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[To be published in the Proceedings of the Symposium on Solid-State Actinide Chemistry and Physics, 192nd American Chemical Society Meeting, Anaheim, California, September 7-12, 1986.]

CONF-860911--25

DE87 004402

Studies of Selected Transuranium and Lanthanide Triiodides Under Pressure Using Absorption Spectrophotometry*

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JAN 27 1987

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*Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy under contracts DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., DE-AS05-76ER04447 with the University of Tennessee (Knoxville), and by the Commission of the European Communities, Joint Research Center, European Institute for Transuranium Elements, Karlsruhe, FRG.

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SUMMARY

The anhydrous triiodides of plutonium, americium, and curium under pressure have been investigated using absorption spectrophotometry. These initial studies on plutonium and curium triiodides together with the published data for americium triiodide show that the rhombohedral (BiI_3-type structure) form of these compounds can be converted to the same orthorhombic ($PuBr_3$-type structure) form by applying pressure at room temperature. Absorption spectrophotometry can often differentiate between two crystallographic forms of materials and has been used in the present high pressure studies to monitor the effects of pressure on the triiodides. A complication in these studies of the triiodides is a significant shift of their absorption edges from the near UV to the visible spectral region with pressure. With curium triiodide this shift causes interference with the major f-f absorption peaks and precludes identification by absorption spectrophotometry of the high pressure phase of CmI_3.

INTRODUCTION

The development of diamond anvil cells has facilitated greatly solid state research of materials under pressure. One area of such research has been studies of actinides under pressure, which are aimed at investigating how the 5f electrons of these materials are perturbed by the application of pressure. Our initial efforts in this area were concerned with studying selected actinide metals using X-ray diffraction

techniques [1-5]. Subsequently, solid state absorption spectrophotometric studies of actinide halides under pressure have been performed, which extended our earlier spectrophotometric studies of such materials carried out at room temperature and normal pressure.

The absorption of the trivalent transuranium elements in the 8-32 x 10^3 cm^{-1} spectral region is due mainly to f-f (Laporte forbidden) transitions and therefore their absorption spectra should reflect perturbations of these 5f-levels. Changes in oxidation state or electronic configuration should have major effects but smaller perturbations can also bring about significant changes in the spectra. For example, the characteristic features of a solid state absorption spectrum can in many cases be correlated with specific properties (interatomic distances, coordination number of the metal ion, crystal field, etc.) of the crystalline matrix of the solid. This sensitivity to environment permits the use of absorption spectrophotometry for monitoring the effects of pressure on the crystal form of many actinide compounds. An important requirement for this technique is that the material being monitored transmit adequate light during the course of the study.

Several of the transuranium halides are candidates for such high pressure spectrophotometric investigations, and studies of AmI_3 [6], $CfBr_3$ [7], and $CfCl_3$ [8,9] have been reported recently. The transuranium triiodides provide an interesting group of compounds to study under pressure due to their potential for formation of polymorphs, and their electronic alterations such as oxidation/reduction, transient charge transfer reactions, etc., as a result of the applied pressure. Reported here are the initial results of our studies of PuI_3, CmI_3,

LaI_3, and GdI_3 using absorption spectrophotometry to monitor the effects of the pressure applied to the compounds.

EXPERIMENTAL

Materials

The plutonium-242 and the curium-248 (97% Cm-248, 3% Cm-246) isotopes used in this work were obtained directly, or indirectly as decay products, from products of irradiation in the High Flux Isotope Reactor and separated in the Transuranium Processing Plant at the Oak Ridge National Laboratory. The metals were prepared by reducing milligram quantities of the respective fluorides with lithium metal vapor [10]. Lanthanum and gadolinium metals (99.9% rare earth content) were obtained from a commericial supplier and were used as received.

The anhydrous triiodides were prepared by direct reaction of the metals with iodine at elevated temperatures in sealed quartz tubes. After distilling away the excess iodine, the triiodides were melted and recooled to assure homogeneous, well-crystallized products. The triioide products were analyzed by both X-ray powder diffraction and absorption spectrophotometry at room temperature and atmospheric pressure prior to introducing each sample into the high pressure cells.

Investigative Techniques

The high pressure spectrophotometric techniques for studying these triiodides employed a diamond anvil cell and a microscope spectrophotometer. Both the cell [11] and the spectrophotometer [12] have been described. The procedure consists of placing the triiodide sample into the cell together with silicone oil and ruby chips; the silicone oil served as the pressure-transmitting medium and the ruby chips permitted the determination of the pressure via the shift in their argon-ion-laser-excited fluorescence [13]. The pressure cell was loaded and assembled in a helium-filled gloved box. The study of the sealed samples under pressure was carried out in air.

