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Letter

Vibrational spectra of Sn_2TiO_4 Enrique J. Baran^{a,*}, Ana C. González-Baró^a, Nobihiru Kumada^b,
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ABSTRACT

The infrared and Raman spectra of the recently synthesized tin(II) titanate, Sn_2TiO_4 , were recorded and briefly discussed on the basis of its structural peculiarities.

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1. Introduction

Double oxides containing transition metals and Sn(II) are relatively scarce [1] and, in particular, mixed titanium(IV)/tin(II) oxides were not known until recently when a material of composition Sn_2TiO_4 could be prepared and characterized [2].

On the other hand, only a reduced number of oxometallates containing octahedral TiO_6 -units has been thoroughly investigated by vibrational spectroscopic methods [3–5]. Therefore, this new material offers a good opportunity to advance in a better knowledge of the vibrational properties of this type of oxide moieties.

2. Experimental

Black stick shaped single crystals of Sn_2TiO_4 were obtained by high temperature solid state reaction working with stoichiometric amounts of TiO_2 , K_2CO_3 and SnCl_2 in an evacuated quartz tube, as described earlier [2]. The obtained samples were characterized by X-ray powder diffractometry.

The infrared spectra in the range $4000\text{--}400\text{ cm}^{-1}$ were recorded with a FTIR-Bruker-EQUINOX-55 instrument, using the KBr pellet technique. Spectra measured with suspensions of the compounds in Nujol mulls gave identical results. Raman spectra in the same spectral range were measured on powdered samples using the FRA 106 Raman accessory of an IF66 Bruker spectrophotometer. Radiation from a Nd:YAG solid-state laser (1064 nm) was used for excitation.

3. Results and discussion

3.1. Structural characteristics

Sn_2TiO_4 crystallizes in the tetragonal system, space group $P4_2/mbc$ with $Z=4$ formula units per cell and it is structurally related to the low-temperature form of Pb_3O_4 [1,2,6]. The structure is built up by one-dimensional chains of slightly distorted TiO_6 -octahedra sharing edges along the c -axis and the chains are connected by Sn^{2+} cations having a stereochemically active electronic lone pair.

The TiO_6 units present four longer (1.986(7) Å) and two shorter (1.965(8) Å) Ti–O distances [2], showing that the actual symmetry of these groups is D_{4h} . On the other hand, the Sn(II) cations present a trigonal SnO_3 coordination with one longer (2.21(1) Å) and two shorter (2.093(6) Å) Sn–O distances [2].

3.2. Vibrational spectra

On the basis of the commented structural characteristics and in order to attempt an assignment of the vibrational spectra of Sn_2TiO_4 , it seems useful to make a spectral analysis based on the D_{4h} distortion of the quasi-octahedral TiO_6 units present in the material [7]. This correlation is presented in Table 1.

From the three active Raman vibrations, the MO_6 -octahedra usually shows a very strong and well-defined line, at the highest energy, corresponding to the totally symmetric M–O stretching ($\nu_1(A_{1g})$), whereas those at lowest energy corresponds to one of the

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Table 1Correlation between the vibrational modes of an octahedral O_h -species and the derived D_{4h} -species.

TiO ₆ -octahedron	TiO ₆ -D _{4h} -symm.
A _{1g}	A _{1g}
E _g	A _{1g} + B _{1g}
F _{1u}	A _{2u} + E _u
F _{1u}	A _{2u} + E _u
F _{1g}	B _{2g} + E _g
F _{2u}	B _{2u} + E _u
Activity	
A _{1g} , E _g , F _{1g} : Ra	A _{1g} , B _{1g} , B _{2g} , E _g : Ra
F _{1u} : IR; F _{2u} : ia	A _{2u} , E _u : IR; B _{2u} : ia

Table 2Description of the vibrational modes of the TiO₆-moieties with *trans*-D_{4h}-symmetry.

Vibrational mode	Description	Activity
ν_1 (A _{1g})	ν_s (Ti-O _{equatorial})	Raman
ν_2 (A _{1g})	ν_s (Ti-O _{axial})	Raman
ν_3 (A _{2u})	ν_{as} (Ti-O _{axial})	IR
ν_4 (A _{2u})	π (TiO ₄)	IR
ν_5 (B _{1g})	ν (TiO ₄)	Raman
ν_6 (B _{2g})	$\delta_{sciss.}$ (TiO ₄)	Raman
ν_7 (B _{2u})	δ (TiO ₄)	Inactive
ν_8 (E _g)	$\delta_{sciss.}$ (TiO ₆)	Raman
ν_9 (E _u)	ν_{as} (TiO ₆)	IR
ν_{10} (E _u)	δ (Ti-O _{equatorial})	IR
ν_{11} (E _u)	δ (Ti-O _{axial})	IR

deformational modes (ν_5 (F_{1g})). Between these two lines a second M–O stretching (ν_2 (E_g)), usually with very low intensity, is found [8].

The IR spectrum generally presents two strong and relatively broad bands corresponding to the antisymmetric M–O stretching (ν_3 (F_{1u})) and bending (ν_4 (F_{1u})) vibrations. The remaining F_{2u} mode, corresponding to another deformational mode, is inactive.

In the case of D_{4h}-symmetry, and as shown in Table 1, splitting of the double and triple degenerated vibrational modes are expected, and concomitant band splitting, in relation to the O_h schema, can be predicted. Concretely, in this case five Raman active and five infrared active bands related to the TiO₆ vibrations in the Sn₂TiO₄ lattice are expected. The origin of these bands is described in detail in Table 2 and the characteristics of these vibrational modes are nicely depicted in an earlier paper of Preetz et al. [9].

