LOW TEMPERATURE HEAT CAPACITIES OF MECHANICALLY ALLOYED La-DOPED PbWO₄ SYSTEM

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Abstract

Heat capacity measurements were carried out on $Pb_{1-x}La_xWO_{4+x/2}$ (x=0.2) and $Pb_{1-x}La_{2x/3}WO_4$ (x=0.2, 0.5) solid solutions prepared by sintering and mechanical alloying (MA) methods. For all the solid solutions, sintered samples showed slightly larger heat capacity around 100 K in comparison with MA samples, which was presumably caused by the excitation of mobile oxide ion motion. For sintered scheelite-type structured $PbWO_4$s, high-temperature synthesis introduced oxide ion interstitials even for the $Pb_{1-x}La_{2x/3}WO_4$ system, which resulted in the excess heat capacity at low temperature for excitation. On the other hand, for the samples prepared by room-temperature MA technique, oxide ion seemed to occupy the regular sites rather than interstitial ones and excess heat capacities were not observed.

Keywords: defect structure, heat capacity, mechanical alloying, oxide ion conductor, PbWO₄, scheelite-type structure

Introduction

The conduction property of PbWO₄ with the scheelite-type structure was rather of a poor electronic nature. A large enhancement in oxide ion conduction occurs at high temperatures when the lanthanum ions are partly substituted for the lead site as typically represented by $Pb_{1-x}La_xWO_{4+x/2}$ or $Pb_{1-x}La_{2x/3}WO_4$ [1–3]. The transport numbers of these materials are approximately unity for both types of substitution. Powder density measurements and the neutron diffraction experiments revealed that, in the former system, oxide ion interstitials were formed to compensate the charge balance for the lanthanum substitution, which would facilitate the oxide ion conduction [2, 4]. Neutron diffraction study showed that oxide ion interstitials seemed to localize at a little shifted position from the center of quasi-fluorite subcell at room temperature [5]. On the other hand, in the latter system, $Pb_{1-x}La_{2x/3}WO_4$, cation deficiency would

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play an important role of the charge compensation. Room-temperature neutron diffraction study also predicted that oxide-ion interstitials were unlikely to be created in lattice for this system [5]. Nevertheless, small amounts of oxide ions were supposed to occupy the interstitial site for Pb$_{1-x}$La$_{2x/3}$WO$_4$ at high temperatures [2], assuming that conduction mechanism of Pb$_{1-x}$La$_{2x/3}$WO$_4$ system is essentially the same as that of Pb$_{1-x}$La$_x$WO$_{4+x/2}$ system, i.e. oxide ions were transferred through the interstitial site.

Recently, we have showed that the mechanical alloying (MA) method using high-energy ball mills was available for preparing the scheelite-type structured PbWO$_4$s [4]. As relatively sharp X-ray diffraction peaks of single phase could be observed for the MA samples, the resultant materials of MA sample were supposed to be rather homogeneous solid solutions, and would be suitable for discuss about the defect structure and physicochemical properties. In Pb$_{1-x}$La$_x$WO$_{4+x/2}$ system, mechanically alloyed samples showed smaller powder densities in comparison with the sintered samples, while those obtained by two types of synthesis route were found to coincide in Pb$_{1-x}$La$_{2x/3}$WO$_4$ system. Therefore, the MA samples would be difficult to contain the oxide-ion interstitials, if oxide ions prefer to occupy the regular sites rather than the interstitial positions in scheelite-type structure. In view of the defect investigations, especially for the ionic conductors, it is meaningful to compare the physical and chemical properties of the sample sets with the same composition and with simply different defect structures. In the La-doped PbWO$_4$s, it is easy to prepare the different defect structured samples by using conventional sintering and MA methods. In the present study, we measured the low-temperature heat capacities of lanthanum-doped PbWO$_4$s prepared by sintering and MA methods, since sintering would not proceed during such a low temperature measurement and heat capacity data generally depend upon the bulk nature rather than macroscopic morphology such as closed pores.

