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Evidence of a stable binary CdCa quasicrystalline phase

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Quasicrystals with a primitive icosahedral structure and a quasilattice constant of 5.1215 Å have been synthesized in a binary Cd–Ca system. The thermal stability of the quasicrystal has been investigated by *in situ* high-temperature x-ray powder diffraction using synchrotron radiation. It is demonstrated that the binary CdCa quasicrystal is thermodynamic stable up to its melting temperature. The linear thermal expansion coefficient of the quasicrystal is $2.765\times10^{-5}\,\mathrm{K}^{-1}$.
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Since the discovery of the icosahedral phase (*i* phase) in rapidly quenched Al-based alloy systems,[1] there have been extensive studies on quasicrystals.[2–8] More than ten stable quasicrystals containing at least three metallic elements have been prepared.[9] Recently, Tsai *et al.*[10] reported that stable quasicrystals are found in the binary CdYb system. This result will be important for the understanding of structure and properties in quasicrystals. Here we report the formation of quasicrystals in the binary CdCa system and verify the thermodynamic stability of the novel quasicrystals by performing *in situ* high-temperature x-ray powder diffraction using synchrotron radiation.

The Cd_xCa_{100-x} ($x=80-90$ at. %) alloys were prepared from the elements (Alfa with 99.9 purity) in a sealed quartz tube with a vacuum of around 10^{-5} mbar at 923 K for a few hours. The structure of as-solidified alloys was studied by a Philips PW 1820 x-ray powder diffractometer with Cu $K\alpha$ radiation. Some selected samples were measured by *in situ* high-temperature (up to 973 K) x-ray powder diffraction using synchrotron radiation at beamline I711 at the MAX II synchrotron in Lund, Sweden, utilizing a Huber G670 imaging plate Guinier camera. The wavelength, 1.513 852 Å, was determined using a Si standard.[11] The powder sample, ground from the recovered sample, was placed in an amorphous quartz capillary, pumped down to 10^{-5} mbar and then sealed, and rotated during data collections. The diffraction patterns were all collected in the range $30°-50°$ in 2θ steps of 0.005°, and accumulated for 5 min. An oven was used for high temperature measurements in steps of 30 K. The temperature at sample was calibrated using the known temperature dependence of lattice parameter for pure silicon powder at the sample position.[12]

Figure 1 shows an x-ray powder diffraction pattern recorded at 295 K from an as-solidified $Cd_{82}Ca_{18}$ alloy using Cu $K\alpha$ radiation. A primitive icosahedral structure was found to be the most promising indexing scheme. The icosahedral Miller indices are generated by cyclic permutations of $(q_x,q_y,q_z)=(\pm1\pm\delta,0)$.[2] Six independent vectors are expressed by: $q_1=(1,\delta,0)$; $q_2=(1,-\delta,0)$; $q_3=(0,1,\delta)$; $q_4=(0,1,-\delta)$; $q_5=(\delta,0,1)$; and $q_6=(-\delta,0,1)$, where δ is the golden mean, 1.618. As an example, the (110 000) peak is found at $q=Q_0(q_1+q_2)=(2,0,0)$ and $Q_0=2\pi/a$, where a is the quasilattice constant. The quasilattice constant at room temperature is found to be $a=5.1215$ Å. The peak ($2\theta\approx33°$, $q\approx2.32\,\text{Å}^{-1}$) is a choice for the basic (100 000) reciprocal lattice vector. It is found that binary CdCa quasicrystals together with tiny Cd, Cd_6Ca, or $Cd_{51}Ca_{14}$ phases are formed in the as-solidified Cd_xCa_{100-x} ($x=81-86$ at. %) alloys. To ascribe the stability of the binary CdCa quasicrystals, a large number of *in situ* high-temperature x-ray powder diffraction measurements for several quasicrystal alloys in a temperature range from 295 to 973 K (above melting temperature) were performed. Figure 2 exemplifies *in situ* x-ray powder diffraction patterns recorded for the as-solidified $Cd_{83}Ca_{17}$ sample at various temperatures using a wavelength of 1.513 852 Å. At 303 K, the pattern can be indexed with the CdCa quasicrystal phase together with a broadened peak for the Cd phase at $2\theta\approx37.8°$. With increasing temperature, the peaks for the Cd phase ($2\theta\approx31.2°$ and 37.8°) become narrow while peaks for quasicrystals just slightly shift to lower angles due to thermal expansion. At 573 K, new peaks at $2\theta\approx33.5°$, 34.3°, 38°, and 39.6°, indexed to the Cd_6Ca phase, appear while the peaks for the Cd phase almost disappear. This infers that the reaction between Cd (melting point is around 594 K) and any Ca-containing components occurs to form the Cd_6Ca phase. Both quasicrystal and Cd_6Ca phases coexist up to 783 K. At 843 K, the quasicrys-

