Structure refinement for $(Cd,Zn)_3As_2$

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HIGHLIGHTS

We study single crystals of two $(Cd_{1-x}Zn_x)_3As_2$ phases α'' and α''', with x = 0.4 and 0.6, respectively. The crystals were grown using the horizontal Bridgman method. Powder and single-crytal X-ray diffraction analysis shows the expected tetragonal structures of $(Cd_{0.4}Zn_{0.6})_3As_2$ (*I*4_1*/amd* space group) and $(Cd_{0.6}Zn_{0.4})_3As_2$. (*P*4_2*/nmc* space group). The cation distribution among three cationic sites is determined.

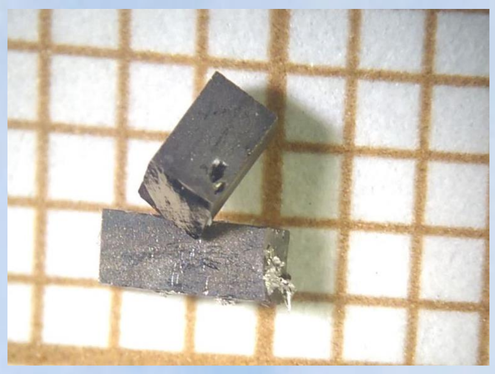

Figure 1. Single crystasl of $(Cd_{0.4}Zn_{0.6})_3As_2$.

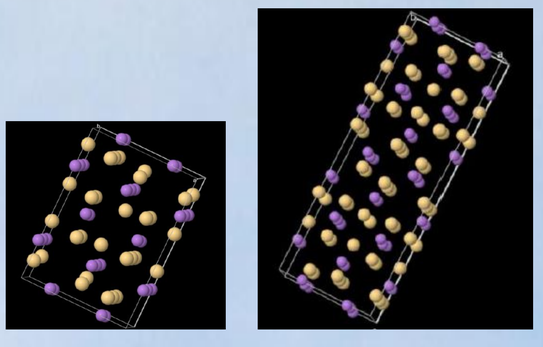

Figure 2. Structure of α'' phase (left) and the superstructure α''' phase (right).

INTRODUCTION

$(Cd_{1-x}Zn_x)_3As_2$, is an alloy system of inverted gap semiconductor, Cd_3As_2 and direct-gap semiconductor, Zn_3As_2. Basic electronic and optical properties of such materials have been determined in [Turner, 1961]. The interest in $(Cd_{1-x}Zn_x)_3As_2$ has been renewed after discovery of Dirac semimetal character of Cd_3As_2 [Borisenko, 2011] in connection with expected topological phase transition to the open-gap semiconductor for some *x* [Nishihaya, 2018].

- Cd and Zn atoms have similar electronic structure. However, the $(Cd_{1-x}Zn_x)_3As_2$ system is not a solid solution, but including the side binaries it is built from structurally closely related tetragonal phases. All of these phases have a meaningful solubility range.
- Among them, the ternary α'' phase (*P*4_2*/nmc*) extends up to x = 0.45 and above x = 0.80, whereas the superstructure α''' phase (*I*4_1*/amd*) is stable between x = 0.45 and x = 0.80 (aee Fig. 2).
- In this work we study the crystal structure of one α'' and one α''' single crystal.