Experimental

Pb$_{1-x}$La$_x$WO$_{4+x/2}$ (x=0.2) and Pb$_{1-x}$La$_{2x/3}$WO$_4$ (x=0.2 and 0.5) samples were obtained through the two types of preparation procedure, i.e. conventional sintering method and mechanical alloying (MA) one. In the former procedure, stoichiometric mixture of PbO, La$_2$O$_3$ and WO$_3$ powders were calcined at 973 K, then palletized and sintered again at 1123 to 1173 K for 10 h. The obtained sample pellets were cut into the thin plate shape for the heat capacity measurements. For MA method, PbO, La$_2$O$_3$ and WO$_3$ powders of stoichiometric composition were put into a zirconia pot with 30 zirconia balls of approximately 90 g in mass; the mass ratio of sample powder to balls was selected to be 1/10. MA experiments have been carried out with a planetary ball-milling machine (Fritsch P-5), which was operated at 260 rpm for 12 h. Obtained sample powders were compacted under the hydrostatic pressure of 200 MPa and cut into thin plate shape. To remove H$_2$O or CO$_2$ inclusion which might be introduced during milling, samples were allowed to be evacuated at 403 K.

Heat capacities were measured by relaxation-type calorimeter (Quantum Design, PPMS) in the temperature range from 4 to 300 K. Approximately 7 mg sample with 0.5 mm in thickness was placed on an alumina platform with Apiezon grease, which was

suspended on the heat sink via small wires. Heat capacity data are derived from fitting the temperature relaxation curve assuming two types of the relaxation time.

Results and discussion

Figure 1 shows the measured heat capacities of $Pb_{1-x}La_xWO_{4+x/2}$ (x=0.2), where circle and triangle symbols denoted those for MA and sintered samples, respectively. Both of them were very close and developed from almost zero at low temperatures toward the classical value (3NR) with increasing temperature. They were converted into Debye characteristic temperatures assuming 18 freedoms and were compared in the temperature range 50 to 150 K as shown in Fig. 2. Molecular mass of 442.979 g mol^{-1} was used for the both samples in this case. The MA sample was found to show slightly larger Debye temperatures than the sintered sample in this temperature range.
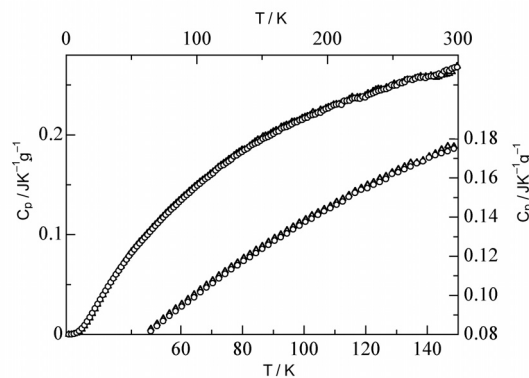

Fig. 1 Measured heat capacities of $Pb_{1-x}La_xWO_{4+x/2}$ (x=0.2) prepared by sintering (Δ) and MA (o) methods. The data in the temperature range from 50 to 150 K were also plotted in an enlarged scale
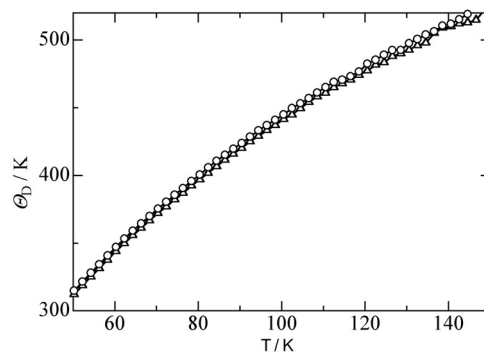

Fig. 2 Debye characteristic temperature of $Pb_{0.8}La_{0.2}WO_{4.1}$ prepared by sintering and MA methods, assuming 18 freedoms. 441.979 g mol^{-1} was used as the molecular mass for both samples

The obtained heat capacity difference was still larger than that of the standard deviation at fitting the relaxation curve or the precision of sample weighing. Structural defects in ionic conductors sometimes cause the extravibrational modes at low frequencies [6] and we had at first assumed that a large amount of defects introduced during milling would allow the lattice in the MA sample to be soft and decrease the Debye temperatures. However, the obtained data was inconsistent with the above assumption. As mentioned above, the most characteristic difference in structure between these two compounds were thought to be the number of oxide ion interstitials, and especially in this system, MA sample was supposed to contain a negligibly small amount of oxide ion interstitials. As the oxide ion interstitial apt to move easily rather than that of WO_4 tetrahedra, heat capacity enhancement of the sintered sample would be attributed to the excitation of oxide ion motion or low-frequency local vibration around the interstitial site.

