Observation of the interplay of microstructure and thermopower in the $Al_{71}Pd_{21}Mn_{8-x}Re_x$ quasicrystalline system

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In an effort to garner further insight into the behavior of thermopower in quasicrystalline materials, a series of quartenary $Al_{71}Pd_{21}Mn_{8-x}Re_x$ polygrain quasicrystals was synthesized. X-ray data confirm that the addition of a fourth element does not alter the quasiperiodicity. It is found that there is an intricate interplay of the microstructure and the magnitude and temperature dependence of the thermopower in this series of materials. Results are presented relating the temperature dependence of the thermopower to the presence and nature of secondary phases within the microstructure.

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INTRODUCTION

Quasicrystals are a class of materials that exhibit long-range rotational order without the translational symmetry of a crystal. These materials are cluster-based structures in which electrical conduction occurs primarily through electron-electron interaction, weak localization, or variable-range hopping. Atoms are arranged nonperiodically. Quasicrystals may be viewed as being structurally ordered on a short-range scale and behave electronically in a manner similar to that of a semimetal while thermally behave like a glass.[1] Since the discovery of stable quasicrystalline phases, extensive work has been preformed to assimilate the mechanisms which govern the electrical transport in these materials.[2] Two predominant symmetries exist in quasicrystalline materials: icosahedral [fivefold with three-dimensional (3D) quasiperiodicity] and decagonal (tenfold with 2D quasiperiodicity and 1D periodicity).[3]

The thermopower in quasicrystals does not behave like a ''typical'' material. Nominal Al-Pd-Mn and Al-Pd-Re quasicrystals have been observed to exhibit thermopower values as large as 80 and 70 μV/K, respectively.[4,5] Many quasicrystalline materials are composed primarily (~70%) of aluminum. Metals such as Cu, Ag, and Au as well as ''metallic-like'' materials such as amorphous metals typically have low thermopower values at room temperature, on the order of 1–10 μV/K, while the thermopower in quasicrystalline materials is observed to be much larger.

Small variations in the quality or preparation of quasicrystals can greatly influence the electrical properties of these materials.[6] This reflects a small variation in the total number of conduction electrons, which can become very important when the Brillouin zone is nearly full. We also know that small amounts of impurities in quasicrystals may substantially enhance the thermopower.[7] Given this background, a series of $Al_{71}Pd_{21}Mn_{8-x}Re_x$ quasicrystals were synthesized where $x=0$, 0.08, 0.25, 0.4, 0.8, 2, 5, and 8 in an effort to systematically investigate the effect of substitutional doping in these materials. Systematic doping between two well-characterized materials may provide a method in which subtle changes in the thermopower due to differences in composition can be more fully understood. Thermopower in both the Al-Pd-Mn and Al-Pd-Re systems appears to be large and predominately p type ($S \leqslant +85$ and $+120$ μV/K, respectively).[8,9] AlPdMn and AlPdRe form with comparable levels (~10%) of Re or Mn, making a solid solution possible.[10]

In this paper, we demonstrate evidence indicating that the thermopower in quasicrystalline systems is a strong function of sample microstructure. This is observed through powder x-ray diffraction (XRD), electron microscopy, electron microprobe analysis (EMPA), and measurements of the temperature dependence of thermopower on the series of quartenary $Al_{71}Pd_{21}Mn_{8-x}Re_x$ quasicrystals. We report on the thermoelectric properties of quaternary quasicrystals as related to the interplay of microstructure with electrical and/or thermal properties.

EXPERIMENTAL DESCRIPTION

Powder XRD was carried out on the series of $Al_{71}Pd_{21}Mn_{8-x}Re_x$ quasicrystals using Cu$K\alpha$ radiation on a Scintag XDS-2000 Θ-Θ diffractometer with a resolution of ~0.03°. High-angle diffraction data were used to identify the crystal structure of the sample. EMPA was used to determine the composition of all the samples using a Cameca SX-50 with a 15-keV accelerating voltage, a 60-nA beam current, and a minimum (1.5 ± 0.5 μm) spot size. Backscattered electron images were obtained for each sample using EMPA. Thermopower was measured on these samples between $10\,K<T<300\,K$ as described elsewhere.[11]

RESULTS AND DISCUSSION

XRD data for several compositions of $Al_{71}Pd_{21}Mn_{8-x}Re_x$ are shown in Fig. 1 and indicate that samples are quasicrystalline when compared to previous XRD results.[12] Note that the peaks are shifted to slightly smaller angle with increasing levels of Re, indicating a larger lattice, which is expected

