Raman and X-ray diffraction studies of superconducting $FeTe_{1-x}Se_x$ compounds

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Abstract. Iron-based superconducting layered compounds have the second highest transition temperature after cuprate superconductors. Their discovery is a milestone in the history of high-temperature superconductivity and will have profound implications for high-temperature superconducting mechanism as well as industrial applications. We have measured X-ray diffraction and Raman spectra of poly-crystalline $FeTe_{1-x}Se_x$ samples with x = 0.0, 0.5 and 1 at room temperature. X-ray profile of FeTe and $FeTe_{0.5}Se_{0.5}$ confirmed the primitive tetragonal unit cell. FeSe is found to be in double phase with tetragonal phase (about 66.62%) and orthorhombic (33.38%). A_{1g} and B_{1g} phonon modes were observed in Raman spectra. At room temperature, these lines are located at 95 and 130 cm^{-1} for FeTe, 93 and 129 cm^{-1} for $FeTe_{0.5}Se_{0.5}$ and 93 and 129 cm^{-1} for FeSe samples.

1. Introduction

The recent discovery of superconductivity in quaternary, rare-earth transition-metal oxypnictides, and especially the subsequent raising of the superconducting transition temperature (T_c) has drawn great interest in the condensed matter community [1-2]. $REFeAsO_{1-x}F_x$, which was abbreviated as FeAs-1111, is the first series of superconductors showing such high T_c values without copper-oxide planes as traditionally observed in cuprate superconductors [3]. As such, it provides a new system, quite different from the cuprate superconductors, in which the mechanisms of high-temperature superconductivity were understand in recent years. It has been thought that superconductivity in the FeAs-based series may have a direct connection to a spin-density-wave (SDW) anomaly occurring in the FeAs layer [4]. In particular, superconductivity emerges when such SDW order is suppressed by chemical doping [5] or by high pressures [6]. However, all these series of iron-based superconductors contain the element As, which is toxic on its own and would be even more so when oxidized to As_2O_3 and/or related compounds [7]. Therefore, there was a quest for search of alternate compound s/elements to serve As role and make these systems user and environment friendly as well. In continuation, as a substitute, FeSe with some Se deficiency, which is less toxic and easier to handle than arsenides, was found to exhibit superconductivity [3]. Among the iron-based superconductors, these systems, called the 11 system. The FeSe/Te superconductor is a remarkable material. The structural simplicity of FeCh4 (Ch = S, Se, Te), in which the conducting layers are not separated by any third-atom layers, offers the best tool for investigating the nature of superconductivity and

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magnetism in Fe-based compounds [8]. Either the pressure or the chemical composition distort the FeCh4 tetrahedron and tune the electronic properties.

However, pure FeTe is not superconducting and the two end compounds FeSe and FeTe are structurally isomorphic but revels different physical and magnetic properties [9]. Density functional calculations on FeS, FeSe and FeTe indicated that the strength of spin density wave (SDW) in FeTe and the possibility of higher T_c in doped FeTe alloy compared to FeSe [10]. Further, the enhancement of T_c in Te substituted FeSe explained on the basis of the density functional calculations. When partially substituting Se for Te in the antiferromagnetic FeTe, the Se substitution affects the structure and must be kept under control for tuning the structure deformation and the electronic properties. In fact, the superconducting state exists over quite a wide range of doping in the Fe (Se, Te) system (up to 90% Te substitution for Se in polycrystalline samples) with a maximum of 15 K [11]. FeSe has been studied quite extensively [9], a key observation is that the phase pure superconducting sample exists only for those samples prepared with intentional Se deficiency. In this paper, we report Raman-scattering results obtained on $FeTe_{1-x}Se_x$ bulk samples. The zone-center optical modes were classified by a group-theoretical analysis and the Raman-active phonons assigned accordingly.

