Supporting information

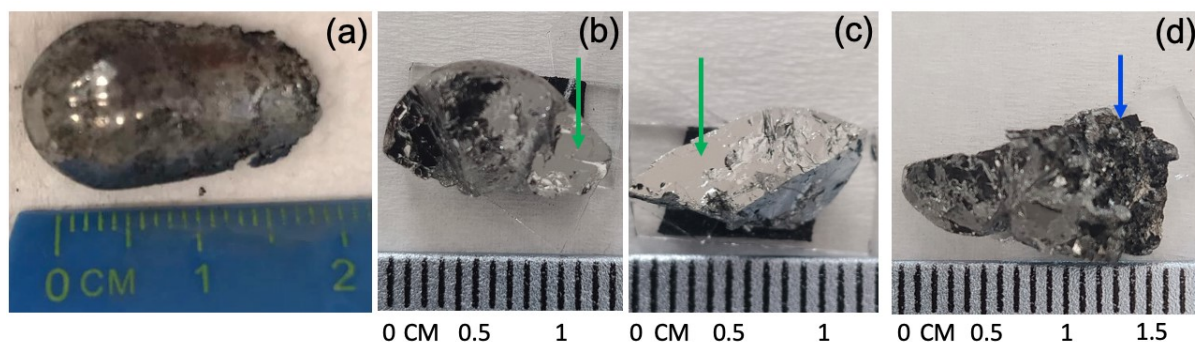

Figure S1: Photographs of a representative ingot with the nominal composition $Bi_{1.85}Cr_{0.15}Se_3$ (a) after removing it from the quartz ampoule and (b)-(d) after cracking it into macroscopic pieces. Large crystals of Cr-doped Bi_2Se_3 can be found inside the ingot (green arrows in (b) and (c). Cr-rich secondary phases are clearly visible in the outer shell of the ingot as in (d) (blue arrow). The XRD pattern reported in Fig. 1 was obtained by pulverizing crystallites from different parts of the ingot, i.e. Cr-doped Bi_2Se_3 and Cr-rich secondary phases, to obtain an XRD pattern that can be used to identify all phases present in the ingot.
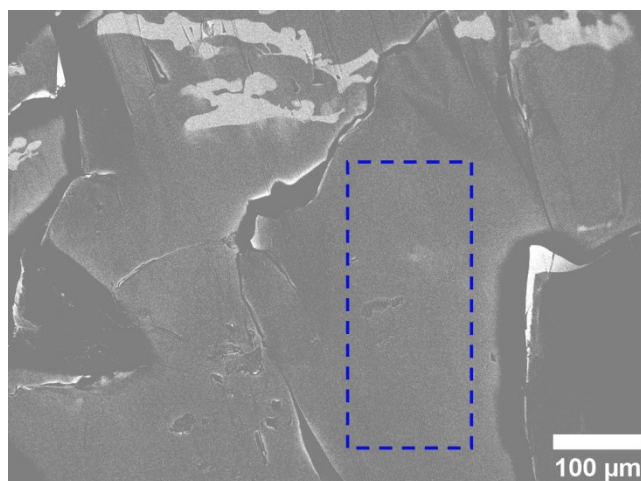

Figure S2: Back scattered electron image of large domain of $Bi_2Cr_4Se_9$ (minor phase). The EDX spectrum collected within the blue rectangle is shown in Fig. 2(c).

