Infrared-Active Lattice Vibrations in a Few Fluorite-type Crystals

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In an attempt to obtain information about the crystalline force field, we have observed the infrared absorptions of three metal oxides with fluorite-type lattices, namely, uranium dioxide (UO_2), thorium dioxide (ThO_2), and cerium dioxide (CeO_2).

The sample of UO_2 was prepared by the Mitsubishi Metal Mining Company, that of ThO_2 was prepared by the Linsay Chemical Company (U.S.A.), and that of CeO_2 was prepared by Dr. Hiroshi Takahashi (the University of Tokyo), who kindly placed it at our disposal. The fact that all three of these samples fluorite-type crystal structures[1] was ascertained by an X-ray diffraction method.* The infrared absorption measurement was carried out by the use of a far-infrared spectrophotometer constructed by Professor H. Yoshinaga and his collaborators.[2] Each of the samples were mounted on the spectrophotometer in the form of a dispersion in a polyethylene film[3] (mostly with 200 mg. of oxide per 1.5 g. of polyethylene and 0.2 mm. thick).

The results of our infrared absorption measurement are shown graphically in Fig. 1. As may be seen in the figure, each of these oxides shows only one strong absorption band in the spectral region 4000～200 cm^{-1}. This is just what was expected from the crystal structure of these oxides. In a previous paper,[4] it has been shown that the fluorite (CaF_2)-type lattice (space group O_h^5) has only one infrared-active (F_{1u}) lattice vibration, and that its frequency ν (cm^{-1}) is given approximately by

$$4\pi^2c^2\nu^2=(4/3)K(\mu_F+2\mu_{Ca}) \tag{1}$$

In this equation, c is the velocity of light, K, the stretching force constant of the Ca-F bond, and μ_F and μ_{Ca}, the reciprocal masses of the F and Ca atoms respectively. Table I gives the observed frequencies ν of the oxides in question and the metal-oxygen bond stretching force constants K as calculated by Eq. 1. In the third column of Table I, the metal-oxygen bond distances,[1] r, are also given.

As may be seen in Table I, the metal-oxygen bond is strongest in UO_2, next strongest in

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1) V. M. Goldschmidt and L. Thomassen, *Videnskapsselsk. Skr.*, 5, 12 (1923).

* In an X-ray diffraction examination kindly made by Dr. Y. Iitaka (the University of Tokyo), the sample of CeO_2 used gave sharp reflections: at d=0.81569, 0.82518, 0.85549, and 0.91454 Å (the calibration has been made by the use of silicon powder). These reflections are indexed as (622), (533), (620), and (531) respectively, with a fluorite-type cell and with a=5.411 Å. The exact cell dimension has been obtained, by an extrapolation at $2\theta=180°$ (2θ being the angle of diffraction), as a=5.4108 Å. On the basis of the results of the examination and by referring, for example, to " Standard X-ray Diffraction Powder Patterns " (United States Departmet of Commerce, National Bureau of Standards), the sample used may be considered to be practically pure CeO_2 for the present purposes.

2) H. Yoshinaga, S. Hujita, S. Minami, A. Mitsuishi, R. A. Oetjen and Y. Yamada, *J. Opt. Soc. Am.*, **28**, 315 (1958).

3) H. Yoshinaga and R. A. Oetjen, ibid., **45**, 1085 (1955).

4) T. Shimanouchi, M. Tsuboi and T. Miyazawa, *J. Chem. Phys.*, **35**, 1597 (1961).

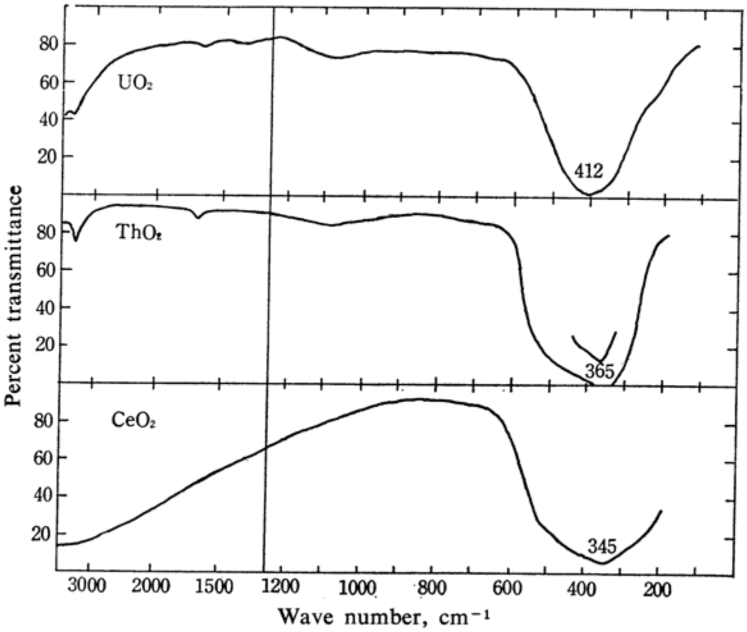

Fig. 1. Infrared absorptions of uranium dioxide, thorium dioxide, and cerium dioxide crystals, all of which have the fluorite type structures.

TABLE I

	Frequency ν cm^{-1}	Force constant, K mdyn./Å	Bond length, r Å
UO_2	412	1.057	2.36
ThO_2	365	0.827	2.42
CeO_2	345	0.685	2.34

ThO_2, and weakest in CeO_2. (However, the metal-oxygen bond length is shortest in CeO_2.) It is noticeable that the metal-oxygen bond stretching force constants in the oxides in question are much greater than the Ca-F bond stretching force constant (0.31 mdyn./Å) in fluorite crystal[4] or the Na–Cl bond stretching force constant (0.11 mdyn./Å) in sodium chloride crystal,[4] where the Ca–F or the Na–Cl bond is considered to be ionic. On the other hand, the metal-oxygen bond stretching force constants in question are much smaller than the C–C, C–Si, or U–O bond stretching force constants (2.8, 2.0, or 1.7 mdyn/Å respectively) in diamond,[4] silicon carbide,[5]** or α-uranium trioxide[6] crystals respectively; where the C–C, C–Si, or U–O bond is considered to be rather covalent.

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[5] M. Tsuboi, ibid., **40**, 1326 (1964).

** For hexagonal silicon carbide, the stretching force constant of the C-Si bond (1.890 Å in length) along the c axis is slightly lower than that of the C-Si bond (1.886 Å in length), which makes a nearly tetrahedral angle with the c axis. The difference, however, was found to be less than 0.1 mdyn./Å. It was also found that the force constant of the latter C-Si bond is practically equal to the force constant of the C-Si bond (1.886 Å in length) in cubic silicon carbide.

[6] M. Tsuboi, M. Terada and T. Shimanouchi, *J. Chem. Phys.*, **36**, 1301 (1962).