Composition-dependent variations in displacement, occupational and density modulation waves in plagioclase feldspar [$Na_{1-x}Ca_x(Si_{3-x}Al_{1+x}O_8)$] solid solution with incommensurately modulated structure

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Plagioclase feldspars [$Na_{1-x}Ca_x(Si_{3-x}Al_{1+x}O_8)$] are the most abundant minerals in the earth's crust. Although crystal structures for end members of albite (Ab = $NaSi_3AlO_8$) and anorthite (An = $CaSi_2Al_2O_8$) are relatively simple, the structures for intermediate plagioclase feldspars (from ~An20 to ~An75) with incommensurate modulations are very complicated at low temperature, and are not simple mixtures of albite and anorthite subunits [1]. The crystal structures and formation mechanism of the modulated structure in intermediate plagioclase have been an enigma for decades beginning with the first discovery in 1940 [2]. The modulated structure and its formation mechanism affect our understanding about mineral associations of plagioclase feldspars and their subsolidus reactions like ordering and exsolution. All proposed structure models based on X-ray diffraction and transmission electron microscopic studies can be categorized into two groups: (1) periodic alternating lamellae with anorthite ($I\bar{1}$) structure in anti-phase relationship with a stacking vector of ½ ***c***, and (2) periodic alternating lamellae with anorthite ($I\bar{1}$) and albite ($C\bar{1}$) structures [3].

Our recent results from Z-contrast imaging and single-crystal XRD indicate that the modulated structure changes from Na-rich plagioclase with $C\bar{1}$ symmetry (~An20) to Ca-rich plagioclase with $\mathrm{I}\bar{1}$ symmetry (~An75). As the composition of plagioclase increases in Ca (at ~ An20), plagioclase with $C\bar{1}$ symmetry transforms to an incommensurately modulated structure characterized by the first-order satellite or *e*-reflections only. Structural refinement results show displacement modulation wave of Ca-Na atoms and weak occupational modulation wave resulted from Si-Al ordering and coupled Ca-Na ordering. As the Ca increases to ~An40, it transforms to another modulated structure characterized by both first-order (*e*-) and second-order (*f*-) satellite reflections. Structural refinement results show density modulation wave together with the displacement modulation and occupational modulation waves. As the composition changes further, the amplitudes of all the three modulation waves increases. The wave vector (i.e., modulation direction) changes and modulation period increases from ~ 4 nm to ~ 12 nm as Ca increase in the plagioclase feldspars. The modulated structure transforms to a lock-in phase with $\mathrm{I}\bar{1}$ symmetry at a composition about An75. Our results also support that the incommensurately modulated structure has a stable field in plagioclase phase diagram [4, 5]. The findings about the coupled modulation waves in the intermediate plagioclase feldspars may help us to better understand or explore similar modulated structures in synthetic materials.

References:

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