# Electronic and Vibrational Spectra of Ordered Perovskites

G. BLASSE AND A. F. CORSMIT

*Solid State Chemistry Department, Physical Laboratory, State University, Utrecht, Netherlands*

This paper describes electronic absorption and emission spectra of ordered perovskites $A_2BWO_6$. The charge-transfer absorption of the tungstate group depends on the choice of A and B. The $WO_6$ group in $Ba_2MgWO_6$ shows two different emissions, a blue and a yellow one. Further, the vibrational spectra of a number of ordered perovskites are reported and interpreted. Their use in crystal–chemical problems is outlined.

## 1. Introduction

Roland Ward and his coworkers have investigated thoroughly the possibility of cation substitution in oxidic perovskite-like phases following the work of Steward and Rooksby (1) on compounds with formula $A_3WO_6$ ($A$ = alkaline earth). Part of the work of Ward's school is summarized in Refs. 2–7. Because of its simplicity the ordered perovskite structure has solicited many investigations on the physical properties of compounds with this structure. A great part of this work has been induced by Ward's studies at the University of Connecticut. Figure 1 shows a detail of the structure. Compounds of this type have the general formula $A_2BB'O_6$, where the $A$ ions are in 12 coordination (the Ca site of perovskite, $CaTiO_3$) and $B$ and $B'$ in 6 coordination (the Ti site of perovskite). The $B$ and $B'$ ions are ordered and both form an fcc lattice. Their coordination octahedra share corners only.

Some arbitrary examples of physical investigations that depend strongly on the special properties of this structure are the recent work of one of Ward's pupils, Sleight (8), on the magnetic and electrical properties of ordered perovskites $Ba_2MReO_6$ (where, depending on M, ferri- and antiferromagnetism and metallic and semi-conduction is found) and the work of Goodenough *et al.* on the conductivity of $Sr_2MgReO_6$ compared to that of $ReO_3$ (9).

One of us has been strongly influenced by his visit to Roland Ward's department in 1962. The

ordered perovskite structure was indispensable in his work on ferromagnetic interactions in nonmetallic oxides [$La_2MMnO_6$ (10)], long-range magnetic interactions [$A_2BWO_6$ and $A_2BMoO_6$ (11)] and the nature of the $Eu^{3+}$ emission [in $Ba_2GdNbO_6$ (12)].

We have now started work on the optical properties of compounds with ordered perovskite structure with the aim to elucidate the lumi-
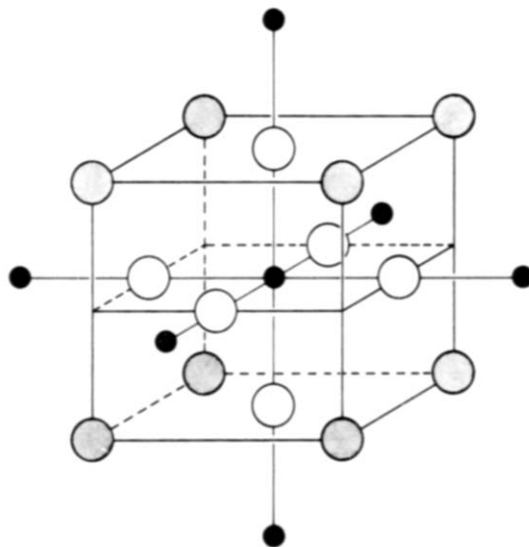


FIG. 1. Ordered perovskite structure of compounds $A_2BB'O_6$. Black circles $B$; small, hatched circle $B'$; open circles $O^{2-}$; large, hatched circles $A$.

nescence mechanism of groups consisting of a highly charged cation with noble gas configuration and oxygen ions. Examples are the tungstate ($WO_6$) and the niobate ($NbO_6$) group. In view of its high symmetry and its ability of extended cation substitution the ordered perovskite structure is again of great help. In the next section some electronic spectra are considered, in the last one some vibrational spectra are discussed. In view of the fact that Ward has also worked in the field of luminescence [see, e.g., (13)] this combination of luminescence and ordered perovskites seems very suitable to honour Roland Ward.