The procedure for the pressure studies consisted of spectrophotometrically analyzing the triiodides in the cell, first at atmospheric pressure and then after each increase or decrease in the applied pressure. After each change in pressure, the pressure on the sample was determined.

In the case of CmI_3, samples were also studied under pressure using X-ray diffraction (MoKα radiation) employing double-sided X-ray film. A Merrill-Bassett-type diamond anvil cell was used in these latter experiments. The loading and operational procedure for this cell were essentially the same as described for the pressure cell used for the spectrophotometric work.

RESULTS AND DISCUSSION

From studies of AmI_3 [14] it was determined that a significant difference exists between the formula volumes of the two crystal forms of AmI_3. This suggested that applying pressure on the rhombohedral form (CN=6) may convert it to the more dense, orthorhombic form (CN=8). In a study of AmI_3 [6] under pressure at room temperature, it was determined that the rhombohedral form underwent an irreversible phase transformation at a pressure of ~2 GPa to the orthorhombic form. With increasing pressure up to 10 GPa the absorption spectrum of AmI_3 remained essentially unchanged except that its absorption edge shifted to lower frequency, approaching 18×10^3 cm^{-1} (which corresponds to 560 nm). This cutoff of transmitted light obscured several absorption peaks of AmI_3 but did not prevent the use of peaks found at even lower frequencies (higher wavelengths) for monitoring the sample under pressure. After the release of pressure, the absorption edge of the samples did not shift back to their original positions and the samples were visibly much darker in color. A similar phenomena, discussed later in this section, was observed with samples of PuI_3, CmI_3, and LaI_3 but not with GdI_3. A smaller shift and less intense color change have been observed in samples of $CfBr_3$ [7] under pressure but the effects were reversible with pressure. Such an effect has not been observed in samples of $CfCl_3$ [8,9] under pressure.

In the case of CmI_3, only a BiI_3-type rhombohedral form had been reported previously [15]. Based on the crystallizing behavior of the lanthanide triiodides [16] and the relative radii of the trivalent

lanthanide and actinide ions [17], preparation of CmI_3 at elevated temperatures was expected to yield this rhombohedral form. This is in accord with our experience where the rhombohedral form was the only form obtained via thermal treatment. In view of the difference that is expected between the formula volumes of the rhombohedral and orthorhombic forms of CmI_3, it was felt that it should be possible to form the more dense, orthorhombic form of CmI_3 by applying pressure on its rhombohedral form. In Figure I is shown the solid state absorption spectrum of CmI_3 both at room pressure and at 10 GPa. Although an excellent spectrum can be obtained at room pressure, the shift of the absorption edge with pressure to 18×10^3 cm^{-1} blocks the major absorption peaks of the CmI_3 and precludes the use of absorption spectrophotometry for monitoring the effect of pressure on this compound. As in the case of AmI_3, the shifted absorption edge of CmI_3 persisted after the pressure was released, negating the hope that if a transition had occurred, it might be detected by changes in the absorption spectrum obtained subsequently at normal pressure. Thus, owing both to the nature of the absorption of CmI_3 and the irreversible shift of the absorption edge with pressure, it was evident that absorption spectrophotometry was not a viable method for monitoring this compound as a function of pressure.

A subsequent investigation of CmI_3 under pressure was carried out using X-ray diffraction. This preliminary study by X-ray diffraction has indicated that the rhombohedral form of CmI_3 does indeed convert under $\sim$6 GPa of pressure to form its orthorhombic polymorph, which is retained after the pressure is released. Due to experimental problems with determining a camera constant for the pressure cell during this

study and the limited number (8) of diffraction lines obtained, the diffraction data for CmI_3 could only be considered qualitative and used only to identify the crystal type of the CmI_3. For example, one useful difference in the diffraction patterns is the presence of a strong single line (hkl = 021) for the rhombohedral form as compared to a doublet (hkl = 112, medium intensity and hkl = 113 + 023, strong intensity) for the orthorhombic form.

