Solved: The enigma of labradorite feldspar with incommensurately modulated structure

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ABSTRACT

Intermediate plagioclase feldspars are the most abundant minerals in the Earth’s crust. Their incommensurately modulated structure has puzzled geologists and crystallographers for decades since the phenomenon in a labradorite was reported in 1940. Solving the structure is a necessary step toward mapping the complex subsolidus phase relations of plagioclase solid solution. The structure of a homogeneous labradorite (An$_{51}$) single crystal from a metamorphic rock is solved and refined from single-crystal X-ray diffraction. The result structure can be simplified as alternating I$_1$-like lamellae domains related by inversion twins. The inversion boundary shows an anorthite-like structure with I$_T$ symmetry and is richer in Ca than the neighboring domains with opposite polarity. No albite-like subunits appear in the e-plagioclase structure. The modulated structure displays a unique Al-Si ordering pattern. A density modulation with a variation of 17 mol% in composition is also observed and can be properly described only by applying second-order harmonic waves for the atomic modulation functions. The modulated structure reveals details that cannot be observed from refinement with only main reflections and may be used to assess the ordering state and cooling rate of its host rock. The homogeneity of the crystal indicates the closure of the solvus for Bøggild intergrowth at low temperature. The highly ordered modulation supports the thermodynamic stability of e-plagioclase. Both Al-Si ordering and Ca-Na ordering are the driving force for formation of the incommensurately modulated structure.

Keywords: Intermediate plagioclase, incommensurate, modulated structure, density modulation, single-crystal XRD, e-plagioclase, labradorite, aperiodic crystal, Invited Centennial article

INTRODUCTION

Plagioclase feldspars, which form a coupled solid solution between albite (Ab; NaAlSi$_3$O$_8$) and anorthite (An; CaAl$_2$Si$_2$O$_8$), are the most abundant group of minerals in the Earth’s crust, and they can be found in most igneous and metamorphic rocks. However, the complicated crystal structure and subsolidus phase relation has been puzzling mineralogists for decades. The most enigmatic feature of plagioclase is the incommensurately modulated structure (e-plagioclase) that appears in low plagioclase composition range with composition between $\sim$An$_{15}$ and $\sim$An$_{75}$ (Bown and G. Gay 1959; Ribbe 1983; Smith and Brown 1988). The crystal structure of e-plagioclase has been an enigma since its first discovery in 1940 (Chao and Taylor 1940). Several different models for e-plagioclase have been raised over the decades, yet none of them solved the structure satisfactorily. All previous models are based on alternating anorthite domains with antiphase relation to one another, while some display density modulation by inserting albite-like CT domains in between I$_T$ domains (Cinnamon and Bailey 1971; Grove 1977; Horst et al. 1981; Kumao et al. 1981; McConnell and Fleet 1963; Megaw 1960a, 1960b, 1960c; Nakajima et al. 1977; Smith and Ribbe 1969; Steurer and Jagodzinski 1988; Toman and Frueh 1976a, 1976b; Wenk and Nakajima 1980) (Fig. 1).

Most single-crystal X-ray analyses of e-plagioclase have been done on labradorite (Boysen and Kek 2015; Horst et al. 1981; Toman and Frueh 1976a, 1976b; Yamamoto et al. 1984), with An composition about 50, which is about the middle of entire compositional range of e-plagioclase. As the An composition increases, so do the intensities of satellite reflections and the modulation period (Smith and Brown 1988). Labradorite is an ideal specimen as the satellites are separate enough to be easily discerned and strong enough for quality refinement. However, igneous plagioclase of this composition often exhibit iridescent color from the Bøggild intergrowth. All the labradorite samples studied previously actually consist of two phases with different compositions and modulation periods (Boysen and Kek 2015; Horst et al. 1981; Yamamoto et al. 1984), which was considered a serious problem (Ribbe 1983), because the reflections from the two components overlap and a

![Figure 1](image-url)