Taking heat capacity of MA sample to be the normal one, a base-line was smoothly drawn based on the measured data of the MA sample. The excess heat capacity was obtained by subtracting the base-line from the measured data of sintered sample, and was shown as the circles in Fig. 3. Whereas the plots were considerably scattered above 200 K, heat capacity anomaly with a broad hump shape appeared around 100 K, which was similar to that of the Schottky-type anomaly. In the region below 20 K, the MA sample showed slightly larger heat capacities, which might be caused by the 'disordered' nature or slight amorphization in MA sample [7].
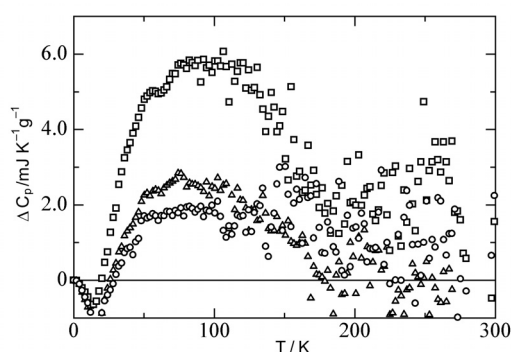

Fig. 3 Heat capacity differences between the sintered and the MA samples.
o – $Pb_{1-x}La_xWO_{4+x/2}$ (x=0.2); $\triangle$ – $Pb_{1-x}La_{2x/3}WO_4$ (x=0.2) and
□ – $Pb_{1-x}La_{2x/3}WO_4$ (x=0.5)

Heat capacity measurements were also carried out on another type of the system $Pb_{1-x}La_{2x/3}WO_4$, where the powder densities of the sintered and the MA samples were reported to coincide to each other [4], as mentioned in the Introduction. Figure 4 showed the heat capacities of $Pb_{1-x}La_{2x/3}WO_4$ (x=0.2) prepared by sintering (triangles) and MA (circles) methods. As made in the above system, the obtained heat capacity data were converted into the Debye characteristic temperatures and these data were
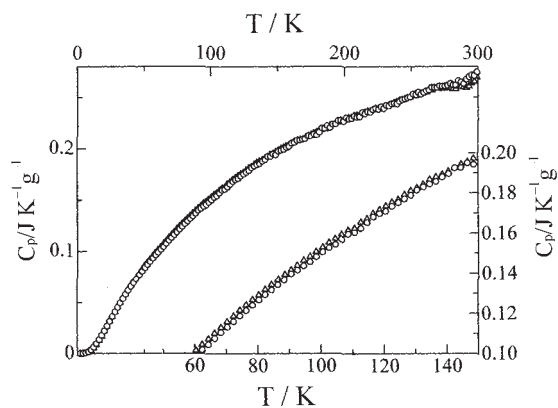
Fig. 4 Heat capacities of Pb$_{1-x}$La$_{2x/3}$WO$_4$ (x=0.2) prepared by sintering and MA methods. The data in the temperature range from 50 to 150 K were also plotted in an enlarged scale
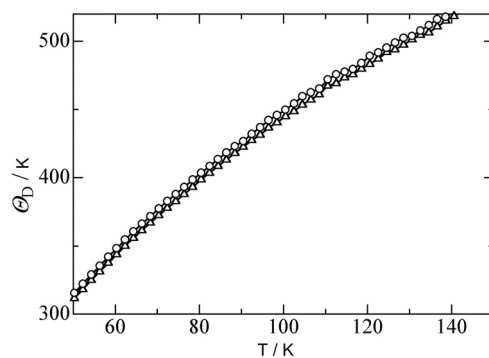