## 2. Experimental

Samples were prepared by usual techniques [see, e.g., (14)]. They were checked by X-ray analysis. Diffuse reflection spectra were measured on a Perkin–Elmer EPS–3T spectrofotometer. Excitation spectra were measured using an $H_2$ lamp, a Beckmann monochromator, a photomultiplyer and Na salicylate as standard. The emission spectra were measured as described by De Gruijter (15). Infrared spectra were measured in KBr and CsI pellets using a Hitachi EPI–G3 grating spectrometer and a Grubb Parsons DM4 spectrometer with a CsI prism. Raman spectra were measured on a Spectra Physics 700 Raman spectrometer using an argon ion laser (courtesy Dr. J. H. van der Maas).

## 3. The Electronic Spectra

### Reflection Spectra

The reflection spectra of compounds $A_2BWO_6$ reveal that the absorption edge of these compounds is only weakly influenced by the choice of $B$ and depends markedly on the choice of $A$ (Table I). The larger the ionic radius of $A$, the longer the wavelength corresponding to the absorption edge. This is illustrated in Fig. 2. It must be realized that, although the error in the values presented may be some nm, the difference between these values is real.

It is generally assumed [see, e.g., Ref. (17)] that the absorption edge of tungstates is due to absorption in the tungstate group corresponding to a so-called charge-transfer transition in which an electron is transferred from the highest filled molecular orbital (localized on the oxygen ions) to the lowest empty molecular orbital [localized on the tungsten ion, mainly $5d(t_{2g})$].

### TABLE I

POSITION OF THE ABSORPTION EDGE OF COMPOUNDS $A_2BWO_6$ IN DEPENDENCE ON THE IONIC RADII OF A (TWELVE-COORDINATION) AND B (SIX-COORDINATION)

| Compound | Absorption edge (nm) | Ionic radii (A) according to Ref. 16 |
|---|---|---|
| $Ba_2MgWO_6$ | 314 | 1.60 (Ba) |
| $Sr_2MgWO_6$ | 304 | 1.40 (Sr) |
| $Ca_2MgWO_6$ | 300 | 1.35 (Ca) |
| $Ba_2MgWO_6$ | 314 | 0.72 (Mg) |
| $Ba_2ZnWO_6$ | 317 | 0.75 (Zn) |
| $Ba_2CdWO_6$ | 317 | 0.95 (Cd) |
| $Ba_2CaWO_6$ | 318 | 1.00 (Ca) |
| $Ba_2SrWO_6$ | 316 | 1.13 (Sr) |
| $Ba_2BaWO_6$ | 320 | 1.36 (Ba) |

The dependence of the absorption edge on the choice of $A$ and $B$ in the formula $A_2BWO_6$ is at first sight surprising, because the $B$ ions are the nearest neighbours of the tungstate group. In Fig. 3 we have drawn the coordination of the $O^{2-}$ ions in $A_2BWO_6$. The anion is linearly coordinated by one $B^{2+}$ and one $W^{6+}$ ion and at larger distances by a square of four $A^{2+}$ ions, this square being perpendicular to the collinear array $B^{2+}$–$O^{2-}$–$W^{6+}$. The orbitals relevant to the lowest charge-transfer transition have also been drawn. In the ground state these are the oxygen
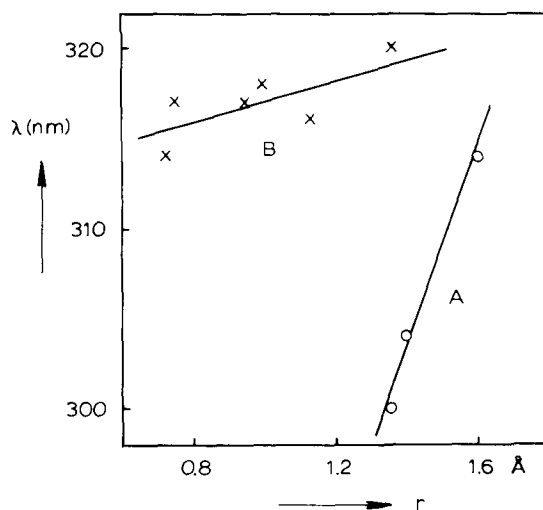


