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Comparison of the Force Field in Various Pyrochlore Families

II. Phases Presenting Structural Defects

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A previous study of various $A_2B_2O_6O'$ pyrochlore families by vibrational spectroscopy allowed the analysis of the ir and Raman spectra and the force fields of pyrochlore phases presenting structural defects. The spectra of the following compounds were compared: (i) ideal pyrochlore $Cd_2Ta_2O_7$, (ii) lacunary $Tl_2Ta_2O_6$, (iii) nonstoichiometric $Pb_{1.5}Ta_2O_{6.5}$, and (iv) $Pb_{2.3}Ta_2O_{7.3}$ exhibiting regular shear planes. If the tridimensional network of TaO_6 octahedra is not modified and the perturbations concern only the A_4O' tetrahedra network, a slight modification of the vibrational spectra and a weak decrease in the Ta–O stretching and O–Ta–O bending force constants are observed. But, if the octahedra network is perturbed, large modifications appear on the spectra, revealing unambiguously the existence of new types of bonds created by the defects in the structure. The Raman intense lines observed in the low frequency range in lead compounds is also discussed.

Introduction

In an earlier paper, we studied different families of $A_2B_2O_7$ pyrochlore compounds by vibrational spectroscopy (*1*). We showed that for some of them, the structure determined by X-ray diffraction is statistically cubic, and that local distortions may occur in the BO_6 octahedra. Our present paper is concerned with oxides that differ from the ideal pyrochlore structure and exhibit structural defects such as vacancies, nonstoichiometry or shear planes. These structural defects may be related to the ir and Raman spectra. Among all the compounds we have studied, we have chosen to compare in this paper the results obtained for different tantalates.

Experimental Results

The compounds are synthesized by heating a mixture of the oxides or carbonates (pure at 99.9%) placed in an electric furnace CIF SM5. The mixture in stoichiometric quantities is first finely ground, then pressed into disks at 200 kg/cm^2 pressure. The disks are put in platinum crucibles which are placed in alumina cages. We obtained well-crystallized compounds for the conditions summarized on Table I.

The infrared spectra were recorded with a Perkin–Elmer 580 spectrometer between 4000 and 180 cm^{-1}. For the lower frequencies, we used a Perkin–Elmer 180 spectrophotometer or a NPL-Grubb Parson Fourier transform interferometer. The samples were in form of powder dispersed in caesium iodide disks or in polyethylene films.

The Raman spectra were recorded with Raman spectrometers Coderg PH1 and

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TABLE I

SYNTHESIS CONDITIONS OF THE STUDIED TANTALATES

Compounds	Mixtures	Heating treatment
$Cd_2Ta_2O_7$	$CdO + Ta_2O_5$ (2/1)	6 to 12 hr at 1200°C in air
$Tl_2Ta_2O_6$	$Tl_2CO_3 + Ta_2O_5$ (1/1)	6 hr at 300°C under vacuum then 24 hr at 600°C (N_2 atmosphere)
$Pb_{1.5}Ta_2O_{6.5}$	$PbO + Ta_2O_5$ (3/2 with 3–4% PbO in excess)	6 hr at 1200°C in air
$Pb_{2.3}Ta_2O_{7.3}$	$PbO + Ta_2O_5$ (1.15/1)	0.5 to 6 hr at 800–1200°C in air

T800 using krypton radiation at 647.1 nm and argon radiation at 514.5 nm, with a power of about 400 mW and a slit width varying between 1 and 2 cm^{-1}. The spectrum of $Pb_{2.3}Ta_2O_{7.3}$ was recorded on a RCI Brucker spectrometer which allowed data accumulation and using krypton radiation at 647.1 nm and a slit width of 1 cm^{-1}. For black $Tl_2Ta_2O_7$, we cannot obtain a Raman spectrum of sufficient quality.

Method of Calculation

Force field calculations were carried out by the previously described method (*1*): we have used Wilson's method (*2*) and Schachtschneider's programs (*3*); according to Shimanouchi's method (*4*), we have considered tridimensional infinite crystals and used the Born von Karman's approximation. We have chosen the generalized valence force field already used for the ideal pyrochlores (*1*). The force constants were calculated for each compound (*5, 6*); the average error $r = \Sigma f(\text{observed}) - f(\text{calculated})/\Sigma f(\text{observed})$ is always lower than 2.5%. The difference between the calculated and observed frequencies is less than 15 cm^{-1}.

