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Positron Annihilation Spectroscopic Studies of Cu_2Te Thermoelectric Material

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Abstract. Positron annihilation lifetime spectroscopy (PALS) and coincident Doppler-broadening spectroscopy (CDBS) have been used for investigating the evolution of vacancy-type defects in the thermoelectric material Cu_2Te which annealed at different temperatures. The results of PALS show that a fraction of positrons has got annihilated at the surfaces and the sample which annealed at 450 ˚C has the highest concentration of surface defects. The average positron lifetime and the S parameter have the same trends which gradually increase with the increase of the annealing temperature. This change implies that the total concentration of the defects has been changed with the change of the annealed temperatures. The results of the CDBS ratio spectrum and S-W plot indicate that the defect species have no change after annealing at different temperatures.

1. Introduction

Thermoelectric (TE) materials have attracted much attention because of their importance in solving environmental problems caused by burning fossil fuels and so on[1,4]. However, in most of the TE materials, the conversion efficiency is still too weak to be used for application. The efficiency of a TE material is decided by the dimensionless thermoelectric figure of merit that defined as $\mathrm{ZT} = \mathrm{S}^2\sigma T / \kappa$ (S, σ and κ are the Seebeck coefficient, electrical conductivity and total thermal conductivity, respectively). So in order to have high efficiency, we need to have low thermal conductivity ($\kappa = \kappa_\mathrm{L} + \kappa_e$, where κ_L is the lattice contribution and κ_e is the electronic contribution) and high power factors ($S^2\sigma$). Recent years, some laboratory results have suggested that high efficiency can be realized in several families of materials [5, 7]. Copper chalcogenides $Cu_{2-x}X$ (X=S, Se or Te), which have simple chemical formula but quite complex atomic arrangements, have been verified with high ZT . In such chalcogenides, the copper ions are highly disordered and superionic with liquid-like mobility, which could result in an intrinsically low lattice thermal conductivity and get high zT [8]. To our knowledge, other properties of such copper chalcogenides are still not very clear so far, which should to be intensively studied. We all know that the defects play a very important role in controlling some useful properties, so it is necessary to study the variation of the defects.

Positron annihilation spectroscopy (PAS) is highly sensitive to the change in properties of structural defects [9, 10]. The positron annihilation lifetime spectroscopy (PALS) and the coincident Doppler-broadening spectroscopy (CDBS) are the two most used methods, which are very efficient in giving important information of the vacancy defects, especially in semiconductor. In this work, we studied the Cu_2Te samples which were treated with different annealing temperatures.

2. Experimental details

The Cu_2Te samples were prepared following the method reported in *Refs. 8*. After that we obtained the powders and pressed them into green compacts, then the green compacts were annealed at different temperatures (400, 450 and500˚C) for 2 h in vacuum. Finally, the samples were down to the room temperature naturally. For convenience, the samples with different annealing temperatures of 400 ˚C, 450˚C and 500˚C are named as 1#, 2# and 3#, respectively.

The powder X-Ray diffraction (XRD) with Cu-Kα radiation (Rigaku-TTR III) was used for investigating the purity and crystallinity of all the samples. The defects were then studied through PALS and CDBS techniques. The PALS measurement was carried out using a 40 μCi ^{22}Na positron source which was sandwiched between the identical samples. The plastic scintillator coupled with photomultiplier tubes were used as detectors and the gamma-gamma coincidence spectrometer had a resolution of 230 ps. Each spectrum contained total counts of more than two million events to ensure the repeatability of the measurements. The CDBS measurement was undertaken using two HPGe detectors which had 1.5 keV energy resolutions at the energy of 511 keV. The counting rate approximately 100 cps and about eight million events were generated in each CDBS spectrum.

3. Results and discussion

Fig.1 shows the X-Ray diffraction patterns of the Cu_2Te samples annealed at different temperatures. They both crystallize in a hexagonal structure (PDF Card#:40-1325) and all of them exhibited excellent purity and phase composition. The results mean that the crystal structures of Cu_2Te have no changed after annealed at different temperatures.

