PHYSICAL REVIEW VOLUME 138, NUMBER 5A 31 MAY 1965

Dielectric Dispersion of Some Perovskite Zirconates

C. H. PERRY AND D. J. MCCARTHY*
Spectroscopy Laboratory† and Research Laboratory of Electronics,‡
Massachusetts Institute of Technology, Cambridge, Massachusetts

AND

G. RUPPRECHT
Tyco Laboratories, Inc.,§ Waltham, Massachusetts

(Received 6 January 1965)

The assignment of the normal-mode spectrum in perovskites has been achieved by a comparison of the vibrations of calcium, strontium, barium, and lead titanates and zirconates. In addition, for the antiferroelectric material lead zirconate, about 90% of the value of the low-frequency dielectric constant is the result of a low-frequency optically active mode.

INTRODUCTION

THE dielectric properties of perovskites have been the subject of many investigations, but a direct correlation between the dielectric constant and a normal optically active lattice mode has been convincingly established only in the case of the *paraelectric* strontium titanate.[1] The identification of this so-called "soft" mode is still debated.[2–9] Such an assignment of the normal-mode spectrum in perovskites has been achieved here by a comparison of the normal modes of titanates and zirconates. In addition, evidence is presented that also in the case of an *antiferroelectric* material, lead zirconate, the low-frequency dielectric constant is the result of a low-frequency optically active mode, at $K=0$, whose contribution to the dielectric constant ϵ accounts for about 90% of its value at room temperature.

RESULTS

The normal modes were obtained from reflectance measurements relative to a front-aluminized mirror on polished polycrystalline ceramic samples. The data were recorded at room temperature over a frequency range from 4000 to 25 cm^{-1} on instruments which were described previously.[10] The reflectance data of the zirconates (Fig. 1) were evaluated by a Kramers-Kronig analysis to yield the real and imaginary part of the dielectric constant[11,12] (Fig. 2). A list of the normal modes is shown in Table I; direct comparison can be made with the results from titanates.[5,7]

DISCUSSION

For an $AB\text{O}_3$ perovskite material of cubic symmetry there should be three sets of triply degenerate infrared active modes of symmetry F_{1u}, and one "silent" optically inactive mode of symmetry F_{2u}.[13] This F_{2u} mode, however, can become active on account of distortions of

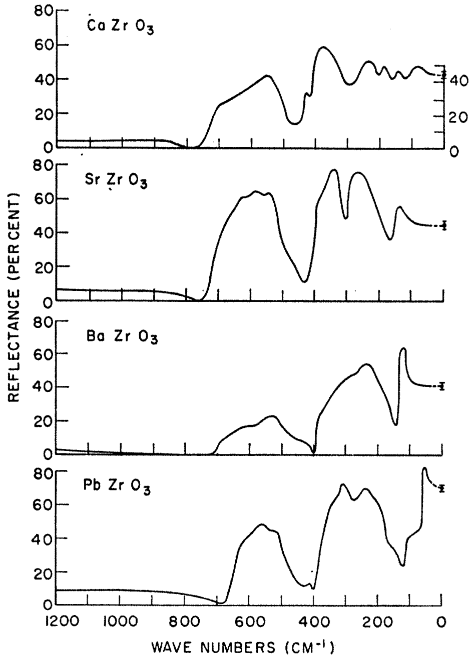

FIG. 1. Reflectance measurements.

---

* Present address: National Video Corporation, Chicago, Illinois.

† The work of this laboratory is supported in part by a grant from the National Science Foundation, Number G-19637.

‡ The work of the laboratory is supported in part by the Joint Services Electronics Program under Contract DA 36-039-AMC-03200(E).

§ This work was supported in part by the Energetics Branch, Air Force Cambridge Research Laboratory under Contract AF 19(628)2845.

[1] A. S. Barker, Jr. and M. Tinkham, Phys. Rev. **125**, 1427 (1962).

[2] J. T. Last, Phys. Rev. **105**, 1740 (1957).

[3] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).

[4] C. H. Perry, B. N. Khanna, and G. Rupprecht, Phys. Rev. **135**, A408 (1964).

[5] R. A. Cowley, Phys. Rev. **134**, A981 (1964).

[6] V. N. Murzin and A. I. Demeshina, Fiz. Tverd. Tela **6**, 182 (1964) [English transl.: Soviet Phys.—Solid State **6**, 144 (1964)].

[7] J. Ballantyne, Quarterly Progress Report No. 73, Research Laboratory of Electronics, MIT, 1964 (unpublished); Ph.D. thesis, Department of Electrical Engineering, MIT, 1964, (unpublished).

[8] R. I. Joseph and B. D. Silverman, J. Phys. Chem. Solids **24**, 1349 (1963).

[9] R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963).

[10] C. H. Perry, Techniques of Far Infrared Spectroscopy, Quarterly Progress Report No. 70, Research Laboratory of Electronics, MIT, 1963 (unpublished).

[11] T. S. Robinson, Proc. Phys. Soc. (London) **B65**, 910 (1952).

[12] F. Abeles and J. Mathieu, Ann. Phys. (Paris) **3**, 5 (1958).

[13] G. R. Hunt, C. H. Perry and J. Ferguson, Phy. Rev. **134**, A688 (1964).