FIG. 2. Position of the absorption edge of ordered perovskites $A_2BWO_6$ vs the ionic radii of $A$ and $B$ (values according to Ref. 16). Curve A is for $A_2MgWO_6$; curve B for $Ba_2BWO_6$.
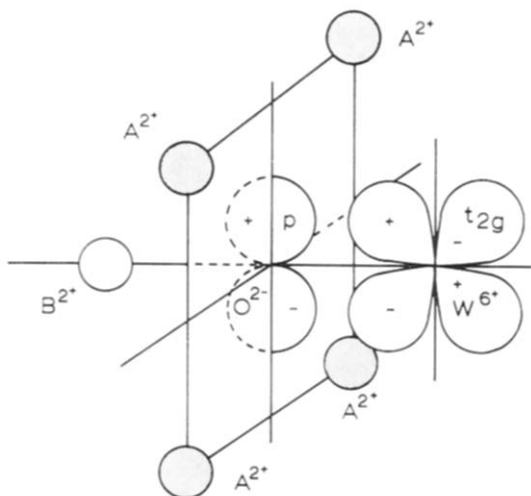
FIG. 3. Anion coordination in ordered perovskite $A_2BWO_6$ (see text).

$2p$ orbitals situated in the square (occupied) and the $t_{2g}$ orbitals of the $W^{6+}$ ion (empty). The absorption corresponds to an electronic transition from the $2p$ orbitals to the $t_{2g}$ orbitals.

It has been argued previously (17) that the spectral position of the charge-transfer band depends strongly on the charge and radius of the cations surrounding the anion. It must be expected that for higher charge and smaller radius the charge-transfer absorption is situated at higher energies, since the anion valence electrons will be stabilized by the strong field due to the positive cations. Figure 2 illustrates that this holds also for the perovskites $A_2BWO_6$ for $A$ as well as for $B$. From Fig. 3 it follows that it is not unreasonable to ascribe the stronger dependence on $A$ than on $B$ to the fact that the charge of the $2p$ orbital is directed towards the four $A^{2+}$ ions and not only to the $B^{2+}$ ion. It is evident that further work is necessary to elucidate this problem. It must also be kept in mind that Fig. 3 is a simplification for a great part of the perovskites, because these show distortions from pure cubic symmetry. Let us now turn to the luminescence of these compounds.

*Luminescence Spectra*

Nearly all compounds cited in Table I luminesce at 77 K under ultraviolet excitation. The emission colours range from deep blue to yellow. This agrees with a few observations made by Kröger (18). He reports a green emission for $Sr_3WO_6$ and a blue emission for $Ca_3WO_6$. Only one of our compounds luminesces with reason-

able efficiency at room temperature, viz., $Ba_2MgWO_6$. Until now, we have investigated only this compound in greater detail, because at the moment it seems the most interesting one.

The emission colours of $Ba_2MgWO_6$ at 300 and 77 K are different, viz., yellow-green and blue-green, respectively. This is borne out by the emission spectra presented in Fig. 4. At 300 K there is only one emission band; at 77 K, however, an additional band at shorter wavelengths appears. At 4 K the intensity of the latter band becomes even higher.

This phenomenon is highly remarkable. Usually the tungstate group shows one emission band only [see, e.g., Refs. (18) and (19)]. In view of the crystal structure, we can reject the possibility of two crystallographically different tungstate groups. It can also be excluded that a small amount of the efficient phosphor $MgWO_4$ is present, because its emission band peaks at 490 nm at 300 K (20), whereas the maximum of the emission of $Ba_2MgWO_6$ is situated at about 530 nm at 300 K. We therefore arrive at the conclusion that the tungstate group in $Ba_2MgWO_6$ emits from two different energy levels of one and the same group.

This is also borne out by the excitation spectra which are different for the two emissions. The longer-wavelength excitation band corresponds to the longer-wavelength emission (Fig. 5).