A detailed study of the defects in the Cu_2Te samples was performed by PALS and the positron lifetime spectrum was fitted by LIMETIME9 program. Each spectrum was resolved into three components, which are summarized in Table 1. The longest lifetime τ_3 (~1ns) with negligible intensity I_3 (1.2%) is attributed to the ortho-positronium (o-Ps) annihilation at the surface of the samples or in the source. It hardly helps in giving some useful information of defects in the samples because of the small intensity, so it will be neglected in the following discussion. The shortest lifetime component τ_1 is around 258-270 ps, and it is generally attributed to the average value of lifetime that annihilation in defect-free crystal [11, 13]. The second lifetime τ_2 has a value between 400-420 ps, and in nanosized samples generally we attribute the lifetimes of the order of 400~600ps to the diffused surface defects [14]. From the Table 1 we can see that the lifetime almost has no change after annealing at different temperatures, which means the size of the vacancy clusters on the grain surfaces has no much change. I_2 is the relative intensity of τ_2 and it can be seen that the I_2 increases from 69.8% to 72.9% with increasing annealing temperature from 400˚C to 450˚C, and then decreases to 65.8% after annealing at 500˚C. This indicates that compared with the other two samples, the 2# sample has the highest concentration of surface defects. Average lifetime $\tau_m = (\tau_1 I_1 + \tau_2 I_2)/(I_1 + I_2)$ could present an overall reflection on the defects traps. Therefore, it could provide the details of defect distribution and the electronic structure in the materials. The variation of average positron lifetime τ_m is presented in Fig.2. It is showed that the value of τ_m gradually increases with the increase of annealing temperature, which means that the annealing temperature could influence the concentration of the defects.

In order to obtain more information and give a further support to the analysis above, we also carry out CDBS measurements in the Cu_2Te samples. The S-parameter as a function of the annealing temperature is shown in Fig.3, from which we can see that with the increase of the annealing temperature, the S-parameter increases slowly. The S-parameter reflects the annihilations with low-momentum valence electrons, so it also can reflect the relative concentrations of defects. Therefore, we can obtain the same conclusion about the defects evolution in both PALS measurement and CDBS measurement.

One-dimensional spectra are obtained from the CDBS and then they are divided by an identical spectrum, which is obtained from the defect-free 99.9999% purity Si sample. The results are shown in Fig.4. Some prominent peaks are shown in the ratio curves and the most prominent of them appears at ~11×10^{-3} m_0c.Generally, this peak mainly results from positron annihilation with the 2*p* electrons of oxygen ions that surrounding the cationic vacancies. We can see that the peak height has no obvious change with the change of annealing temperatures, which means the atomic structures of the defects have no change. To demonstrate this, we give the S-W plot, which can be used for distinguishing different defect species. The W parameter will depend linearly on the S parameter if only a single type of vacancy there. From the Fig.5 we can see that the data points fall on a line, indicating that the defect species have not changed after annealing. Thus both the results of the ratio curves and the S-W plot demonstrate that the defect species have no change after annealing at different temperatures.

4. Conclusion

In summary, a detailed study of the X-Ray diffraction and positron annihilation spectra have been used for investigating the properties of Cu_2Te thermoelectric material annealed at different temperatures. The conclusions have been summarized as follows:

(1) All the samples have the crystal structure of Cu_2Te without any other impurity phases within the limited detection.

(2) Compared with the other two samples, the 2# sample has the highest concentration of surface defects.

(3) The total concentration of detects increases with the increase of annealing temperatures.

(4) The results of S-W plot indicates the defect species have no changed after annealing at different temperatures.

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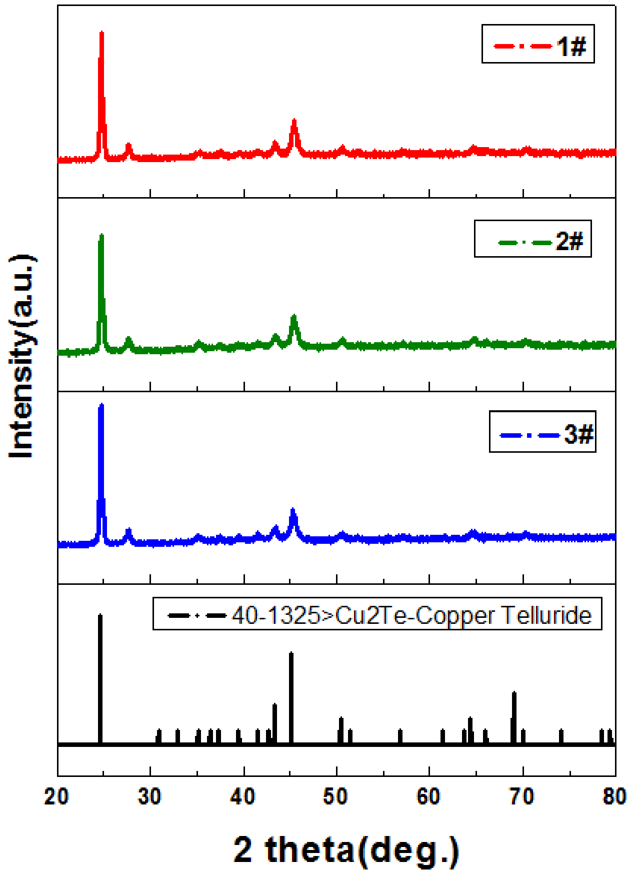

Fig.1 XRD spectra of the Cu_2Te samples.