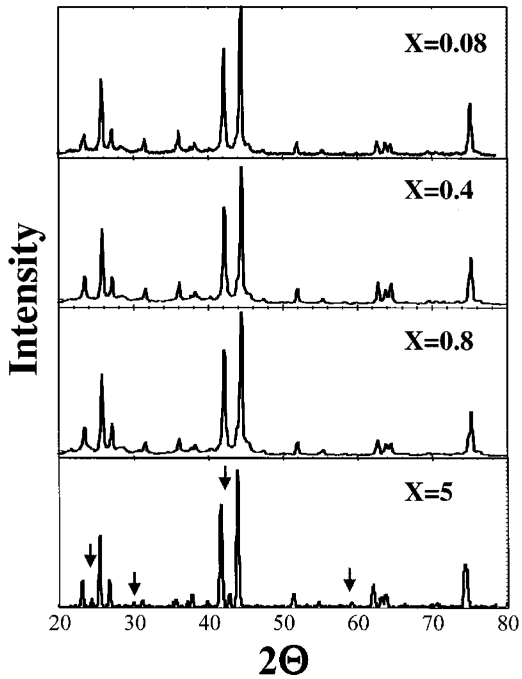

FIG. 1. X-ray diffraction data for $Al_{71}Pd_{21}Mn_{8-x}Re_x$ indicate that all patterns are quasicrystalline with a secondary phase of either decagonal Al-Pd-Mn or crystalline Al_3Pd_2 occurring when $x=5$. The presence of the secondary phase is identified by the emergence of a new set of small intensity peaks, some (≈4 of 8) of which are indicated by the arrows.

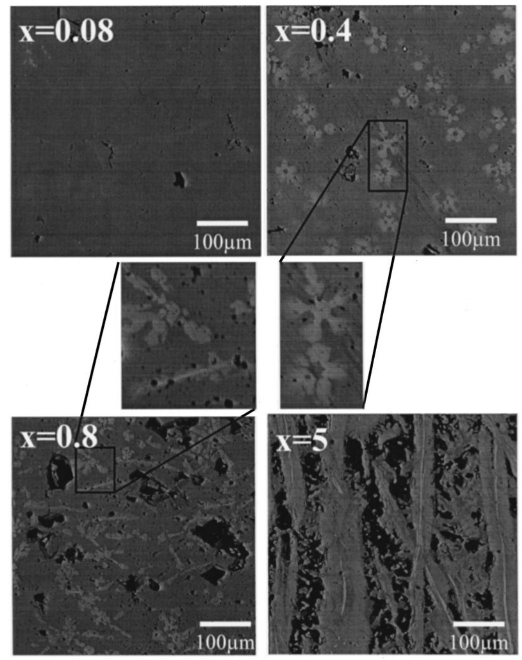

FIG. 2. Backscattered images of several concentrations of $Al_{71}Pd_{21}Mn_{8-x}Re_x$ displaying a secondary phase. As x increases, small threefold or fivefold rosettes develop and appear to elongate into dendrites for higher x. Insets are enlarged regions of the indicated sections.

due to the larger size of Re (atomic radius $r \approx 1.37$ Å) when substituted for Mn($r \approx 1.27$ Å). For small additions of Re, $x \leqslant 2$, no changes are observed in the XRD other than a slight peak shift. For intermediate concentrations of Re, $2 \leqslant x \leqslant 5$, additional small intensity peaks are detected that are not consistent with the primary quasicrystalline icosahedral phase. The emerging secondary phase is much less prevalent in the bulk quasicrystal than that of the icosahedral phase. The arrows in Fig. 1 indicate a few of these peaks. The emerging peaks are evidence of a secondary phase believed to be either a decagonal phase or crystalline Al_3Pd_2. No evidence of elemental Re is present in the samples. Except for the parent quasicrystals and systems with very low levels of Re doping, all samples contain mixed phases.

Backscattered electron (BSE) images were taken of each $Al_{71}Pd_{21}Mn_{8-x}Re_x$ quasicrystal in order to assess homogeneity of the compound. These images are shown in Fig. 2 for various concentrations of Re. Here EMPA indicates the presence of two phases. Lighter regions in the micrograph are areas with higher average atomic number, indicating that these regions have more Re than Mn present ($M_{\mathrm{Re}} \approx 3.5 M_{\mathrm{Mn}}$). Darker regions still have a composition consistent with being quasicrystalline.

Pure Al-Pd-Mn and Al-Pd-Re appear to be homogeneous, and for compositions of $Al_{71}Pd_{21}Mn_{8-x}Re_x$ where $x \leqslant 0.25$, a uniform appearance is observed (see upper left-hand corner of Fig. 2). All of these samples are determined to have stoichiometry consistent with quasicrystalline composition with no observable secondary phases present. These samples also have very low porosity as determined by visual inspection in an Olympus metallurgical microscope with up to 500× magnification. For the region where $0.4 \leqslant x \leqslant 2$, XRD indicates pure icosahedral phase quasicrystals. It must be noted that XRD is not extremely sensitive and low levels of a secondary phase may be present in these quasicrystals.