This situation reminds one of similar observations on the niobate group which is isoelectronic with the tungstate group (21, 22). In this case, however, the low-temperature emission is the longer-wavelength emission. We have recently observed that this longer-wavelength emission corresponds to a longer-wavelength excitation band (23).
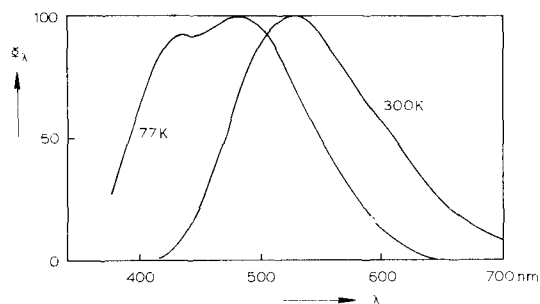


FIG. 4. Spectral energy distribution of the emission of $Ba_2MgWO_6$ under 254 nm excitation at 77° and 300°K. $\Phi_\lambda$ gives the radiant power in arbitrary units per constant wavelength interval.
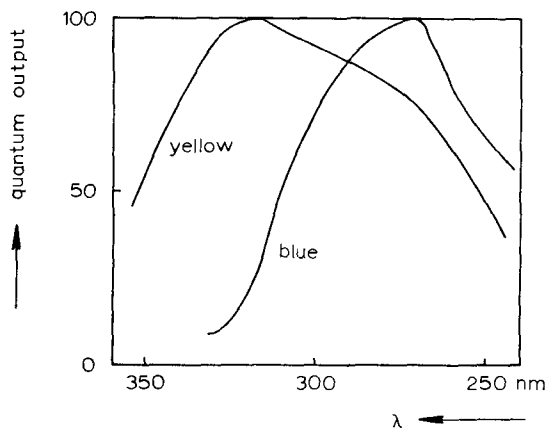
FIG. 5. Relative excitation spectra of the yellow and blue emission of $Ba_2MgWO_6$ at 77°K.

For a satisfactory explanation further measurements and molecular orbital calculations will be necessary. It seems obvious, however, that the double emission of the tungstate group in

$Ba_2MgWO_6$ is related to the complicated nature of the first excited state of the tungstate group that contains singlet as well as triplet levels (21, 22). In view of its high symmetry the ordered perovskites seem very suitable to investigate this problem further. It is also possible to study the influence of the surroundings on these effects. For $Sr_2MgWO_6$, for example, the emission spectrum at 77 K consists of an emission band with a shoulder on the high-energy side; $Ba_2CdWO_6$, however, shows one single emission band at 77 K only.

## 4. Vibrational Spectra

Since the $WO_6$ group can be considered as a molecular unity within the lattice, it seemed interesting to study also the vibrational spectra of these compounds in order to obtain information on the symmetry and the chemical bond in the tungstate group.

An $MO_6$ octahedron has 15 internal degrees of

TABLE II

VIBRATIONAL SPECTRA AND ASSIGNMENTS OF THE MOLECULAR GROUP $MO_6$ IN ORDERED PEROVSKITES $A_2BMO_6$ (VALUES IN $CM^{-1}$)[a]

|  |  | $A_{1g}$ $\nu_1$ | $E_g$ $\nu_2$ | $T_{1u}$ $\nu_3$ | $T_{1u}$ $\nu_4$ | $T_{2g}$ $\nu_5$ |
|---|---|---|---|---|---|---|
| $M^{7+}O_6$ | $Ba_2NaIO_6$ | 722 | — | 688 | 427 | 435 |
| $M^{6+}O_6$ | $Ba_2MgWO_6$ | 818 | 670 | 620(sh) | 435; 386; 355 | 445 |
|  | $Ba_2NiWO_6$ | 833 | — | 602(sh) | 426; 375; 353 | 447 |
|  | $Ba_2CuWO_6$ | 830 | — | 685; 609 | 395; 355; 328 | — |
|  | $Ba_2ZnWO_6$ | 825 | — | 605(sh) | 344(sh) | 431 |
|  | $Ba_2CoWO_6$ | 820 | — | 599(sh) | 364(sh) | — |
|  | $Sr_2MgWO_6$ | 865 | — | 668(sh) | 390(sh) | 457 |
|  | $Ca_2MgWO_6$ | 846 | — | 650(sh) | 440, 400 | 480 |
|  | $Ca_3WO_6$ | 833 | — | 690; 608; 560 | 418; 381; 355 | 477; 432 |
|  | $Ba_2MgUO_6$* | — | — | 610 | 356 | — |
|  | $Ca_3UO_6$* | — | — | 645; 580; 528 | 381 (sh); 351 | — |
|  | $Sr_2NiTeO_6$ | 760 | 598 | 695(sh) | 398(sh) | 412 |
|  | $Ba_2CaTeO_6$ | 752 | 618 | 685 | 400 | 412 |
|  | $Ca_3TeO_6$ | 727 | 612; 596 | 684(sh); 668 | 461; 432(sh) | 455(sh); 445 |
|  | $Ba_2CaMoO_6$ | 813 | 651 | 648(sh); 600 | 358(sh) | 417 |
| $M^{5+}O_6$ | $SrLaMgNbO_6$ | 790 | — | 619(sh) | 433; 388 | 440(sh) |
|  | $Ba_2YNbO_6$ | 830(sh); 765 | — | 650; 560 | 340(sh) | 394 |
| $M^{4+}O_6$ | $La_2MgTiO_6$ | 725 | — | 600(br) | 460; 412 | 487; 499(sh) |