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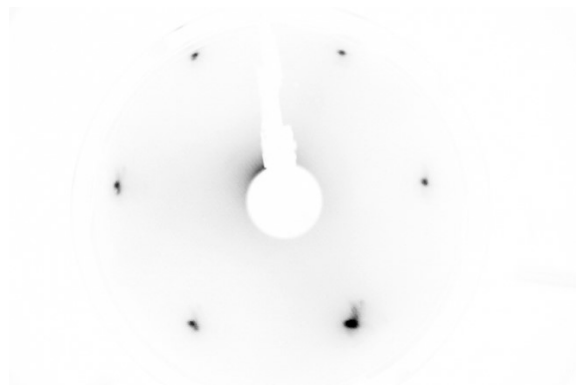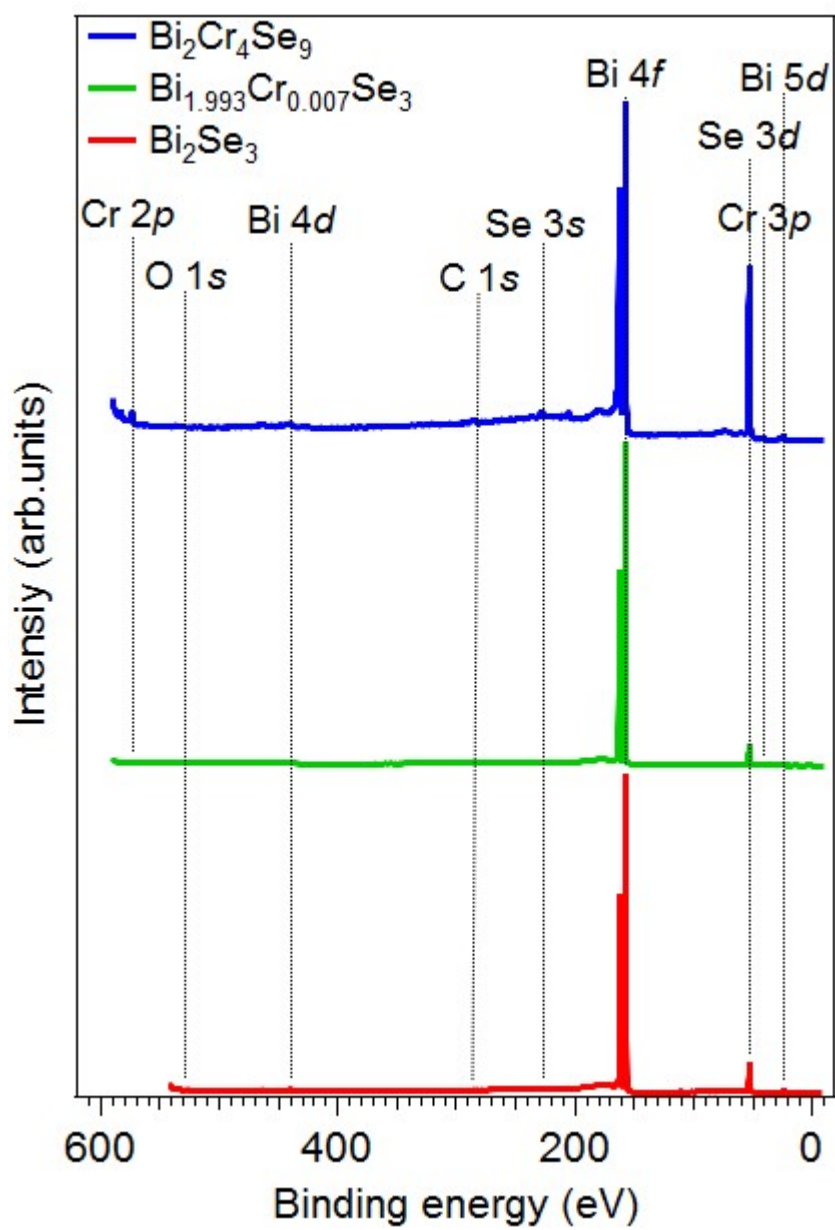*Figure S3: LEED pattern measured on $Bi_{1.993}Cr_{0.007}Se_3$ with primary electron energy of 48.3 eV.*