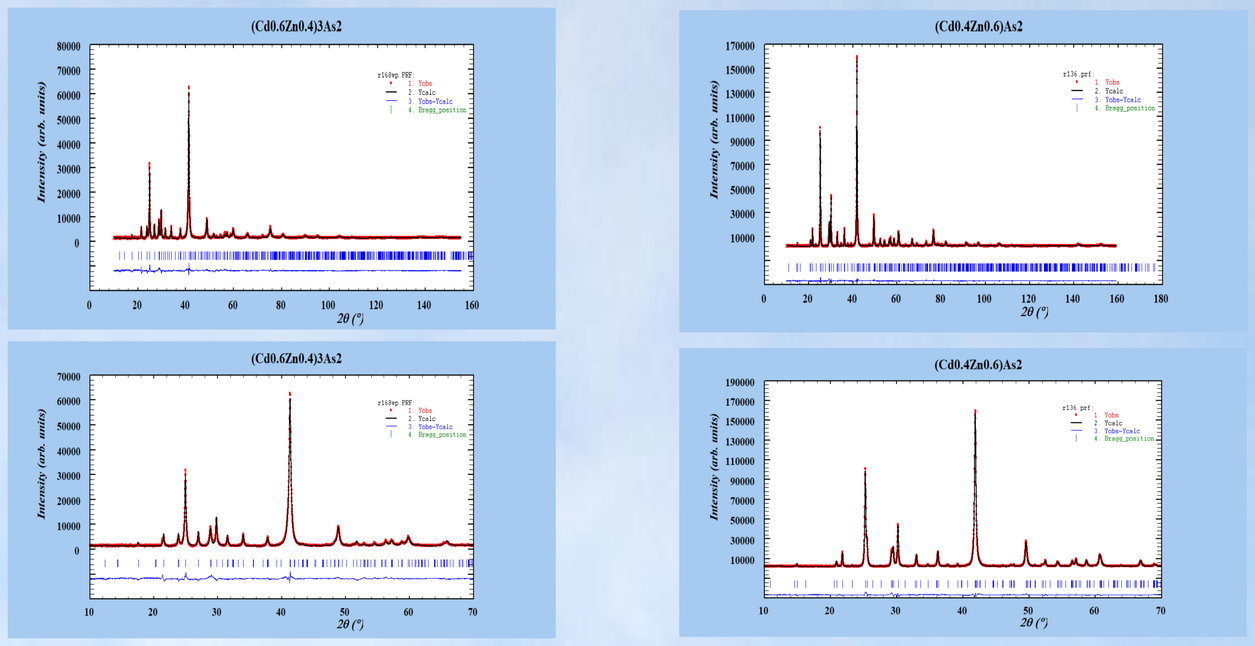

Figure 3 Rietveld refinement of the α'' (left) and α''' (right) phases.
The lower panels represent the magnified low-angle part of the refined patterns.

CRYSTAL GROWTH

The $(Cd_{1-x}Zn_x)_3As_2$ crystals were prepared from 5N and 6N Cd, Zn, and As. The growth was preceded by (i) additional purification of As, (ii) synthesis of $(Cd_{1-x}Zn_x)_3As_2$. The growth was then carried out by horizontal Bridgman method in quartz ampoules pulled through temperature gradient at a rate of 7 mm/h. We have fabricated a sequence of crystals with various *x* value (see an example in Fig. 1).

X-RAY DIFFRACTION METHODS APPLIED IN THE STUDY

X-ray powder diffraction measurements were performed using the X'pert MPD diffractometer ($CuK\alpha_1$ radiation) equipped with a Johansson monochromator and a strip detector. The structures of the powders were refined by the Rietveld method, employing the Fullprof2k,v.5.30 software. Single-crystal diffraction measurements were performed on an Oxford Diffraction X'calibur diffractometer, employing the graphite-monochromated MoKα radiation. Data collection and reduction were performed using the CrysAlis CCD and CrysAlis RED programs (Rigaku Oxford Diffraction). The crystal structures were refined by full-matrix least-squares methods on F^2 using the SHELX-2014 crystallographic software package.

RESULTS AND CONCLUSIONS

- Phase analysis shows that the crystals are single phase; a trace foreign reflection is ascribed to quartz (the ampoule material). The refinement was performed assuming the standardized starting structure models of compositionally related crystals, available in ICSD database.
- The result of Rietveld refinement are displayed in Figure 3. The data refined by powder XRD and single-crystal XRD, describing the unit cell are presented in Table 1.
- The reduced lattice parameters agree with the trends described in [Zdanowicz, 1964] (see Fig. 4). The atomic coordinates differ marginally from those reported for Zn-rich crystal [Volodina, 2013] (the $(Cd_{0.4}Zn_{0.6})_3As_2$ case, phase α'''), and from unpublished evaluations quoted in ICSD database ($(Cd_{0.6}Zn_{0.4})_3As_2$ case, phase α''). The refined *x* values differ by several percent (α''' case) and 20% (α'' case) from the technological composition. The cation distribution for α''' is in line (but with different absolute values) with the result of [Volodina, 2013]. That for α'' demonstrates the earlier-unknown differences in cation distribution among the three cationic sites. These distributions define the substitutional disorder.