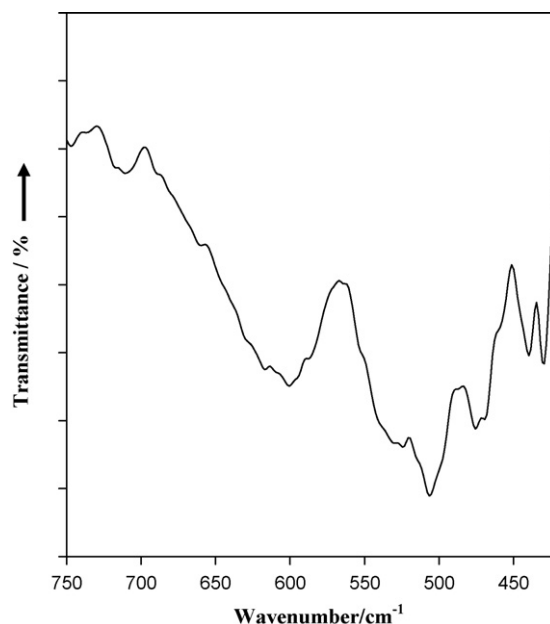
The FTIR and Raman spectra of one of the measured Sn₂TiO₄ samples are shown in Figs. 1 and 2, respectively. A first inspection of the IR spectrum immediately shows the presence of two strong and relatively broad bands centered at about 600 and 500 cm⁻¹, which are usually considered as characteristic of non-isolated octahedral TiO₆ moieties [4,10].

The proposed assignment is shown in Table 3, and briefly discussed as follows:

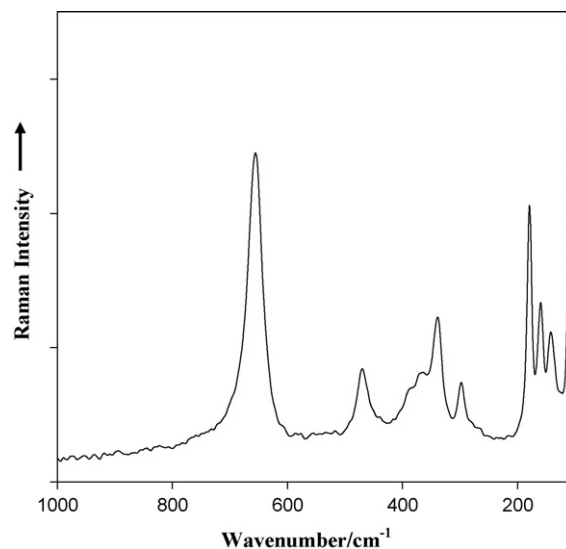
Table 3Wavenumbers (in cm⁻¹) and assignment of the vibrational spectra of Sn₂TiO₄.

IR	Raman	Assignment
618 sh	655 vs	ν_1 (A _{1g}), ν_2 (A _{1g}) (?)
600 vs, br		ν_3 (A _{2u})
530 m		ν_9 (E _u)
506 vs		ν_4 (A _{2u})
476 s, 470 sh		ν_{10} (E _u)
	470 s	ν_{11} (E _u)
440 m, 430 s		ν_8 (E _g)
	380 sh, 360 m	ν_6 (B _{2g})
	339 s, 298 m	
	180 vs, 160 s, 142 m, 108 vs	Lattice vibrations

vs, very strong; s, strong; m, medium; br, broad; sh, shoulder.

**Fig. 1.** FTIR spectrum of Sn₂TiO₄ in the spectral range between 750 and 400 cm⁻¹.

- The strongest Raman line can be confidently assigned to totally symmetric stretching vibration of the four equatorial Ti–O bonds.
- The two components derived from the octahedral E_g mode (A_{1g} + B_{1g}) could not be identified. The A_{1g} component may be eventually overlapped with the ν_1 (A_{1g}) vibration, as suggested in Table 3, whereas the other one probably does not attain enough intensity.
- In the IR spectrum the two components of the original F_{1u} modes ($\nu_3 + \nu_9$ and $\nu_4 + \nu_{10}$, respectively) lie close together, as expected. The ν_{11} (E_u) mode lies near to ν_{10} , in agreement with their similar origin. The observed weak splitting of this band may be a consequence of a site-symmetry effect.
- The situation is rather more complex for the components derived from the original F_{1g} mode, since in the region below 470 cm⁻¹ the TiO₄-vibrations can be coupled with SnO modes [11]. The active Raman vibration ν_8 (B_{2g}) apparently presents a similar energy than ν_{11} whereas the ν_6 (B_{2g}) mode is also seen as a weakly splitted doublet.

**Fig. 2.** FT-Raman spectrum of Sn₂TiO₄ in the spectral range between 1000 and 100 cm⁻¹.

As it can be seen from Fig. 2 and Table 3 the Raman spectrum shows some additional bands; those at 339 and 298 cm^{-1} can, eventually, be related to vibrational modes that retain a certain Sn–O character whereas the other four are surely external (“lattice”) vibrations.

4. Conclusion

In summary, the performed analysis of the IR and Raman spectra of Sn_2TiO_4 is clearly compatible with the structural characteristics of the compound, containing non-isolated and slightly distorted octahedral TiO_6 moieties, and extends our knowledge on the vibrational properties of this type of materials.

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