2. Experimental

The bulk polycrystalline $FeTe_{1-x}Se_x$ samples with x = 0.0, 0.5 and 1, were synthesized through a standard solid state reaction route via vacuum encapsulation. The high purity chemicals Fe, Se, and Te were weighed in the stoichiometric ratio and ground thoroughly in a glove box having pure Argon atmosphere. The mixed powder was subsequently pelletized and then encapsulated in an evacuated (10^{-3} Torr) quartz tube. The encapsulated tube was then heated at 750 °C for 12 hours and slowly cooled to room temperature. The heating schedule was repeated couple of times with intermediate grinding. The x-ray diffraction (XRD) pattern was recorded at room temperature in the scattering angular (2θ) range of 10° to 60° in equal 2θ steps of 0.02° using a Rigaku Diffractometer with Cu Kα (λ = 1.54 Å). Raman spectra were recorded with Horiba Jobin Yvon T6400 Micro Raman using a He–Ne Laser operating at λ = 632.8 nm.

3. Results and discussions

Figure 1 shows the x-ray diffraction profile and results of Rietveld refinement. The x-ray profile of FeTe, $FeTe_{0.5}Se_{0.5}$ and FeSe confirmed the primitive tetragonal unit cell and the space group P4/nmm, z-coordination parameter = 0.2850). The FeTe and $FeTe_{0.5}Se_{0.5}$ samples are in single phase as confirm from the Rietveld refinement. However, FeSe is found to be in double phase, were in, tetragonal phase (about 66.62%) and orthorhombic with space group *Cmcm* (33.38%). The estimated values of lattice parameter a and c from the refinement results are listed in table 1 and both were found to be decreasing with the selenium concentration. Similar trends also true for volume concentration. Further, the bond length of Fe–Te = 2.648 Å, Fe–(Se,Te) = 2.505 Å and Fe-Se = 2.33 Å were calculated using the Vesta software and found that the bond length to be decreasing as the concentration of Se increases. Observation of such trend in bond length is quite consistent as the smaller ionic radius of Se over the Te, presumably creates the positive chemical pressure.

Figure 2 shows the comparison of phonon Raman spectra between the parent compound FeTe and the superconducting $FeTe_{0.5}Se_{0.5}$ and FeSe. From the group theory considerations [12], Γ- point phonon modes of the tetragonal Fe(Te,Se) can be expressed as $\Gamma = A_{1g} + 2A_{2u} + B1g + 2E_g + 2E_u$. Fe and Te ions occupy 2a and 2c Wyckoff positions, respectively. Symmetry analysis shows that there are four Raman-active modes [A_{1g}(Te) + B_{1g}(Fe) + $2E_g$(Te, Fe)] and two infrared active modes [A_{2u}(Te, Fe) + E_u(Te, Fe)] [13]. Acordingly, the Raman tensors take the form:

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \quad (1)$$

$$B_{1g} = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{2}$$

$$E_g = \begin{pmatrix} 0 & 0 & -e \\ 0 & 0 & e \\ -e & e & 0 \end{pmatrix}, \tag{3}$$

are the Raman active modes and

$$B_{2g} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{4}$$

is the Raman inactive mode.

Table 1. Structural parameters obtained from the Rietveld refinement analysis of $FeTe_{1-x}Se_x$ at 300 K. Space group: *P4/nmm* (# 129) and Space group: *Cmcm* (# 63) . Atomic positions: Fe: 2a (3/4, 1/2, 0); Te: 2c (1/2,1/2, 0.28); respectively.

