Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Hiroaki Saito, Ryoichi Suzuki, Kaori Nishi, Hidemi Nagao, Kizashi Yamaguchi & Kiyoshi Nishikawa (2003): Molecular Dynamics Simulation of Metal Oxides Including Ag, Molecular Crystals and Liquid Crystals, 379:1, 501-506

To link to this article: http://dx.doi.org/10.1080/713738602

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 501-506

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090958

Molecular Dynamics Simulation of Metal Oxides Including Ag

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$AgPb_6CO_9$ crystal has been simulated by means of molecular dynamics calculational method. A new simple interatomics potential model for this crystal was developed so that the crystal structure remans quite stable for all the simulation time steps. By analysis of the mean squared displacement, we studied the atomic motions in this crystal structure in detail.

Keywords: Molecular Dynamics; superconductitity

INTRODUCTION

Since the discovery of high T_c superconductivity (SC), exotic superconductivity has become a focus of interest in physics and chemistry. In particular, Ba-La-Cu-O system[1] evoked a considerable interest on perovskite like mixed valency copper compounds.

Recently, we have investigated the field-induced superconductivity in molecular crystals by using a two-band model[2,3] and applied this two-band model to CuO_2 plane of copper oxides and the field-effect transister (FET) configuration of anthracene, quadruthiophene (QTP), and C_{60} crystals[4].

Since 1980, Ag compounds were termed solid electrolytes or superionic conductors, and this interdisciplinary research field became very active. According to Ratner and Nitzan[5], it is known that Ag compounds are characterized as follows: (i) the bondings show the high ionicity; (ii) the mobile ions are, generally, polarizable and heavy; (iii) the Debye temperature is low.

Recently, D. Djurek *et al.*, have investigated the powdered mixtures $PbCO_3$, $2PbO + Ag_2O$ and $PbCO_3$ prefired in CO_2 and annealed in $CO_2 + O_2$ atmosphere[6]. The samples exhibit resistive properties characteristic for superconductivity with room temperature T_c.

In this study, we pay attentions to Ag compounds and report the results of molecular dynamics (MD) calculations on $AgPb_6CO_9$ crystal. Most calculations are carried out with a simple tow-body potential and we could obtain the stable structure of this crystal. Its thermodynamic properties in MD calculations are briefly discussed.

THE STRUCTURE OF $AgPb_6CO_9$ CRYSTAL

From the X-ray analysis[6], the crystal structure is assumed to be hexagonal with Ag channels along hexagonal c-axis and carbon channels along edges of a hexagonal prism. Pb^{2+} cations are octahedrally coordinated by oxygen forming $(Pb_2O_3)^{2-}$ complexes with a rather short Pb-Pb distance of 3.21 Å. Oxygen octahedral are distorted sharing faces and vertices. From spatial considerations the hexagonal unit cell could be estimated a = 6 Å and c = 6.42 Å. The unit formula derived from proposed structure is shown in Figure 1 and atomic positions are shown in Table 1.

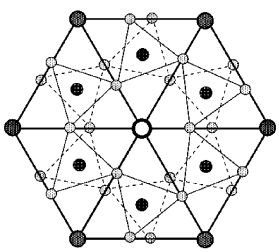

FIGURE 1 Structure of $AgPb_6CO_9$.

TABLE 1. Atomic positions in unit cell [6].

	x	y	x		x	y	z		x	y	z
Ag	0	0	0	C2	1	1	-1/2	O4	0.6	0	-1/2
Pb1	3/4	3/8	0	O1	0	0.4	1/2	O5	1	0.6	-1/2
Pb2	3/8	3/4	0	O2	0.4	1	1/2	O6	0.4	0.4	-1/2
C1	1	0	1/2	O3	0.6	0.6	1/2				

POTENTIAL MODEL

The $AgPb_6CO_9$ crystal structure consists of Ag, Pb, C, and O atoms with different ionic charges. The simple 2-body potential energy function $\Phi(r_{ij})$ without the weak van der Waals interaction is used to represent the complicated interatomic interactions of the system;

$$\Phi(r_{ij}) = \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}} + f_0(b_i + b_j)\exp\left[\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right].$$

Here, the first term is the coulombic potential between two charged ions, whereas the second term is the short-range repulsive potential of the Gilbert-Ida-Busing type describing an overlap repulsion of the electron cloud. ε_0 is the dielectric constant of vacuum and $r_{ij} = | r_i - r_j |$ is an inter-atomics distance of ions i and j. z_i, a_i and b_i are the ionic charge, the ionic radius and the ionic softness parameter of ion i, respectively. f_0 is a constant that sets the appropriate dimensions.