At $x=0.4$ a secondary phase is observed and takes on the form of rosettes. Some rosettes have fivefold symmetry and are compact and well formed. Threefold rosettes are also observed. Twofold, threefold, and fivefold symmetry patterns are observed in electron diffraction patterns of quasicrystals.[13] It would be expected that a twofold symmetry might be observed for some of the rosettes, but this has yet to be observed in this microstructure. Some rosettes appear to be elongated and look like ''snowflake'' structures. Bulk materials which contain intermediate levels of Re are more porous than quasicrystals with lower levels of Re doping.

At $x=0.8$, we observe that the rosettes have elongated to form dendrites. The dendritic needles are not perfectly formed, and remnant rosette structures remain (see Fig. 2 for $x=0.8$). Rosettes appear to be elongating from the nucleation site of the rosette ($x \leqslant 0.8$) and forming the dendritic structure observed for all higher-level doping of Re($x \geqslant 0.8$). Porosity of the $x=0.8$ sample increases substantially over that for smaller levels of Re doping. At larger concentrations of Re doping ($x \geqslant 2$), the samples become much more porous (porosity increasing from ∼5% to ∼50%) and the quasicrystal is now composed of interpenetrating needles which are once again primarily single phase and a mixture of Al, Pd, Mn, and Re. A small dendrite, however, is in the

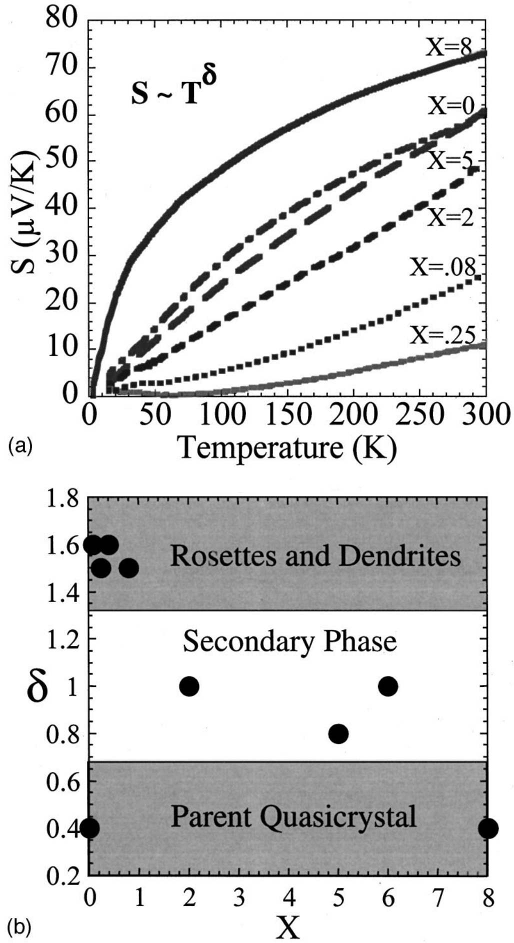

FIG. 3. (a) Thermopower vs temperature for several compositions of quasicrystalline $Al_{71}Pd_{21}Mn_{8-x}Re_x$. (b) It is observed that thermopower behaves as T^{δ} where $\delta\approx 0.4$, 1, and 1.5 for different levels of Re doping.

center of some of the bulk needles and is observed to have a higher Re concentration than the rest of the material. XRD measurements indicate that the secondary phase does not appear until $x\geqslant 2$, although secondary phases for $x<2$ may have been too small to be detected by XRD. It is noted that the composition of the rosettes and dendrites is not consistent with crystalline Al_3Pd_2. Secondary phases may be explained by preferential formation of quasicrystalline AlPdRe over quasicrystalline AlPdMn. Formation of the needlelike structures for $x\geqslant 2$ may be due AlPdRe growing in platelets.