TABLE I. Frequencies (in cm^{-1}) and symmetry of infrared modes obtained from Kramers-Kronig analysis of the reflectance data in perovskite-titanates and -zirconates.

Titanates

Sample	Crystal symmetry	ν_1 (Ti-O stretch)	ν_2 (Ti-O$_3$ torsion)	ν_3 (O-Ti-O bend)	ν_4 (cation-TiO$_3$ lattice mode)
CaTiO$_3$	Orthorhombic (multiple cell)	549 (B_1,B_2,A_1)	443 (B_1,B_2,A_2)	179 (B_1,B_2,A_1)	148 (B_1,B_2,A_1)
SrTiO$_3$	Cubic $O_h^1(P_m3_m)$	555 (F_{1u})	—(F_{2u})	185 (F_{1u})	100 (F_{1u})
BaTiO$_3$	Tetragonal	491 (E_u,A_1)	— (B_1,E_u)	175 (E_u,A_1) 184	12 (E_u,A_1)
PbTiO$_3$	Tetragonal	530 (E_u,A_1)	400 (B_1,E_u)	220 (E_u,A_1) 172	83 (E_u,A_1)

Zirconates

Sample	Crystal symmetry	ν_1 (Zr-O stretch)	ν_2 (Zr-O$_3$ torsion)	ν_3 (O-Zr-O bend)	ν_4 (cation-ZrO$_3$ lattice mode)
CaZrO$_3$	Orthorhombic (multiple cell)	515 (B_1,B_2,A_1)	340 (B_1,B_2,A_2) (377) (418)	228 (B_1,B_2,A_1) 186	153 (B_1,B_2,A_1) 96
SrZrO$_3$	Cubic (multiple cell)	522 (B_1,B_2,A_1)	325 (B_1,B_2,A_2) (357) (379)	240 (B_1,B_2,A_1)	143 (B_1,B_2,A_1)
BaZrO$_3$	Cubic	505 (F_{1u})	— (F_{2u})	210 (F_{1u})	115 (F_{1u})
PbZrO$_3$	Tetragonal (multiple cell)	508 (E_u,A_1)	290 (B_1,E_u)	221 (E_u,A_1)	80 (E_u,A_1) 34

the crystal lattice from the ideal cubic structure. The perturbation need only be slight and would of course split the degeneracies in all modes (e.g., $F_{2u}-B_1$, B_2, A_2). Although Kramers-Kronig analysis does not always bring out this feature, mode splitting can indeed be noticed in a number of cases on the reflectance data. An estimate of these split-off frequencies is included in parentheses in Table I.

Since ν_2 is missing in the undistorted lattices (see, for instance, BaZrO$_3$ in Fig. 2), this vibration is identified as the optically inactive torsional mode F_{2u}. To render F_{2u} active, the B cation can no longer be at a center of symmetry, a condition which is easily realized if the lattice is slightly sheared. This, according to Megaw's x-ray data, appears to be a common phenomenon among these structures.[14,15]

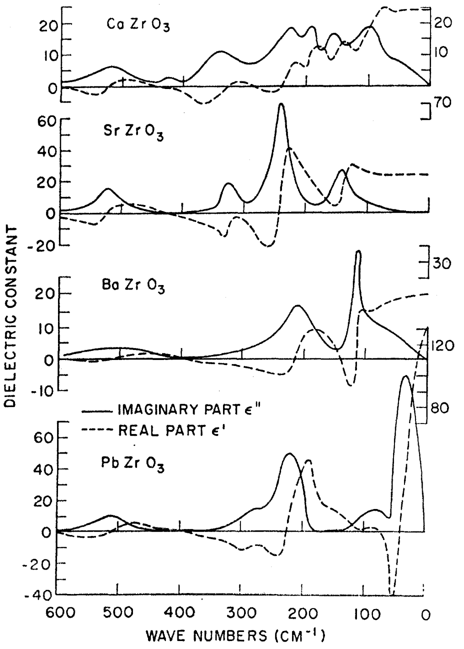

FIG. 2. Dielectric-constant measurements.

The modes ν_1 and ν_3 do not depend upon the A cation (Table I). ν_4, on the other hand, shows a definite trend as a function of the A-cation mass. Therefore it is concluded that ν_4 represents the A-(BO$_3$) lattice mode. The assignment of ν_1 and ν_3 as stretching and bending mode, respectively, is based upon the common experience that the stretching mode is usually of higher frequency than the bending mode. In view of the data presented the mode assignment for the perovskites probably represents the physical reality to a good approximation.

In Fig. 2 it is shown for the first time that in the case of antiferroelectric PbZrO$_3$[16] the main contribution to the low frequency dielectric constant (i.e., about 90%) is caused by a low frequency "soft" lattice mode which is well separated from the other modes.

ACKNOWLEDGMENTS

The authors wish to thank John Stampfel of the Research Laboratory of Electronics, MIT, for help in the preparation of the results. All computation work was performed with the IBM 7094 at the MIT Computation Center.

---

[14] H. D. Megaw, Proc. Phys. Soc. (London) **58**, 133 (1946).

[15] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, England, 1962).

[16] G. Shirance, E. Sawaguchi, and Y. Takagi, Phys. Rev. **84**, 476 (1951).