[a] Compounds for which the Raman spectra could not be obtained due to strong absorption of the laser line or due to luminescence are marked with an asterisk. (sh) means that the given band is accompanied by a shoulder.

freedom or normal vibrations. Group-theoretical considerations represent them as:

$$A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$$

The modes $A_{1g}$, $E_g$ and $T_{2g}$ are Raman active, the two modes $T_{1u}$ are I–R active, whereas $T_{2u}$ is inactive (24, 25). Deviation from $O_h$ symmetry will result in line broadening or even splitting. Complete removal of symmetry will result in 15 bands.

The compounds $A_2BMO_6$ have one $MO_6$ octahedron per primitive unit cell with site symmetry $O_h$. We have indeed observed for these compounds three bands in the Raman spectra and two bands in the ir spectra and in addition a number of bands at lower wavenumbers (external modes) (14). Even in those cases, where the X-ray diagrams do not show departure from cubic symmetry, at least part of the ir bands of the $MO_6$ group showed a shoulder. The number of investigated compounds $A_2BMO_6$ has now been extended with those with serious deviations from cubic symmetry. In Table II the frequency assignments are given.
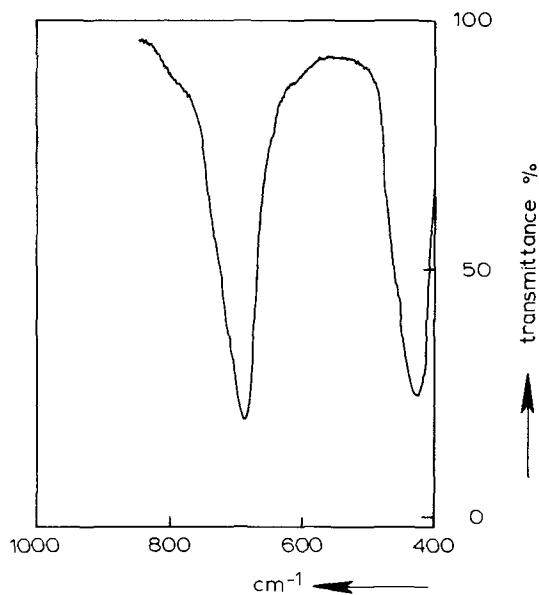
For $Ba_2CaTeO_6$ the frequency assignment was controlled by force constant calculations starting with the simple Urey–Bradley force field (UBFF). The three force constants $K$, $F$ and $H$ were derived from the well-defined Raman bands. These calculations were refined using an orbital-valence force field (OVFF) (26). Results are given in Table III. The agreement is satisfactory.