Structural Data

Ideal structure. The ideal pyrochlore structure has the general formula $A_2B_2O_6O'$. It is composed of a network of BO_6 octahedra linked by their corners to form hexagonal vacancies where A_4O' tetrahedra, constituting a second network, are situated. A cations must have rather large ionic radii (≥0.1 nm) in comparison to those of B cations (0.06 to 0.09 nm) (*7–9*). The cubic structure with space group $Fd3m$ (O_h^7) contains eight formulas per unit cell and the following crystallographic sites are occupied (origin on B; $R\bar{3}m$): 16(*d*) for A cations, 16(*c*) for B cations, 48(*f*) for oxygen atoms O, 8(*b*) for oxygen atoms O′.

Vacancies and nonstoichiometry. The BO_6 octahedra network is essential to the cohesion of the crystal as is shown by the high values of the stretching constants of the B–O bonds (1.3 to 1.5 N · cm^{-1}) in comparison to those of the A–O and A–O′ bonds (0.12 to 0.35 N · cm^{-1}). Therefore, vacancies are essentially encountered in the A_4O' network. The environment of the A cations is presented on Fig. 1. We have studied two types of compounds (*5, 6*):

—$A_2B_2O_6$ oxides in which the oxygen atoms O′ are missing. In this case, A cations are only bonded to six oxygen atoms O, and the A_4O' tetrahedra do not exist (*10*). Thallium tantalate belongs to this structural type.

—Nonstoichiometric $Pb_{1.5}Nb_2O_{6.5}$ and $Pb_{1.5}Ta_2O_{6.5}$ oxides in which only 75% of 16(*d*) sites (Pb^{2+}) and 50% of 8(*b*) sites (O′) are occupied. The tetrahedra network is therefore very perturbated (*11–13*).

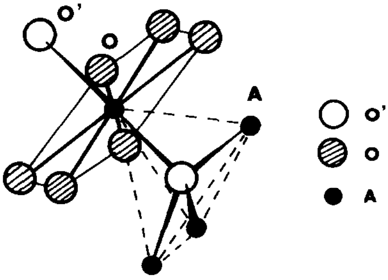

FIG. 1. Environment of A cations and oxygen atoms O′ in the pyrochlore structure.

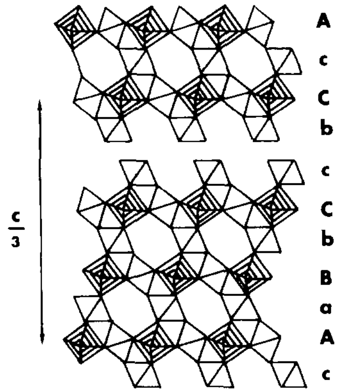

FIG. 2. Projection of the structure of the rhombohedral pyrochlore $Pb_{2.3}Ta_2O_{7.3}$ (*11*).

Defect of packing in the octahedra network. Bernotat-Wulf (*11, 14*), Saine (*15*), and Scott (*16*) after Roth (*13*) and Brusset *et al.* (*17*) studied the structure of five rhombohedral or hexagonal lead niobates. The first three authors propose the following description of the structure: cubic pyrochlore blocks are separated by regular shear planes; the cohesion between two blocks is ensured by Pb–O bonds as is shown on Fig. 2. Tantalates are supposed to be isostructural to niobates. We have studied some oxides of general formula nPbO,B_2O_5 (B = Nb, Ta; $1.5 < n \leq 2.5$), and we consider here only the tantalate with $n = 2.3$ (*18*).

Spectroscopic Results

For an ideal pyrochlore structure, the group theory predicts six Raman active lines ($A_{1g} + E_g + 4\ F_{2g}$) and seven ir active absorption bands (all F_{1u}). Table II gives the principal contributions of stretching and deformation modes to the potential energy distribution for each characteristic frequency of ideal $Cd_2Ta_2O_7$. It can be seen that only the modes of highest frequencies (600–500 cm^{-1}) are due to B–O stretching modes. Within the range 500–300 cm^{-1}, there are couplings between B–O stretching and O–B–O bending modes. Below 300 cm^{-1} the two modes that are due to the A_4O' network appear at 270 and 245 cm^{-1}. The two lowest frequencies at 103 and 70 cm^{-1} exhibit couplings of the A–O and A–O′ bonds stretching and O–A–O and O–A–O′ bending modes. According to our previous work (*1*) the influence of A cations upon the BO_6 network is expected to be weak, therefore the comparison between tantalates of cadmium, thallium, and lead is available. On Table II are also reported the values of the observed frequencies for the other tantalates. On Figs. 3 and 4 we present ir and Raman spectra of the compounds, and the principal calculated force constants are given on Table III.

