

Fig. 2. Electron diffraction patterns of the Ca-free phase projected along the [001] and [111] directions.

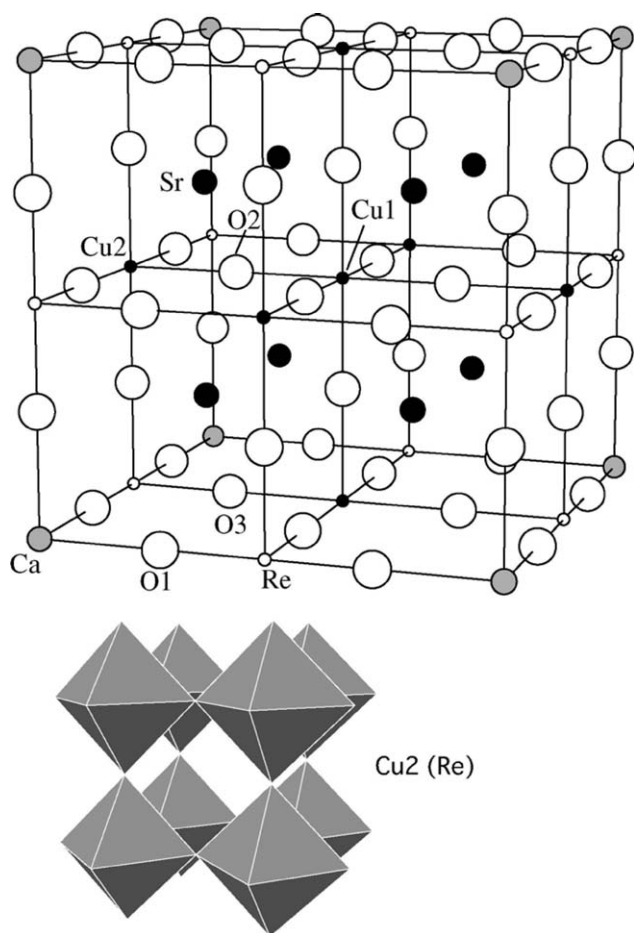


Fig. 3. Crystal structure of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$. The lower part indicates a network of the Cu2 (or Re) sites.

analysis which was constructed based on the space group $Pm-3m$. In this model, the unit cell consists of eight perovskite-like subcells and the A -sites of the subcells are occupied exclusively by Sr. The B -sites are occupied by Ca, Re and Cu in an ordered way, i.e., Ca at the $1a$ sites, Re at the $3d$ sites and Cu at the $1b$ and $3c$ sites. The Rietveld refinement based on this model

was quite successful to result in reliability factors of $R_{\text{wp}}=6.96$ and $R_1=5.64$. Observed and calculated X-ray patterns, final structure parameters and selected bond lengths are shown in Fig. 4 and Tables 1 and 2, respectively.

From the structure model in Fig. 3, a stoichiometric composition of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$ is derived for the Ca-containing phase and the unit cell includes one formula unit ($z=1$). This composition is converted to $\text{Sr}(\text{Ca}_{0.125}\text{Re}_{0.375}\text{Cu}_{0.5})\text{O}_3$ and is slightly different from the nominal one of $\text{Sr}(\text{Ca}_{0.175}\text{Re}_{0.325}\text{Cu}_{0.5})\text{O}_{3.15}$ from which we obtained the best phase purity. If Ca is simply replaced by Sr in Fig. 3, the stoichiometric composition of the Ca-free phase becomes $\text{Sr}_9\text{Re}_3\text{Cu}_4\text{O}_{24}$ ($\text{Sr}_{1.125}\text{Re}_{0.375}\text{Cu}_{0.5}\text{O}_3$) and this is also slightly different from the “best” nominal composition of $\text{Sr}_{1.15}\text{Re}_{0.35}\text{Cu}_{0.5}\text{O}_3$.

In the Rietveld analysis, we refined the occupation factors for the B -site atoms of Ca, Re and Cu. However, they converged to unity within a few percent uncertainties confirming the stoichiometric composition. The EPMA measurement for the Ca-containing phase gave a composition of $\text{Sr}_{1.0}\text{Ca}_{0.15}\text{Re}_{0.35}\text{Cu}_{0.5}\text{O}_y$, where the experimental error is the order of ~ 0.01 . This composition is closer to the stoichiometric composition than the nominal one but the Ca/Re ratio is still larger than 1/3 beyond the experimental uncertainty. This may suggest partial substitution of Ca for Re. Magnetic properties of the phases depend drastically on the nominal oxygen content (see below). This fact seems to indicate the possibility of oxygen-vacancy introduction under a low-oxygen-pressure synthesis condition. We did not constrain any temperature factors, and the temperature factors of the oxygen sites, in particular, those of O1 and O3 become noticeably large (Table 1) which may suggest that these sites are partially vacant. In addition, the temperature factor of the Ca site is considerably small. However, by the X-ray powder diffraction pattern alone, it is hard to elucidate more details of the structure. Neutron diffraction study is in progress and