An inspection of Table II shows that the decrease of the frequencies in the sequence $M^{7+}O_6$ to $M^{4+}O_6$ is less marked than expected (note especially $\nu_1$). This phenomenon will be studied further.
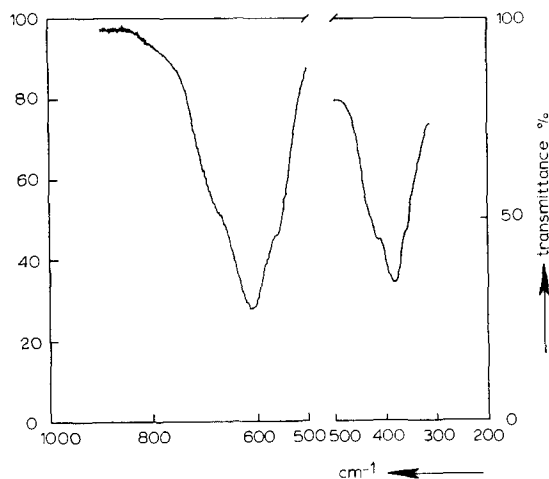


FIG. 6. Infrared spectrum of $Ba_2NaIO_6$.

In many cases we noted a splitting of the bands and lines. This is illustrated in Figs. 6 and 7, where the infrared-active $\nu_3$ and $\nu_4$ have been drawn for $Ba_2NaIO_6$ and $Ca_3WO_6$, respectively. In the case of the iodate there is practically no splitting; in the case of the tungstate the bands show three components. Indeed, it is known that $Ca_3WO_6$ shows a strong deviation from cubic symmetry (27). However we also observed a splitting of the ir bands in the case of perovskites that do not show a deviation from cubic symmetry detectable by X-ray analysis. This is inter-

TABLE III

FORCE CONSTANTS CALCULATION ON $Ba_2CaTeO_6$. ALL FREQUENCIES IN $CM^{-1}$, ALL FORCE CONSTANTS IN MDYN/Å

| | UBFF I | OVFF II | OVFF III | OVFF IV | Observed |
|---|---|---|---|---|---|
| $\nu_1$ | 752 | 737 | 745 | 745 | 752 |
| $\nu_2$ | 618 | 596 | 604 | 598 | 618 |
| $\nu_3$ | 719 | 704 | 709 | 708 | 685 |
| $\nu_4$ | 341 | 374 | 399 | 403 | 400 |
| $\nu_5$ | 412 | 380 | 416 | 405 | 412 |
| $K$ | 3.24 | 3.16 | 3.04 | 3.15 | |
| $D$ | — | 0.18 | 0.43 | 0.305 | |
| $F$ | 0.11 | 0.49 | 0.55 | 0.52 | |
| $F'$ | — | −0.10 | −0.05 | −0.10 | |
| $H$ | 0.52 | — | — | — | |



FIG. 7. Infrared spectrum of $Ca_3WO_6$ (note the threefold splitting of the bands).

preted as a deviation from cubic site symmetry and will possibly be of importance for the interpretation of the luminescence spectra. We conclude that infrared spectroscopy is a sensitive method to investigate the site symmetry of the $MO_6$ group in ordered perovskites $A_2BMO_6$.

It is interesting to note that the infrared bands of $Ba_2CuWO_6$ are not further split than in the case of $Ba_2ZnWO_6$ and $Ba_2NiWO_6$. The compound $Ba_2CuWO_6$ shows a strong tetragonal deviation from cubic symmetry due to the Jahn–Teller effect working on the $Cu^{2+}$ ions (28). The present results show that the $WO_6$ group in this compound is not seriously distorted whereas the $Cu^{2+}O_6$ octahedron is (29).

For $Ba_2YNbO_6$ we observed three Raman lines in the $\nu_1$ region, whereas only one is expected. The X-ray diagram does not show superstructure lines due to ordering of the $Y^{3+}$ and $Nb^{5+}$ ions. These, however, are not expected due to the small difference between the scattering powers of $Y^{3+}$ and $Nb^{5+}$. In our opinion the appearance of more than one line in the $\nu_1$ region is due to incomplete ordering. This shows that the vibrational spectra can also be used to study ordering phenomena between cations in those cases where X-ray analysis is not sensitive. More examples will be published elsewhere.