Our results show the crystallographic data for $(Cd_{1-x}Zn_x)_3As_2$ single crystals grown by the Bridgman method. The refined structures are in line with the alloy phase diagram proposed in [Zdanowicz, 1964]. Both compounds exibit a substitutional disorder; the cation distribution among the sites is determined.

Table 1. Unit cells of the investigated crystals, as obtained from powder and single-crystal diffraction.

feature	powder XRD	SC XRD	SC XRD	powder XRD
phase	$(Cd_{0.6}Zn_{0.4})_3As_2$	$(Cd_{0.4}Zn_{0.6})_3As_2$	$(Cd_{0.4}Zn_{0.6})_3As_2$	$(Cd_{0.4}Zn_{0.6})_3As_2$
temperature [K]	297(2)	150 K	295 K	297(2)
space group	$P4_2/nmc$	I41/amd	I41/amd	I 41/a m d
lattice parameter a [Å]	8.78092(49)	8.6072(2)	8.6316(2)	8.62845(16)
lattice parameter c [Å]	12.3264(11)	24.2533(9)	24.3273(14)	24.3257(6)
unit cell volume [Å^3]	94178(11)	1796.49(14)	1812.49(13)	1811.05(0.06)
density	5.855 g/cm3	6.02142	5.93946	5.810 g/cm3
axial ratio	1.40377	2.8178	2.8184	2.81924
cleavage plane (*)	(100)	-	-	(102)
nominal Zn fraction in the ingot	0.400	0.600	0.600	0.600
Zn fraction from refinement [at%]	0.510	0.566	0.580	0.645

(*) As deduced from fitting of various preferred orientation direction models.

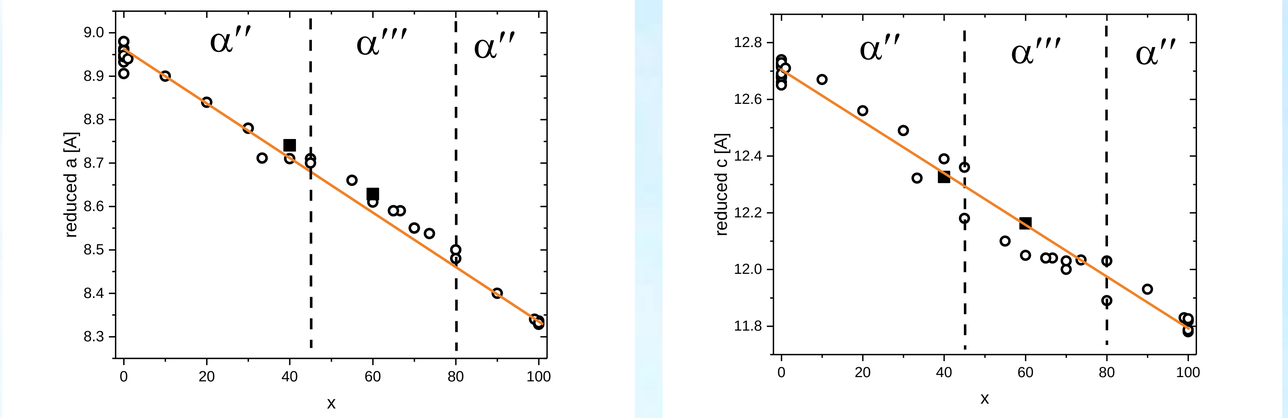

Figure 4. Variation of the reduced lattice parameter of tetragonal phases in the studied system. Various literature data are represented by open circles, the present data – by full squares.

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