Discussion

When the tridimensional BO_6 network is

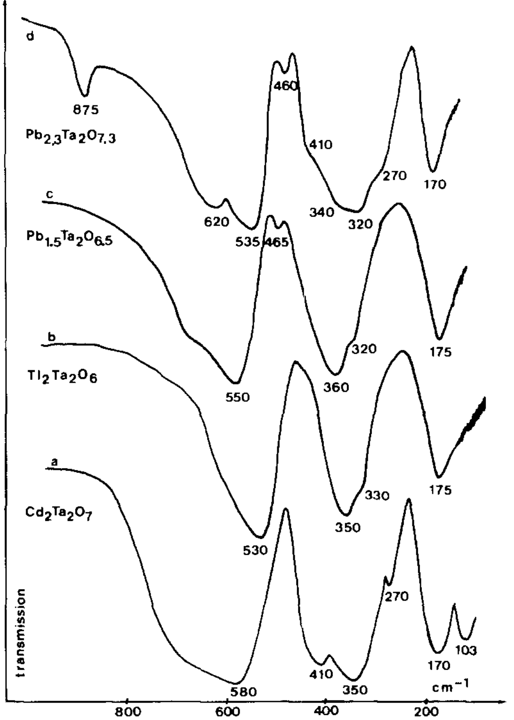

FIG. 3. Infrared absorption spectra of the studied compounds.

TABLE II

OBSERVED FREQUENCIES AND THEIR ASSIGNMENT FOR THE DIFFERENT TANTALATES

	$Cd_2Ta_2O_7$		$Tl_2Ta_2O_6$	$Pb_{1.5}Ta_2O_{6.5}$		$Pb_{2.3}Ta_2O_{7.3}$		
Mode	ir	Raman	ir	ir	Raman	ir	Raman	Assignment
						890	892	Ta–O (terminal)
						612	705	Ta–O (edge-sharing octahedra)
F_{1u}	580		530	550		530		Ta–O
F_{2g}		575			580			
$F_{2g} + A_g$		524			518 + 510		522	Ta–O + O–Ta–O
F_{1u}	410		350	360		458		
F_{1u}	350		330	320		320		
E_g		333			330		356	
F_{2g}		298			302		290	Pyrochlore
F_{1u}	170		175	175		175		
F_{1u}	270		x	NO^a		NO^a		A–O′ + O–A–O′
F_{2g}		245			242–200		246	
F_{1u}	103		NO^a < 100	78		NO^a < 100		A–O + A–O′ + O–A–O + O–A–O′
F_{1u}	70		NO^a < 100	50		NO^a < 100		
					118		135–128	Pb–O of a new type or Pb–Pb
					62		65–50	

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[a] NO = Not observed.

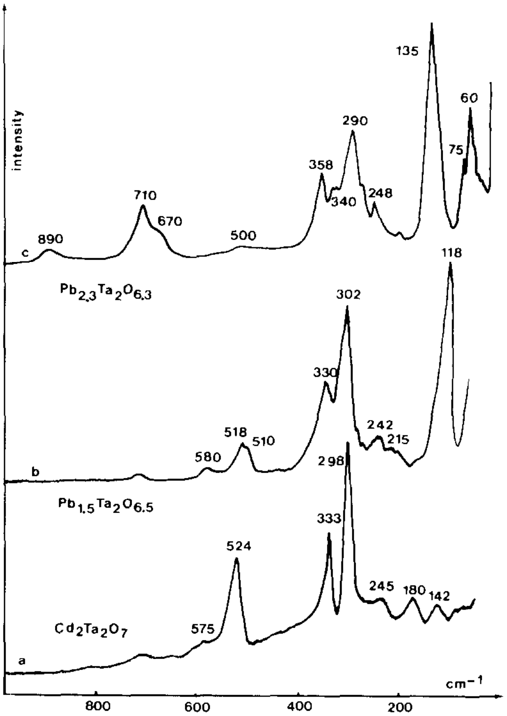

FIG. 4. Raman spectra of the studied compounds.

identical, as in the ideal structure, the profile of the spectra remains quite unchanged (Figs. 3a,b,c; Figs. 4a,b); we note that only two frequencies, observed at 580 and 410 cm^{-1} in $Cd_2Ta_2O_7$ are shifted to about 530 and 360 cm^{-1} in $Tl_2Ta_2O_6$ and $Pb_{1.5}Ta_2O_{6.5}$. Frequencies assigned to *A*–O stretching or O–*A*–O bending modes are also very close for these three tantalates. Therefore, even an important perturbation of the A_4O' network has a weak influence on the BO_6 network and on the rigidity of the structure. From a vibrational point of view, the two networks are practically energetically independent.