Finally we mention the vibrational spectra of $Sr_3MgNb_2O_9$, a perovskite with $1:2$ ordering between the octahedral cations (30). Due to this ordering the structure becomes hexagonal. The space group is $P\bar{3}m1$ $(D_{3d}^3)$ with 2 Nb per unit cell at site symmetry $C_{3v}$. As a consequence the bands will split. Here we only mention the case of $\nu_3$ which splits in a weaker band at 540 cm$^{-1}$ and a stronger one at 660 cm$^{-1}$ due to the trigonal field at the $Nb^{5+}$ site. The centre of gravity of $\nu_3$ is situated at about 620 cm$^{-1}$. This is the same frequency as observed in the case of $SrLaMgNbO_6$ (see Table II), where practically no splitting has been observed. More details will be published elsewhere.

The present examples were only given to demonstrate the usefulness of vibrational spectroscopy in crystal–chemical studies of ordered perovskites.

## Acknowledgments

## References

1. E. G. STEWARD AND H. P. ROOKSBY, Acta Crystallogr. 4, 503 (1951).
2. E. J. FRESIA, L. KATZ, AND R. WARD, J. Amer. Chem. Soc. 81, 4783 (1959).
3. A. W. SLEIGHT AND R. WARD, J. Amer. Chem. Soc. 83, 1088 (1961).
4. J. LONGO AND R. WARD, J. Amer. Chem. Soc. 83, 2816 (1961).
5. F. GALASSO, J. R. BARRANTE, AND L. KATZ, J. Amer. Chem. Soc. 83, 2830 (1961).
6. A. W. SLEIGHT, J. LONGO, AND R. WARD, Inorg. Chem. 1, 245 (1962).
7. A. W. SLEIGHT AND R. WARD, Inorg. Chem. 1, 790 (1962).
8. A. W. SLEIGHT AND J. F. WEIHER, J. Phys. Chem. Solids 33, 679 (1972).
9. A. FERRETTI, D. B. ROGERS, AND J. B. GOODENOUGH, J. Phys. Chem. Solids 26, 2007 (1965).
10. G. BLASSE, J. Phys. Chem. Solids 26, 1969 (1965).
11. G. BLASSE, Proc. Int. Conf. Magnetism, 350 (1964).
12. G. BLASSE, A. BRIL, AND W. C. NIEUWPOORT, J. Phys. Chem. Solids 27, 1587 (1966).
13. R. WARD, Trans. Electrochem. Soc. 93, 171 (1948).
14. A. F. CORSMIT, H. E. HOEFDRAAD, AND G. BLASSE, J. Inorg. Nucl. Chem. 34, 3401 (1972).
15. W. C. DE GRUIJTER, J. Solid State Chem. 6 (1).
16. R. D. SHANNON AND C. T. PREWITT, Acta Crystallogr. B25, 925 (1969).
17. G. BLASSE AND A. BRIL, Z. Phys. Chem. N.F. 57, 187 (1968).
18. F. A. KRÖGER, "Some Aspects of the Luminescence of Solids," Elsevier, Amsterdam (1948).
19. G. BLASSE AND A. BRIL, J. Solid State Chem. 2, 291 (1970).
20. A. BRIL, in "Luminescence of Organic and Inorganic Materials" (Kallman and Spruch, Eds.), p. 479, John Wiley, New York (1962).
21. G. BLASSE AND A. BRIL, J. Lumin. 3, 109 (1970).
22. G. BLASSE AND A. BRIL, J. Solid State Chem. 3, 69 (1971).
23. G. P. M. VAN DEN HEUVEL AND G. BLASSE, unpublished results.
24. G. HERZBERG, "Infrared and Raman Spectra," D. VAN NOSTRAND, New York (1945).
25. E. B. WILSON JR., J. C. DECIUS, AND P. C. CROSS, "Molecular Vibrations," McGraw–Hill, New York (1955).
26. S. N. THAKUR AND D. K. RAI, J. Mol. Spectrosc. 19, 341 (1966).
27. I. N. BELYAEV, V. S. FILIPEV, AND E. G. FESENKO, Zh. Strukt. Khim. 4, 719 (1963).
28. G. BLASSE, J. Inorg. Nucl. Chem. 27, 993 (1965).
29. YU. N. VENEVTSEV, Mater. Res. Bull. 6, 1085 (1971).
30. F. GALASSO AND J. PYLE, J. Phys. Chem. 67, 1561 (1963).