Journal of Physics and Chemistry of Solids 115 (2018) 1–5

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Vibrational and elastic properties of $Ln_2Sn_2O_7$ (Ln = La, Sm, Gd, Dy, Ho, Er, Yb, or Lu)

S. Akbudak [a,*], A.K. Kushwaha [b]

[a] Department of Physics, Faculty of Arts and Sciences, Adiyaman University, 02100 Adiyaman, Turkey
[b] Department of Physics, K.N. Govt. P.G. College, Gyanpur, Bhadohi 221304, India

ARTICLE INFO

Keywords:
Elastic property
Phonon
Stannate pyrochlore
Vibrational property

ABSTRACT

In this study, an eight-parameter bond-bending force constant model was used to calculate the zone center phonon frequencies, elastic constants, and related properties of the stannate compounds $Ln_2Sn_2O_7$ (Ln = La, Sm, Gd, Dy, Ho, Er, Yb, or Lu) with a pyrochlore structure. We found that the Sn—O bond strengths dominate the Ln-O and O—O bonds. We also found that all of the materials are ductile and anisotropic in nature. The anisotropic nature of the compounds increases in the order of: $La_2Sn_2O_7$ < $Sm_2Sn_2O_7$ < $Gd_2Sn_2O_7$ < $Dy_2Sn_2O_7$ < $Ho_2Sn_2O_7$ < $Er_2Sn_2O_7$ < $Yb_2Sn_2O_7$ < $Lu_2Sn_2O_7$.

1. Introduction

Due to their stability and carcinogenic characteristics, all of the organic materials and heavy metal ions present in industrial wastes are a potential threat to human health. Most of these contaminants are generally resistant to biological decomposition, especially dyes. Thus, it is difficult to remove them via known biological processes. However, chemical and biological processes such as chlorination, ozonization, absorption, and microfiltration are still effective for eliminating industrial wastes in various environments. Identifying effective methods for removing pollution from industrial waste is still a challenging problem. Thus, finding alternative effective methods and synthesizing new materials for this purpose are major research objectives, where one of the most effective recently developed approaches is photocatalysis [1–5].

Photocatalysts speed up photoreactions where oxidation is activated in the presence of ultraviolet light. In the presence of light, photocatalysis can remove harmful compounds by decomposing them into carbon dioxide and water. Photocatalysis can help to clean the environment without using fossil fuels and hazardous chemicals. Photocatalysts can be applied to different pollutants and they are highly efficient for cleaning the environment. Semiconductors and metal blends can also be used as photocatalysts. The valence electrons of photocatalysts are activated when they are exposed to sunlight. The waste energy from the activated electrons allows the electrons to cross to the valence band of the photocatalysts, and negatively charged electrons and positively charged vacancies are obtained. Thus, the photocatalyst gains the capacity for very strong reduction and oxidation.

Among the various compounds with semiconducting behavior, pyrochlore ($A_2B_2O_7$) lattice structured materials obtained at temperatures above 1300 °C have unique properties, which make them promising for applications in catalysis [6,7], superconductors [8,9], thermal barrier coatings [10–12], fuel cells [13,14], and nuclear waste removal [15] because of their low thermal conductivity and high temperature phase stability.

In recent years, the stannate pyrochlore $La_2Sn_2O_7$ compounds with a cubic structure have attracted much attention among experimental and theoretical researchers because of their possible applications. Thus, Zhang et al. synthesized lanthanide stannate pyrochlores $Ln_2Sn_2O_7$ (Ln = Y, La, Pr, Yb) via a hydrothermal method [16]. Qu et al. used phonon scattering theory to analyze the thermal conduction behavior of $A_2B_2O_7$-type pyrochlore structures [17] where the samples were prepared via a co-precipitation method. Li et al. synthesized and controlled the particle size of yttrium tin ($Y_2Sn_2O_7$) pyrochlores by using a soft chemical method [18]. Chen et al. fabricated $La_2Sn_2O_7$ via a hydrothermal method and they observed the photocatalytic performance of $La_2Sn_2O_7$ based on CO_2 reduction with H_2O [19]. Stranska et al. synthesized and investigated the properties of inorganic-based pyrochlore compounds obtained with different lanthanides using solid state reaction and suspension mixing of materials methods [20]. Wang et al. used a simple hydrothermal method to synthesize $Ln(IO_3)_3$ (Ln = Ce, Nd, Eu, Gd, Er, Yb) polycrystals and they showed that $Ln(IO_3)_3$ has excellent photocatalytic properties [21]. Chen et al. enhanced the photocatalytic