Figure S4: Core level spectra measured on (a) $Bi_2Cr_4Se_9$, (b) $Bi_{1.993}Cr_{0.007}Se_3$ and (c) Bi_2Se_3 phases measured with hυ=700 eV.
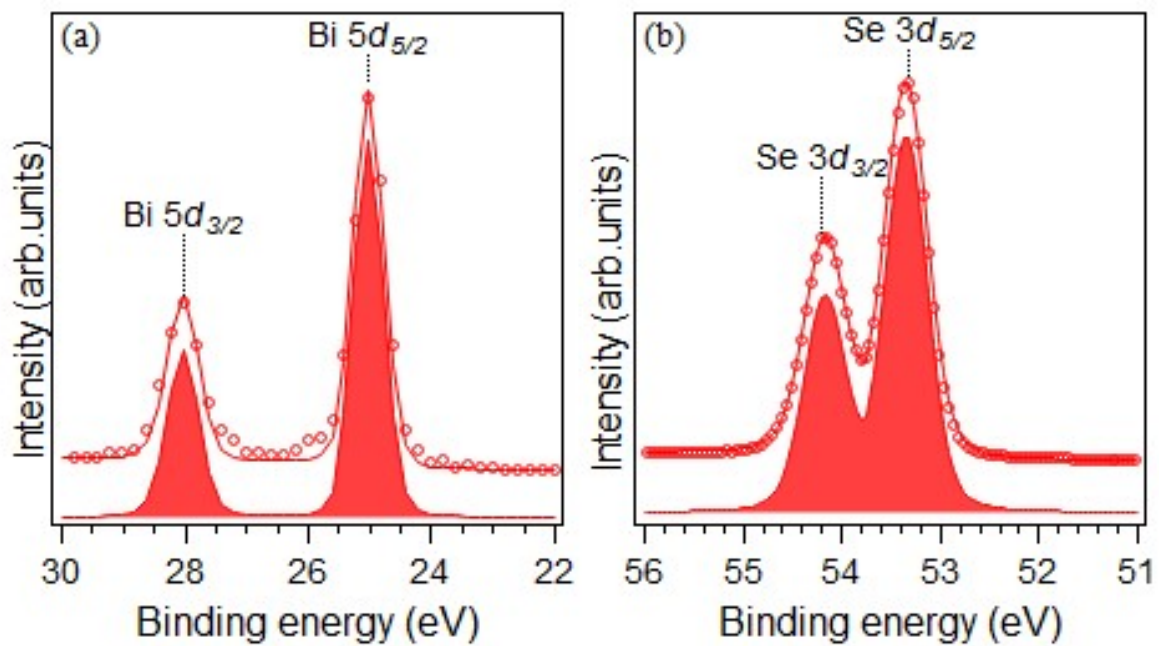

Figure S5: (a) Bi 5d and (b) Se 3d core level spectra measured on Bi_2Se_3 with hυ=650 eV.

		Bi1 (Bi 5d)	Bi2 (Bi 5d)	Se1 (Se 3d)	Se$_2$ (Se 3d)
Bi$_2$Cr$_4$Se$_9$	Peak Position BE (eV)	25.00	24.85	53.30	53.80
	ghm (eV)	0.81	1.46	0.74	0.68
	FWHM (eV)	0.90	1.5	0.70	0.80
Bi$_{1.993}$Cr$_{0.007}$Se$_3$	Peak Position BE (eV)	25	-	53.3	-
	ghm (eV)	0.73		0.66	-
	FWHM (eV)	0.35		0.80	
Bi$_2$Se$_3$	Peak Position BE (eV)	25		53.3	
	ghm (eV)	0.55		0.45	
	FWHM (eV)	0.70		0.50	
	Spin orbit split (eV)	**3.05**	**-**	**0.84**	**-**
	Branching ratio	**1.4**	**-**	**1.77**	**-**
	***lhm* (eV)**	**0.10**		**0.10**	

Table S1: The fitting parameters of Bi 5d and Se 3d core level spectra measured on Bi$_2$Cr$_4$Se$_9$ and Bi$_{1.993}$Cr$_{0.007}$Se$_3$ phases. The position of the peaks in BE (eV), spin orbit splitting (eV), branching ratio, Lorentzian width (eV) and the gaussian width (eV) obtained by fitting using Voigt function are reported.
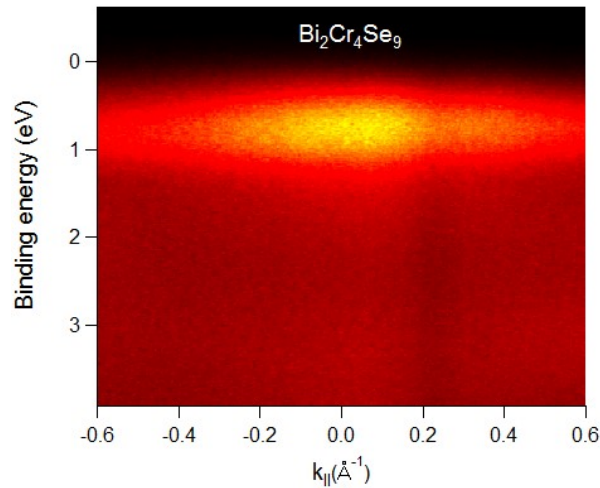

Figure S6: Electronic band structure measured near E$_F$ by means of ARPES on Bi$_2$Cr$_4$Se$_9$ phase with hν = 45 eV.