The formation of an orthorhombic form of CmI_3 under pressure is consistent with the behavior of the lanthanide triiodides, based on the fact that the ionic radius of Cm(III) is similar to that of Sm(III) [17]. By using X-ray diffraction Beck and Gladrow [18] have determined by diffraction that the rhombohedral forms of the lanthanide triiodides through DyI_3 convert to the $PuBr_3$-type orthorhombic form at elevated temperatures (up to 500°C) and under pressure (3-6 GPa), even though at normal pressure only the orthorhombic form is observed through neodymium triiodide [16]. From radii considerations, an orthorhombic form of the actinide triiodides through einsteinium or fermium should be generated under pressure. Because of the high specific radioactivity and limited quantities of these actinides, such experiments with EsI_3 or FmI_3 are not practical, but they can be carried out with CfI_3. Due to the increasing stability of the divalent state in progressing across the actinide series, applying pressure on CfI_3 may bring about changes in addition to a crystal modification, such as the reduction of the californium (Cf(III) → Cf(II)) or a transient charge transfer reaction.

An orthorhombic form of PuI_3 has been known for several years [19] and recently a rhombohedral form has been shown to exist [20]. Studies of PuI_3 comparable to those described above for AmI_3 and CmI_3 have also

been carried out [20]. From such studies it has been determined that the rhombohedral form of PuI_3 under pressure also converts to an orthorhombic form, which is retained after the release of pressure. Details of these studies will be reported separately but the key results are noted here to point out that absorption spectrophotometry was used successfully to monitor the structural changes of PuI_3 with pressure. Although the absorption edge of the PuI_3 samples also shifted to longer wavelengths with the application of pressure, a sufficient number of PuI_3 absorption peaks could be evaluated at lower frequencies (longer wavelengths) for structural analysis.

Both LaI_3 and GdI_3 were examined under the same experimental conditions used for the other triiodides studied in this work to determine if similar shifts in their absorption edges and color changes would be noted in these materials under pressure. Both of these compounds lack absorption peaks in the spectral region of interest (8-32 x 10^3 cm^{-1}). At normal pressure their absorption spectra appear to be essentially scattering curves, as shown for LaI_3 in Figure II. The LaI_3 samples exhibited the $PuBr_3$-type orthorhombic crystal modification while the GdI_3 samples exhibited the BiI_3-type rhombohedral structure, as expected from the literature [16] and confirmed by X-ray diffraction. Upon applying pressure to the LaI_3 sample, the material acquired a reddish color and an intense absorption band in the 18 x 10^3 cm^{-1} region (see Figure II). Both effects were found to be reversible with pressure. In contrast, applying pressure up to 13 GPa on the GdI_3 did not generate a change in its spectrum or color.

Changes in color and shifts in the absorption edge with pressure have been reported for many inorganic and organic materials and can

arise from a variety of effects [21]. The reason for the shift in the position of the absorption edge of the triiodide samples with increasing pressure, which also coincided with the visual darkening of the samples' color, is not understood. If this red-shift had resulted from a change in the charge- transfer band, from the decrease in the ligand-to-metal bond lengths, or from a compression of electronic orbitals, then the absorption edge should have reverted to its original position when the pressure was released. The color and the shifted absorption edge are not characteristic of either crystal modification of these actinide triiodides. The generation of small amounts of iodine in these samples with pressure could account for such observed changes, but the presence of iodine suggests that a reduced species of the metal was also generated. Spectral or X-ray evidence for such reduced metal species was not observed but it is possible that the amounts present may have been too small or that their absorption peak(s) were obscured by other absorbing material. Additional work is necessary to resolve this question.

The conversion of the rhombohedral form of PuI_3, AmI_3, and CmI_3 to their orthorhombic form with pressure probably resulted from the more favorable packing efficiency in the latter form. In the case of AmI_3 [6] at room temperature, the formula volume of its rhombohedral form is ~18% greater than that of its orthorhombic form. Similarly, it has been shown that the $AlCl_3$-type monoclinic form of $CfBr_3$ under pressure (1.7-3.4 GPa) converts to the $PuBr_3$-type orthorhombic form, a form which has not been prepared directly by thermal treatment and has a 19% smaller formula volume at room temperature and normal pressure. In contrast, studies of both the UCl_3-type hexagonal form (up to 22 GPa)

and the $PuBr_3$-type orthorhombic form (up to 35 GPa) of $CfCl_3$ have not shown a pressure induced transformation between these forms [8,9]. Significantly, the difference between the room temperature-normal pressure formula volumes of $CfCl_3$ is less than 1%. Beck and Gladrow [18] have discussed structural transformations for several comparable lanthanide halides as a function of temperature and pressure and have proposed a correlation of structure with the relative density of the various crystalline forms.