* Corresponding author.
E-mail address: salihakbudak19@gmail.com (S. Akbudak).

https://doi.org/10.1016/j.jpcs.2017.11.030
Received 5 July 2017; Received in revised form 28 November 2017; Accepted 30 November 2017
Available online 2 December 2017
0022-3697/© 2017 Published by Elsevier Ltd.

activity of $La_2Sn_2O_7$ for CO_2 reduction [22].

Liu et al. theoretically investigated the elastic stiffness, structural stability, and thermal conductivity of $La_2T_2O_7$ (T = Ge, Ti, Sn, Zr, Hf) based on first principles density functional theory calculations [23]. Pruneda and Artacho studied the elastic and structural parameters of $La_2X_2O_7$ (X = Ti, Zr, Hf, Sn) within the framework of density functional theory together with the local density approximation (LDA) method [24]. The zone-center Raman and infrared phonon frequencies were calculated for stannate pyrochlore compounds $A_2Sn_2O_7$ (A = La, Sm, Yb, Lu) by Gupta et al. [25] using a short range force constant model, where the zone center phonons were calculated using six stretching and three bending force constants.

The stannate $Ln_2Sn_2O_7$ compounds (Ln = La, Sm, Gd, Dy, Ho, Er, Yb, or Lu) with pyrochlore structures have interesting properties that may be useful in various areas, such as spintronics and catalysis, but few theoretical studies have considered these compounds. Experimental studies are expensive and they may require numerous trials, so theoretical studies that provide insights into the technological applications of pyrochlore structures are of great importance. Therefore, in this study, we used an eight-parameter bond-bending force constants model to calculate the zone-center Raman and infrared phonon frequencies, elastic constants, and related properties.

2. Crystal structure and potential model

The ideal pyrochlore structure $La_2Sn_2O_7$ crystallizes in a cubic structure with space group Fd3m and the unit cell contains eight molecules. The cations A and B are metals that occupy the positions at sites 16d (1/2, 1/2, 1/2) and 16c (0, 0, 0). The anions, i.e., oxygen, occupy the positions at sites 8f (x, 1/8, 1/8) and 8b (3/8, 3/8, 3/8). The pyrochlore structure permits a broad range of atomic substitutions at the A, B, and O sites, and thus these compounds have many unique properties.

Group theoretical analysis provides the total number of zone center modes that are present for each species of the space group:

$$\Gamma = A_{1g} + E_g + 2F_{1g} + 4F_{2g} + 3A_{2u} + 3E_u + 8F_{1u} + 4F_{2u}, \quad (1)$$

where A_{1g}, E_g, and $4F_{2g}$ are Raman active modes, $8F_{1u}$ are infrared active phonon modes, and $2F_{1g}$, $3A_{2u}$, $3E_u$, and $4F_{2u}$ are optically inactive phonon modes.

The potential energy ϕ of the $La_2Sn_2O_7$ can be expended using the Taylor series and written as:

$$\phi = \sum_{lmn}\left[\frac{1}{r}\left(\frac{d\phi}{dr}\right)_{|r|=|r_k|}\left\{r^{\circ}_{lmn}(S_{lmn}-S_{\circ})\frac{1}{2}|S_{lmn}-S_{\circ}|^2\right\} + \frac{1}{2}\left\{\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi}{dr}\right)\right\}_{|r|=|r_k|}\left\{r^{\circ}_{lmn}\cdot(S_{lmn}-S_{\circ})\right\}^2\right], \quad (2)$$

where $\mathbf{S_0}$ and $\mathbf{S_{lmn}}$ are the displacements of the central ion and its first neighbor ions from their equilibrium position, respectively, r°_{lmn} represents the position coordinates of neighboring ions in equilibrium, l, m, and n, represent the direction cosines of the line joining the central ion and the nearest neighbor ions, and $|\mathbf{r_k}|$is the nearest neighbor distance.