X	0.0	0.5	1 (*P4/nmm*)	1 (*Cmcm*)
a (Å)	3.822	3.794	3.809	5.241
b (Å)	3.822	3.794	3.809	4.572
c (Å)	6.281	6.017	5.389	1.292
V (Å^3)	91.757	86.624	66.62	33.38

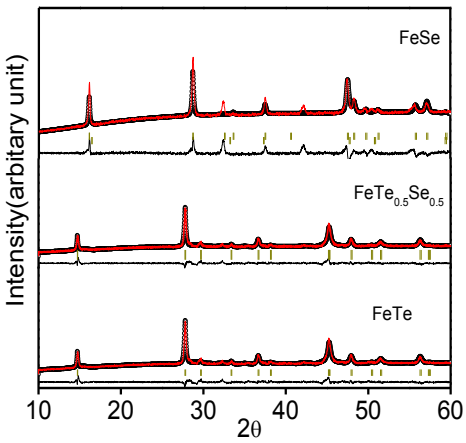

Figure 1. X-ray diffraction data along with the Rietveld refinement results of $FeTe_{1-x}Se_x$ samples.

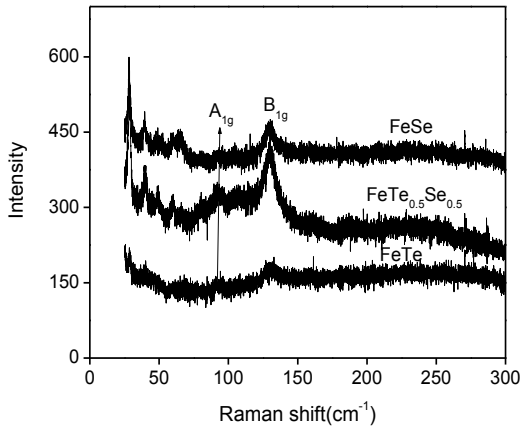

Figure 2. Comparison of phonon Raman spectra between the parent sample FeTe and superconducting $FeTe_{0.5}Se_{0.5}$ and FeSe samples. Vertical line shows the shifting of A_{1g} mode.

Herein, the Raman-active modes, $\Gamma_{Raman} = A_{1g} + B_{1g} + 2E_g$ can be assigned to the observed frequencies. However, we have observed A_{1g} and B_{1g} modes in our measurements. At room temperature, these lines are located at 95 and 130 cm^{-1} for FeTe, 93 and 129 cm $^{-1}$ for $FeTe_{0.5}Se_{0.5}$ and 93 and 129 cm $^{-1}$ for FeSe samples. The peak position of A_{1g} is found to be decreasing as the Se concentration increases. Such observation could be due the Fe magnetic moment and anharmonicity [13]. As mentioned above, the A_{1g} type of Te vibrations plays the important role for the mode vibration

in the chalcogen's tetrahedral formation. Only chalcogen's antiphase vibrations that occurred perpendicular to the Fe layer has an internal source of anharmonicity. While the peak position of B_{1g} has been shifted slightly to lower energy with increasing Se concentration. It is instructive to mention that Fe magnetic moment and anharmonicity may not alter the B_{1g} modes. Therefore, the B_{1g} vibration of Fe ions should not be affected by this structure due to the Fe layer topology. In other phonon Raman-scattering measurements, Okazaki et al. [14] have observed these modes at 158 and 202 cm^{-1} on single crystal $Fe_{1.074}Te$ sample. Similar results were also reported by Xia et al. [15] at 159.1 and 196.3 cm^{-1} for single crystal $FeTe_{0.92}$ and Kumar et al. [16] at 160 and 224 cm^{-1} on polycrystalline $FeSe_{0.82}$ sample.

4. Conclusions

We have measured X-ray diffraction and Raman spectra of poly-crystalline $FeTe_{1-x}Se_x$ samples with x = 0.0, 0.5 and 1 at room temperature. X-ray profile of FeTe and $FeTe_{0.5}Se_{0.5}$ confirmed the primitive tetragonal unit cell. FeSe is found to be in double phase with tetragonal phase (about 66.62%) and orthorhombic (33.38%). A_{1g} and B_{1g} phonon modes were observed in Raman spectra. The peak position of A_{1g} is found to be decreasing as the Se concentration increases. While the peak position of B_{1g} has been shifted slightly to lower energy with increasing Se concentration.

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