Thermopower in quasicrystalline materials is known to be a strong function of composition and annealing conditions of the sample.[14] Figure 3(a) shows the thermopower as a function of temperature from $10\,K<T<300\,K$ for this series of samples. Also, note the variability in the magnitude of the thermopower with composition. The thermopower in the $Al_{70}Pd_{20}Mn_{10}$ system increases almost monotonically with temperature, varying as $T^{0.4}$ at high temperatures. The thermopower in the $Al_{70}Pd_{20}Re_{10}$ system increases rapidly at low temperatures and then increases gradually above 35 K, going also to a $T^{0.4}$ dependence at higher temperatures ($T>50\,K$). Below 40 K the conduction in AlPdRe is governed by variable-range hopping ($S\sim T^{1/2}$), which may explain the increase in magnitude of AlPdRe over AlPdMn.[15]

With the growth of secondary phases in the bulk quasicrystal, the resulting transport properties in the $Al_{71}Pd_{21}Mn_{8-x}Re_x$ system are significantly affected. AlPdRe and AlPdMn have reasonably high room-temperature thermopower values (70 and 64 μV/K, respectively). With the addition of $x=0.08$, the thermopower is seen to reduce to 27 μV/K. With larger Re doping ($0.25\leqslant x\leqslant 0.8$), the thermopower is seen to drop even further to $\sim$10 μV/K. However, it is noted that with additional Re($2\leqslant x\leqslant 6$) the thermopower begins to increase, though it never exceeds the thermopower of the parent AlPdRe system [Fig. 3(a)].

The thermopower behavior is clustered into three distinct regions as shown in Fig. 3(b). In the first region, the parent materials AlPdMn and AlPdRe show a temperature dependence where $S\sim T^{0.4}$ above $T\approx 50\,K$. In the second region ($2\leqslant x\leqslant 6$), the thermopower increases linearly with temperature, indicating a diffusionlike thermopower. In this region, XRD indicates the presence of a secondary phase in addition to the icosahedral phase. A diffusionlike thermopower ($S\approx AT$, where A is a constant) would be expected in a crystalline phase, but it is not obvious what the dependence would be for a quasicrystal. Backscattered images indicate the formation of needlelike structures. The thermopower for these compositions exhibit intermediate magnitudes of thermopower with room-temperature values being $\sim$50 μV/K.

In the third region the thermopower increases as $T^{1.5}$. This behavior occurs for quasicrystals with relatively low concentrations of Re doping ($0.08\leqslant x\leqslant 0.8$). Here XRD indicates pure icosahedral phase quasicrystals. Backscattered images indicate several different microstructures. The third region involves quasicrystals with no secondary phases or quasicrystals with rosettes and dendrites. Values of the thermopower are reduced with room-temperature magnitudes of the thermopower ($S\leqslant 30\,\mu$V/K).

By coupling results from the temperature dependence of the thermopower with the results from the microstructure (XRD, EMPA, and EBS), we observe a pattern relating the thermopower and microstructure. The temperature dependence of the thermopower is clustered into three distinct regions: $S\sim T^{0.4}$, $S\sim T$, and $S\sim T^{1.5}$, as seen in Fig. 3(b). Low concentrations of Re exhibit rosettes and needlelike dendrites, lower values of thermopower ($S\approx 20\,\mu$V/K), and the strongest temperature dependence $\delta\approx 1.5$. The intermediate concentrations of Re exhibit the presence of the secondary phase, intermediate values of the thermopower ($S\approx 50\,\mu$V/K), and approximately a linear temperature dependence, i.e., $\delta\approx 1$. The end members or pure parent quasicrystals Al-Pd-Mn and Al-Pd-Re exhibit a thermopower that increases as $T^{0.4}$ and yields the highest values of the thermopower ($S\approx 75\,\mu$V/K). The XRD data indicate icosahedral quasicrystals, and the EMPA shows no secondary phase. BSE shows AlPdMn to be dense, while AlPdRe is porous. The thermopower for these quasicrystals has the largest magnitude. These results could be key in the understanding of the thermopower in many quasicrystalline systems. Work in progress includes a full investigation of the electrical resistivity, thermopower, and thermal conductivity in this series of samples and relating these results to this microstructure in this series of $Al_{71}Pd_{21}Mn_{8-x}Re_x$ materials.

SUMMARY

The addition or substitution of Re to the AlPdMn system drastically changes the electrical transport properties and the microstructure of these quasicrystalline materials. The addition of Re results in the growth of secondary phases. We believe the secondary phase to be either decagonal Al-Pd-Mn or crystalline Al_3Pd_2. Further work is in progress to elucidate which phase is dominating or if possibly both phases are present. Thermoelectric properties are substantially changed with the addition of Re in the AlPdMn system. The mechanisms governing thermopower in this system of materials are difficult to understand. Thermopower is observed to be very sensitive to doping with small, impurity levels of Re, which results in a substantial decrease of the thermopower and begins to increase again with further increases in Re doping. More work is needed to understand the electrical and thermal transport in this fascinating class of materials. Extensive characterization of the electrical resistivity, thermal conductivity, and heat capacity of this series of materials is in progress. These results point out the important role that the composition and microstructure play in the electrical and thermal transport in quasicrystals.

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