Let A_k be the bond-stretching force constant defined by the second derivative of the potential energy ϕ as follows.

$$\frac{e^2}{V}A_k = \left.\frac{d^2\phi}{dr^2}\right|_{|r|=|r_k|} \quad (3)$$

The bond-bending force constant B_k is expressed as the first derivative of the potential energy ϕ:

$$\frac{e^2}{V}B_k = \left.\frac{1}{r}\frac{d\phi}{dr}\right|_{|r|=|r_k|}, \quad (4)$$

where k = 1, 2, 3, and 4 for the first, second, third, and fourth neighbors, respectively.

3. Results and discussion

3.1. Optical properties (phonons at Γ = 0)

We considered four bond-stretching and four bond-bending interactions, i.e., A_1, A_2, A_3, and A_4, and B_1, B_2, B_3, and B_4, between the ions Sn—O, Ln—O (Ln = La, Sm, Gd, Dy, Ho, Er, Yb, or Lu), O—O, and O—O′. Four bond-stretching (A_1, A_2, A_3, and A_4) and four bond-bending (B_1, B_2 B_3, and B_4) force constants were calculated for the compounds by using the experimental values of the Raman modes A_{1g} [25] and the infrared modes F_{1u} [25,26] at the zone-center as input data for $La_2Sn_2O_7$, $Sm_2Sn_2O_7$, $Yb_2Sn_2O_7$, and $Lu_2Sn_2O_7$. The experimental values of A_{1g} have not been reported for $Gd_2Sn_2O_7$, $Dy_2Sn_2O_7$, $Ho_2Sn_2O_7$ and $Er_2Sn_2O_7$, so we considered that the force constant between O—O′ for the

Table 2
Experimental and calculated Raman active modes for $Ln_2Sn_2O_7$ (Ln = La, Sm, Gd, Dy, Ho, Er, Yb, or Lu).

System	A_{1g}	E_g	$F_{2g}(1)$	$F_{2g}(2)$	$F_{2g}(3)$	$F_{2g}(4)$
$La_2Sn_2O_7$						
This study	497	342	605	532	415	301
Exp. [25]	495	340	600	530	416	304
Cal. [23]	511	354	613	512	384	306
$Sm_2Sn_2O_7$						
This study	503	347	612	533	410	305
Exp. [25]	500	344	608	530	410	308
Cal. [25]	520	365	623	512	387	307
$Gd_2Sn_2O_7$						
This study	504	352	615	534	412	306
$Dy_2Sn_2O_7$						
This study	505	356	617	534	413	307
$Ho_2Sn_2O_7$						
This study	507	358	619	535	414	307
$Er_2Sn_2O_7$						
This study	509	360	621	536	414	309
$Yb_2Sn_2O_7$						
This study	511	362	622	536	416	310
Exp. [25]	508	360	618	530	417	312
Cal. [25]	528	377	632	515	395	301
$Lu_2Sn_2O_7$						
This study	512	363	624	537	417	309
Exp. [25]	510	360	620	530	418	312
Cal. [25]	527	379	632	517	396	301

Table 1
Values of the force constants (kdynes/cm) for $Ln_2Sn_2O_7$ (Ln = La, Sm, Gd, Dy, Ho, Er, Yb, or Lu).

Compound	A_1 Sn—O	B_1 Sn—O	A_2 Ln—O	B_2 Ln—O	A_3 O—O	B_3 O—O	A_4 O—O′	B_4 O—O′
$La_2Sn_2O_7$	51.31	7.18	48.67	5.78	23.12	2.68	20.14	1.97
$Sm_2Sn_2O_7$	58.19	7.93	53.86	6.93	18.56	1.94	16.98	1.53
$Gd_2Sn_2O_7$	60.49	8.63	56.52	7.34	17.13	1.82	15.86	1.19
$Dy_2Sn_2O_7$	62.11	9.04	57.95	8.02	15.98	1.65	15.65	1.19
$Ho_2Sn_2O_7$	63.89	9.58	60.01	8.99	14.24	1.59	13.77	1.19
$Er_2Sn_2O_7$	65.23	10.24	61.33	9.32	12.45	1.37	11.79	1.19
$Yb_2Sn_2O_7$	67.91	10.99	62.11	9.69	11.13	1.21	9.54	0.75
$Lu_2Sn_2O_7$	69.81	12.09	63.45	10.43	9.68	0.96	8.17	0.69

Download English Version:

https://daneshyari.com/en/article/7920381

Download Persian Version:

https://daneshyari.com/article/7920381

Daneshyari.com