These studies of the triiodides under pressure were part of a larger on-going program to determine if applied pressure can perturb the 5f orbitals of the actinides sufficiently to be detected by absorption spectrophotometry. Structural changes have been the major effect of applying pressure in our studies of compounds to date. Additional studies at higher pressures will pursue further what perturbations may occur to the 5f electrons as a result of applying pressure. However, the present work provides additional evidence that absorption spectrophotometry can be a rapid and sensitive means of monitoring selected actinide materials under pressure.

ACKNOWLEDGMENTS

The authors are indebted for the use of plutonium-242 and curium-248 in this work to the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, through the transplutonium elements production facilities at the Oak Ridge National Laboratory. The authors are indebted also for efforts of G. M. Begun in the ruby fluorescence measurements.

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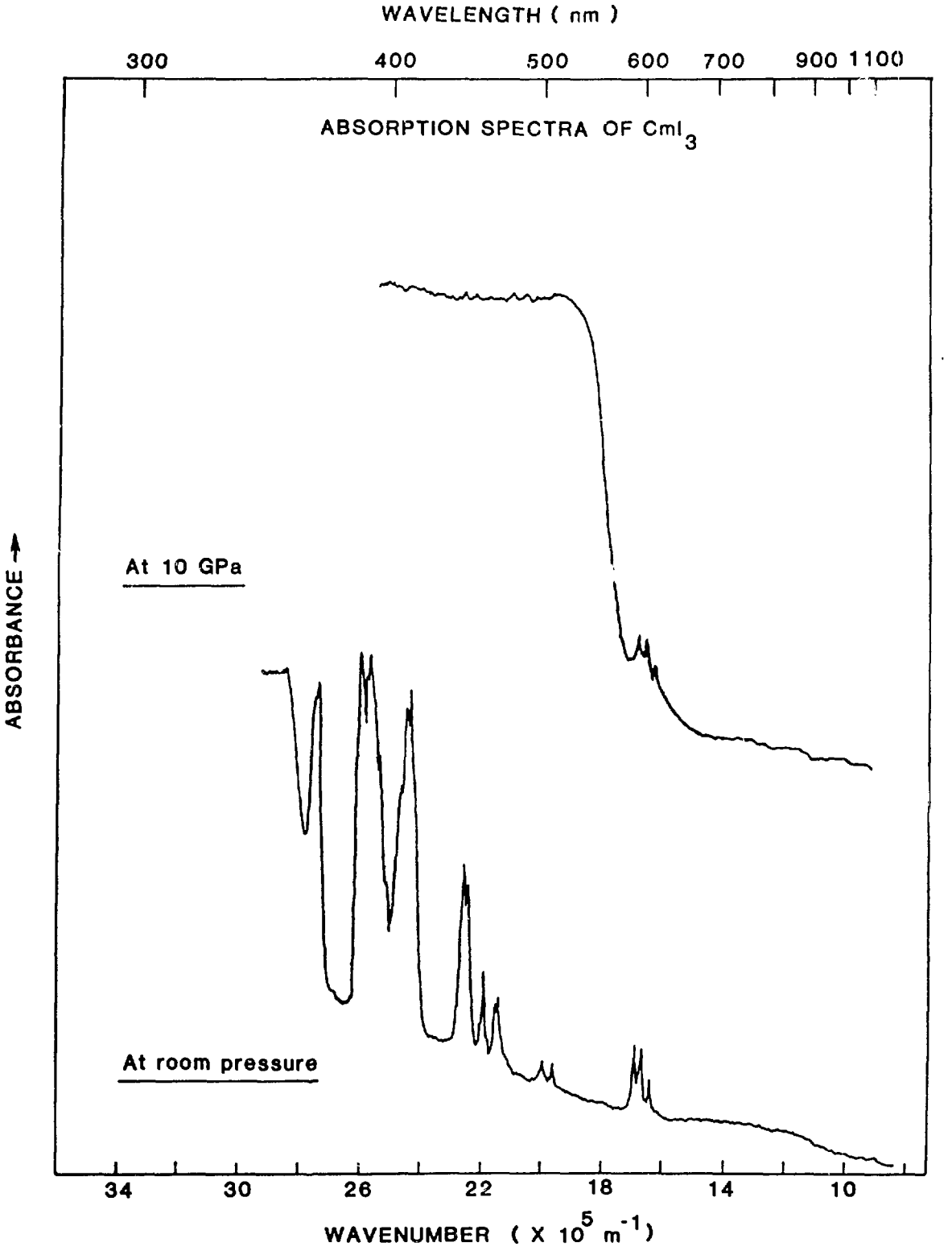
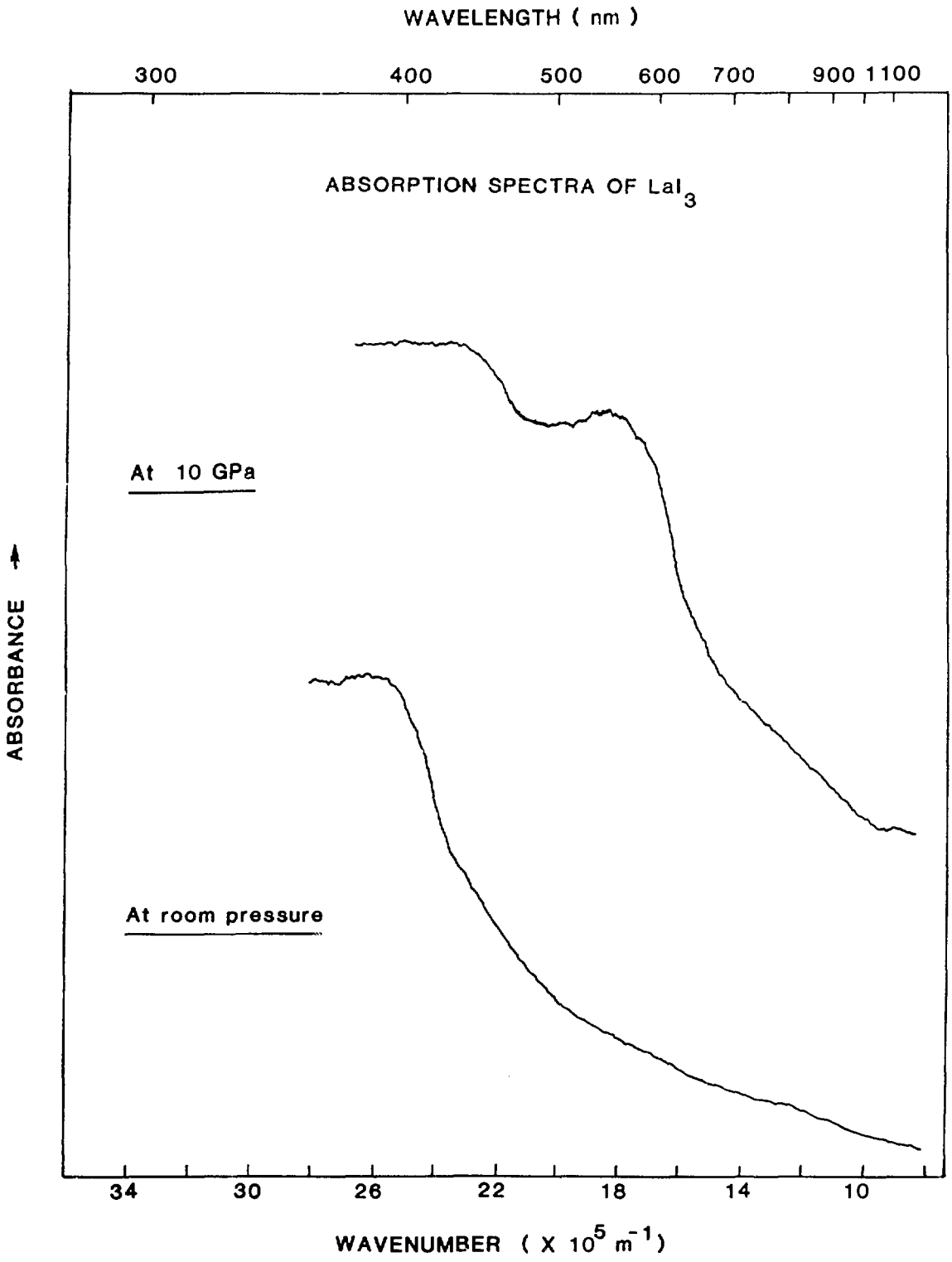
FIGURE CAPTIONS

Figure I. Absorption Spectra of CmI_3 at Room Pressure and at 10 GPa.

Figure II. Absorption Spectra of LaI_3 at Normal Pressure and at 10 GPa.

ORNL DWG 86-18331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