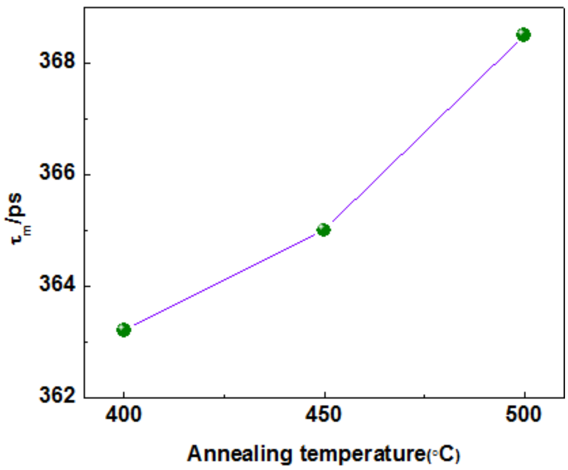

Fig.2 Average lifetime as a function of the annealing temperatures for Cu_2Te samples.

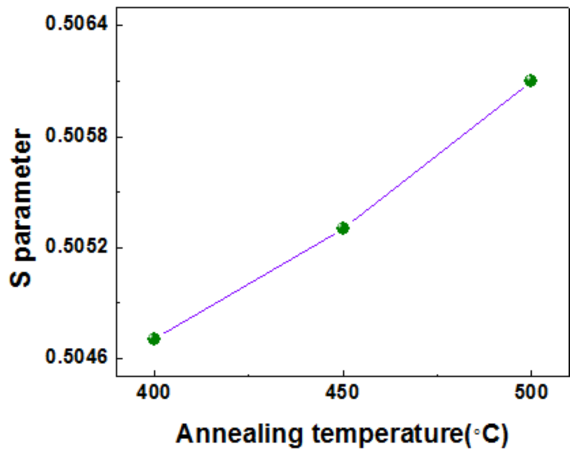

Fig.3 The S-parameter as a function of the annealing temperatures for Cu_2Te samples.

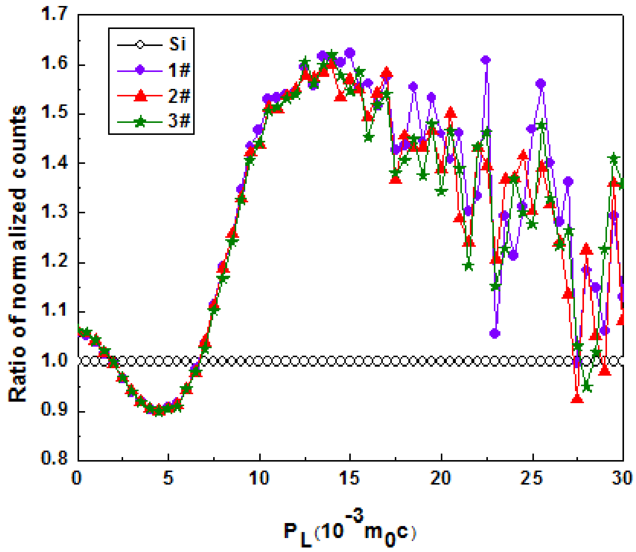

Fig.4 The ratio curves generated with respect to Si from the CDB spectra.

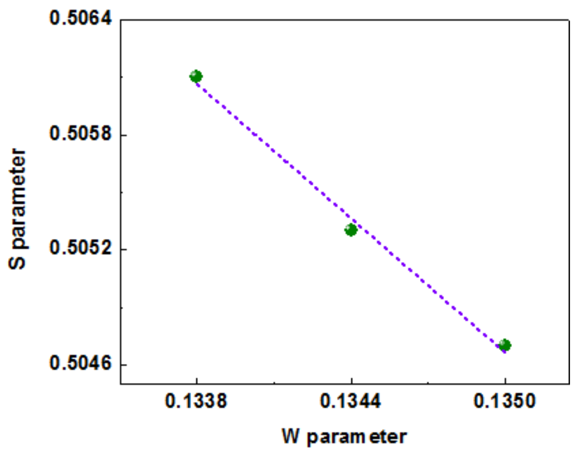

Fig.5 The variation of S- versus W-parameter for Cu_2Te samples.

Table 1 Positron lifetime results.

Sample	$\tau_1(ps)$	$I_1(\%)$	$\tau_2(ps)$	$I_2(\%)$	$\tau_3(ns)$	$I_3(\%)$
1#	259.3(0.0057)	29.9(1.5)	407.7(0.0021)	69.8(1.5)	1.41(0.14)	0.388(0.059)
2#	258(0.034)	25.9(9.7)	403(0.022)	72.9(9.7)	0.94(0.22)	1.2(1.0)
3#	270(0.022)	33.7(7.2)	419(0.016)	65.8(7.2)	1.31(0.33)	0.5(0.32)

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