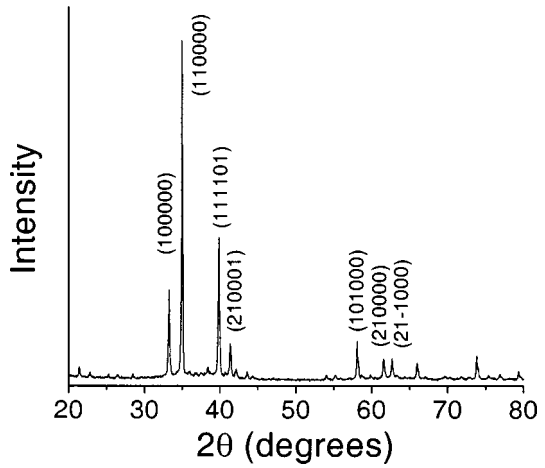

FIG. 1. X-ray powder diffraction pattern recorded with Cu $K\alpha$ radiation for the as-solidified $Cd_{82}Ca_{18}$ alloy.

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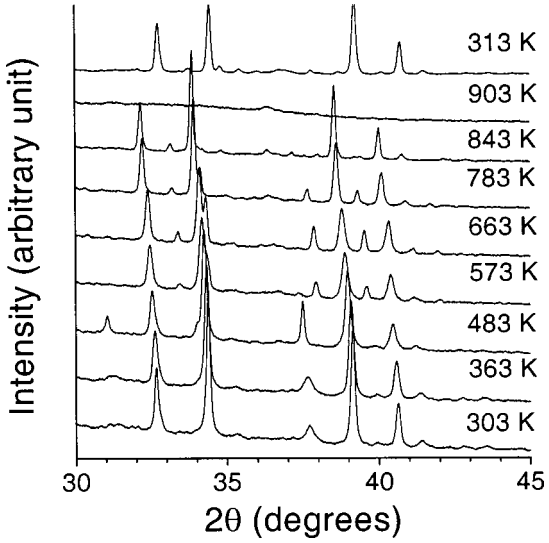

FIG. 2. *In situ* high-temperature x-ray powder diffraction patterns recorded with synchrotron radiation with wavelength 1.513 852 Å for the as-solidified $Cd_{83}Ca_{17}$ alloy.

tals remain while the Cd_6Ca phase disappears. This is consistent with the Cd–Ca phase diagram,[13] in which Cd_6Ca becomes unstable above 838 K. At 873 K, no quasicrystals were detected and the sample is composed of a liquid phase and a tiny solid $Cd_{51}Ca_{14}$ phase. At 903 K, the sample is in the liquid state. When the liquid phase resolidifies, the quasicrystals reappear, as indicated in the pattern recorded at 313 K. The results obtained from our *in situ* x-ray powder diffraction measurements strongly demonstrate that the binary CdCa quasicrystals formed here constitute a thermodynamic stable phase up to their melting point. Figure 3 shows that the quasilattice constant is a linear function of temperature. The data can be well fitted (solid line) with $a = 5.0791\ \text{Å} + 1.4155\times10^{-4}\,T$. The linear thermal expansion coefficient, $\alpha=(da/dT)/a(300\,\text{K})$, is $2.765\times10^{-5}\,\text{K}^{-1}$. This is larger than the value $1.4\times10^{-5}\,\text{K}^{-1}$ for $Al_{72}Pd_{20}Mn_8$ quasicrystals,[14] $1.33\times10^{-5}\,\text{K}^{-1}$ for $Al_{70.3}Pd_{21.7}Mn_8$ quasicrystals at 300 K,[15] and $1.3\times10^{-5}\,\text{K}^{-1}$ for $Al_{70}Pd_{20}Mn_{10}$ quasicrystals.[16]

In conclusion, binary CdCd quasicrystals have been synthesized and their thermodynamic stability has been investigated by *in situ* high-temperature x-ray powder diffraction using synchrotron radiation. It is found that the quasicrystalline phase is stable up to its melting temperature. The quasilattice constant increases linearly with temperature, $a = 5.0791\ \text{Å} + 1.4155\times10^{-4}\,T$, having a thermal expansion coefficient of $2.765\times10^{-5}\,\text{K}^{-1}$ at 300 K. The stable binary CdCa quasicrystal will be a good candidate for the determination of the basic atomic structure of quasicrystals.

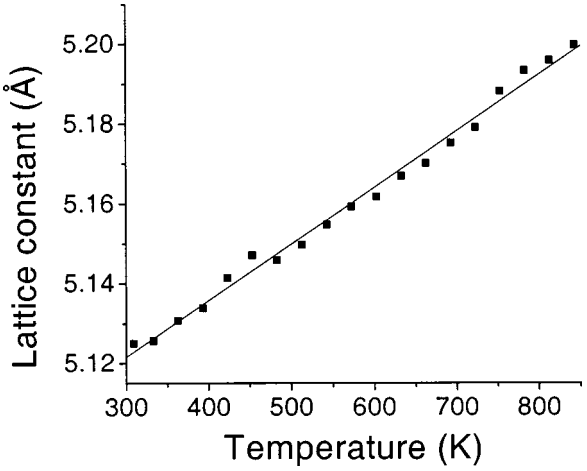

FIG. 3. Linear thermal expansion of as-solidified $Cd_{83}Ca_{17}$ quasicrystals.

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