Fig. 5 Debye characteristic temperature of sintered (Δ) and MA (o) samples of Pb$_{1-x}$La$_{2x/3}$WO$_4$ (x=0.2) assuming 18 freedoms. Molecular mass was set to be 432.118 g mol^{-1} for both samples

compared in Fig. 5. It was found that in Pb$_{1-x}$La$_{2x/3}$WO$_4$ system, the Debye characteristic temperature of MA sample around 100 K was also a little larger than that of sintered sample like the above system. Therefore, there seemed to remain a small amount of oxide ion interstitials in the sintered sample and they would contribute to the heat capacity enhancement around 100 K. Considering that MA process was essentially performed at the room temperature while sintered sample had once undergone the high temperature treatment at the synthesis, oxide ion occupancy at the interstitial positions might be very low for the MA sample. Namely these observed heat capacity difference between two samples were supposed to be ascribed by the difference for the amount of oxide-ion interstitials introduced at high-temperature reaction.

To check the reproducibility, we made additional heat capacity measurements on the sample set for Pb$_{1-x}$La$_{2x/3}$WO$_4$ (x=0.5). The obtained Debye characteristic temperatures were represented in Fig. 6. In this composition, the MA sample also showed

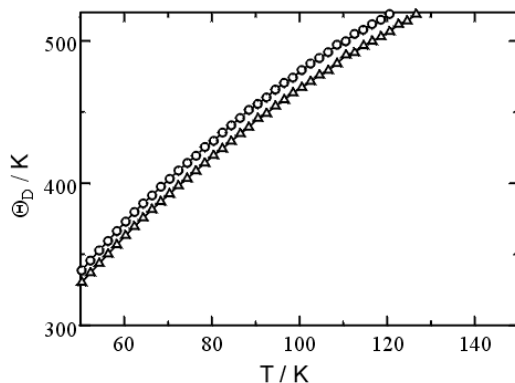**Fig. 6** Debye characteristic temperature of $Pb_{1-x}La_{2x/3}WO_4$ (x=0.5) prepared by
sintering (Δ) and MA (o) methods, assuming 18 freedoms. Molecular mass was
set to be 397.739 g mol^{-1} for both samples

larger Debye temperatures in comparison with the sintered one, the tendency of
which agreed with the results of the above compositions. Excess heat capacity also
showed broad hump shape as the rectangles in Fig. 3. Accordingly, it was confirmed
that in this system a small amount of oxide ion interstitials remained in the sintered
sample would contribute to the heat capacity anomaly around 100 K. While above
discussions were made between the sample sets with the same compositions, it was
difficult to explain the compositional dependence of heat capacity anomaly by such
qualitative discussions. Compared the excess heat capacities in Fig. 3, the enhance-
ment in heat capacity in $Pb_{1-x}La_{2x/3}WO_4$ system around 100 K seemed to be larger
than that of $Pb_{1-x}La_xWO_{4+x/2}$, whereas the latter system was supposed to contain a
larger amount of oxide ion interstitials. Moreover, the difference of Debye tempera-
ture was apparent in x=0.5 of $Pb_{1-x}La_{2x/3}WO_{4+x/2}$ (Fig. 6) in comparison with x=0.2
(Fig. 5), contrary to the ionic conductivity at high temperatures. However, in our
qualitative consideration, such discrepancies across the composition cannot be dis-
cussed. Indeed, distributions of lanthanum ions and cation vacancies depend on the
composition and the potentials around oxide ion interstitials would be altered. MD
simulation might provide some information about the compositional dependence of
anomalous heat capacity.

Conclusions

Heat capacity measurements were carried out on $Pb_{1-x}La_xWO_{4+x/2}$ (x=0.2) and
$Pb_{1-x}La_{2x/3}WO_4$ (x=0.2 and 0.5). In $Pb_{1-x}La_xWO_{4+x/2}$ system, the mechanically alloyed
sample showed slightly larger heat capacities around 100 K, which was supposed to
be ascribed to the low-frequency component related to the local vibration of oxide
ions around the interstitial site. Similar heat capacity enhancement for sintered sam-
ple was also observed in the $Pb_{1-x}La_{2x/3}WO_4$ (x=0.2, 0.5). Therefore a small amount of
oxide ions was incorporated to the interstitial sites for the sample prepared by

sintering method and the room-temperature prepared MA sample contains far less oxide ion interstitials.

In addition to these insights, we have showed that the low-temperature heat capacity measurement is an appropriate method to characterize the defect structure.

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