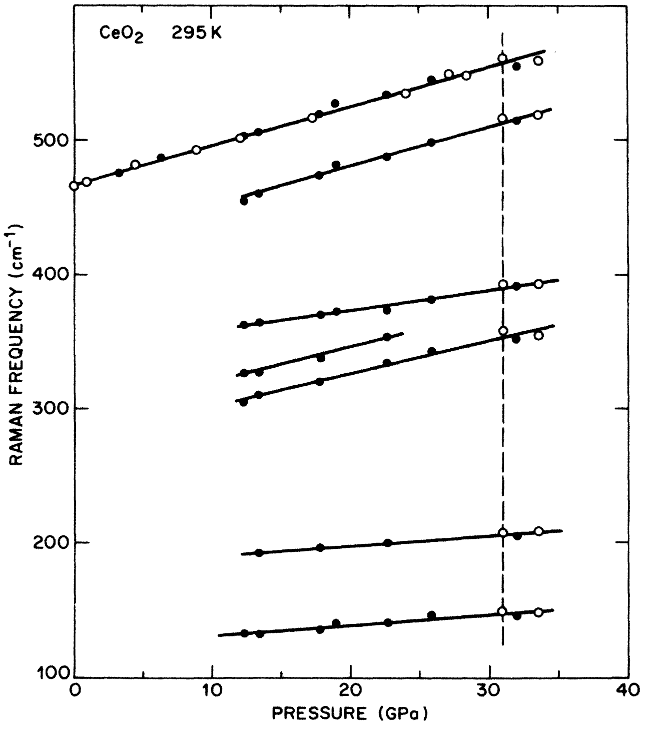

FIG. 3. The effect of pressure on the Raman spectrum of CeO_2. Only the topmost Raman peak (fluorite F_{2g} mode, indicated by open circles) is observed on increasing pressure cycle up to 31 GPa. Then a phase transition occurs with six new Raman peaks (also marked by open circles). On releasing pressure the Raman peaks of the high-pressure phase (indicated by solid circles) are present down to 12 GPa where they suddenly disappear and the fluorite peak comes in place.

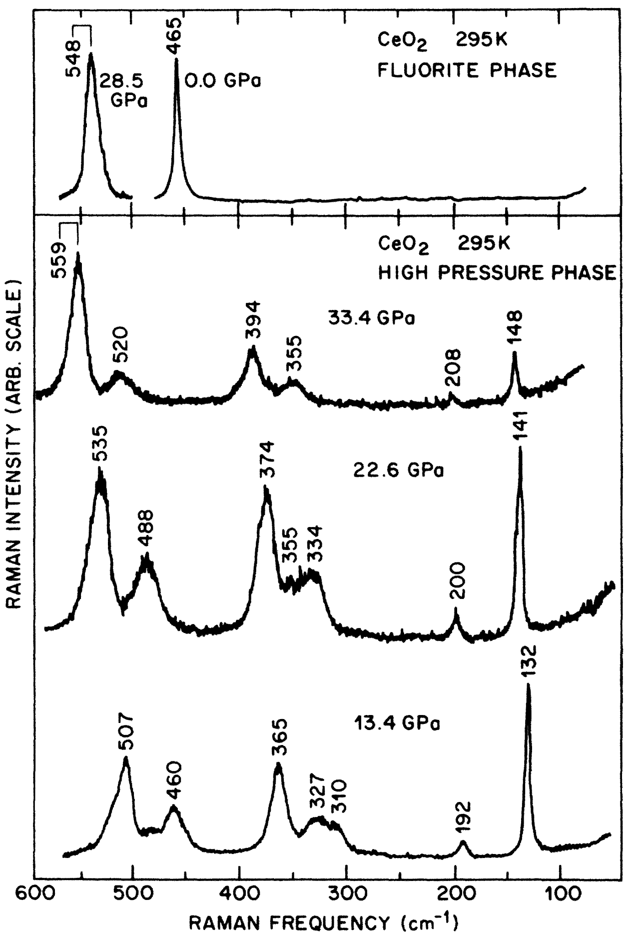

FIG. 4. The Raman spectrum of the fluorite phase of CeO_2 at two different pressures (topmost) and of the high-pressure phase at three different pressures. The spectra at 22.6 and 13.4 GPa were taken on releasing pressure cycle. Except the lowest frequency peak all the others are broad, indicating possible overlapping modes.

obtained from *Restrahlen* measurements.[11] However, the ω_{TO} derived from the same measurement seems to agree quite well with the calculated frequency. Using the experimentally derived ω_{LO} and ω_{TO} values and the phonon dispersion data we have indicated the possible origin of the observed second-order features in Table I. The experimentally obtained pressure coefficients and the calculated Grüneisen γ also given.