When the regular packing of the BO_6 octahedra network is broken by shear planes, the vibrational spectra exhibit important modifications (Fig. 3d; Fig. 4c); the principal feature is the appearance of two new frequency ranges at about 890 and 700–640 cm^{-1}. One of the present authors (E. H.) has studied various families of niobates and tantalates with different types of linkage of the BO_6 octahedra together (*19*) and therefore different types of bonding. By comparison with these studies, we can assign the frequencies at 890 cm^{-1} to the stretching of short terminal Ta–O bonds; their force constant should be close to 5 N · cm^{-1}. The range 700–640 cm^{-1} is characteristic of strong Ta–O–Ta bridged bonds such as those encountered in structures exhibiting a edge-sharing linkage of the BO_6 octahedra; their force constant should be close to 2.5 N · cm^{-1}. The vibrational spectra of the perovskite $Ca_2Nb_2O_7$ where the same type of shear planes exists, also exhibit additional modes at 880 and 720 cm^{-1} (*20*). The

TABLE III

PRINCIPAL CALCULATED FORCE CONSTANTS

Definition		$Cd_2Ta_2O_7$		$Tl_2Ta_2O_6$		$Pb_{1.5}Ta_2O_{6.5}$	
d	Ta–O	1.45		$d - d^0 = 1.18$		1.57	
d^0	O–Ta/Ta–O[a]	0.16				0.15	
a	O–Ta–O	1.21	1.08	0.73	0.82	0.96	0.98
a′		0.95		0.90		1.00	
D	*A*–O	0.125		0.11		0.13	
b	O–*A*–O	0.08		0.10		0.06	
D′	*A*–O	0.30		x		0.06 or 0.14	
b′	O–*A*–O′	0.17		x		0.06	

[a] Bond angle: 180°.

observation of a frequency range at about 700 cm^{-1} in perovskite or pyrochlore compounds which are BO_6 octahedra corner-sharing structures, may be due to a strengthening of the non-terminal Ta–O bonds situated along the shear planes.

Vibrational spectroscopy is a very useful technique to reveal the existence of such defects; while electron microscopy studies are absolutely necessary to show shear planes, the record of vibrational spectra is a simple and fast experiment making it possible to confirm whether or not these defects are present, something not rapidly revealed on X-ray films.

The A_4O' tetrahedra network is more difficult to study insofar as it contributes weakly to vibrational energy and therefore to the profile of the spectra:

—In the ideal pyrochlore, only two modes are characteristic of it: the Raman line at 240 cm^{-1} and the ir band at 270 cm^{-1}.

—Moreover, when this network is perturbed, A cations and oxygen atoms O′ may be displaced from their ideal position, creating in the crystal a large distribution of A–O bonds having different lengths and a different chemical environment. This fact can explain the observation of low frequency modes, particularly on Raman spectra. But according to various authors, Maroni and Spiro, for example (*21, 22*), these features may also be assigned to the existence of Pb–Pb bonds; Maroni and Spiro observed, on the Raman spectra of $Bi_6(OH)_{12}^{6+}$ and $Pb_4(OH)_4^{4+}$ in the low-frequency range, intense lines that they assigned to Bi–Bi or Pb–Pb bonding. On the other hand, it is interesting to report here the results obtained for the vibrational study of lead oxides PbO_α, PbO_β, and Pb_3O_4 (*23, 24*). In these oxides, Pb–O bonds stretching modes are observed above 200 cm^{-1} but Pb–Pb "interactions" play an important role: they are responsible for most modes observed below 200 cm^{-1} and among them, intense Raman lines at about 145 and 80 cm^{-1} in PbO_α and PbO_β (*23*) and at 121 and 74 cm^{-1} in Pb_3O_4 (*24*). In these compounds, the "Pb–Pb interactions" have been described in fact as a quadrupolar interaction between two Pb^{2+} cations and their lone pairs. It is possible that such interactions exist in the lacunary compound $Pb_{1.5}Ta_2O_{6.5}$ and also in $Pb_{2.3}Ta_2O_{7.3}$ along the shear planes.

Conclusion

All of our work using ir absorption and Raman scattering techniques undertaken on various families of pyrochlore compounds has led us to study about 30 oxides exhibiting an ideal structure or a structure with disorder or defects. Our previous paper on ideal pyrochlore families (*1*) permitted us (i) to assign the observed frequencies, (ii) to find out the force field in these structures, (iii) to bring complementary structural information about the statistical position of cations in some families, and (iv) to show that the two networks BO_6 octahedra and A_4O' tetrahedra are energetically independent. The present study has shown the influence of structural defects in a pyrochlore phase upon the vibrational spectra and the force field. The ir and Raman scattering are complementary techniques to X-ray diffraction and electron microscopy because they reveal short-range order and can therefore indicate the existence of new types of chemical bonds created in the structures by the defects.

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