We have optimized the potential parameters a_i and b_i to maintain the $AgPb_6CO_9$ crystal structure in an equilibrium state. Values of the potential parameters used in our calculations are summarized in Table 2.

TABLE 2 The parameter set of the two-body potential.

	Ag	Pb	C	O
z	2	2	4	-2
a(Å)	1.79	1.61	1.80	1.60
b(Å)	0.086	0.090	0.085	0.085
f_0 ($JÅ^{-1}\ mol^{-1}$)			$4.18605*10^3$	

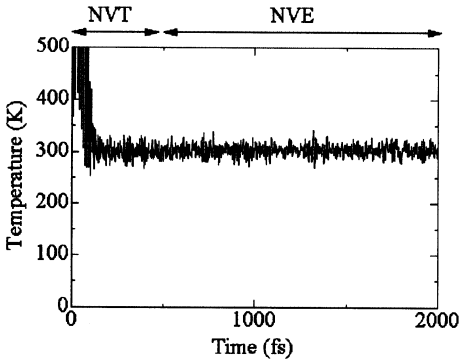

FIGURE 2 The plot of variation temperature vs. time step.

MOLECULAR DYNAMICS SIMULATION

MD calculations were carried out for the $AgPb_6CO_9$ crystal using the program IEMD2[7]. The Verlet algorithm (velocity form) was utilized to integrate the equations of atomic motions[8,9]. The MD basic cell was made up of 1×1×3 unit cells, in which 308 atoms are included.

Calculations were carried out under the standard constant volume condition while keeping the temperature constant by velocity scaling method (NVT ensemble). Simulation was performed for 10000 time steps (corresponding to 20ps) in total, where one MD time step was taken as 2.0 fs (=•τ). To achieve a thermal equilibrium state, the system was stabilized at the constant temperature of 300K for 500 MD time steps (NVT), and then the system was calculated for following 9500 MD time steps under the microcanonical condition without temperature control (NVE ensemble). The variation of temperature as a function of time step is shown in Figure 2. The temperature becomes quite stable at the NVE condition ; the average temperature was found to be around 300 K. To analyze the particle dynamics, we calculated the mean squared displacements (MSD). MSD as a function of time step for Ag, Pb, C and O atoms are shown in Figure 3. All MSD values are almost constant. Hence, all atoms vibrate around the initial position, however C atom is weakly held at the initial position and vibrates with rather large amplitude.

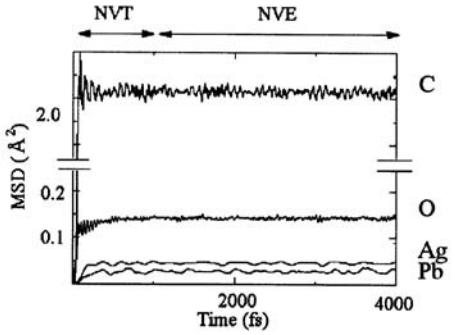

FIGURE 3 Mean squared displacements of Ag, Pb, C and O atoms for $AgPb_6CO_9$ crystal.

CONCLUSION

Here we performed the MD calculations for the $AgPb_6CO_9$ crystal. The set of repulsive potential parameters was optimized so as to retain and keep the $AgPb_6CO_9$ structure in an equilibrium state. Starting from the experimentally determined atomic positions for this crystal, the calculated MSD values Ag and Pb atoms were found to be less than 0.05 $Å^2$, the MSD of O atoms was about 0.14 $Å^2$, and the MSD of C atoms was about 2.20 $Å^2$ at the equilibrium state (= 300K).

In summary, we have developed a simple potential model for $AgPb_6CO_9$ crystal and simulated the complicated $AgPb_6CO_9$ crystal system using the MD calculation method; our resultant potential successfully reproduces the complicated $AgPb_6CO_9$ crystal structure with a stable equilibrium configuration.

Acknowledgements

H. N is grateful for a financial support of the Ministry of Education, Science and Culture of Japan (Research No. 12020234 and No. 13740328). H. N and K. Y. are grateful for financial support of the Ministry of Education, Science and Culture of Japan (Research No. 10146101 and Research No. 10149105).

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