PRESSURE-INDUCED PHASE TRANSITION

From high-pressure Raman and x-ray diffraction studies[1,2,5,12,13] the occurrence of a pressure-induced phase transition from the fluorite-type structure to the $PbCl_2$-type structure has been established in several alkaline-earth difluorides and PbF_2. Phase transitions in HfO_2,[3] ZrO_2,[14,15] and TbO_2 (Ref. 3) from the fluorite-type structure to the so-called cottunite ($PbCl_2$ type), or to a distorted cottunite type[3] have been also reported in samples quenched after high-pressure high-temperature treatment. Further, for CeO_2, UO_2, and ThO_2 a pressure-induced transition to the orthorhombic Ni_2Si-type structure[3] has been suggested as a possible postfluorite phase. However, in CeO_2 no definite evidence for a phase change from the fluorite phase has been seen, so far.[3] Evidently the required transition pressure was not reached in previous studies.

The present high-pressure Raman study clearly establishes the occurrence of a pressure-induced phase transition in CeO_2 near 31 GPa, under ambient temperature. The new phase shows seven Raman peaks (see Table II). With the exception of two low-frequency peaks, all other Raman features are quite broad and may consist of several modes close in frequency. Therefore the conclusion is that the new structure is definitely of a lower symmetry. Further, the spectrum is quite similar to that of the high-pressure phases of BaF_2 or PbF_2, which are known to transform to the $PbCl_2$ structure. The latter has 18 Raman-active modes according to group theoretical analysis.[5] We believe that the high-pressure phase of CeO_2 also has the $PbCl_2$-type structure. This is the only postfluorite phase known at present in which a higher than eightfold coordination, namely ninefold, is reached in the case of AX_2 compounds. Whether other types of structural transitions could lead to higher density and account for the observed Raman spectrum of the high-pressure phase of CeO_2 is hard to decide, without an *in situ* high-pressure x-ray diffraction study. We intend to carry out such a study.

The bulk modulus of CeO_2 is a factor of 2 or 3 higher compared to that of the alkaline-earth difluorides.[2] From

TABLE I. The observed first- and second-order Raman peaks in the fluorite phase of CeO_2, their designation, pressure dependence, and mode Grüneisen parameter γ.

	First order			Second order		
Activity	ω (cm^{-1})	$d\omega/dP$ (cm^{-1}/GPa)	γ	ω_R (cm^{-1})	Designation	$d\omega/dP$ (cm^{-1}/GPa)
ω_R	465 (F_{2g})	3.29	1.44	580	$\omega_{TO}(X)+LA(X)$	5.4
				660	$\omega_R(X)+LA(X)$	7.0
ω_{ir}	275 (F_{1u},ω_{TO})			880	$\omega_{LO}+\omega_{TO}$	5.0
ω_{ir}	585 (F_{1u},ω_{LO})	4.2	1.5	1030	$2\omega_R(X)$	4.6
				1160	$2\omega_{LO}$	12.0

TABLE II. Observed Raman peak frequencies, their $d\omega/dP$, and the mode Grüneisen parameters γ of the high-pressure phase extrapolated to 1 atm. from high-pressure data. The bulk modulus B of CeO_2 was assumed to be the same as that of ThO_2 [$B=204$ GPa (Ref. 16)].

ω (cm^{-1})	$d\omega/dP$ (cm^{-1}/dP)	$\gamma=(B/\omega_0)(d\omega/dP)$
468	2.91	1.27
421	3.0	1.45
344	1.5	0.9
291	2.76	1.93
277	2.44	1.80
183	0.71	0.79
125	0.73	1.19

this, a higher transition pressure may be expected for CeO_2, and this is definitely the case. Attempts to scale the transition pressure with the reciprocal of the unit-cell volume seem to work for the alkaline-earth difluorides,[2] but CeO_2 does not fit into this scaling. This might indicate a different structure for the high-pressure phase. However, all the available evidence at the present time, in particular the Raman data, support the conclusion that the high-pressure phase is $PbCl_2$ type.

ACKNOWLEDGMENT

We wish to thank R. G. Maines, Sr. for assistance in the high-pressure experiments.

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